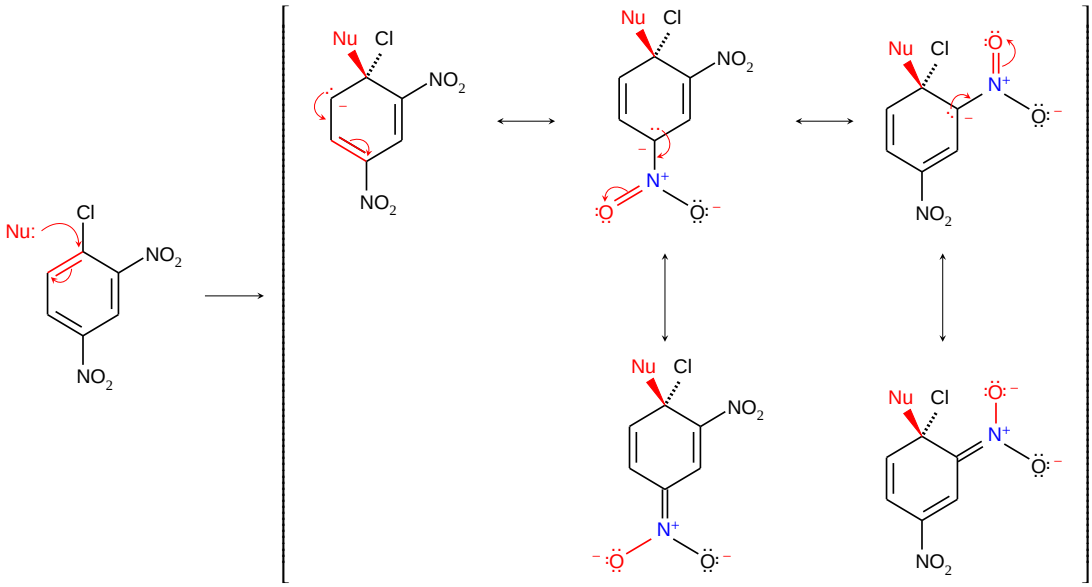
Shinsaku Fujita

XyMTEX: Reliable Tool for Drawing Chemical Structural Formulas



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Manual for XyMTEX Versions 1.01–5.01 (S. Fujia, September 01, 2013) ©

If the logos XyMTEX and LaTeX are not available, the title of this document should be printed: "XyMTeX: Reliable Tool for Drawing Chemical Structural Formulas". This document has been typeset by the PDF-compatible mode and the resulting dvi file has been converted into a PDF file by using the `dvipdfmx` converter.

Preface

XyMTEX and Interdisciplinary Chemistry/Mathematics Books

The development of the XyMTEX system highly reflects the personal history of my researches aiming at the integration of chemistry and mathematics. In 1991, I published an interdisciplinary monograph for linking chemistry and mathematics:

S. Fujita, *Symmetry and Combinatorial Enumeration in Chemistry* (Springer-Verlag, 1991),

where the TEX/LATEX system was used to typeset the manuscript. Because of interdisciplinary nature, this book contains many structural formulas of organic compounds along with mathematical equations. Such mathematical equations were successfully typeset by means of the original utilities of the TEX/LATEX system. However, the structural formulas contained in this book were drawn manually and pasted on the camera-ready manuscript, because the TEX/LATEX system supported no reliable utility for drawing structural formulas at that time.

For the purpose of pursuing my interdisciplinary researches, it was desirable to develop a reliable LATEX tool for drawing structural formulas, so that the XyMTEX system was developed and released in 1993. The manual was published as a book in 1997:

S. Fujita, *XyMTEX—Typesetting Chemical Structural Formulas* (Addison-Wesley Japan, 1997).

In 2001, I published a monograph on the concept of imaginary transition structures (ITSs), which serves as computer-oriented representation of organic reactions:

S. Fujita, *Computer-Oriented Representation of Organic Reactions* (Yoshioka Shoten, 2001).

Although such ITSs can be regarded as extended structural formulas with colored bonds (par-bonds, out-bonds, and in-bonds), the XyMTEX system at that time did not support utilities of coloring bonds. It follows that the ITSs contained in this book were drawn manually and pasted on the camera-ready manuscript.

After the PostScript-compatible mode of the XyMTEX system was developed, it was applied to typeset structural formulas of high quality, which were incorporated in a book for surveying organic compounds for color photography:

S. Fujita, *Organic Chemistry of Photography* (Springer-Verlag, 2004).

Along with chemical or mathematical equations, this book contains 480 figures, each of which consists of several structural formulas drawn by the XyMTEX system.

More recently, I have published two monographs on combinatorial enumeration of compounds as three-dimensional structures. These books contain many mathematical equations as well as structural formulas because of interdisciplinary nature, where the mathematical equations were typeset by the original TEX/LATEXutilities and the structural formulas were drawn by the XyMTEX system.

- The book published in 2007 deals with a new concept *mandalas*, which I have proposed as a basis for rationalizing enumeration of three-dimensional structures:

  S. Fujita, *Diagrammatical Approach to Molecular Symmetry and Enumeration of Stereoisomers*, Mathematical Chemistry Monographs Series Vol. 4 (Kragujevac, 2007),

- The book published in 2013 is concerned with the *proligand method*, which I have proposed to enumerate three-dimensional structures:

  > S. Fujita, *Combinatorial Enumeration of Graphs, Three-Dimensional Structures, and Chemical Compounds*, Mathematical Chemistry Monographs Series Vol. 15 (Kragujevac, 2013).

  This book indicates that the proligand method for enumerating three-dimensional structures can be degenerated into the Pólya's method for enumerating graphs.

Because the present version of the XƎMTEX system (the PostScript-compatible mode and the PDF-compatible mode) supports utilities for coloring structural formulas, the book published in 2001 would be rewritten with maintaining bond colors (par-bonds, out-bonds, and in-bonds). This will be briefly discussed in Section 39.4 in the present manual.

By the publication of the interdisciplinary chemistry/mathematics books described above, the XƎMTEX system has been proven to be a reliable tool for publishing books of high printing quality which contain structural formulas along with mathematical equations.

About the Present Manual

The present manual consists of 10 parts, each of which subdivided into several chapters.

- Part I (General Principles and Conventions) consists of six chapters (Chapters 1–6), where basic techniques of the XƎMTEX system are discussed. The XƎMTEX system supports three modes (TEX/LATEX-compatible mode, PostScript-compatible mode, and PDF-compatible mode) as described in Chapter 1 (Introduction). To obtain structural formulas of higher quality, you should select the PostScript-compatible mode or the PDF-compatible mode according to the setting of your computer. Chapter 2 (General Principles of XƎMTEX Commands) briefly describes the substitution technique based on (yl)-functions, the addition technique for drawing fused rings, and the replacement technique for drawing spiro rings. Chapter 3 (XƎMTEX Commands for General Use: Syntax) deals with three- to six-membered heterocycles and others as XƎMTEX commands for general use, where general features of required arguments (e.g., substitution lists ⟨subslist⟩ and atom lists ⟨atomlist⟩) and those of optional arguments (e.g., bond lists ⟨bondlist⟩, skeletal bond lists ⟨skelbdlist⟩, and deleted bond lists ⟨delbdlist⟩) are discussed. Chapter 4 (Fusing Units: Syntax) describes three- to six-Membered fusing units, which are used in the addition technique. Chapter 5 (Size Reduction) and Chapter 6 (Fonts and Related Matters) deal with additional items for general conventions.

- Part II (Carbocyclic Compounds) consists of seven chapters (Chapters 7–13), where commands for specific use are discussed to draw carbocyclic compounds. These commands are regarded as short-cut commands, which are defined by fixing one or more arguments of commands for general use: Chapter 7 (Six-Membered Carbocycles), Chapter 8 (Five- or Lower-Membered Carbocycles), Chapter 9 (Carbocycles with Fused Six-to-Six-Membered Rings), Chapter 10 (Carbocycles with Fused Six-to-Five-Membered Rings), Chapter 11 (Fused Tricyclic Carbocycles), Chapter 12 (Chair Forms and Further Carbocyclic Compounds), and Chapter 13 (Steroid Derivatives).

- Part III (Heterocyclic Compounds) consists of five chapters (Chapters 14–18), where commands for specific use are discussed to draw heterocyclic compounds. These commands are regarded as short-cut commands, which are defined by fixing one or more arguments of commands for general use: Chapter 14 (Six-Membered Heterocycles), Chapter 15 (Five- or Lower-Membered Heterocycles), Chapter 16 (Heterocycles with Fused Six-to-Six-Membered Rings), Chapter 17 (Heterocycles with Fused Six-to-Five-Membered Rings), and Chapter 18 (Pyranoses and Furanoses).

- Part IV (Aliphatic Compounds) consists of three chapters (Chapters 19–21), where commands for specific use are discussed to draw aliphatic compounds. Chapter 19 (Aliphatic Compounds of Lower Carbon Contents) discusses commands for drawing planar forms of tetrahedral compounds and for drawing trigonal units. Chapter 20 (Tetrahedral Units with Wedged Bonds) discusses commands for drawing tetrahedral units or trigonal bipyramidal units with stereochemical configurations. Chapter 21 (Zigzag Polymethylene Chains) discusses commands for drawing zigzag polymethylene chains of carbon content 2 to 10.

- Part V (Other Building Blocks and Utilities) consists of two chapters (Chapters 22 and 23). Chapter 22 (Polymers) introduces delimiters for polymers, a polymethylene unit, a polystyrene unit, and so on. Chapter 23 (Lone Pairs and Radicals) deals with various commands for drawing lone pairs.
- Part VI (Techniques for Combining Structures) consists of five chapters (Chapters 24–28), which develop more detailed discussions on the substitution technique, the replacement technique, the addition technique, and other related techniques. Chapter 24 (LaTeX Picture Environment for Combining Structures) deals with most basic techniques for combining two or more moieties by using the LaTeX `picture` environment. Chapter 25 ((yl)-Functions and the Substitution Technique) discusses the substitution technique by declaring a (yl)-function in the ⟨subslist⟩ of a command. Chapter 26 (Linking Units Coupled with (yl)-Functions) discusses commands for inserting a unit between a parent structure and a substituent due to a (yl)-function. Chapter 27 (The Replacement Technique for Drawing Spiro Rings and Related Techniques) discusses the application of (yl)-functions to the replacement technique for drawing spiro rings. Chapter 28 (The Addition Technique for Ring Fusion and Related Techniques) deals with the application of fusing units to the addition technique for drawing fused rings.
- Part VII (Advanced Techniques for Drawing Structures) consists of four chapters (Chapters 29–32). Chapter 29 (Stereochemistry) contains more detailed discussions on stereochemical expressions based on wedges, hashed wedges, wavy bonds, and so on. Chapter 30 (Drawing by Low-Level Commands) deals with low-level commands for straight-lined bond, wedges, hashed wedges, etc., which are used in the LaTeX `picture` environment or the XyMTeX `XyMcompd` environment. In particular, regular pentagons, heptagons, etc. are constructed as building blocks for drawing structural formulas. Chapter 31 (New Commands for Drawing Five-, Seven-, and Eight-Membered Rings) discusses the definition of commands for drawing regular pentagons, heptagons, etc., which are applied to draw complicated natural products such as maitotoxin and ciguatoxin. Chapter 32 (Dirty Tricks) discusses non-standard applications of the replacement technique and the addition technique.
- Part VIII (Molecular Formulas and Reaction Schemes) consists of five chapters (Chapters 33–37). Chapter 33 (Arrows) deals with arrows used in chemical equations or in diagrams of electron shifts. Chapter 34 (Compound Numbers and Compound Boxes) discusses compound numbers and derivative numbers as well as environments or boxes for giving such compound or derivative numbers. Chapter 35 (Commands for Printing Chemical Formulas and Environments for Printing Chemical Equations) deals with the `ChemEquation` environment etc., which correspond to such mathematical environments as the `equation` environment. Chapter 36 (Formatting Reaction Schemes) discusses the drawing reaction schemes which contain structural formulas drawn by the XyMTeX system. Chapter 37 (Math Versions) deals with new math versions “chem” and “boldchem” in addition to the usual math version “normal” and “bold”.
- Part IX (Coloring Chemical Compounds and Reaction Schemes) consists of three chapters (Chapters 38–40), which discusses various XyMTeX utilities for coloring structural formulas: Chapter 38 (Coloring Substituents and Substitution Bonds), Chapter 39 (Coloring Skeletal Bonds and Double Bonds), and Chapter 40 (Coloring Chemical Schemes).
- Part X (Appendices) consists of two chapters (Chapters 41 and 42). Chapter 41 (EPS Files Containing XyMTeX Formulas) discusses the generation of EPS (encapsulated PostScript) files, which have the data of bounding boxes. And then the incorporation of the resulting EPS files into chemical documents is demonstrated. Chapter 42 (PDF Files Containing XyMTeX Formulas) is devoted to the generation of PDF files, the evaluation of their bounding boxes, and the incorporation of them into chemical documents.

If readers pursue a short-cut to practical features of the XyMTeX drawing of structural formulas, they get along well by reading Parts I and VIII selectively (and Part VI desirably). The chapters contained in the remaining parts are independent of each other, so that they may be referred to when they become necessary to the readers.

Kanagawa, Japan Shinsaku Fujita
September 2013

About the author:

Shinsaku Fujita was born in Kita-Kyushu City, Japan in 1944. He received his undergraduate training at Kyoto University. After earning a Master's degree in 1968, he started as a research instructor and received a Dr. Eng. degree at Kyoto University under the guidance of Prof. Hitosi Nozaki. In 1972, he joined Ashigara Research Laboratories, Fuji Photo Film Co., Ltd., where he was engaged in the R&D of organic compounds for instant color photography and in the R&D of the organic reaction database until 1997. From 1997 to 2007, he has been Professor of Information Chemistry and Materials Technology at the Kyoto Institute of Technology. In 2007, he has started Shonan Institute of Chemoinformatics and Mathematical Chemistry as a private laboratory. He was awarded the Synthetic Organic Chemistry Award in 1982 and the Society of Computer Chemistry Japan Award in 2002. His research interests have included reactive intermediates (nitrenes), synthetic organic chemistry (cylophanes, strained heterocycles, and organic compounds for photography), organic photochemistry, organic stereochemistry (theoretical approach), mathematical organic chemistry (combinatorial enumeration), and the organic reaction database (imaginary transition structures). He is the author of *Symmetry and Combinatorial Enumeration in Chemistry* (Springer-Verlag, 1991), *XYMTEX—Typesetting Chemical Structural Formulas* (Addison-Wesley Japan, 1997), *Computer-Oriented Representation of Organic Reactions* (Yoshioka Shoten, 2001), *Organic Chemistry of Photography* (Springer-Verlag, 2004), *Diagrammatical Approach to Molecular Symmetry and Enumeration of Stereoisomers*, Mathematical Chemistry Monographs Series Vol. 4 (Kragujevac, 2007), *Combinatorial Enumeration of Graphs, Three-Dimensional Structures, and Chemical Compounds*, Mathematical Chemistry Monographs Series Vol. 15 (Kragujevac, 2013), and several books on TEX/LATEX. His homepage on World Wide Web is located at http://xymtex.com/.

Contents

Part I

General Principles and Conventions

Chapter 1

Introduction

1.1 Backgrounds for the Development of the XyMTEX System

The text formatter TEX developed by Knuth [1] is widely used in preparing manuscripts of scientific papers and in the typesetting processes of several scientific journals and books (for an example at the beginning of the 1990s, see [2]). In particular, LATEX, a TEX macro package that was released by Lamport [3], has expanded the society of TEX users because of plainness.

Since the beginning of its history, TEX (LATEX) places special emphasis on mathematics typesetting. Hence, it has been accepted by scientists who have to write mathematic equations. In contrast, the TEX/LATEX typesetting is less popular in chemistry than in mathematics and other fields. One of the reasons is that there are few TEX/LATEX utilities for typesetting chemical structural diagrams.

Although LATEX provides us with a `picture` environment for drawing simple figures, its original commands are so primitive as to be directly applied to the drawing of structural formulas. Hence, the commands should be combined to produce more convenient macros.

Pioneering works by Haas and O'Kane [4] and by Ramek [5] have provided such macros that allow us to typeset structural formulas. The macros of the former approach are available in the public domain, being named ChemTEX. Although they are easier to use than the original `picture` environment of LATEX, they still have some items to be improved. The most inconvenient item is the incapability of accommodating 10 or more substituents. It stems from the fact that one argument is used to assign one substituent (or one object) in each of the macros of Haas-O'kane's approach. Note that the direct usage of arguments enables us only to assign 9 or less substituents, because a macro in TEX/LATEX is capable of taking 9 or less arguments.

For example, the `\steroid` macro reported for typesetting a steroid skeleton takes 9 arguments [4]:

```
\steroid{A1}{A2}{A3}{A4}{A5}{A6}{A7}{A8}{A9}
```

where Argument 1 (`A1`) can take 'D' (a second bond between positions 1 and 2), 'Q' (no action), or 'R^{11}' (a substituent on position 11 and the corresponding double bond); Argument 2 (`A2`) can take 'D' (a second bond between positions 3 and 4), 'Q' (no action), or 'R^{3}' (a substituent on position 3 and the corresponding double bond); Argument 3 (`A3`) can take 'Q' (no action), or 'R^{3}' (a substituent on position 3 and the corresponding single bond); and so on. Through the total statement of arguments, only six substituents are specified, while the skeleton have 20 or more substitution positions to be considered.

Moreover, the specification of the arguments is not systematic, so that many functions are included into the macro within the restriction of the direct usage of arguments.

1. One argument (Argument 2) specifies objects of two different categories *e.g.*, inner double bonds and outer double bonds.

2. Arguments 2 and 3 specify a substituent attaching to the same position (position 3).

3. It is difficult without a reference manual to differentiate between one argument for specifying bonds and another argument for specifying substituents.

4. The argument ‘Q’ is selected to show no modification because this character is hardly ever found in a chemical structure formula. However, the use of this character may become necessary in future. Such explicit description of ‘no action’ should be avoided.

As a result, the formats and contents of arguments are different from one argument to another and from one macro to another such that a typical TEX user, a secretary or a chemist author, may give up to memorize such macros. Hence, more systematic and convenient macros are desirable in order to spread the typesetting of chemical structures with TEX/LATEX.

The XYMTEX system as a package set[a] involves convenient macros for typesetting chemical structural formulas [6]. These macros are based on techniques in which inner bonds, substituents, and hetero-atoms on a skeleton are separately assigned without such limitation of numbers. The package set XYMTEX[b] will be a more versatile tool if it is coupled with the macros which the author has released in a book [7].

1.2 Development of the XYMTEX System

1.2.1 History of the XYMTEX System

The history of the XYMTEX system is summarized in Table 1.1. The XYMTEX system has been improved step by step, where there were three epochs if we focus our attention on final files for browsing and printing:

1. The early versions (up to version 3.00) have been based on the `picture` environment of LATEX and the epic package, where bonds of chemical structural formulas are drawn by using the `line` command enhanced by the epic package. Hence, these versions can be used within the native LATEX system, so that the resulting dvi files can be browsed and printed by means of such an appropriate dvi-ware as dviout. These dvi files can be converted into PDF files by using the dvipdfm(x) converter. This mode of drawing is now supported as *the TEX/LATEX-compatible mode* in the present version of XYMTEX.

2. The next versions (up to version 4.06) have been based on the utilities supported by the PSTricks package, where an appropriate dvi-to-ps converter (e.g., the dvips converter) is necessary to convert dvi files into PostScript files. This mode of drawing is now supported as *the PostScript-compatible mode* in the present version of XYMTEX.
   The resulting PostScript files can be browsed by using the Ghostscript system (coupled with Ghostview). The PostScript files are further transformed into PDF files by using an appropriate converter (e.g., Adobe Distiller). It follows that the PDF printing of XYMTEX structural formulas is available via such a route as

$$< \text{tex with XYMTEX codes} > \overset{\text{TEX/LATEX}}{\longrightarrow} < \text{dvi} > \overset{\text{dvips}}{\longrightarrow} < \text{ps} > \overset{\text{Distiller}}{\longrightarrow} < \text{PDF} >.$$

   On the other hand, structural formulas drawn by the XYMTEX system can also be transformed into EPS (encapsulated PostScript) files by using the Ghostscript utilities so as to be incorporated into PDF files. This means that we are alternatively able to use the dvipdfm(x) converter in order to convert LATEX document files with XYMTEX structural formulas (EPS files) into PDF files, i.e.,

$$< \text{tex with XYMTEX EPS files} > \overset{\text{TEX/LATEX}}{\longrightarrow} < \text{dvi} > \overset{\text{dvipdfm(x)}}{\longrightarrow} < \text{PDF} >.$$

   The PDF printing of XYMTEX structural formulas has been discussed under the title “Articles, Books, and Internet Documents with Structural Formulas Drawn by XYMTEX — Writing, Submission, Publication, and Internet Communication in Chemistry.” [8], where such state-of-the-art routes as described above have been compared to prepare PDF documents with XYMTEX structural formulas.

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[a] LATEX 2ε uses the term ‘package’ to designate a file with .sty extension, while XYMTEX version 1.00 has used the same term to indicate a set of sty files. In order to prevent confusion, we now use the term ‘package set’ to indicate a set of sty files and the term ‘package’ to designate each sty file.

Table 1.1. Versions of XƎMTEX

version	package files and comments
1.00 (1993)	(for LATEX2.09) See Ref. [9,10] aliphat.sty, carom.sty, lowcycle.sty, hetarom.sty, hetaromh.sty, hcycle.sty, chemstr.sty, locant.sty, xymtex.sty
1.01 (1996)	(for LATEX 2_ε) See Ref. [11]. ccycle.sty, polymers.sty, chemist.sty
1.02 (1998)	(not released) Nested substitution by 'yl'-function.
2.00 (1998)	Enhanced version based on the XƎM Notation. See Ref. [12,13,14]. fusering.sty, methylen.sty
2.01 (2001)	(not released) Size reduction, sizeredc.sty (version 1.00)
3.00 (2002)	Size reduction (sizeredc.sty, version 1.01), and reconstruction of the command system. See Ref. [15]
4.00 (2002)	(not released) PostScript printing (xymtx-ps.sty, version 1.00 and chmst-ps.sty, version 1.00)
4.01 (2004)	The xymtx-ps package for PostScript printing and length-variable central atoms [16]
4.02 (2004)	PostScript printing and wedges bonds for stereochemistry
4.03 (2005)	PostScript printing and wavy bonds for stereochemistry. See Ref. [17]
4.04 (2009)	Macros for drawing steroids (steroid.sty, ver 1.00). See Ref. [18]
4.05 (2009)	Macros for drawing Lewis structures of the lewissturc package (lewisstruc.sty, version 1.00), revised and improved macros added to the chemist package (ver 4.05) [and the chmst-ps package (ver 1.02)], and the first release of the chemtimes package (ver 1.00)
4.06 (2009)	The chmst-ps package (ver 1.03) for supporting bent (curved) harpoons. See Refs. [19,20,21]
5.00 (2010)	The xymtx-pdf package (ver 5.00) for supporting PDF printing, the bondcolor package (ver 5.00) for coloring double bonds and skeletal bonds as well as the assurelatexmode package for assuring compatibility of the three modes. This version also contains the chmst-pdf package (ver 5.00) for extending the chemist package to support PDF printing and the assurechemist package for assuring compatibility of the three modes. See Refs. [22].
5.01 (2013)	The present version: Addition of several macros and the release of an integrated manual (this manual).

3. Because PDF files become more and more popular in writing, publication and internet documentation, and because the dvipdfm(x) converter becomes the de facto standard for preparing PDF files, it is highly desirable to develop a direct route for processing dvi files prepared from TEX/LATEX documents with XƎMTEX codes, i.e.,

$$< \text{tex with XƎMTEX codes} > \overset{\text{TEX/LATEX}}{\longrightarrow} < \text{dvi} > \overset{\text{dvipdfm(x)}}{\longrightarrow} < \text{PDF} >.$$

The latest versions (up to version 5.01) have been based on the utilities supported by the pgf package, where an appropriate dvi-to-pdf converter (e.g., the dvipdfmx converter) is necessary to convert a dvi file into a PDF file. This mode of drawing is now supported as *the PDF-compatible mode* in the present version of XƎMTEX.

Recent books on LATEX 2_ε have referred to the XƎMTEX system, e.g., pages 520–540 of [23] and pages 551–598 of Vol. II of [24].

1.2.2 The Name of the Package

The word 'chemistry' stems from an Arabian root 'alchemy', which is, in turn, considered to come from Greek, $\chi\upsilon\mu\epsilon\acute{\iota}\bar{\alpha}$. The XƎM of the name XƎMTEX is an uppercase form of $\chi\upsilon\mu$. This conforms to a rule of coinage, because the name TEX is also a word of Greek origin ($\tau\epsilon\chi$).

The pronunciation of XƎMTEX is recommended to be 'khýmtekh', in which the 'kh' sound may be a Russian 'kh' or more simply an English 'k' and the symbol 'y' is expected to be pronounced like a German

'ü'. The logo XyMTEX should be used to refer to the XyMTEX system, because the command \XyMTeX has been defined in the XyMTEX package to output the logo XyMTEX. If the logo is not available, the simplified form 'XyMTeX' is allowed.

1.3 Three Modes of XyMTEX for Drawing Structural Formulas

The XyMTEX system (version 5.01) consists of the package files listed in Table 1.2, where the inner package xymtx-ps.sty has been developed to realize the PDF-compatible mode; and the inner package xymtx-pdf.sty has been developed to realize the PDF-compatible mode.

The XyMTEX system (version 5.01) supports three modes of structural drawing. They are switched by loading either one of the XyMTEX utility files collected in Table 1.2, i.e.,

- the xymtex package (\usepackage{xymtex} for the TEX/LATEX-compatible mode),
- the xymtexps package (\usepackage{xymtexps} for the PostScript-compatible mode), or
- the xymtexpdf package (\usepackage{xymtexpdf} for the PDF-compatible mode).

The TEX/LATEX mode and the PostScript-compatible mode can be switched in a tex file. On a similar line, the TEX/LATEX mode and the PDF-compatible mode can be switched in a tex file. It should be noted, however, that the PostScript-compatible mode and the PDF-compatible mode cannot coexist in a tex file, because the PostScript-compatible mode depends on utilities based on the PSTricks package, while the PDF-compatible mode depends on utilities based on the pgf/TikZ package.

Because the commands defined in the package files of the XyMTEX Structural Files (Fig. 1.2) are common in the three modes, they are unnecessary to be rewritten even if one selected mode is changed into another. It follows that the PostScript-compatible mode and the PDF-compatible mode can be switched only by exchanging the declarations: \usepackage{xymtexps} ↔ \usepackage{xymtexpdf}.

1.3.1 TEX/LATEX-Compatible Mode of XyMTEX

The declaration of \usepackage{xymtex} in the preamble of a tex file results in the reading of all the package files listed in the XyMTEX Structural Files of Fig. 1.2, which permits XyMTEX drawing according to the LATEX picture environment and the epic package (modified slightly).

Preparation of TEX Files

When xymtex.sty is input, all of the package files of the XyMTEX system (except xymtx-ps and xymtx-pdf) are loaded. A typical template for the TEX/LATEX-compatible mode of XyMTEX is shown as follows:

```
%test1.tex
\documentclass{article}
\usepackage{xymtex}
\usepackage{xcolor}
\usepackage{graphicx}

\begin{document}
(formula)
\end{document}
```

To reduce formula sizes, epic.sty is automatically loaded. This mode draws β-bonds as thick lines and α-bonds as dotted lines. To draw chemical equations, the package files chemist and assurechemist are also loaded automatically. The packages xcolor and graphicx are loaded separately to enhance graphics.

LATEX Processing

For the purpose of LATEX processing, you should type the following command in the command prompt:

```
c:> latex test1
```

Table 1.2. Package Files of XyMTEX and Related Files

package name	included functions
XyMTEX Structural Files	
aliphat.sty	macros for drawing aliphatic compounds
carom.sty	macros for drawing vertical and horizontal types of carbocyclic compounds
lowcycle.sty	macros for drawing five-or-less-membered carbocycles.
ccycle.sty	macros for drawing bicyclic compounds etc.
hetarom.sty	macros for drawing vertical types of heterocyclic compounds
hetaromh.sty	macros for drawing horizontal types of heterocyclic compounds
hcycle.sty	macros for drawing pyranose and furanose derivatives
chemstr.sty	basic macros for atom- and bond-typesetting
locant.sty	macros for printing locant numbers
polymers.sty	macros for drawing polymers
fusering.sty	macros for drawing units for ring fusion
methylen.sty	macros for drawing zigzag polymethylene chains
sizeredc.sty	macros for size reduction
steroid.sty	macros for drawing steroid derivatives contained in the steroid package
lewissturc	macros for drawing Lewis structures
bondcolor	macros for coloring double bonds and skeletal bonds (XyMTEX Version 5.00)
assurelatexmode	dummy declaration for compatibility of the three modes (XyMTEX Version 5.00)
Packages for PostScript- and PDF-Compatible Modes	
xymtx-ps.sty	macros for PostScript printing (XyMTEX Version 4.02). These macros are substituted for several macros contained in the chemstr package.
xymtx-pdf.sty	macros for PDF printing (XyMTEX Version 5.00). These macros are substituted for several macros contained in the chemstr package.
Related Files	
chemist.sty	commands for using ‘chem’ version and chemical environments
assurechemist.sty	dummy commands for compatibility of the three modes (Version 5.00)
chmst-ps.sty	macros for PostScript printing. These macros are substituted for several macros contained in chemist package.
chmst-pdf.sty	macros for PDF printing. These macros are substituted for several macros contained in chemist package.
XyMTEX Utilities for Switching	
xymtex.sty	a package for calling all package files (listed in XyMTEX Structural Files) as well as chemist and assurechemist. Without loading xymtx-ps.sty and xymtx-pdf.sty (for the TEX/LATEX mode)
xymtexps.sty	a package for calling all package files (listed in XyMTEX Structural Files) and xymtx-ps (for the PostScript-compatible mode) as well as chemist, assurechemist, and chmst-ps. Not with xymtx-pdf
xymtexpdf.sty	a package for calling all package files (listed in XyMTEX Structural Files) and xymtx-pdf (for the PDF-compatible mode) as well as chemist, assurechemist, and chmst-pdf. Not with xymtx-ps.sty

Thereby, we obtain the corresponding dvi file named “test1.dvi”, which can be browsed or printed by using a dvi-ware such as dviout. The dvi file can be further converted into a PostScript file (e.g., by using dvips) or a PDF file (e.g., by using dvipdfmx).

The above procedure is a traditional one, in which a tex file is prepared by an editor and processed by using a command line of the Windows command prompt. Note that the LATEX processing depends on your system, if your system is an integrated one which combines an editor and the LATEX-system.

1.3.2 PostScript-Compatible Mode of X∑MTEX

The declaration of `\usepackage{xymtexps}` in the preamble of a tex file results in the reading of the xymtx-ps package as well as all the package files listed in the X∑MTEX Structural Files of Fig. 1.2. The drawing of structural formulas is based on the LATEX picture environment and the PSTricks package [25].

Preparation of TEX Files

When xymtexps.sty is input, all of the package files of the X∑MTEX system (also xymtx-ps.sty except xymtx-pdf.sty) are loaded. A typical template for the PostScript-compatible mode of X∑MTEX is shown as follows:

```
%test2.tex
\documentclass{article}
\usepackage{xymtexps}
\usepackage{xcolor}
\usepackage{graphicx}
\begin{document}
(formula)
\end{document}
```

To draw chemical equations, the packages chemist, assurechemist, and chmst-ps are automatically loaded. The packages xcolor and graphicx are loaded separately to enhance graphics.

This mode draws β/α-bonds in one format selected from a pair of wedged bonds/hashed dash bonds (default), a pair of wedged bonds/hashed wedged bonds, and a pair of dash bonds/hashed dash bonds.

LATEX Processing

Then the file (named “test2.tex” tentatively) is compiled by means of the LATEXsystem by inputting the following command in the command line of a personal computer.

```
C:> latex test2
```

Thereby, the LATEX processing starts to include the xymtx-ps package along with all of the X∑MTEX structural files collected in Table 1.2. The xymtx-ps.sty package internally includes pstricks.sty, pstricks.tex, and pstricks.con, which are distributed as part of the PSTricks package. After the processing, we obtain the corresponding dvi file (“test2.dvi”).

Conversion of dvi Files into PostScript Files

The resulting dvi file (named test2.dvi) should be converted into the corresponding PostScript file (named “test2.ps”) by inputting the following command:

```
C:> dvips test2
```

The resulting PostScript file (“test2.ps”) is browsed or printed by an appropriate PostScript viewer (e.g., Ghostscript and GSview) or printer.

Conversion of PostScript Files into PDF files

PostScript files such as “test2.ps” can be converted into PDF files by using the Adobe Distiller or the pdfwrite converter which is acceptable from the GSview.

1.3.3 PDF-Compatible Mode of X∑MTEX

The declaration of `\usepackage{xymtexpdf}` in the preamble of a ztex file results in the reading of the xymtx-pdf package as well as all the package files listed in the X∑MTEX Structural Files of Fig. 1.2. The drawing of structural formulas is based on the LATEX picture environment and the pgf package [26]. A dvi file produced by TEX/LATEX processing should be further converted into a PDF file by dvipdfm(x) in order to browse or printing X∑MTEX structural formulas.

Preparation of TEX Files

The macro codes for the PDF-compatible mode of XƎMTEX are defined in xymtx-pdf.sty, which is incompatible with xymtx-ps.sty for the PostScript-compatible mode. The following template (named "test3.tex") indicates a typical format for loading xymtexpdf.sty for the PDF-compatible mode of the XƎMTEX system.

```
%test3.tex
\documentclass{article}
\usepackage{xymtexpdf}
\usepackage{xcolor}
\usepackage{graphicx}
\begin{document}
(formula)
\end{document}
```

This mode draws β/α-bonds in one format selected from a pair of wedged bonds/hashed dash bonds (default), a pair of wedged bonds/hashed wedged bonds, and a pair of dash bonds/hashed dash bonds.

When you load the utility package xymtexpdf.sty by using `\usepackage` as above, all the package files listed in XƎMTEX Structural Files (Table 1.2) as well as xymtx-pdf.sty for the PDF-compatible mode of the XƎMTEX system are loaded to draw structural formulas. In addition, the packages chemist, assurechemist, and chmst-pdf are automatically loaded to draw chemical equations. The packages xcolor and graphicx are loaded separately to enhance graphics.

LATEX Processing

For the purpose of LATEX processing, you should type the following command in the command prompt:

```
c:> elatex test3
```

where the extended eTEX version of LATEX is used. Thereby, the corresponding dvi file ("test3.dvi") is produced.

Conversions by dvipdfm(x)

The dvi file is ready to be processed by the dvipdfm(x) converter by typing the following command in the command prompt:

```
c:> dvipdfmx test3
```

Thereby, we obtain a PDF file (named "test3.pdf"), which contains structural formulas drawn by the XƎMTEX system.

The resulting PDF file ("test3.pdf") is browsed or printed by an appropriate PDF viewer (e.g., Adobe Reader) or printer.

LATEX Processing With "dvips" Option

The standard PDF-compatible mode described above produces a dvi file suitable to the subsequent processing by the dvipdfm(x) converter, where the dvi file is converted into a PDF file. The PDF-compatible mode can alternatively produce a dvi file suitable to the dvips converter, which generates a PostScript file.

For the latter purpose, you should use a tex file in accord to the following template (named "test4.tex"), where the xymtexpdf package is loaded with the option "dvips":

```
%test4.tex
\documentclass{article}
\usepackage[dvips]{xymtexpdf}
\usepackage{xcolor}
\usepackage{graphicx}
\begin{document}
(formula)
\end{document}
```

For the purpose of LATEX processing, you should type the following command in the command prompt:

```
c:> elatex test4
```

where the extended eTEX version of LATEX is used. Thereby, the corresponding dvi file ("test4.dvi") is produced. The dvi file is ready to be processed by the dvips converter by typing the following command in the command prompt:

```
c:> dvips test4
```

The resulting PostScript file (named "test4.ps") contains structural formulas drawn by the XMTEX system.

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Chapter 2

General Principles of XMTEX Commands

2.1 How to Communicate Information on Organic Compounds

As found in textbooks on organic chemistry [1–4], information on organic compounds is communicated by the pairwise use of IUPAC names [5] and structural formulas. It follows that students, teachers, researchers, and engineers in the fields of organic chemistry are expected to be able to draw a structural formula by hearing an IUPAC name and reversely to remember an IUPAC name by glimpsing a structural formula. This way of communicating information on organic compounds suggests that an ultimate target of a drawing tool is to develop utilities of drawing structural formulas by inputting an IUPAC name. The XMTEX system pursues the ultimate target with appropriate and rational modifications for meeting the methodology of the TEX/LATEX system:

Main principle: The main and most important principle of the XMTEX system is that a XMTEX command is consistent with the way of the IUPAC nomenclature as far as possible.

The way of constructing IUPAC names consists of two steps:

1. A parent structure (or more specifically a parent hydride) is first selected and named in order to characterize an organic compound to be named.
2. Additional information on atoms, bonds, and others is specified by attaching prefixes, suffixes, etc. to the name of the selected parent structure.

Various operations for dividing the structure of a given organic compound into a parent structure and additional information are defined in the IUPAC recommendations [5].

According to the way of the IUPAC nomenclature, the way of constructing a XMTEX command consists of two steps in drawing the structural formula of a given organic compound:

1. A XMTEX command for specifying a parent structure is first selected.
2. Additional information on atoms, bonds, and others is treated by means of arguments and/or optional arguments attached to the XMTEX command.

The main principle of XMTEX commands provides us with an advantage that the inspection of a XMTEX command enables us to reproduce the structural formula without drawing it. This means that XMTEX commands can be used as a communication tool for digital communication. Thus, XMTEX commands can be regarded as linear notations, so that they are systematized to give the XM notation [6], which is further sophisticated to develop the XMML (XM markup language) for internet communication [7,8].

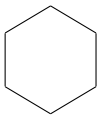
It should be emphasized again that structural formulas are not merely diagrams but have their own chemical meanings. Hence, codes for drawing structural formulas in themselves are desirable to aim at having

chemical meanings, as XeLaTeX commands are aiming at. In contrast, note that codes for drawing diagrams have no chemical meanings in themselves. In this context, it is worthwhile to mention that the selection of the XeLaTeX system (i.e., the selection of codes having chemical meanings) in preference to other systems based on commands of basic levels (i.e., codes having no chemical meanings) is akin to the selection of LaTeX in preference to plain TeX as well as the selection of programming languages of higher level (e.g., the C-language and the Java language) in preference to an assembly language as a low-level programming language.

In addition, an educational advantage of the XeLaTeX system should be mentioned, because the process of learning the IUPAC nomenclature is parallel to the process of conducting the XeLaTeX drawing. For the purpose of teaching compounds of a given type, for example, a XeLaTeX command corresponding to the parent structure of the type can be used to draw a compound at issue. At the same time, this drawing process can be linked to the naming due to the IUPAC nomenclature.

The following examples demonstrate the above-described features of XeLaTeX commands.

Example 2.1. A cyclic saturated hydrocarbon of carbon content 6 (**2-1**) is called *cyclohexane*, which is regarded as a **parent structure**, or more specifically as a **parent hydride** (P-12.1 of [5]). The structural formula of cyclohexane as a parent structure is shown as follows:



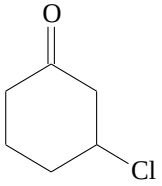
2-1

This formula is drawn by the following XeLaTeX command:

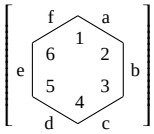
```
\cyclohexanev{}
```

where the suffix `v` of the command `\cyclohexanev` specifies the vertical direction of the printed formula. The empty pair of braces represents the absence of substituents to be specified. □

Example 2.2. In order to name a compound, various formal **operations** must be carried out (P-12.1 of [5]). For example, the structure shown bellow (**2-2**) is named *3-chlorocyclohexanone*.



2-2



2-3

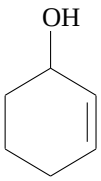
In this naming, the parent hydride ‘cyclohexane’ is selected first. Then the suffix ‘one’ and the prefix ‘chloro’, indicating **substitution** of the hydrogen atoms of cyclohexane, are attached to the name of the parent hydride, where the locant number 1 for the ‘one’ (in the full name *3-chlorocyclohexan-1-one*) is omitted because such omission provides no confusion.

The formula **2-2** is drawn by the XeLaTeX code shown below:

```
\cyclohexanev{1D==O;3==Cl}
```

where `1D==O` corresponds to the suffix ‘one’ and `3==Cl` corresponds to the prefix ‘chloro’. The locant numbering of the command `\cyclohexanev` is given in the diagram shown in **2-3**. Although the carbonyl group and the chloro substituent are differently expressed by the suffix ‘one’ and the prefix ‘chloro’ in terms of the IUPAC nomenclature, the above XeLaTeX command regards them as substituents in a unified fashion, where such substituents are written in the attached pair of braces. □

Example 2.3. The mode of unsaturation is represented by the suffix ‘ene’. For example, the structure shown bellow (**2-4**) is named *cyclohex-2-en-1-ol*.



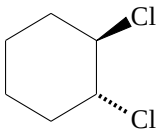
2-4

The formula **2-4** is drawn by the following XƎMTEX command:

```
\cyclohexanev[b]{1==OH}
```

where the optional argument `[b]` corresponds to the suffix 'ene', while the regular argument `{1==OH}` corresponds to the suffix 'ol'. Because the suffix 'ene' is considered to represent a 'substitution' on a bond (not on a hydrogen or not on a vertex diagrammatically), the XƎMTEX command uses the optional argument `[b]` with a pair of bracket, where the letter `b` represents a double-bond modification of the bond specified by such a locant alphabet as `a`, `b`, . . ., or `f` (**2-3**). The suffix 'ol' is treated as a usual substituent on a hydrogen (or on a vertex diagrammatically), which appears as a regular argument in the pair of braces, i.e., `{1==OH}`. □

Example 2.4. The most common way to represent spatial configuration is through the insertion of special bond types, e.g., bold, hashed, dashed, and/or wedged, among an otherwise planar depiction of straight-lined bonds [9]. For example, the compound named *trans-1,2-dichlorocyclohexane* is depicted below.



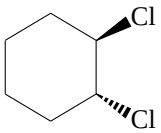
2-5

The formula **2-5** is drawn by the following XƎMTEX command:

```
\cyclohexanev{2B==Cl;3A==Cl}
```

where the prefix '*trans*-1,2-dichloro' corresponds to the argument `{2B==Cl;3A==Cl}`. Note that the bond modifier `B` is used to output a β-bond depicted by a solid wedge, while the bond modifier `A` is used to output a α-bond depicted by a hashed bond. Thus, the combination of a solid wedge and a hashed bond is selected as a default way to represent spatial configuration in the XƎMTEX system (the PostScript-compatible mode and the PDF-compatible mode). Note that the command `\wedgehasheddash` is globally declared to select the combination of a solid wedge and a hashed bond under a default condition. □

Example 2.5. On the other hand, the combination of a solid wedge and a hashed wedge is selected as a preferred representation of spatial configuration in the IUPAC recommendations 2006 "Graphical Representation of Stereochemical Configuration (IUPAC Recommendations 2006)" [9]. Although an unwedged hashed bond is recognized to be acceptable, the majority of the IUPAC recommendations 2006 [9] is concerned with the proper use of hashed wedged and solid wedges bonds. If we obey the IUPAC recommendations 2006, the structural formula of *trans*-1,2-dichlorocyclohexane is depicted below.



2-6

The formula **2-6** is drawn by the following XƎMTEX command:

```
{\wedgehashedwedge
\cyclohexanev{2B==Cl;3A==Cl}
}
```

where the command `\wedgehashedwedge` is locally declared to select the combination of a solid wedge and a hashed wedge. If the command `\wedgehashedwedge` is globally declared in the preamble of a tex file:

```
\documentclass{article}
\usepackage{xymtexpdf}%%PDF-compatible mode
%\usepackage{xymtexps}%%PostScript-compatible mode
\wedgehashedwedge%global declaration
\begin{document}
\cyclohexanev{2B==Cl;3A==Cl}
\end{document}
```

the combination of a solid wedge and a hashed wedge (**2-6**) is selected as a default mode of drawing spatial configuration in the XyMTEX system (the PostScript-compatible mode and the PDF-compatible mode). □

2.2 Parent Structures and Parent Hydrides

Chapter P-2 of the IUPAC Provisional Recommendations 2004 [5] summarizes various **parent structures** (or more specifically **parent hydrides**). Although the ultimate target of the XyMTEXsystem is to be equipped with commands for drawing respective parent structures, the state of the art of the XyMTEX system supports representative parent structures, which aim at the preparation of papers and books on organic chemistry, e.g. [10]. Note that the selection of parent structures is concerned with the first step itemized in page 11, because such parent structure are linked with the names of the XyMTEX commands.

2.2.1 XyMTEX Commands for Specific Use

Among such parent structures, Fig. 2.1 collects examples of monocyclic parent hydrides and heterocyclic parent hydrides, which have been selected from the lists of the IUPAC Provisional Recommendations 2004 [5, P-22.1 and P-22.2]. As shown below the structural formulas in Fig. 2.1, the XyMTEX commands correspond to the parent structures of specific kinds, which are designated by the IUPAC names. They have the abstract syntax:

```
\ComSpec[⟨bondlist⟩]{⟨subslist⟩}
```

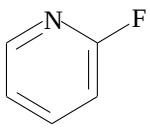
where the command name `\ComSpec` corresponds to the IUPAC name (or an appropriate related name) of a compound to be typeset. It is usually attached by a suffix `v` or `h`, which respectively denotes a vertical or horizontal representation of the structural formula, e.g., `\cyclopropanev` (**2-7**) and `\cyclopropaneh`. The command name is attached by a further suffix `i`, e.g., `\cyclopropanevi` and `\cyclopropanehi`, if alternative orientations are possible. If the optional argument ⟨bondlist⟩ is not declared, a preselected bond pattern is typeset, dependent of the IUPAC name based on the command `\ComSpec`. The optional argument ⟨bondlist⟩ is used to change the preselected bond pattern. The argument ⟨subslist⟩ is used to list substituents. More details of the syntax will be described later.

Remember the two steps itemized in page 11. The command name `\ComSpec` corresponds to the first step, while the argument ⟨subslist⟩ as well as the optional argument ⟨bondlist⟩ is concerned with the second step.

Commands for Monocyclic Compounds

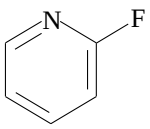
As examples of `\ComSpec`, the XyMTEX commands listed in Fig. 2.1 are capable of drawing monocyclic compounds in accord with the way described in Section 2.1.

Example 2.6. The compound named *2-fluoropyridine* is drawn in various ways:



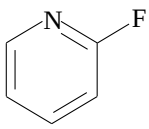
2-20

`\pyridinev{2==F}`



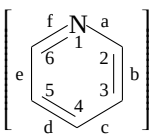
2-21

`\pyridinev[bdf]{2==F}`



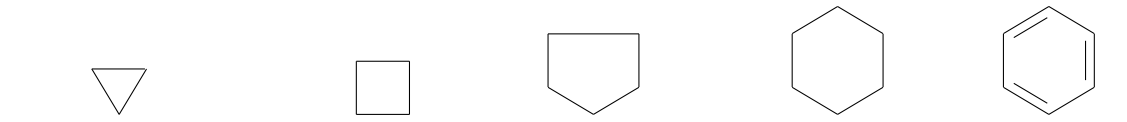
2-22

`\pyridinev[ace]{2==F}`



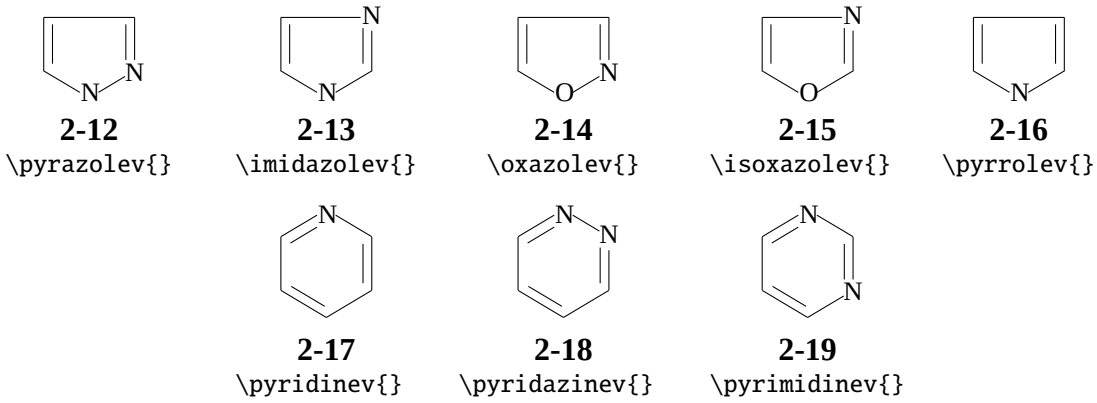
2-23

Monocyclic hydrocarbons (P-22.1 [5])



2-7 `\cyclopropanev{}` **2-8** `\cyclobutane{}` **2-9** `\cyclopentanev{}` **2-10** `\cyclohexanev{}` **2-11** `\benzenev{}`

Heterocyclic parent hydrides (P-22.2 [5])



2-12 `\pyrazolev{}` **2-13** `\imidazolev{}` **2-14** `\oxazolev{}` **2-15** `\isoxazolev{}` **2-16** `\pyrrolev{}`

2-17 `\pyridinev{}` **2-18** `\pyridazinev{}` **2-19** `\pyrimidinev{}`

Figure 2.1. Examples of monocyclic parent hydrides. The XƎMTEX commands shown below the structural formulas correspond to the respective IUPAC names, where each vacant pair of braces is used to specify substituents if necessary. These commands are categorized as XƎMTEX commands for specific use (`\ComSpec`).

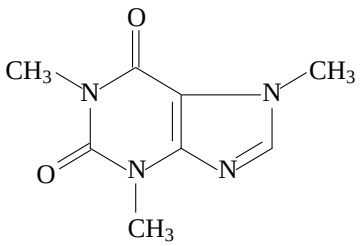
The formulas **2-20**–**2-22** are drawn by the XƎMTEX commands shown below the respective structural formulas, where `2==F` corresponds to the prefix '2-fluoro'. The optional argument ⟨bondlist⟩ is used to change the bond pattern of **2-20** (with no ⟨bondlist⟩), which is preselected by setting `[bdf]` in the argument ⟨bondlist⟩, as shown in **2-21**. The preselected bond pattern can be changed into an alternative expression of **2-22** (`ace`: a bond list) as well as other expressions described below (cf. mancude-ring systems). □

Commands for Fused Ring Systems

On the other hand, Fig. 2.2 collects examples of fused cyclic parent hydrides, which have been shown in the lists of the IUPAC Provisional Recommendations 2004 [5, P-25.1]. The XƎMTEX commands shown below the structural formulas have the abstract syntax shown above (`\ComSpec`), where the names for `\ComSpec` correspond to the respective IUPAC names. Each vacant pair of braces is used to specify substituents if necessary.

The XƎMTEX commands listed in Fig. 2.2 are capable of drawing derivatives in accord with the way described in Section 2.1.

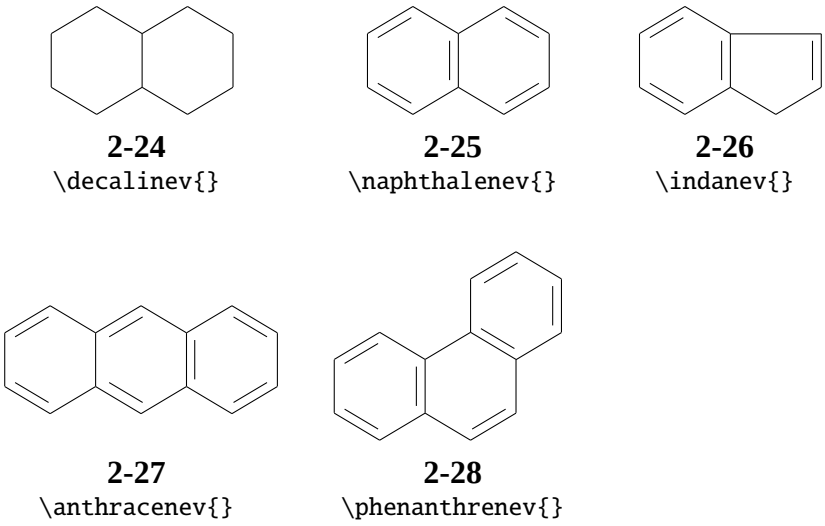
Example 2.7. Caffeine, the IUPAC name of which is 1,3,7-trimethyl-1*H*-purine-2,6(3*H*,7*H*)-dione, is represented by the following structural formula:



2-35

The formula **2-35** is drawn by the following XƎMTEX command:

Fused hydrocarbons as parent hydrides (P-25.1 [5])



Fused heterocyclic parent hydrides (P-25.1 [5])

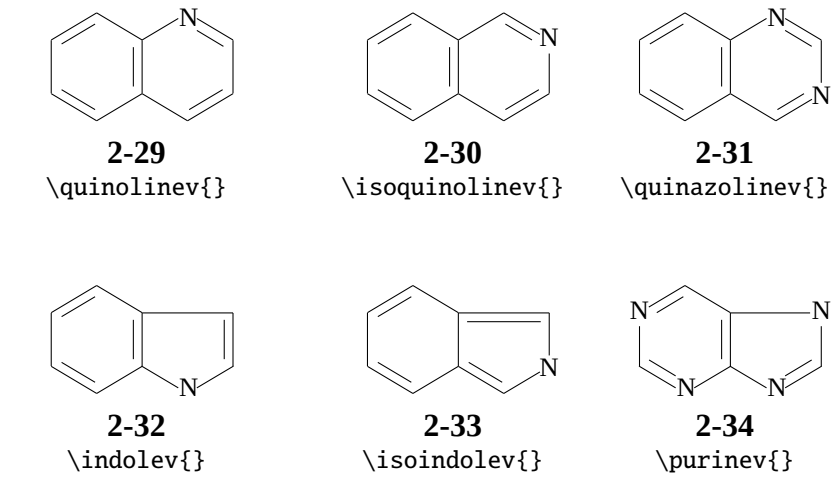
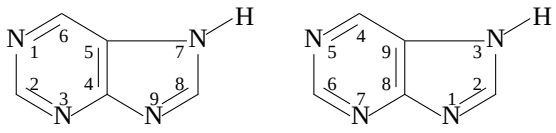


Figure 2.2. Examples of fused heterocyclic parent hydrides. The XƎMTEX commands shown below the structural formulas correspond to the respective IUPAC names, where each vacant pair of braces is used to specify substituents if necessary. These commands are categorized as XƎMTEX commands for specific use (\ComSpec).

```
\purinev[aj]{4D==O;6D==O;3==CH$_{3}$;5==CH$_{3}$;7==CH$_{3}$}
```

where a purine skeleton is selected as a parent structure.

The locant numbering of the IUPAC name of purine (**2-36**) is rather irregular, because it is regarded as a six-membered pyrimidine ring fused by a five-membered imidazole ring.



The XƎMTEX numbering shown in the formula **2-37** is selected to be good for at other 6-5 fused rings. Thus, the locant numbering of `\purinev` (**2-34**) shown in **2-37** is common to those of `\indanev` (**2-26**), `\indolev` (**2-32**), and `\isoindolev` (**2-33**). □

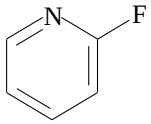
Mancude-Ring Systems as Parent Structures

A ring having (formally) the maximum number of non-cumulative double bonds is termed *mancude* [11, page 1348]. A mancude ring system or a fully saturated ring system is selected as a parent structure in the IUPAC nomenclature [5].

When a mancude ring system is selected as a parent structure, its preselected double bonds are printed out by using a XƎMTEX command for specific use without declaring ⟨bondlist⟩ (cf. Figs. 2.1 and 2.2). Because such a mancude ring system can be drawn as alternative diagrams with one or more modes of printing double bonds, it is convenient to draw these alternative diagrams optionally within the methodology of the XƎMTEX system. The output mode of double bonds can be changed by designating locant alphabets one by one, as found by comparing between **2-20** (with no ⟨bondlist⟩) and **2-22** (with the ⟨bondlist⟩ `[ace]` as a bond list).

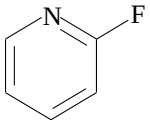
In addition to the *one-by-one declaration* of ⟨bondlist⟩, another mode of declaration (a *bond-pattern declaration*) is available in the usage of XƎMTEX commands of specific use.

Example 2.8. In place of no declaration of ⟨bondlist⟩ (**2-20**) as well as a one-by-one declaration `[bdf]` (**2-39**), a bond-pattern declaration `[r]` (a right-hand bond pattern) in the ⟨bondlist⟩ of `\pyridinev[r]{2==F}` is permissible to draw the same structural formula (**2-38**) as a mancude ring system.



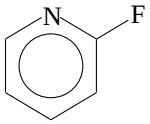
2-38 (= 2-20)

`\pyridinev[r]{2==F}`



2-39 (= 2-22)

`\pyridinev[l]{2==F}`



2-40

`\pyridinev[A]{2==F}`

In place of a one-by-one declaration `[ace]` (**2-21**), a bond-pattern declaration `[l]` (a left-hand bond pattern) in the ⟨bondlist⟩ of `\pyridinev[l]{2==F}` is permissible to draw the same structural formula (**2-39**) as a mancude ring system.

When a bond-pattern `[A]` (an aromatic bond pattern) is declared in the ⟨bondlist⟩ of the code `\pyridinev[A]{2==F}`, a structural formula (**2-40**) is obtained as an alternative expression, in which an inner circle denotes a conjugated double-bond system. □

2.2.2 XƎMTEX Commands for General Use

It is impossible that XƎMTEX commands for specific use cover all of the parent structures listed in the IUPAC nomenclature [5]. Hence, it is desirable to develop XƎMTEXcommands for general use, which support a wider range of compounds at the cost of additional specification. They have the abstract syntax:[a]

```
\ComGen[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}
```

where the command name `\ComGen` corresponds to the name of a compound type to be typeset. The above-mentioned suffixes `v` and `h` along with `i` are also effective to this type of commands. If the optional argument ⟨bondlist⟩ is not declared, no preselected bond pattern is typeset. The optional argument ⟨bondlist⟩ is used to change the preselected bond pattern. The argument ⟨atomlist⟩ is used to list atoms for replacing skeletal vertices. The argument ⟨subslist⟩ is used to list substituents. More details of the syntax will be described later.

Remember again the two steps itemized in page 11. The command name `\ComGen` corresponds to the first step, while the arguments ⟨atomlist⟩ and ⟨subslist⟩ as well as the optional argument ⟨bondlist⟩ are concerned with the second step.

[a] This syntax is a simplified format, where optional arguments non-essential to the present discussions are omitted. The full form of the syntax will be discussed in Chapter 3.

Examples of XeLaTeX commands for general use (\ComGen) are collected in Fig. 2.3, where the arguments ⟨atomlist⟩ and ⟨subslist⟩ are vacant and the optional argument ⟨bondlist⟩ is omitted.

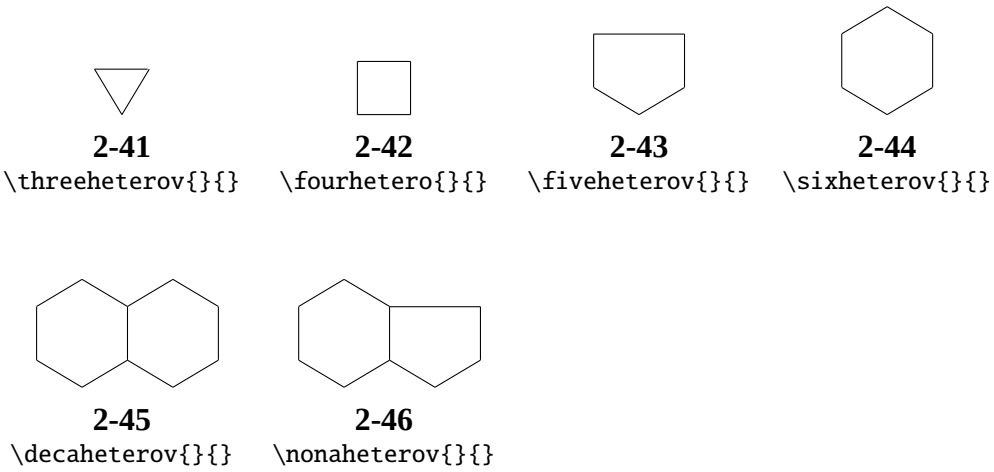
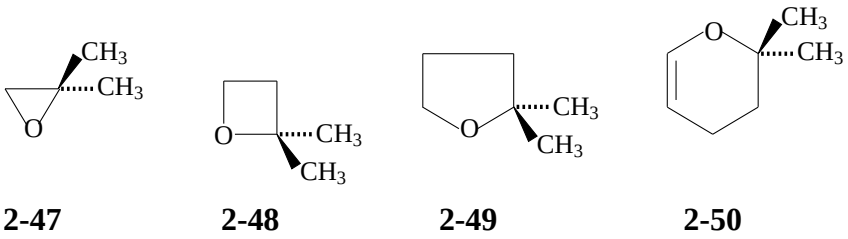


Figure 2.3. Examples of parent structures drawn by the XeLaTeX commands for general use (\ComGen), where each vacant pair of braces is used to specify skeletal atoms or substituents if necessary.

Example 2.9. By using the XeLaTeX commands for general use, 2,2-dimethyloxirane (**2-47**), 2,2-dimethyloxetane (**2-48**), 2,2-dimethyltetrahyrofurane (**2-49**), and 2,2-dimethyl-3,4-dihydro-2*H*-pyrane (**2-50**) are drawn as follows:



2-47 **2-48** **2-49** **2-50**

The modes of specifying arguments are shown below:

```
\threeheterov{1==O}{2SA==CH$_{3}$;2SB==CH$_{3}$}
\fourhetero{1==O}{2SA==CH$_{3}$;2SB==CH$_{3}$}
\fiveheterov{1==O}{2SA==CH$_{3}$;2SB==CH$_{3}$}
\sixheterov[e]{1==O}{2SA==CH$_{3}$;2SB==CH$_{3}$}
```

Heteromonocyclic parent hydrides are named in terms of the Hantzsch-Widman system, e.g., oxirane and oxetane [5, P-22.2]. These examples can be regarded as demonstrating replacement operations, which will be discussed later. □

2.3 Operations in the IUPAC Nomenclature

Operations in the IUPAC nomenclature [5, P-13] are structural modifications, by which parent structures are modified to give the IUPAC names of their derivatives. The modes of such operations correspond to the modes of structural modifications in the XeLaTeX system. Note that such operations are concerned with the second step itemized in page 11, where they are linked with the arguments ⟨subslist⟩, ⟨bondlist⟩, and/or ⟨atomlist⟩ appearing in XeLaTeX commands for specific use (\ComSpec) and for general use (\ComGen).

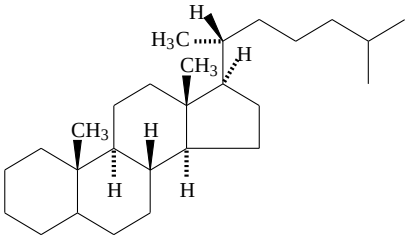
The arguments ⟨subslist⟩, ⟨bondlist⟩, and ⟨atomlist⟩ in the XeLaTeX system respectively support the substitution technique, the addition technique, and the replacement technique, which are linked to the respective operations in the IUPAC Nomenclature.

This section is devoted to a brief explanation on operations in the IUPAC Nomenclature in order to give an introduction to the techniques of the XƎMTEX system (the substitution technique, the addition technique, and the replacement technique).

2.3.1 Substitutive Operation

The substitutive operation [5, P-13.1] involves the exchange of one or more hydrogen atoms for another atom or group of atoms, as already described in Sections 2.1 and 2.2. Substitutive operation in the general principles of XƎMTEX commands would be demonstrated more clearly by referring to complicated natural compounds as examples. Let us consider steroid derivatives as such complicated compounds.

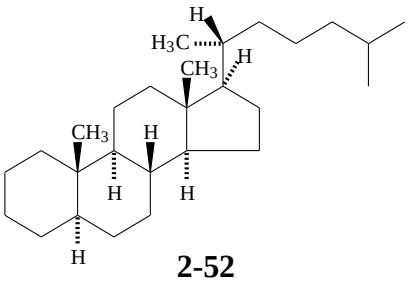
Example 2.10. Cholestane (**2-51**), which is a kind of steroid, is regarded as a parent hydride [5, P-101.2.5]). Such a complicated structure can be drawn by inputting a simple XƎMTEX command, i.e., `\cholestane{}`.



2-51

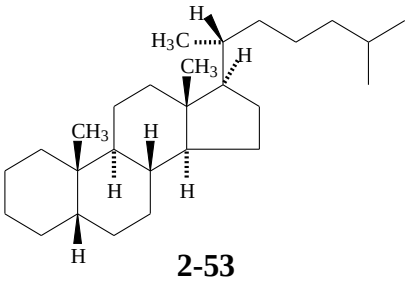
IUPAC name: cholestane
XƎMTEX command: `\cholestane{}`

The command `\cholestane` is a XƎMTEX command for specific use. The configuration at the 5-position is denoted by the argument ⟨subslist⟩ as shown in **2-52** and **2-53**:



2-52

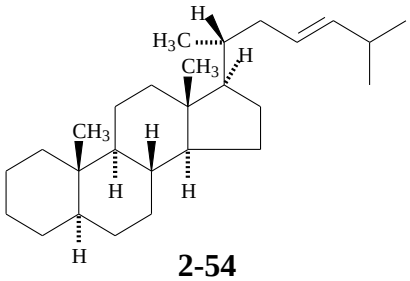
IUPAC name: 5α-cholestane
XƎMTEX command: `\cholestane{5A==H}`



2-53

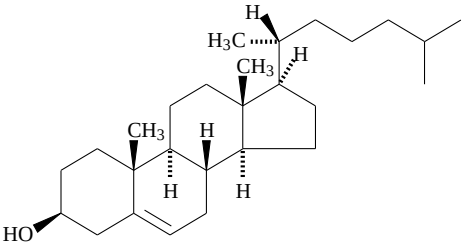
IUPAC name: 5β-cholestane
XƎMTEX command: `\cholestane{5B==H}`

The cholestane structure as a parent hydride is used to draw a derivative **2-54** with a double bond at the side chain by specifying the optional argument ⟨bondlist⟩. The 5α-configuration is specified by the argument ⟨subslist⟩. In a similar way, cholesterol (**2-55**), the IUPAC name of which is cholest-5-en-3β-ol, is drawn by using the optional argument ⟨bondlist⟩ and the argument ⟨subslist⟩.



2-54

IUPAC name:
(23*E*)-5α-cholest-23-ene [5,P-101-6.2]
XƎMTEX command: `\cholestane[@{Zd}]{5A==H}`



2-55

common name: cholesterol
IUPAC name: cholest-5-en-3β-ol
XeTeX command: `\cholestane[e]{3B==HO}`

A XeTeX command such as `\cholestane` for specific use can be regarded as a short-cut of a XeTeX command for general use or of a set of commands of lower level. This point will be discussed later in detail. Note that the input `[@{Zd}]` contains an ad-hoc declaration of '@', which avoids an erroneous result during the processing. □

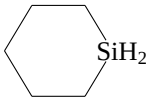
2.3.2 Replacement Operation

The replacement operation [5, P-13.2] involves the exchange of one group of atoms or single non-hydrogen atom for another. Example 2.9 shows several examples by starting from the parent structures drawn by the XeTeX commands for general use (Fig. 2.3). Although the case of Example 2.9 is categorized to be substitution operation in IUPAC Provisional Recommendations 2004 [5], it is discussed here for the sake of convenience.

Skeletal Replacement ('a') Nomenclature

Skeletal replacements of carbon atoms by O, S, N, Si, etc. produce organic compounds regarded as subsidiary parent structures [5, P-13.2.1]. So-called replacement ('a') prefixes (e.g., oxa, thia, aza, sila, etc.) represent the elements being introduced [5, P-15.4].

Example 2.11. Let us draw silacyclohexane (**2-56**). The XeTeX command `\cyclohexanev` for specific use (`\ComSpec`) is incapable of specifying skeletal replacements. Hence, we should use the XeTeX command `\sixheterov` or `\sixheteroh` for general use (`\ComGen`), where the argument ⟨atomlist⟩ is used to accomplish the skeletal replacement.

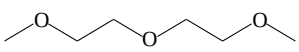


2-56

IUPAC name: silacyclohexane
XeTeX command: `\sixheteroh{4==SiH$_{2}$}{}`

The 'a' prefix 'sila' represents the replacement of the carbon atom for a silicon atom. □

Example 2.12. Let us next draw diethylene glycol dimethyl ether (**2-57**), which is named '2,5,8-trioxanonane' in terms of the IUPAC replacement procedure. We use the XeTeX command `\nonamethylene` for general use (`\ComGen`), where the argument ⟨atomlist⟩ is used to accomplish the skeletal replacement.



2-57

common name: diethylene glycol dimethyl ether
IUPAC name: 2,5,8-trioxanonane
XeTeX command: `\nonamethylene{2==O;5==O;8==O}{}`

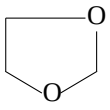
The 'a' prefix 'trioxa' represents the replacement of three carbon atoms for oxygen atoms. For an educational purpose, we are able to define a new XeTeX command `\nonane`, which demonstrates more clearly the correspondence between the XeTeX command and the IUPAC name '2,5,8-trioxanonane':

```
\let\nonane=\nonamethylene
\nonane{2==O;5==O;8==O}{}
```

This code typeset the same structural formula as **2-57**. □

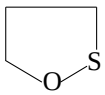
Hantzsch-Widman Names

As shown in Example 2.9, heteromonocyclic parent hydrides are named in terms of the Hantzsch-Widman system [5, P-22.2]. Following examples use the XeTeX command `\fiveheterov` for general use, where the argument ⟨atomlist⟩ is used to specify skeletal replacements.



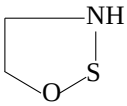
2-58

IUPAC name: 1,3-dioxolane
XeTeX command: `\fiveheterov{1==O;3==O}{}`



2-59

IUPAC name: 1,2-oxathiolane
XeTeX command: `\fiveheterov{1==O;2==S}{}`



2-60

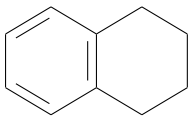
IUPAC name: 1,2,3-oxathiazolidine
XeTeX command: `\fiveheterov{1==O;2==S;3==NH}{}`

2.3.3 Additive Operation

The additive operation involves the addition of component parts without loss of original atoms or groups [5, P-13.3].

Use of an Additive Prefix

One way of additive operations [5, P-13.3.1] is exemplified by the derivation of 1,2,3,4-tetrahydronaphthalene from naphthalene, where the prefix 'hydro' means the addition of one hydrogen atom.



2-61

common name: tetraline
IUPAC name: 1,2,3,4-tetrahydronaphthalene
XeTeX command: `\naphthalenev[fhk]{}`

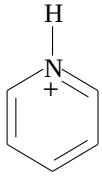
The command `\naphthalenev[@]{}` for specific use cancels all the preselected setting, when the vain argument `[@]` (as ⟨bondlist⟩) is declared. Hence, the resetting of `[fhk]` is necessary to draw the left-hand aromatic ring.

Because `\tetralinev` and `\decalinev` are equipped as XeTeX commands for special use, the following codes depict the same structural formula as **2-61**:

```
\tetralinev{}
\decalinev[fhk]{}
```

Use of an Additive Suffix

Another way of additive operations [5, P-13.3.2] is exemplified by the derivation of pyridinium from pyridine, where the suffix 'ium' means the addition of one H^+.

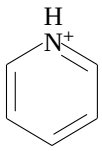


2-62

IUPAC name: pyridinium
XeTeX command: `\pyridinev[{1+}ace]{1==H}`

The designation `{1+}` in the optional argument ⟨bondlist⟩ prints out a plus charge. The designation `[ace]` is necessary to revive the double bonds of the pyridine ring.

If the bond between N^+—H is not desirable, the XeTeX command `\sixheterov` for general use can be used as follows:



2-63

IUPAC name: pyridinium
XƎMTEX command: `\sixheterov[ace]{1==\upnobond{N\rlap{$^{+}$}}{H}}{}`

The designation `\upnobond{N\rlap{$^{+}$}}{H}` prints out the group $\overset{H}{N^+}$ at the top vertex of the hexagonal diagram.

2.3.4 Other Operations

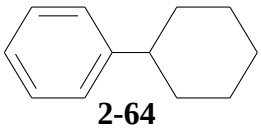
Chapter P-1 of the IUPAC Provisional Recommendations 2004 [5] describes other operations, e.g., conjunctive operation [5, P-13.5], multiplicative operation [5, P-13.6], and fusion operation [5, P-13.7]. The latter two operations will be explained after naming methods of monovalent substituent groups are discussed.

2.4 Monovalent Substituent Groups and a (yl)-Function for the Substitution Technique

Chapter P-2 of the IUPAC Provisional Recommendations 2004 [5] has discussed the general methodology for naming substituent groups [5, P-29.2].

1. In terms of 'specific method' [5, P-29.2.1], the suffixes 'yl', 'ylidene', and 'ylidyne' replace the ending 'ane' of the parent hydride name, e.g., 'cyclohexane' is converted into 'cyclohexyl'.
2. In terms of 'general method' [5, P-29.2.2], the suffix 'yl', 'ylidene', or 'ylidyne' is added to the name of the parent hydride with elision of the terminal letter 'e', e.g., 'propane' is converted into 'propan-2-yl'.

Such a monovalent substitution group is supplied to substitution of a hydrogen atom of a parent structure. For example, cyclohexylbenzene corresponds to the following structural formula (**2-64**):



2-64

where a benzene ring is selected as a parent structure and the substituted cyclohexyl group is a monovalent substitution group derived by the 'specific method' [5, P-29.2.1].

> The XƎMTEX commands of specific and general use support a *(yl)-function* in order to treat both the specific method [5, P-29.2.1] and the general method [5, P-29.2.2] for generating substituent groups.

For example, suppose that a (yl)-function is declared in the argument ⟨subslist⟩ of the command `\cyclohexaneh`. Then, the original control point (0,0) of the drawing area assigned to the command `\cyclohexaneh` is moved to the position designated by the (yl)-function, as shown in Fig. 2.4. The parent structure **2-65** is drawn by inputting `\cyclohexaneh{1==H}`, where the hydrogen to be substituted in terms of the 'specific method' [5, P-29.2.1] is designated explicitly. By declaring a (yl)-function as found in `\cyclohexaneh{1==(yl)}`, the control point (0,0) is shifted onto the new vertex of locant number 1, as designated by a red solid circle in **2-66**.

Thereby, the resulting cyclohexyl group (**2-66**) is ready to occupy an appropriate position of a given parent structure.

Example 2.13. Let us draw the structural formula of cyclohexylbenzene (**2-64**). What you should do is to include the code of the cyclohexyl group (**2-66**) in the code of benzene as a parent structure. Thereby, we are able to obtain the following structure:

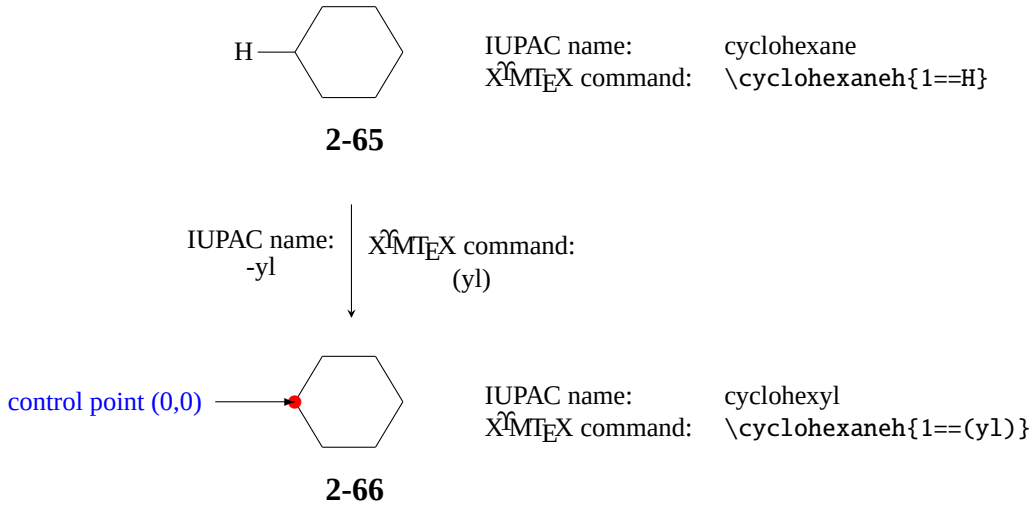
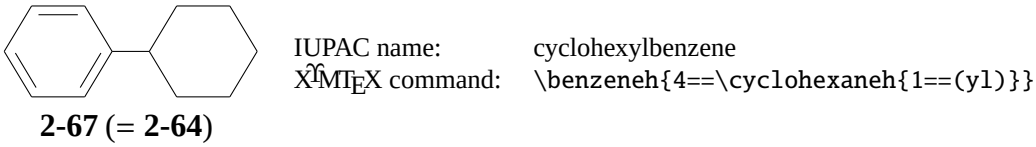
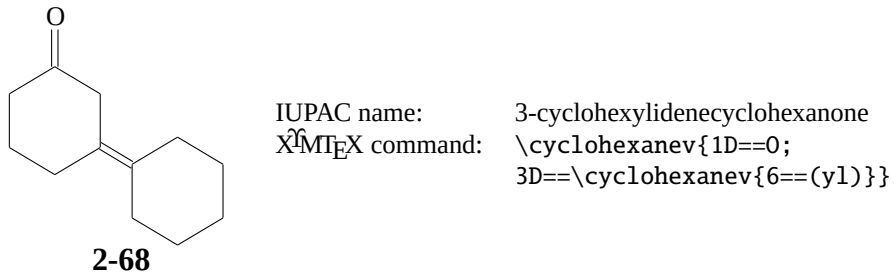


Figure 2.4. Substituent produced by a (yl)-function. The original control point of a XeLaTeX command is shifted to a new position to be attached.



The control point (0,0) of **2-66** is located at the endpoint of a single bond of a parent benzene.

A monovalent substituent group generated by a (yl)-function is used as a moiety of -ylidene along with a moiety of -yl, as shown in the following example:

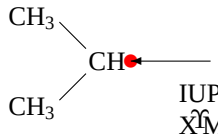


Note that such a moiety as **2-66** retains no valence bond on the vertex of the control point (0,0). Whether a linking bond is single or double is determined by the absence or presence of a bond modifier `D` in the argument ⟨subslist⟩ of the parent structure. □

As shown in Example 2.13, the declaration of a substituent generated by a (yl)-function in the ⟨subslist⟩ of a parent structure is a versatile methodology for drawing a substitution derivative of the parent structure.

Substitution technique: Hereafter, the methodology using the ⟨subslist⟩ of a parent structure is called *the substitution technique*, because it mimics the substitutive operation of the IUPAC nomenclature (cf. Subsection 2.3.1).

Example 2.14. Let us draw the structural formula of cumene (IUPAC name: propan-2-ylbenzene). A propan-2-yl moiety as a substituent group is generated by using a (yl) function in a XeLaTeX command `\ltrigonal` for specific use, which draws a central atom with three substituents through bonds. One of the three substituents is a hydrogen to be replaced in accord with the 'general method' [5, P-29.2.2], so that the declaration of a (yl)-function produces a propan-2-yl moiety as a substituent group:

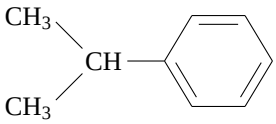


IUPAC name: propan-2-yl
XeLaTeX command:

2-69

```
\ltrigonal{0==CH;1==(yl);2==CH$_{3}$;3==CH$_{3}$}
```

This code is involved in the argument ⟨subslist⟩ of `\benzeneh` for drawing a parent structure. Thereby, we obtain the structural formula of cumene (IUPAC name: propan-2-ylbenzene).



2-70

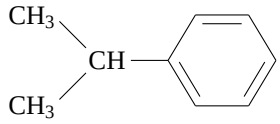
common name: cumene
IUPAC name: propan-2-ylbenzene
XeLaTeX command:

```
\benzeneh{1==%
\ltrigonal{0==CH;1==(yl);2==CH$_{3}$;3==CH$_{3}$}}
```

In order to write a succinct code, we can define a short-cut command:

```
\def\propanIIyl{\ltrigonal{0==CH;1==(yl);2==CH$_{3}$;3==CH$_{3}$}}
```

Then, the new command `\propanIIyl` is used in place of the original code due to `\ltrigonal`, so as to give the same structure as **2-70**.

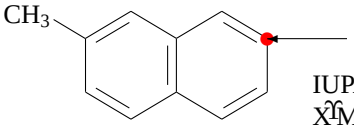


2-70′

common name: cumene
IUPAC name: propan-2-ylbenzene
XeLaTeX command: `\benzeneh{1==\propanIIyl}`

By using such a short-cut command as `\propanIIyl`, the correspondence between the IUPAC name and the XeLaTeX command becomes traceable easily. □

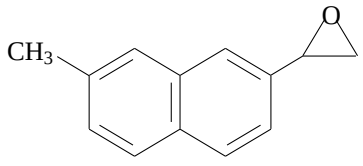
Example 2.15. The general method [5, P-29.2.2] is applied to all mancude rings and ring systems (mancude: maximum number of non-cumulative double bond), as described in [5, P-29.3.4]. For example, 7-methylnaphthalen-2-yl is derived from 2-methylnaphthalene in term of the general method by declaring a (yl)-function in the argument ⟨subslist⟩ of the XeLaTeX command `\naphthalenev`.



IUPAC name: 7-methylnaphthalen-2-yl
XeLaTeX command: `\naphthalenev{2==(yl);7==CH$_{3}$}`

2-71

Let us consider oxirane as a parent structure, which is drawn by using the XeLaTeX command `\threeheterovi` for general use. The above-mentioned code for drawing 7-methylnaphthalen-2-yl is involved in the argument ⟨subslist⟩ of `\threeheterovi`. Thereby, we obtain the structural formula to be drawn:



IUPAC name: 2-(7-methylnaphthalen-2-yl)oxirane
XeLaTeX command:

```
\threeheterovi{1==O}{%
3==\naphthalenev{2==(yl);7==CH$_{3}$}}
```

2-72

Note that the locant numbers (1 to 3) of the command `\threeheterovi` are fixed in a clockwise fashion by starting from the top vertex of a triangle. □

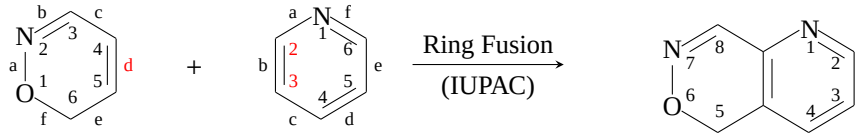
2.5 Fused Ring Systems and the Addition Technique

The fusion operation involves the union of two rings or ring systems so that atoms or atoms and bonds are common to each. Spiro systems have one atom in common; fused ring systems have both atoms and bonds in common [5, P-13.7]. More detailed descriptions on fused and bridged fused systems appear in [5, P-25].

2.5.1 IUPAC Fusion Names

IUPAC fusion names are constructed in terms of the combination of a parent component with attached components [5, P-25.3]. The parent component is selected by applying criteria of seniority [5, P-25.3.2.4], where the name of the parent component is used as the stem of a fusion name. The names of attached components are formed by replacing the last letter 'e' by 'o' in the name of the attached component.

As an example, let us construct an IUPAC name for the structure represented by **2-75**, i.e., 5*H*-pyrido[2,3-d][1,2]oxazine. Because one of the criteria of seniority [5, P-25.3.2.4] is to select a component containing the greater number of heteroatoms of any kind, 6*H*-1,2-oxazine (**2-73**) is selected as a parent component, which is characterized by locant numbers for the six vertices as well as by locant alphabets for six edges (bonds). On the other hand, pyridine is selected as an attached component, which is also characterized by locant numbers for the six vertices and by locant alphabets for six edges (bonds).



2-73 (6*H*-1,2-oxazine) + **2-74** (pyridine) → **2-75** (5*H*-pyrido[2,3-d][1,2]oxazine)

The ring fusion between the two rings occurs at the *d*-bond of the parent component **2-73** and at the 2,3-bond of the attached component **2-74**, so that the numbers and letters are enclosed in square brackets, i.e., [2,3-*d*], and placed immediately after the designation 'pyrido' of the attached component. Finally, an indicated hydrogen atom, i.e., 5*H*, is added to the name, using a locant number characterizing the fused system **2-75**. Thereby, we are able to obtain the IUPAC name: 5*H*-pyrido[2,3-d][1,2]oxazine.

XƎMTEX commands for ring fusion mimic the above-mentioned methodology of constructing IUPAC names for fused rings, except that locant alphabets are used to designate both the fusion positions of parent components and attached components.

2.5.2 XƎMTEX Commands for Ring Fusion

To treat fused ring systems, the XƎMTEX system supports several commands for typesetting three- to six-membered cyclic fusing units. They have the abstract syntax:[b]

```
\ComFuse[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}{⟨fuse⟩}
```

where the command name `\ComFuse` corresponds to the name of units to be typeset. The newly-introduced argument ⟨fuse⟩ indicates the locant alphabet of a bond (edge) at which the fusion of the unit occurs.

Example 2.16. Let us draw 5*H*-pyrido[2,3-d][1,2]oxazine (**2-75**), where the parent component **2-73** is drawn by using `\sixheterov` (as `\ComGen`), while the attached component **2-74** is drawn by using `\sixfusev` (as `\ComFuse`).

2-76 (6*H*-1,2-oxazine) `\sixheterov[bf]{5==O;6==N}{}`

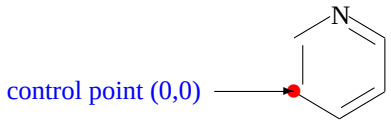
2-77 (pyridine) `\sixfusev[ace]{1==N}{}{}`

These commands have the common locant numbers and alphabets, which are fixed as designated in **2-76** and **2-77**. The locant alphabets are attached to edges by starting from the top vertex of the hexagon in a clockwise fashion, where each edge is characterized by a lowercase alphabet, while the two endpoints of each edge are characterized by a pair of lowercase and uppercase alphabets, i.e.,{a, A}, {b, B}, . . . , or {f, F}.

[b] This syntax is a simplified format, where optional arguments non-essential to the present discussions are omitted. The full form of the syntax will be discussed in Chapter 4.

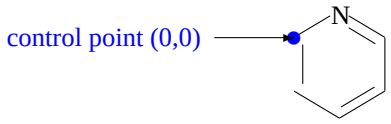
The XeLaTeX command `\sixfusev` with the value `e` or `E` for the argument ⟨fuse⟩ results in the printing **2-78** or **2-79**. The declaration of the argument ⟨fuse⟩ results in the selection of a control position and in the deletion of a skeletal bond, as shown in Fig. 2.5(a).

(a) Attached components produced by `\sixfusev` with the value `e` or `E`



2-78

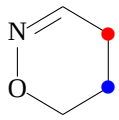
IUPAC name: pyrido[2,3-?]
XeLaTeX command: `\sixfusev[ace]{1==N}{}{e}`



2-79

IUPAC name: pyrido[2,3-?]
XeLaTeX command: `\sixfusev[ace]{1==N}{}{E}`

(b) Parent component produced by `\sixheterov`



2-80

IUPAC name: 6*H*-1,2-oxazine (the *d*-double bond deleted)
XeLaTeX command:

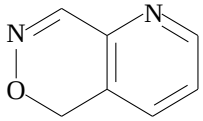
```
\sixheterov[f%
{b\redx{\circle*{50}}}%
{B\bluex{\circle*{50}}}%
]{5==O;6==N}{}
```

Figure 2.5. Mechanism of ring fusion in the XeLaTeX system. The correct fusion is accomplished by the superposition of the red solid circle of **2-78** on the blue solid circle of **2-80** or by the superposition of the blue solid circle of **2-79** on the red solid circle of **2-80**.

The lowercase and uppercase alphabets of each pair correspond to the endpoints of the edge at issue (cf. **2-77**). Their positions of the endpoints are selected as control points, each of which is designated by a red or blue solid circle in **2-78** or **2-79**,

On the other hand, the XeLaTeX command `\sixheterov` for general use prints out a red solid circle in **2-80** by designating `{b\redx{\circle*{50}}}` in the optional argument ⟨bondlist⟩, while it prints out a blue solid circle by designating `{B\bluex{\circle*{50}}}` in the optional argument ⟨bondlist⟩ (Fig. 2.5(b)). Note that the locant alphabets are attached to edges by starting from the top vertex of the hexagon in a clockwise fashion, as described above (cf. **2-76**).

By keeping the above discussions in mind (Fig. 2.5), let us draw 5*H*-pyrido[2,3-d][1,2]oxazine, where we consider the ring fusion between the *d*-bond of 6*H*-1,2-oxazine (**2-80**, the *d*-double bond deleted) and the 2,3-positions of pyridine ring (**2-78** or **2-79**). To realize a correct fusion for generating 5*H*-pyrido[2,3-d][1,2]oxazine, the `\redx{\circle*{50}}` of `{b\redx{\circle*{50}}}` can be replaced by the code for generating **2-79** or alternatively the `\bluex{\circle*{50}}` of `{B\bluex{\circle*{50}}}` can be replaced by the code for generating **2-78**. The following formula is drawn by the combination of **2-79** and **2-80** (cf. `{b\redx{\circle*{50}}}`).



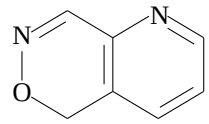
2-81 (= **2-75**)

IUPAC name: 5*H*-pyrido[2,3-d][1,2]oxazine
XeLaTeX command:

```
\sixheterov[f{b\sixfusev[ace]{1==N}{}{E}}]{5==O;6==N}{}
```

(or `\sixheterov[f{B\sixfusev[ace]{1==N}{}{e}}]{5==O;6==N}{}`)

The same compound as **2-81** can be alternatively drawn by using the XeLaTeX command `\decaheterov` for general use, which supports the drawing 6-6 fused ring systems.



2-82 (= **2-81**)

IUPAC name: 5*H*-pyrido[2,3-d][1,2]oxazine
XeLaTeX command:
```
\decaheterov[achk]{1==N;6==O;7==N}{}
```

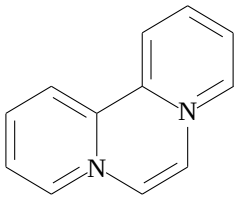
Although this shortcut drawing does not mimic the IUPAC nomenclature in this case, there are many cases in which such a shortcut drawing *does* mimic the IUPAC nomenclature. □

As shown in Example 2.16, the declaration of a fusing component in the ⟨bondlist⟩ of a parent structure is a versatile methodology for drawing a fused-ring derivative of the parent structure. The ring fusion of the IUPAC nomenclature can be regarded as a kind of additive operation described in Subsection 2.3.3, because the ring fusion is common to the additive operation in the fact that it is based on the addition to a skeletal bond.

Addition technique: Hereafter, the methodology using the ⟨bondlist⟩ of a parent structure is called *the addition technique*, because it mimics the additive operation of the IUPAC nomenclature (cf. Subsection 2.3.3).

A parent component can be fused with two or more attached components. Two representative examples are shown below:

Example 2.17. The structural formula of dipyrido[1,2-a:2′,1′-c]pyrazine is drawn by the scheme 6→6←6, where the central six-membered pyrazine is attached by two pyridine rings.

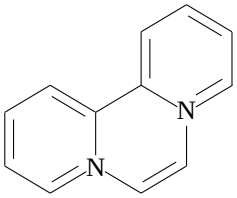


2-83

IUPAC name: dipyrido[1,2-a:2′,1′-c]pyrazine
XeLaTeX command:
```
\sixheterov[c%
{a\sixfusev[ace]{4==\null}{}{D}}%
{e\sixfusev[ace]{3==\null}{}{B}}%
]{2==N;5==N}{}
```

Note that the locant set ‘1,2-a’ in the IUPAC name corresponds to the combination a—D in the argument ⟨bondlist⟩, while the locant set ‘2′,1′-c’ corresponds to the combination e—B in the argument ⟨bondlist⟩. The declaration of `\null` in each inner command `\sixfusev` assures an open space for a nitrogen atom, which has been already drawn in the pyrazine ring by the outer command `\sixheterov`.

The same compound **2-83** can be alternatively drawn by using `\decaheterov` and `\sixfusev` as follows:

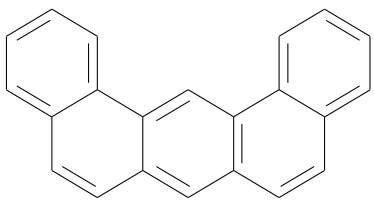


2-83′

IUPAC name: dipyrido[1,2-a:2′,1′-c]pyrazine
XeLaTeX command:
```
\decaheterov[cegi%
{a\sixfusev[ace]{4==\null}{}{D}}%
]{2==N;{4a}==N}{}
```

This construction is schematically represented by 6-6←6, which is not directly linked to the IUPAC name. □

Example 2.18. The structural formula of dibenzo[*a*,*j*]antheracene (**2-84**) is drawn by the scheme 6→6-6-6←6 as follows:



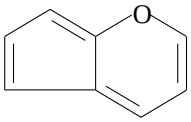
2-84

IUPAC name: dibenzo[*a*,*j*]antheracene
XeLaTeX command:
```
\anthracenev[cfhlo%
{a\sixfusev[ace]{}{}{D}}%
{j\sixfusev[bdf]{}{}{C}}]{}
```

The parent component 6-6-6 is drawn by using the XeTeX command `\anthracenev` for specific use. Each of the two attached components is drawn by using the fusion command `\sixfusev`. □

The XeTeX system supports `\fivefusevi` as a command (`\ComFuse`) for drawing five-membered attached components. The following examples show the construction of 5-6 and 5-5 fused ring systems by using the command `\fivefusevi`. Note that `\fivefusevi` outputs the upward mirror image of the structure drawn by `\fivefusev`.

Example 2.19. The structural formula of cyclopenta[b]pyran is drawn by the scheme 5→6 as shown below:

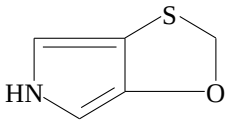


2-85

IUPAC name: cyclopenta[b]pyran
XeTeX command:
```
\sixheterov[bd{e\fivefusevi[ad]{}{}{B}}]{1==O}{}
```

The parent component 'pyran' is drawn by `\sixheterov`, while the attached component is drawn by `\fivefusevi`. □

Example 2.20. The structural formula of *2H,5H*-[1,3]oxathiolo[4,5-*c*]pyrrole is drawn by the scheme 5←5 as shown below:



2-86

IUPAC name: *2H,5H*-[1,3]oxathiolo[4,5-*c*]pyrrole
XeTeX command:
```
\fiveheterov[ac{b\fivefusevi[]{1==S;3==O}{}{d}}]{5==HN}{}
```

The parent component 'pyrrole' is drawn by `\fiveheterov`, while the attached component is drawn by `\fivefusevi`. □

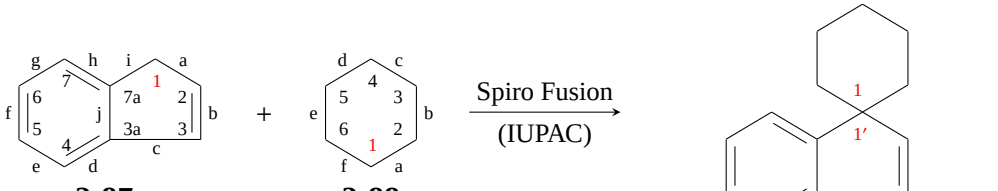
2.6 Spiro Ring Systems and the Replacement Technique

If a spiro-ring system is regarded as a parent ring with an attached ring unit, the process of constructing such a spiro-ring system resembles the skeletal replacement ('a') nomenclature described in Subsection 2.3.2. This resemblance is a basis of the replacement technique.

2.6.1 IUPAC names of Spiro Ring Systems

A 'spiro union' is a linkage between two rings that consists of a single atom common to both rings [5, P-24.1]. A typical procedure for naming such a spiro ring system is the specification of both the rings accompanied by a specification of a spiro union at issue [5, P-24.5].

Let us examine a spiro fusion for generating spiro[cyclohexane-1,1′-indene] (**2-89**), in which a spiro union is a linkage designated by 1 and 1′. The spiro ring system of **2-89** is generated by combining the indene component (**2-87**) and the cyclohexane component (**2-88**), where the position 1 of **2-87** is superposed onto the position 1 of **2-88** to give the spiro union represented by 1,1′, as shown in the IUPAC name: spiro[cyclohexane-1,1′-indene].



2-87
(indene)

2-88
(cyclohexane)

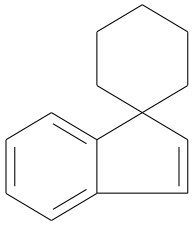
2-89
(spiro[cyclohexane-1,1′-indene])

XeTeX commands for spiro ring fusion mimic the above-mentioned methodology of constructing IUPAC names for spiro ring systems.

2.6.2 (yl)-Function Applied to Spiro Ring Fusion

A (yl)-Function has been described to draw a monovalent substituent group (Section 2.4), where the monovalent substituent group is contained in the argument ⟨subslist⟩ of a XyMTEX command for specific use (`\ComSpec`) and for general use (`\ComGen`). The same monovalent group can be used to construct a spiro ring system, if it is contained in the argument ⟨atomlist⟩ of a XyMTEX command for general use (`\ComGen`). Note that the monovalent group can be produced from a XyMTEX command for specific use (`\ComSpec`) as well as for general use (`\ComGen`).

Example 2.21. For example, the indene component (**2-87**) is drawn by using the command `\decaheterov` for general use, while the cyclohexane component (**2-88**) is drawn by applying a (yl)-function to the command `\cyclohexanev` for specific use. The resulting command `\cyclohexanev` with a (yl)-function is contained in the argument ⟨atomlist⟩ of for the command `\decaheterov`, where an atom locant (1) with an atom modifier (`s`), i.e., `1s`, is used for specifying the cyclohexane component. Thereby, we obtain the following structural formula to be drawn (**2-90** = **2-89**).



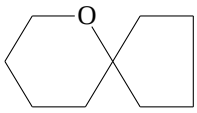
2-90 (= **2-89**)

IUPAC name: spiro[cyclohexane-1,1′-indene]
XyMTEX command:

```
\nonaheterovi[bdfh]{1s==\cyclohexanev{4==(yl)}}{}
```

It should be noted that the spiro fusion is akin to the skeletal ‘a’ replacement described in Subsection 2.3.2, where the use of the ⟨atomlist⟩ corresponds to the skeletal specification of the ‘a’ replacement. □

Example 2.22. Heterocyclic spiro compounds are named by skeletal replacement (‘a’) nomenclature in order to specify the hetero atom at issue. For example, the name ‘6-oxaspiro[4.5]decane contains’ the prefix ‘oxa’. In the XyMTEX system, the prefix ‘oxa’ and the prefix ‘spiro’ can be treated in a parallel way according to the replacement technique using ⟨atomlist⟩.



2-91

IUPAC name: 6-oxaspiro[4.5]decane
XyMTEX command:

```
\sixheteroh{3==O;4s==\cyclopentanehi{1==(yl)}}{}
```

Thus, the skeletal oxygen (`3==O`) and the spiro component (`4s==\cyclopentanehi{1==(yl)}}{}`) show such parallelism, because they are declared in the ⟨atomlist⟩ of `\sixheteroh`. □

As shown in Examples 2.21 and 2.22, the declaration of a spiro unit generated by a (yl)-function in the ⟨atomlist⟩ of a parent structure is a versatile methodology for drawing a spiro-ring derivative of the parent structure. The spiro ring fusion of the IUPAC nomenclature can be regarded as a kind of replacement operation described in Subsection 2.3.2, because the skeletal ‘a’ replacement is akin to the spiro fusion described in Examples 2.21 and 2.22.

Replacement technique: Hereafter, the methodology using the ⟨atomlist⟩ of a parent structure is called *the replacement technique*, because it mimics the replacement operation of the IUPAC nomenclature (cf. Subsection 2.3.2).

2.7 Substitution Technique, Replacement Technique, and Addition Technique

The above-mentioned features of the IUPAC nomenclature [5] provide us with important guidelines in developing the syntax for drawing structural formulas. As conclusive remarks of this chapter, we should recall the three techniques supporting the XyMTEX system.

1. (Substitution Technique Using ⟨subslist⟩) Atoms and any substituents are attached to the positions of a given parent skeleton through a bond. These processes are referred to as the IUPAC substitutive operations, as described in Subsection 2.3.1, where character strings such as OH and CH_3 are declared in the ⟨subslist⟩ of a XƎMTEX command. Moreover, substituents generated by (yl)-functions can be declared in ⟨subslist⟩ to be attached to the positions of the parent skeleton through a bond, as described in Section 2.4. Such modes of derivation using ⟨subslist⟩ are called *the substitution technique*.
2. (Replacement Technique Using ⟨atomlist⟩) Atoms and any substituents directly occupy the positions of a given parent skeleton. These processes are referred to as the IUPAC replacement operations, as described in Subsection 2.3.2, where character strings such as O, NH, and SO_2 are declared in the ⟨atomlist⟩ of a XƎMTEX command. Substituents generated by (yl)-functions can be also declared in ⟨atomlist⟩ to be attached directly to the position of the parent skeleton, so as to exhibit spiro fusion as described in Section 2.6.2. Such modes of derivation using ⟨atomlist⟩ are called *the replacement technique*.
3. (Addition Technique Using ⟨bondlist⟩) On the other hand, ring fusion described in Subsection 2.5.2 is regarded as a kind of bond occupation, just as unsaturation is expressed by the addition (occupation) of a line to a skeletal bond, e.g., C–C → C=C. These processes are referred to as the IUPAC additive operations (Subsection 2.3.3), although the process C=C → C–C is adopted in the IUPAC nomenclature, strictly speaking. Such modes of derivation using ⟨bondlist⟩ are called *the addition technique*.

It should be emphasized that the development of the three techniques gives a rational basis to the installation of ⟨subslist⟩, ⟨atomlist⟩, and ⟨bondlist⟩.

References

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Chapter 3

X^ΥMTEX Commands for General Use: Syntax

In Subsection 2.2.2 (page 17), the simplified format of the commands for general use (`\ComGen`) has been discussed briefly. The full form of the syntax is discussed in this chapter, where the commands of this type (stored in the hetarom package of the X^ΥMTEX system) are described in detail.

3.1 Command Names and Syntax

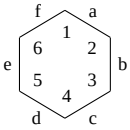
X^ΥMTEX commands for general use, which are represented by `\ComGen` in general, are designed to have a variable set of skeletal heteroatoms. Their command names are selected in accord with parent structures to be drawn (cf. Fig. 2.3), where they are based on commonly-used terms (e.g., `\sixheterov` for six-membered cycles). Most user commands of X^ΥMTEX are suffixed with '`v`', '`vi`', '`h`' and '`hi`'. The suffix '`v`' means that the command prints a structural formula of vertical form. The suffix '`h`' means that the command typesets a structural formula of horizontal form. When alternative orientations are possible, X^ΥMTEX commands are differentiated by an additional suffix '`i`'. Further additional suffixes '`b`' and '`t`' are used to specify six-to-six fused rings. Note that the command `\fourhetero` has no suffix.

The list of X^ΥMTEX commands for general use is shown in Table 3.1, where all of optional arguments are omitted. Several examples of structural formulas drawn by these commands are collected in Fig. 2.3, where no optional arguments are declared.

Table 3.1. X^ΥMTEX Commands for General Use (cf. Fig. 2.3),

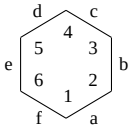
vertical type		horizontal type	
`\...v`	`\...vi`	`\...h`	`\...hi`
`\threeheterov{}{}`	`\threeheterovi{}{}`	`\threeheteroh{}{}`	`\threeheterohi{}{}`
`\fourhetero{}{}`			
`\fiveheterov{}{}`	`\fiveheterovi{}{}`	`\fiveheteroh{}{}`	`\fiveheterohi{}{}`
`\sixheterov{}{}`	`\sixheterovi{}{}`	`\sixheteroh{}{}`	`\sixheterohi{}{}`
`\nonaheterov{}{}`	`\nonaheterovi{}{}`	`\nonaheteroh{}{}`	`\nonaheterohi{}{}`
`\decaheterov{}{}`	`\decaheterovi{}{}`	`\decaheteroh{}{}`	`\decaheterohi{}{}`
`\decaheterovb{}{}`	`\decaheterovt{}{}`		

To show different outputs due to the suffixes '`v`', '`vi`', '`h`', and '`hi`', the command `\sixheterov` and the related commands are used to draw hexagonal diagrams characterized by the respective sets of locant numbers (for vertices) and of locant alphabets (for edges).



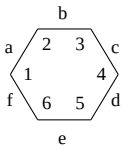
3-1

`\sixheterov{}{}`



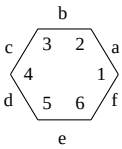
3-2

`\sixheterovi{}{}`



3-3

`\sixheteroh{}{}`



3-4

`\sixheterohi{}{}`

The locant numbers (alphabets) of `\sixheterov` for vertical drawing (**3-1**) start from the top vertex and are placed in a clockwise fashion, while the locant numbers (alphabets) of `\sixheterovi` for inverse vertical drawing (**3-2**) start from the bottom vertex and are placed in an anti-clockwise fashion. On the other hand, the locant numbers (alphabets) of `\sixheteroh` for horizontal drawing (**3-3**) start from the leftmost vertex and are placed in a clockwise fashion, while the locant numbers (alphabets) of `\sixheterohi` for inverse horizontal drawing (**3-4**) start from the rightmost vertex and are placed in an anti-clockwise fashion.

The syntax of a XeLaTeX command of general use (Table 3.1) is represented as follows, where the symbol `\ComGen` is used to represent each command:

Syntax:

`\ComGen`(⟨skelbdlist⟩)[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}[⟨delbdlist⟩]

Arguments:

- ⟨skelbdlist⟩ for specifying modification of skeletal bonds (option),
- ⟨bondlist⟩ for specifying unsaturation (option),
- ⟨atomlist⟩ for specifying modification of skeletal atoms (required),
- ⟨subslist⟩ for specifying substituents (required), and
- ⟨delbdlist⟩ for specifying deleted bonds in a skeleton (option).

Compare this full syntax of `\ComGen` with its simplified syntax shown on page 17, which has one optional argument ⟨bondlist⟩ and two required arguments ⟨atomlist⟩ and ⟨subslist⟩.

3.2 Specification of Required Arguments

The specification of each argument in a XeLaTeXcommand is based on list-treating macros [1]. Thus, items to be specified are listed sequentially with or without appropriate delimiters.

3.2.1 Substitution Lists ⟨subslist⟩

Construction of ⟨subslist⟩

The argument ⟨subslist⟩ lists substituents with bonds. The information on each substituent with a bond is described by a character string, which is delimitated by a semicolon, as represented below:

{ ⟨locNo⟩⟨bdmodifier⟩==⟨subsvalue⟩; ··· }

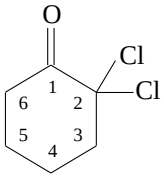
Each character string consists of ⟨locNo⟩ (locant number), ⟨bdmodifier⟩ (one or two characters as a bond modifier), a double equality symbol (==), and ⟨subsvalue⟩ (substitution value). The total list of such character strings with semicolons as delimiters constructs an argument ⟨subslist⟩, which is surrounded by a pair of brace to serve as a required argument of a XeLaTeX command.

For example, the ⟨subslist⟩ argument `{1==Cl;3D==O;...}` means that position 1 takes a chlorine atom (Cl) through a single bond, position 3 takes an oxygen atom (O) through a double bond, and so on. Thus, a character string before every semicolon represents a mode of substitution, where a locant number with a bond modifier is separated from a substituent by means of a double equality symbol (==). The following example shows the output produced by specifying a ⟨subslist⟩ argument as `{1D==O;2Sa==Cl;2Sb==Cl}`

Table 3.2. Locant Numbering and Bond Modifiers for ⟨subslist⟩

Bond Modifiers	Printed structures	Ex.
n or *n*S	exocyclic single bond at *n*-atom	**3-6**, **3-7**
*n*D	exocyclic double bond at *n*-atom	**3-8**
*n*A	alpha single bond at *n*-atom	**3-9**
*n*B	beta single bond at *n*-atom	**3-10**
*n*Sa	alpha (not specified) single bond at *n*-atom	**3-11**
*n*Sb	beta (not specified) single bond at *n*-atom	**3-11**
*n*SA	alpha single bond at *n*-atom (hashed line or hashed wedge)	**3-12**
*n*SB	beta single bond at *n*-atom (wedge or bold line)	**3-12**
*n*Sd	alpha single bond at *n*-atom (hashed line or hashed wedge) with an alternative direction to *n*SA	**3-13**
*n*Su	beta single bond at *n*-atom (wedge or bold line) with an alternative direction to *n*SB	**3-13**
*n*FA	alpha single bond at *n*-atom (hashed line or hashed wedge) for ring fusion	**3-14**,**3-16**
*n*FB	beta single bond at *n*-atom (wedge or bold line) for ring fusion	**3-15**, **3-17**
*n*GA	alpha single bond at *n*-atom (hashed line or hashed wedge) for the other ring fusion	**3-15**, **3-17**
*n*GB	beta single bond at *n*-atom (wedge or bold line) for the other ring fusion	**3-14**, **3-16**
*n*U	single bond at *n*-atom with unidentified configuration (wavy bond)	**3-18**
*n*SU	alpha (not specified) single bond at *n*-atom with unidentified configuration (wavy bond)	**3-19**
*n*SV	beta (not specified) single bond at *n*-atom with unidentified configuration (wavy bond)	**3-19**
*n*FU	single bond at *n*-atom with unidentified configuration (wavy bond) for ring fusion	**3-20**
*n*GU	single bond at *n*-atom with unidentified configuration (way bond) for the other ring fusion	**3-21**

in the command `\sixheterov`, where the other required argument ⟨atomlist⟩ is vacant `{}`, while all the remaining optional arguments are omitted.



IUPAC name: 2,2-dichlorocyclohexanone
XMTEX command: `\sixheterov{}{1D==O;2Sa==Cl;2Sb==Cl}`

3-5

Bond Modifiers

Each bond modifier ⟨bdmodifier⟩ consists of one or two characters listed in Table 3.2, where the letter *n* represents a locant number and the remaining one or two characters represent a bond modifier. The diagrams listed in Fig. 3.1 illustrate these bond modifiers by using a cyclohexane skeleton due to `\sixheterov`.

No specification of a bond modifier or a modifier 'S' outputs an exocyclic single bond (e.g., **3-6** and **3-7**). A modifier 'D' outputs an exocyclic double bond (e.g., **3-8**). When two substituents attach to a common skeletal atom, they are characterized by bond modifiers 'Sa' and 'Sb' (e.g. **3-11**).

When one substituent is selected to specify the configuration of a skeletal atom, it is characterized by a bond modifier 'A' (e.g., **3-9**) or 'B' (e.g., **3-10**), which represents an α- or β-substitution.

When a pair of two substituents is selected to specify the configuration of a skeletal atom, it is characterized by a pair bond modifiers 'SA' and 'SB' (e.g., **3-12**), which represents an α- and β-substitution. The reverse specification (α/β vs. downward/upward) is possible by using bond modifiers 'Sd' and 'Su' (e.g.,

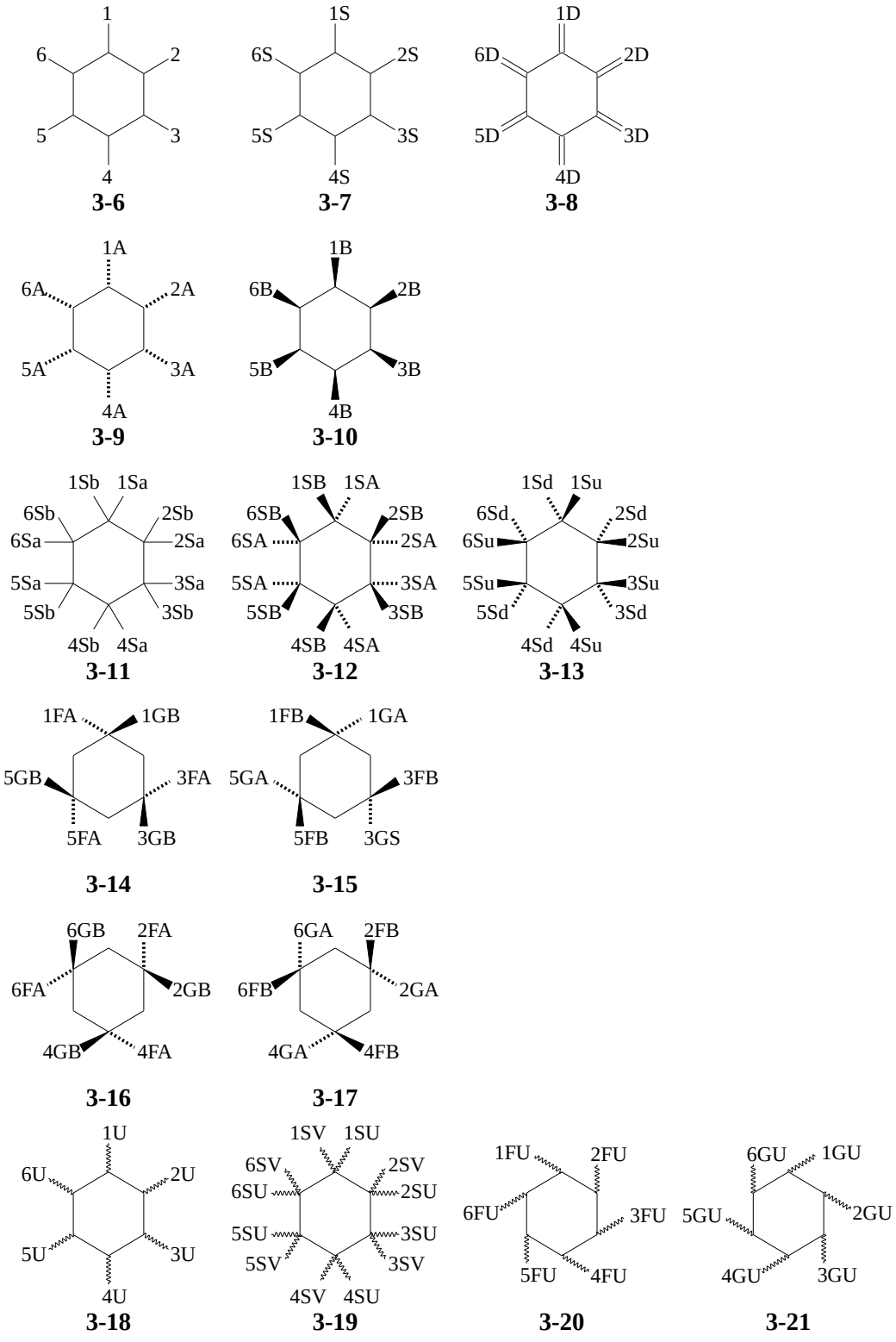
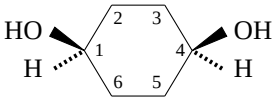


Figure 3.1. Locant numbers and bond modifiers for ⟨subslist⟩. Examples drawn by the command `\sixheterov`.

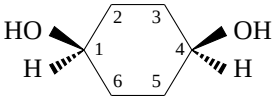
3-13). Such α (downward) bonds are expressed as hashed lines or hashed wedges according to a default mode of the XeTeX system. Such β (upward) bonds are expressed as bold lines or wedges according to a default of the XeTeX system. The default mode can be changed locally and/or globally. In particular, hashed lines (default in this manual) can be changed into hashed wedges by declaring the command

\wedgehashedwedge. Compare the two diagrams of (1*s*, 4*s*)-cyclohexane-1,4-diol shown below (**3-22** and **3-23**):



3-22

IUPAC name: (1*s*, 4*s*)-cyclohexane-1,4-diol
XeTeX command: (default mode)
```
\sixheteroh{}{1SB==HO;1SA==H;4SB==OH;4SA==H}
```



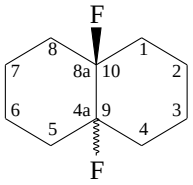
3-23

IUPAC name: (1*s*, 4*s*)-cyclohexane-1,4-diol
XeTeX command: (locally changed)
```
\wedgehashedwedge
\sixheteroh{}{1SB==HO;1SA==H;4SB==OH;4SA==H}
```

For the purpose of designating substitution at such fused positions, the XeTeX system supports further modifiers, 'FA' (e.g., **3-14**,**3-16**), 'FB' (e.g., **3-15**, **3-17**), 'GA' (e.g., **3-15**, **3-17**), and 'GB' (e.g., **3-14**, **3-16**).

Bonds with unidentified configuration are emphasized by using wavy bonds. Bond modifier 'U' (**3-18**), 'SU' (**3-19**), and 'SV' (**3-19**) are supported to draw wavy bonds for the purpose of emphasizing unidentified configuration. Fused positions with unidentified configuration are specified by bond modifiers, 'FU' (**3-20**) and 'GU' (**3-21**), which output wavy bonds.

Although the positions 9 and 10 of a 6-6 fused ring drawn by the XeTeX command \decaheterov for general use are fused positions, it is unnecessary to use a modifier 'FU' or 'GU', because each of the 9- and 10-positions is capable of accommodating only one definite substituent. For example, 9,10-difluorodecaline with unidentified configuration is drawn by using the bond modifiers 'B' and 'U', as follows:



3-24

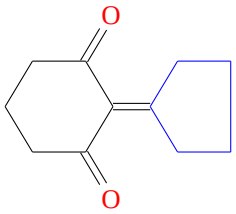
common name: 9,10-difluorodecaline
IUPAC name: 4a,8a-difluorodecahydronaphthalene
XeTeX command:
```
\decaheterov{}{{10}B==F;9U==F}
```

Note that modifiers such as 'FA', 'GA', 'FB', 'GB', 'FU' and 'GU' are used in the cases that operations of ring fusion are taken into consideration.

Values of ⟨subsvalue⟩

The substituent value assigned to ⟨subsvalue⟩ is a substituent represented by a character (e.g., H, F, and O), a character string (e.g., Cl, OH, and NH_2), and a substituent component generated by a (yl)-function. A predefined command for coloring (e.g., \redx, \bluex) can be used to the substituent coloring.

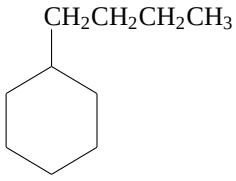
The structural formula of 2-cyclopentylidenecyclohexan-1,3-dione (**3-25**) is drawn by \sixheterohi, in which the ⟨subsvalue⟩ values of the argument ⟨subslist⟩ are found to be two oxygens (carbonyl groups) as well as a substituent component generated by applying a (yl)-function to \fiveheterohi. These substituent values are colored by using \redx and \bluex.



3-25

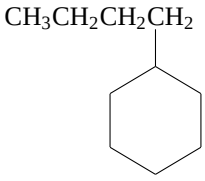
IUPAC name: 2-cyclopentylidenecyclohexan-1,3-dione
XeTeX command:
```
\sixheterohi{}{1D==\bluex{\fiveheterohi{}{1==(yl)}};%
2D==\redx{O};6D==\redx{O}}
```

A substituent declared for the value of ⟨subsvalue⟩ is output in a right-handed or left-handed manner according to the substitution position specified by a locant number. If the substitution is represented by a long character string, e.g., $CH_2CH_2CH_2CH_3$ for a butyl group, a default setting produces the right-handed output in the position 1 of the command \sixheterov, as shown by the formula **3-26**. If a left-handed output is desirable, the LaTeX command \llap can be used effectively, as shown by the formula **3-27**.



3-26

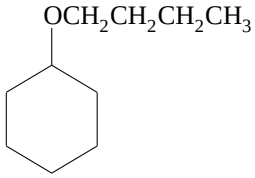
```
\sixheterov{}{1==%
CH$_{2}$CH$_{2}$CH$_{2}$CH$_{3}$}
```



3-27

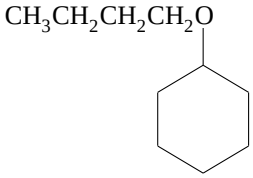
```
\sixheterov{}{1==%
\llap{CH$_{3}$CH$_{2}$CH$_{2}$}CH$_{2}$}
```

If such a long character string has a one-character union (e.g., an oxygen atom of $OCH_2CH_2CH_2CH_3$), its left-handed output can be embodied by using a XeLaTeX command `\lmoiety`. Moreover, such a code as `OCH$_{2}$CH$_{2}$CH$_{2}$CH$_{3}$` can be simplified into `\ChemForm{OCH_2CH_2CH_2CH_3}` by using the XeLaTeX command `\ChemForm`. The following structures show a default right-handed output (**3-28**) and the corresponding left-handed output (**3-29**) due to `\lmoiety`.



3-28

```
\sixheterov{}{1==%
\ChemForm{OCH_2CH_2CH_2CH_3}}
```



3-29

```
\sixheterov{}{1==\lmoiety{%
\ChemForm{CH_3CH_2CH_2CH_2O}}}
```

3.2.2 Atom Lists ⟨atomlist⟩

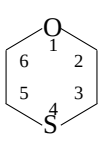
Construction of ⟨atomlist⟩

The argument ⟨atomlist⟩ lists skeletal atoms or spiro components aiming at spiro fusion. The information on skeletal atoms etc. is described by a character string, which is delimitated by a semicolon, as represented below:

{ ⟨locNo⟩⟨spiromodifier⟩==⟨atomvalue⟩; ··· }

Each character string consists of ⟨locNo⟩ (locant number), ⟨spiromodifier⟩ (one character for a spiro union), a double equality symbol (==), and ⟨atomvalue⟩ (atom value). The total list of such character strings with semicolons as delimiters constructs an argument ⟨atomlist⟩, which is surrounded by a pair of brace to serve as a required argument of a XeLaTeX command.

For example, the ⟨atomlist⟩ argument `{1==O;4==S;...}` means that the vertex of lacant number 1 is occupied by an oxygen atom (O) after vertex truncation, the vertex of lacant number 4 is occupied by a sulfur atom (S) after vertex truncation, and so on. Thus, a character string before every semicolon represents a mode of skeletal replacement, where a locant number (with a spiro modifier if necessary) is separated from an atom value by means of a double equality symbol (==). The following example shows the output produced by specifying a ⟨atomlist⟩ argument as `{1==O;4==S}` in the command `\sixheterov`, where the other required argument ⟨subslist⟩ is vacant `{}`, while all the remaining optional arguments are omitted.



3-30

IUPAC name: 1,4-thioxane

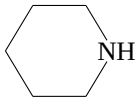
XeLaTeX command: `\sixheterov{1==O;4==S}{}`

Spiro Modifiers and Values of ⟨atomvalue⟩ in the ⟨atomlist⟩

The substituent value assigned to ⟨atomvalue⟩ is a skeletal atom represented by a character (e.g., O and S), a character string (e.g., NH), and a spiro component generated by a (yl)-function. Predefined commands for coloring (e.g., `\redx`, `\bluex`) or for other purposes can be used to give coloring or other printing effects.

When a character or a character string contained in the argument ⟨atomlist⟩ is concerned with a skeletal atom, the ⟨spiromodifier⟩ is not required, i.e., *n*==⟨atomvalue⟩, as exemplified in **3-30**. The truncation of the substitution vertices occurs to assure the spaces for outputting O and S.

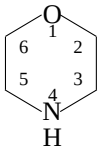
If a character string (NH) is assigned to ⟨atomvalue⟩ of `\sixheteroh` (i.e., `\sixheteroh{4==NH}{}`), the letter N of the NH is typeset at the substitution vertex at issue. The truncation of the substitution vertex occurs to assure the space for outputting the N (of the NH), as found in the structure of piperidine (**3-31**).



3-31

IUPAC name: piperidine
XeTeX command:
`\sixheteroh{4==NH}{}`

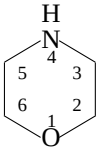
A skeletal atom for ⟨atomlist⟩ may be given in the form of a control sequence (a LaTeX command). For example, the structural formula of morpholine **3-32** can be drawn in such a way as aligned vertically with no vertical bond. The command `\downnobond{N}{H}` is assigned to ⟨atomlist⟩ to output N.



3-32

Common name: morpholine
IUPAC name: 1,4-oxazinane
XeTeX command: `\sixheterov{1==O;4==\downnobond{N}{H}}{}`

Because the reverse counterpart of `\downnobond{N}{H}` is `\upnobond{N}{H}`, it is used to output N, where no vertical bond is depicted between N and H. The example **3-33** is drawn by using the command `\sixheterovi`, which is the reverse counterpart of `\sixheterov`.



3-33

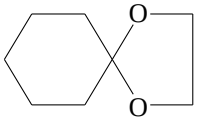
Common name: morpholine
IUPAC name: 1,4-oxazinane
XeTeX command: `\sixheterovi{1==O;4==\upnobond{N}{H}}{}`

If a character string contained in the argument ⟨atomlist⟩ is concerned with a spiro component generated by a (yl)-function for aiming at spiro fusion, either

- a letter '`s`' (for a direct spiro union) or
- a letter '`h`' (for a non-carbon atom spiro union)

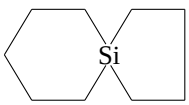
is selected as a value of ⟨spiromodifier⟩, i.e., *n*`s`==⟨atomvalue⟩ or *n*`h`==⟨atomvalue⟩.

If such a spiro component attaches directly to a counterpart component, the spiro modifier '`s`' is used to generate a correct spiro union, as shown in **3-34**. On the other hand, if a spiro union consists of a non-carbon atom (e.g., Si), the spiro modifier '`h`' is used to generate a correct spiro union, as shown in **3-35**.



3-34

IUPAC name: 2,5-dioxaspiro[4.5]decane
XeTeX command:
`\sixheteroh{4s==\fiveheterohi{2==O;5==O}{1==(yl)}}{}`



3-35

IUPAC name: 1-silaspiro[4.5]decane
XeTeX command:
`\sixheteroh{4h==\fiveheterohi{1==Si}{1==(yl)}}{}`

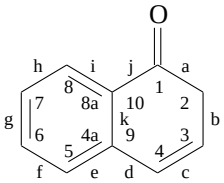
3.3 Specification of Optional Arguments

3.3.1 Bond Lists ⟨bondlist⟩

The optional argument ⟨bondlist⟩ which is surrounded by a pair of square brackets lists the unsaturation of skeletal bonds, if necessary. Each descriptor of the ⟨bondlist⟩ is a locant alphabet ⟨locAlph⟩, a pair of braces containing a locant alphabet and a fusing unit {⟨locAlph⟩⟨fuseunit⟩}, or a pair of braces containing a locant number and a ± sign {⟨locNo⟩⟨± sign⟩}. The specification of ⟨bondlist⟩ in a XeLaTeX command for general use is conducted by the one-by-one declaration of such descriptors aligned sequentially:

[⟨locAlph⟩ ··· {⟨locAlph⟩⟨fuseunit⟩} ··· {⟨locNo⟩⟨± sign⟩} ···]

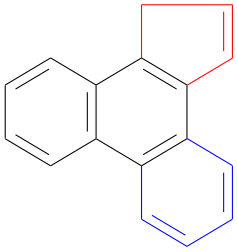
The structural formula **3-36** of naphthalene-1(2*H*)-one is drawn by setting the argument ⟨bondlist⟩ `cegi` with a pair of square brackets in the XeLaTeX command `\decaheterov` for general use. Note that the locant alphabets (`a` to `k`) are attached to the respective skeletal bonds, as shown in the formula **3-36**.



3-36

IUPAC name: naphthalene-1(2*H*)-one
XeLaTeX command: `\decaheterov[cegi]{}{1D==O}`

The construction of fused ring systems has been briefly discussed in Section 2.5, where the mechanism of the setting {⟨locAlph⟩⟨fuseunit⟩} has been explained. The unit represented by ⟨fuseunit⟩ is generated by a cyclic fusing unit `\ComFuse` (e.g., `\fivefusev` and `\sixfusev`), as shown in Subsection 2.5.2. The following example **3-37** is drawn by a scheme 5→ 6-6 ← 6, where a five-membered fusing unit due to `\fivefusev` and a six-membered fusing unit due to `\sixfusev` are used in the setting {⟨locAlph⟩⟨fuseunit⟩}. The two modes of setting along with usual locant alphabets `acfhk` are contained in the optional argument ⟨bondlist⟩ of the XeLaTeX command `\decaheterov` for general use.

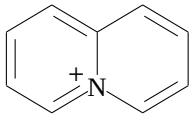


3-37

IUPAC name: 1*H*-cyclopenta[*l*]phenanthrene
XeLaTeX command:

```
\decaheterov[acfhk%                (usual locant alphabets)
{a\fivefusev[b]{}{}{e}}%           (5-membered fusing unit)
{c\sixfusev[bd]{}{}{F}}%           (6-membered fusing unit)
]{}{}
```

Another setting {⟨locNo⟩⟨± sign⟩} is used to draw a plus or minus charge on a skeletal hetero atom. For example, the N^+ unit of a quinolizinium ion (**3-38**) is drawn by setting {9+} along with usual locant alphabets `acegi` in the optional argument ⟨bondlist⟩ of the XeLaTeX command `\decaheterov` for general use.



3-38

IUPAC name: quinolizinium ion
XeLaTeX command: `\decaheterov[acegi{9+}]{9==N}{}`

3.3.2 Skeletal Bond Lists ⟨skelbdlist⟩

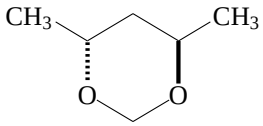
The optional argument ⟨skelbdlist⟩ which is surrounded by a pair of parentheses lists skeletal bonds with configurations. Each descriptor of the ⟨skelbdlist⟩ is a pair of braces containing a locant alphabet and a descriptor of configuration (A for an α bond or B for a β bond), i.e., {⟨locAlph⟩⟨AorB⟩}. The specification

of ⟨skelbdlist⟩ in a XeLaTeX command for general use is conducted by the one-by-one declaration of such descriptors aligned sequentially:

({⟨locAlph⟩⟨AorB⟩} ⋯)

This declaration means that the skeletal bond specified by a locant alphabet ⟨locAlph⟩ is changed into a bold line when ⟨AorB⟩ is B, or into a bold dashed line when ⟨AorB⟩ is B.

The 1,3-dioxane represented by **3-39** is alternatively regarded as the methylene acetal of pentane-2,4-diol. Because pentane-2,4-diol has stereoisomers, the corresponding methylene acetal **3-39** is desirable to be drawn as a structural formula with configurations. For this purpose, the optional argument ⟨skelbdlist⟩ is used as follows:



3-39

common name: pentane-2,4-diol methylene acetal
IUPAC name: 4,6-dimethyl-1,3-dioxane
XeLaTeX command:

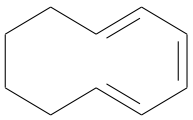
```
\sixheterov({bB}{eA})%
{3==O;5==O}{2==CH$_3$;6==CH$_3$}
```

3.3.3 Deleted Bond Lists ⟨delbdlist⟩

The optional argument ⟨delbdlist⟩ which is surrounded by a pair of square brackets lists skeletal bonds to be deleted, if necessary. Each descriptor of the ⟨bondlist⟩ is a locant alphabet ⟨locAlph⟩, which is declared in ⟨delbdlist⟩ in a one-by-one fashion:

[⟨locAlph⟩ ⋯]

For example, (1*E*,3*Z*,5*E*)-cyclodeca-1,3,5-triene **3-40** is drawn by the following code, where the last pair of square brackets `[k]` indicates the deletion of the skeletal bond (fused bond) specified by the locant alphabet `k`. For the locant alphabets of `\decaheterov`, see **3-36**.

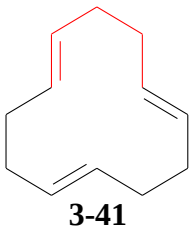


3-40

IUPAC name: (1*E*,3*Z*,5*E*)-cyclodeca-1,3,5-triene
XeLaTeX command:

```
\decaheterov[bdj]{}{}[k]
```

As a more complicated example, (1*E*,5*E*,9*E*)-cyclododeca-1,5,9-triene (**3-41**) is drawn by the technique of ring fusion (Section 2.5).

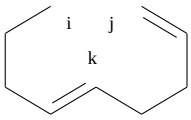


3-41

IUPAC name: (1*E*,5*E*,9*E*)-cyclododeca-1,5,9-triene
XeLaTeX command:

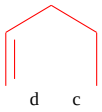
```
\decaheterov[ae%
{j\sixfusev[e]{}{}{C}[d]}%
]{}{}[ijk]
```

The parent component **3-42** is generated by using `\decaheterov` (as `\ComGen`), where three skeletal bonds are deleted by specifying `ijk` in the optional argument ⟨delbdlist⟩. On the other hand, the attached component **3-43** is generated by using `\sixfusev` (as `\ComFuse`) where one skeletal bond is deleted by specifying `d` in the optional argument ⟨delbdlist⟩. Note the bond `c` is deleted because it is the position of ring fusion, which is specified by the argument `C` for ⟨fuse⟩ of `\sixfusev` (as `\ComFuse`). Then, the combination of **3-42** and **3-43** produces the triene **3-41** to be drawn.



3-42

```
\decaheterov[ae]{}{}[ijk]
```



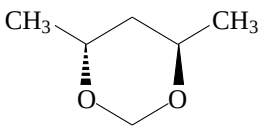
3-43

```
\sixfusev[e]{}{}{C}[d]
```

The bold line and bold dashed line of **3-39** can be replaced by a wedge and a hashed wedges after bond deletion by ⟨delbdlist⟩. Thus, the setting of `be` for ⟨delbdlist⟩ and the setting of the commands:

`2s==\WedgeAsSubst(0,0)(0,-1){150}`	(wedged bond, slope `(0,-1)`)
`6s==\HashWedgeAsSubst(0,0)(0,-1){150}`	(hashed wedged bond, slope `(0,-1)`)

in the argument ⟨atomlist⟩ produce the structural formula represented by **3-44**. Note that such declarations as `2s==...` and `6s==...` in ⟨atomlist⟩ are rather dirty applications of the spiro fusion described on page 37.

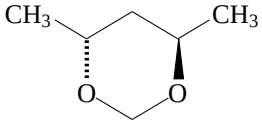


3-44

common name: pentane-2,4-diol methylene acetal
IUPAC name: 4,6-dimthyl-1,3-dioxane
XeLaTeX command:

```
\sixheterov{3==O;5==O;%
2s==\WedgeAsSubst(0,0)(0,-1){150};%
6s==\HashWedgeAsSubst(0,0)(0,-1){150}%
}{2==CH$_3$;6==CH$_3$}[be]%
```

A structural formula due to the default setting of the present manual (wedges and hashed lines), i.e., **3-45**, can be drawn by mixed usage of the techniques described for **3-39** and **3-44**.



3-45

common name: pentane-2,4-diol methylene acetal
IUPAC name: 4,6-dimethyl-1,3-dioxane
XeLaTeX command:

```
\sixheterov({eA}){3==O;5==O;%
2s==\WedgeAsSubst(0,0)(0,-1){150}%
}{2==CH$_3$;6==CH$_3$}[b]%
```

3.4 Details and Examples of XeLaTeX Command for General Use

3.4.1 Drawing Three-Membered Heterocycles

The XeLaTeX commands `\threeheterov` and `\threeheterovi` for general use, which are defined in hetarom.sty for drawing three-membered heterocycles of vertical direction, have the following formats:

```
\threeheterov(⟨skelbdlist⟩)[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}[⟨delbdlist⟩]
\threeheterovi(⟨skelbdlist⟩)[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}[⟨delbdlist⟩]
```

The horizontal counterparts `\threeheteroh` and `\threeheterohi` for general use, which are also defined in hetarom.sty for drawing three-membered heterocycles, have the following formats:

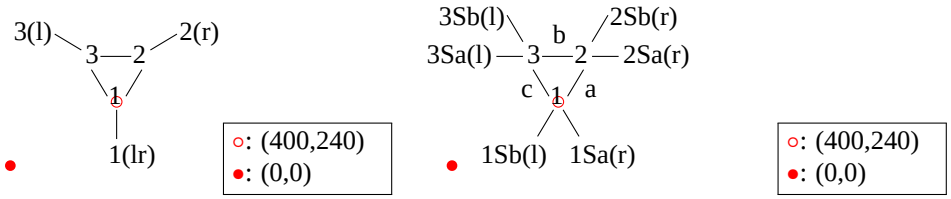
```
\threeheteroh(⟨skelbdlist⟩)[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}[⟨delbdlist⟩]
\threeheterohi(⟨skelbdlist⟩)[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}[⟨delbdlist⟩]
```

The required arguments ⟨atomlist⟩ and ⟨subslist⟩ (cf. Section 3.2) as well as the optional arguments ⟨skelbdlist⟩, ⟨bondlist⟩, and ⟨delbdlist⟩ (cf. Section 3.3) can be declared according to the general format of `\ComGen` (page 32).

The locant numbers and the locant alphabets assigned to the structures depicted by these commands are shown in Figs. 3.2 and 3.3. In each structural diagram, the original control point (0,0) of the drawing area is shown by a red solid circle, and the beginning point of drawing is shown by a red open circle. Note

that the XƎMTEX system is based on the LATEX picture environment, where the unit length is changed into `\unitlength=0.1pt`. Hence, the coordinate (400, 240), for example, represents (40pt, 24pt). The locant numbers (1 to 3) and the locant alphabets (`a` to `c`) are also shown in the diagrams.

(a) Output of `\threeheterov`



(b) Output of `\threeheterovi`

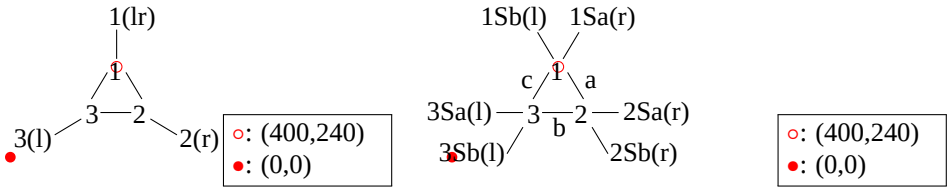
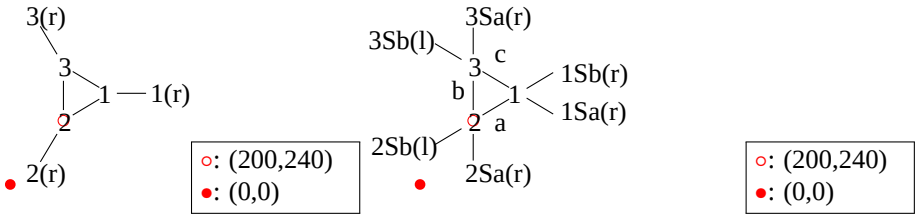


Figure 3.2. XƎMTEX commands for general use, which output three-membered heterocyclic rings of vertical type. Representative declarations of ⟨subslist⟩ are shown, where the symbol (r) or (l) denotes a right-handed or left-handed in a default setting. The symbol (lr) outputs a right-handed substituent but permits a double-sided output.

(a) Output of `\threeheteroh`



(b) Output of `\threeheterohi`

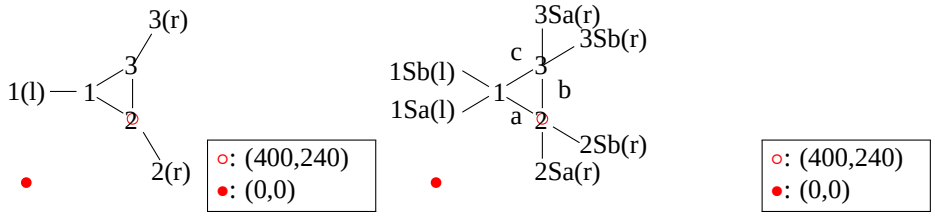


Figure 3.3. XƎMTEX commands for general use, which output three-membered heterocyclic rings of horizontal type. Representative declarations of ⟨subslist⟩ are shown, where the symbol (r) or (l) denotes a right-handed or left-handed in a default setting. The symbol (lr) outputs a right-handed substituent but permits a double-sided output.

The argument ⟨subslist⟩ describes each substituent with a locant number and a bond modifier, as described in Subsection 3.2.1. Representative modes of outputting substituents are shown in Fig. 3.2. The remaining modes (e.g., wedges and dashed lines) are common to those collected in Table 3.2 and Fig. 3.1. The handedness for each oriented or double-sided position is shown with a character set in parentheses, i.e., (l), (r), or (lr). In accord with the default definitions of the macro `\threeheterov`, the right-handed position (2) is designed to take only a right-handed substituent, while the left-handed positions (3) is to take only a left-handed substituent. Such positions (designated with the letter 'r' or 'l') are referred to as 'oriented' positions in this manual. In contrast, the bottom position of the cyclopropane ring (designated with the string 'lr') can accommodate a substituent of both handedness. It is referred to as a 'double-sided' position in this manual.

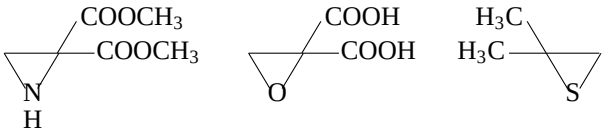
Although the default definition is to put a right-handed moiety, a left-handed substituent can be printed by means of the macro `\lmoiety`.

According to Subsection 3.2.2, the argument ⟨atomlist⟩ takes a usual format with respect to heteroatoms attached to n = 1 to 3, *e.g.*, 1==N for a nitrogen atom at 1-position.

The following examples indicate the declaration of the required arguments ⟨subslist⟩ and ⟨atomlist⟩ in the commands for drawing three-membered heterocycles.

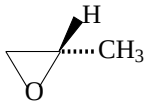
```
\threeheterov{1==\downnobond{N}{H}}{2Sa==COOCH$_{3}$;2Sb==COOCH$_{3}$}
\threeheterov{1==O}{2Sa==COOH;2Sb==COOH}
\threeheterov{1==S}{3Sa==H$_{3}$C;3Sb==H$_{3}$C}
```

For the command `\downnobond`, see the code for drawing **3-32**. These codes produce the following structural formulas:

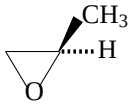


3-46 **3-47** **3-48**

The absolute configurations of (*S*)- and (*R*)-propylene oxide (**3-49** and **3-50**) are drawn by declaring bond modifiers `SA` and `SB` shown in Table 3.2.



3-49
(*S*)-propylene oxide
`\threeheterov{1==O}`
`{2SA==CH$_{3}$;2SB==H}`



3-50
(*R*)-propylene oxide
`\threeheterov{1==O}`
`{2SB==CH$_{3}$;2SA==H}`

Although the optional argument ⟨bondlist⟩ obeys the criterion described in Subsection 3.3.1, several modes added to `\threeheterov` and `\threeheterovi` are collected in Table 3.3, along with the modes of the criterion.

Table 3.3. Argument ⟨bondlist⟩ for commands `\threeheterov` and `\threeheterovi`

Character	Printed structure
none	saturated
a	1,2-double bond
b	2,3-double bond
c	3,1-double bond
A	aromatic circle
{*n*+}	plus at the n-hetero atom (n = 1 to 3)
	n = 4 – outer plus at 1 position
	n = 5 – outer plus at 2 position
	n = 6 – outer plus at 3 position
{0+}	plus at the center of a cyclopropane ring

Two expressions (**3-52** and **3-53**) of a cyclopropenium cation, which is generated by the attack of $SbCl_5$ on **3-51**, are drawn by the declaration of `{1+}` or `{0+}` in the ⟨bondlist⟩ of `\threeheterovi`.

3-51
`\threeheterovi%`
`[b]{}{1==Cl}`

3-52
`\threeheterovi%`
`[b{1+}]{}{}`

3-53
`\threeheterovi%`
`[A{0+}]{}{}`

3.4.2 Drawing Four-Membered Heterocycles

The XeLaTeX command `\fourhetero` is a command for general use, which is capable of giving skeletal atoms as an atom list ⟨atomlist⟩. This command is designed for drawing four-membered heterocycles by using the following format (hetarom.sty).

```
\fourhetero(⟨skelbdlist⟩)[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}[⟨delbdlist⟩]
```

Note that the suffixes `v`, `vi`, etc. are not attached because of the equality of the four directions. The required arguments ⟨atomlist⟩ and ⟨subslist⟩ (cf. Section 3.2) as well as the optional arguments ⟨skelbdlist⟩, ⟨bondlist⟩, and ⟨delbdlist⟩ (cf. Section 3.3) can be declared according to the general format of `\ComGen` (page 32).

The locant numbering and the setting of locant alphabets are shown Fig. 3.4. The handedness for each oriented or double-sided position is shown with a character set in parentheses.

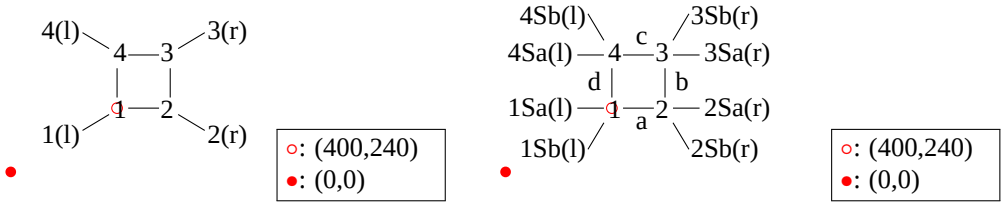


Figure 3.4. XeLaTeX command for general use, which outputs a four-membered heterocyclic ring of horizontal type. See the caption of Fig. 3.2.

For general aspects of ⟨bondlist⟩, see Subsection 3.3.1. The optional argument ⟨bondlist⟩ of `\fourhetero` is used for the bond specification shown in Table 3.4.

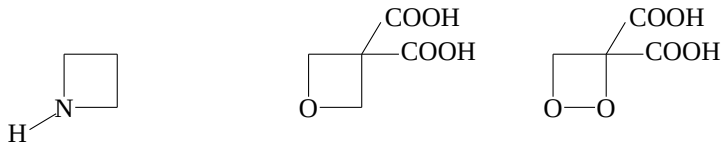
Table 3.4. Argument ⟨bondlist⟩ for Commands `\fourhetero` and others

Character	Printed structure	Character	Printed structure
none	mother compound (fully saturated)		
a	1,2-double bond	b	2,3-double bond
c	3,4-double bond	d	4,1-double bond
{*n*+}	plus at the *n*-nitrogen atom (*n* = 1 to 4)		

According to Subsection 3.2.2, the argument ⟨subslist⟩ takes a usual format with respect to heteroatoms attached to *n* = 1 to 4, *e.g.*, 1==N for a nitrogen atom at 1-position.

The argument ⟨subslist⟩ describes each substituent with a locant number and a bond modifier, as described in Subsection 3.2.1. Representative modes of outputting substituents are shown in Fig. 3.4. The remaining modes are common to those collected in Table 3.2 and Fig. 3.1.

The required arguments ⟨subslist⟩ and ⟨atomlist⟩ in the command for drawing four-membered heterocycles are declared as shown below:



3-54 **3-55** **3-56**

which are generated by writing the following codes:

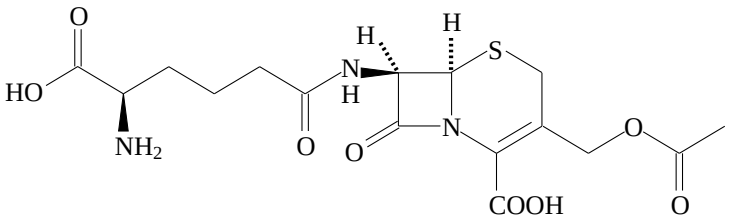
```
\fourhetero{1==N}{1==H}
\fourhetero{1==O}{3Sa==COOH;3Sb==COOH}
\fourhetero{1==O;2==O}{3Sa==COOH;3Sb==COOH}
```

The following example illustrates a combination of the addition technique, the substitution technique, and the replacement technique.

Example 3.1. The structural formula of cephalosporin C (**3-57**) can be drawn by inputting the following code:

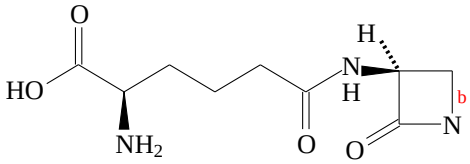
```
\fourhetero[%
{b\sixfusev[c]{1==S;5==\null;%
3s==\pentamethylenei{3==O}{1==(yl);4D==O}}{4==COOH;6GA==H}{e}}%
]{2==N}{1D==O;4Sd==H;%
4Su==\heptamethylenei{7==\downnobond{N}{H}}%
{7==(yl);1W==HO;1D==O;2B==NH$_{2}$;6D==O}}
```

Thereby, we obtain



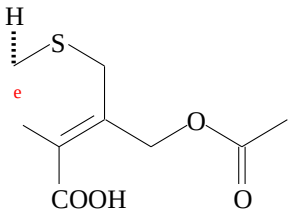
3-57 (cephalosporin C)

The code for drawing **3-57** is an application of the ring-fusion mechanism described in Section 2.5 (the addition technique). As described in Subsection 3.3.1, the bond list ⟨bondlist⟩ is capable of containing a code of an attached component for ring fusion. The above code consists of a four-membered ring **3-58** as a parent component and a six-membered ring **3-59** as an attached component. The former is drawn by using `\fourhetero` and the latter is drawn by using `\sixfusev`.



3-58 (parent component)

```
\fourhetero[]%
{2==N}{1D==O;4Sd==H;%
4Su==\heptamethylenei%
{7==\downnobond{N}{H}}%
{7==(yl);1W==HO;1D==O;%
2B==NH$_{2}$;6D==O}}
```



3-59 (attached component)

```
\sixfusev[c]{1==S;5==\null;%
3s==\pentamethylenei%
{3==O}{1==(yl);4D==O}}%
{4==COOH;6GA==H}{e}
```

The setting of b in the ⟨bondlist⟩ of `\fourhetero` corresponds to the setting of e in the ⟨fuse⟩ of `\sixfusev`, i.e., `[{b...{e}}]`. This correspondence is illustrated by the locant alphabet b of **3-58** and the locant alphabet e of **3-59**.

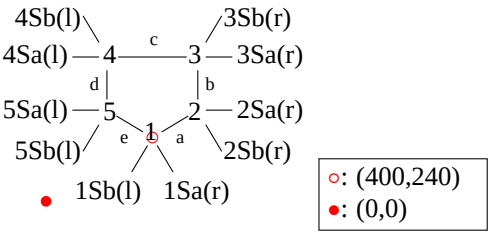
The side chain in the parent component (**3-58**) is placed by the substitution technique, i.e., the declaration of `\heptamethylenei` in the ⟨subslist⟩ of `\fourhetero`. On the other hand, the side chain in the attached component (**3-59**) is placed by the replacement technique, i.e., the declaration of `\pentamethylenei` in the ⟨atomlist⟩ of `\sixfusev`. □

3.4.3 Drawing Five-Membered Heterocycles

The XeTeX commands `\fiveheterov` and `\fiveheterovi` for general use, which are defined in hetarom.sty for drawing five-membered heterocycles of vertical direction, have the following formats:

```
\fiveheterov(⟨skelbdlist⟩)[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}[⟨delbdlist⟩]
\fiveheterovi(⟨skelbdlist⟩)[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}[⟨delbdlist⟩]
```

(a) Output of \fiveheterov



(b) Output of \fiveheterovi

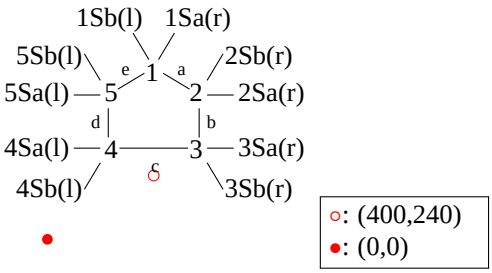
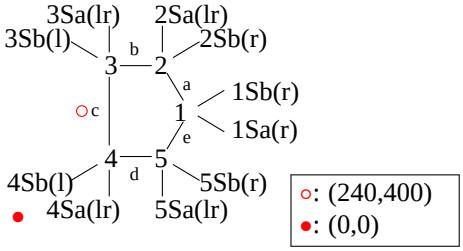


Figure 3.5. XƎMTEX commands for general use, which output five-membered heterocyclic rings of vertical type. For the meanings of the symbols, see the caption of Fig. 3.2.

(a) Output of \fiveheteroh



(b) Output of \fiveheterohi

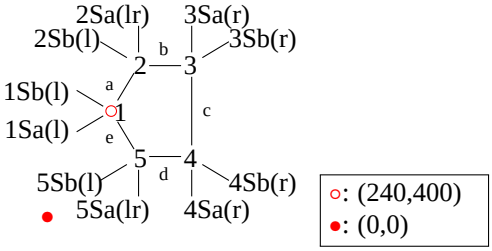


Figure 3.6. XƎMTEX commands for general use, which output five-membered heterocyclic rings of horizontal type. For the meanings of the symbols, see the caption of Fig. 3.2.

Table 3.5. Argument ⟨bondlist⟩ for commands \fiveheterov, \fiveheterovi, \fiveheteroh, and \fiveheterohi

Character	Printed structure	Character	Printed structure
a	1,2-double bond	A	aromatic circle
b	2,3-double bond	{*n*+}	plus at the *n*-nitrogen atom (*n* = 1 to 6)
c	4,3-double bond	{0+}	plus (or minus) at the center
d	4,5-double bond		
e	5,1-double bond		

The horizontal counterparts \fiveheteroh and \fiveheterohi for general use, which are also defined in hetarom.sty for drawing five-membered heterocycles, have the following formats:

```
\fiveheteroh(⟨skelbdlist⟩)[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}[⟨delbdlist⟩]
\fiveheterohi(⟨skelbdlist⟩)[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}[⟨delbdlist⟩]
```

The required arguments ⟨atomlist⟩ and ⟨subslist⟩ (cf. Section 3.2) as well as the optional arguments ⟨skelbdlist⟩, ⟨bondlist⟩, and ⟨delbdlist⟩ (cf. Section 3.3) can be declared according to the general format of \ComGen (page 32).

The locant numbers and the locant alphabets assigned to the structures depicted by these commands are shown in Figs. 3.5 and 3.6, where the locant numbers (1 to 5) are attached to their vertices and the locant alphabets (a to e) are attached to their edges.

The required argument ⟨atomlist⟩ has been discussed in Subsection 3.2.2. A typical embodiment of ⟨atomlist⟩ is a list of heteroatoms, *e.g.*, 1==N for a nitrogen atom at 1-position.

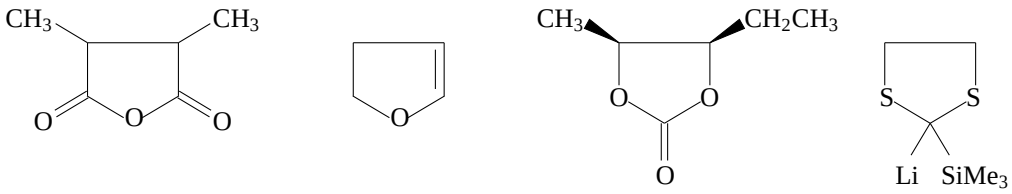
The required argument ⟨subslist⟩ for these macros takes a general format, in which the bond modifiers listed in Table 3.2 are used. The respective modes of output are collected in Fig. 3.1.

The option argument ⟨bondlist⟩ is a character string in a pair of square brackets, where each character indicates the presence of a double bond at the edge specified by the character (Table 3.5).

Examples of \fiveheterov:

```
\fiveheterov{1==O}{2D==O;5D==O;3==CH$_{3}$;4==CH$_{3}$}\qquad
\fiveheterov[b]{1==O}{}\qquad
\fiveheterov{2==O;5==O}{1D==O;3B==CH$_{2}$CH$_{3}$;4B==CH$_{3}$}\qquad
\fiveheterov{2==S;5==S}{1Sa==SiMe$_{3}$;1Sb==Li}
```

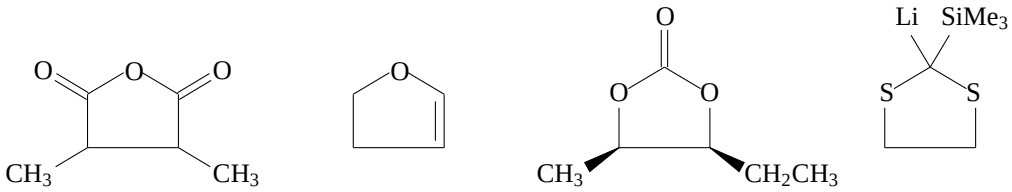
produce



Examples of `\fiveheterovi`:

```
\fiveheterovi{1==O}{2D==O;5D==O;3==CH$_{3}$;4==CH$_{3}$}\qquad
\fiveheterovi[b]{1==O}{}\qquad
\fiveheterovi{2==O;5==O}{1D==O;3B==CH$_{2}$CH$_{3}$;4B==CH$_{3}$}\qquad
\fiveheterovi{2==S;5==S}{1Sa==SiMe$_{3}$;1Sb==Li}
```

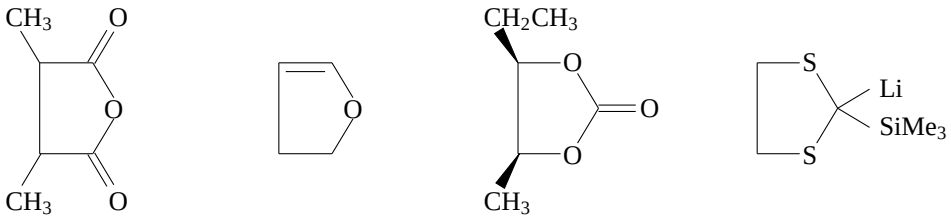
produce



Examples of `\fiveheteroh`:

```
\fiveheteroh{1==O}{2D==O;5D==O;3==CH$_{3}$;4==CH$_{3}$}\quad
\fiveheteroh[b]{1==O}{}\quad
\fiveheteroh{2==O;5==O}{1D==O;3B==CH$_{2}$CH$_{3}$;4B==CH$_{3}$}\quad
\fiveheteroh{2==S;5==S}{1Sa==SiMe$_{3}$;1Sb==Li}
```

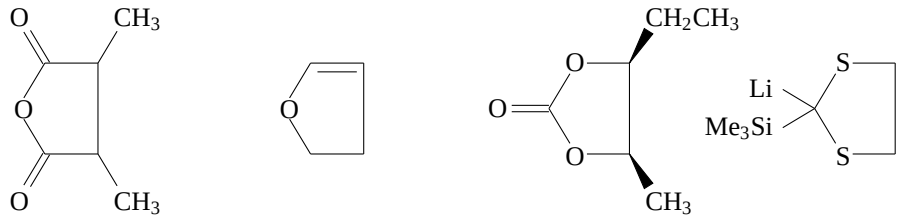
produce



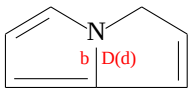
Examples of `\fiveheterohi`:

```
\fiveheterohi{1==O}{2D==O;5D==O;3==CH$_{3}$;4==CH$_{3}$}\qquad
\fiveheterohi[b]{1==O}{}\qquad
\fiveheterohi{2==O;5==O}{1D==O;3B==CH$_{2}$CH$_{3}$;4B==CH$_{3}$}\qquad
\fiveheterohi{2==S;5==S}{1Sa==Me$_{3}$Si;1Sb==Li}
```

produce the following structures:



Example 3.2. According to the ring-fusion mechanism described in Section 2.5, the bond list ⟨bondlist⟩ is capable of containing a code of an attached component for ring fusion, as described in Subsection 3.3.1. For example, the structural formula of 3*H*-pyrrolizine (**3-60**) can be drawn in terms of the scheme 5←5 shown below:



3-60

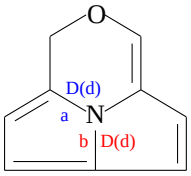
IUPAC name: 3*H*-pyrrolizine

XƎMTEX command:

```
\fiveheterovi[ce%
{b\fivefusevi[b]{5==\null}{}{D}}%
]{2==N}{}
```

The code for drawing **3-60** consists of a five-membered ring (drawn by `\fiveheterovi`) as a parent component and a five-membered ring (drawn by `fivefusevi`) as an attached component. The setting of `b` in the ⟨bondlist⟩ of `\fiveheterov` corresponds to the setting of `D` in the ⟨fuse⟩ of `\fivefusevi`, i.e., `[{b...{D}}]`, where `D` is set in place of the locant alphabet `d` to select the alternative endpoint of the bond (edge) as a fusion union.

The left five-membered ring of the resulting 3*H*-pyrrolizine (**3-60**) can be used as a parent structure for further ring fusion in order to draw the structural formula (**3-61**) of 1*H*[1,4]oxazino[3,4,5-*cd*]pyrrolizine [2, P-25.3.3.2.1].



3-61

IUPAC name: 1*H*[1,4]oxazino[3,4,5-*cd*]pyrrolizine

XƎMTEX command:

```
\fiveheterovi[ce%
{b\fivefusevi[b]{5==\null}{}{D}}%
{a\sixfusev[b]{1==O}{}{D}[c]}%                (added)
]{2==N}{}
```

The code based on the command `\sixfusev` is added to the the ⟨bondlist⟩ of `\fiveheterovi`, where the setting of `a` in the ⟨bondlist⟩ of `\fiveheterovi` corresponds to the setting of `D` in the ⟨fuse⟩ of `\sixfusev`, i.e., `[{a...{D}}]`. □

3.4.4 Drawing Six-Membered Heterocycles

The XƎMTEX commands `\sixheterov` and `\sixheterovi` for general use, which are defined in hetarom.sty for drawing six-membered heterocycles of vertical direction, have the following formats:

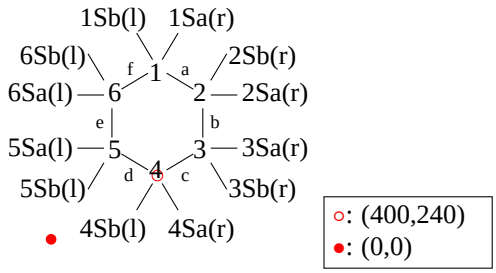
```
\sixheterov(⟨skelbdlist⟩)[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}[⟨delbdlist⟩]
\sixheterovi(⟨skelbdlist⟩)[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}[⟨delbdlist⟩]
```

The horizontal counterparts `\sixheteroh` and `\sixheterohi` for general use, which are also defined in hetarom.sty for drawing six-membered heterocycles, have the following formats:

```
\sixheteroh(⟨skelbdlist⟩)[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}[⟨delbdlist⟩]
\sixheterohi(⟨skelbdlist⟩)[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}[⟨delbdlist⟩]
```

The required arguments ⟨atomlist⟩ and ⟨subslist⟩ (cf. Section 3.2) as well as the optional arguments ⟨skelbdlist⟩, ⟨bondlist⟩, and ⟨delbdlist⟩ (cf. Section 3.3) can be declared according to the general format of `\ComGen` (page 32).

(a) Output of `\sixheterov`



(b) Output of `\sixheterovi`

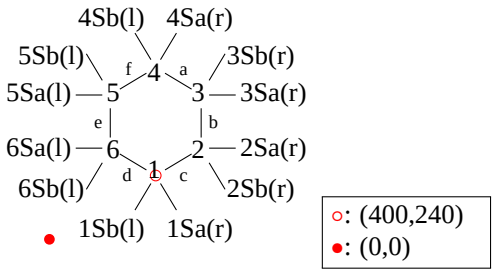
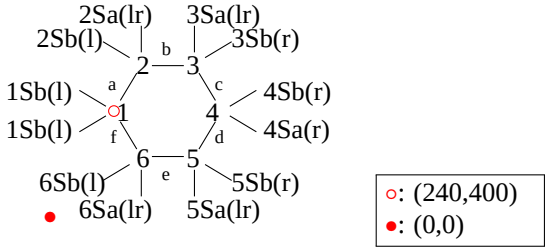


Figure 3.7. XeTeX commands for general use, which output six-membered heterocyclic rings of vertical type. For the meanings of the symbols, see the caption of Fig. 3.2.

(a) Output of `\sixheteroh`



(b) Output of `\sixheterohi`

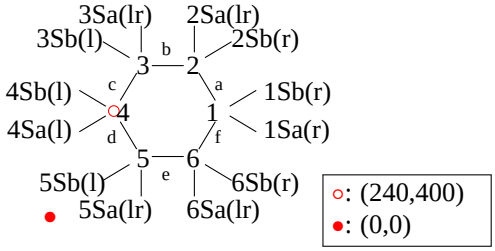


Figure 3.8. XeTeX commands for general use, which output six-membered heterocyclic rings of horizontal type. For the meanings of the symbols, see the caption of Fig. 3.2.

Table 3.6. Argument ⟨bondlist⟩ for commands `\sixheterov`, `\sixheterovi`, `\sixheteroh`, and and `\sixheterohi`

Character	Printed structure	Character	Printed structure
a	1,2-double bond	r	mancude-ring system (right-handed)
b	2,3-double bond	l	mancude-ring system (left-handed)
c	4,3-double bond	none or H or []	fully saturated form
d	4,5-double bond	A	aromatic circle
e	5,6-double bond	{*n*+}	plus at the *n*-hetero atom (*n* = 1 to 6)
f	6,1-double bond		

The locant numbers and the locant alphabets assigned to the structures depicted by these commands are shown in Figs. 3.7 and 3.8. The locant numbers (1 to 6) and the locant alphabets (`a` to `f`) are also shown in the diagrams.

The required argument ⟨atomlist⟩ has been discussed in Subsection 3.2.2. A typical embodiment of ⟨atomlist⟩ is a list of heteroatoms, *e.g.*, 1==N for a nitrogen atom at 1-position. It should be emphasized that, in order to typeset a heteroatom at a given position, the edges incident to the heteroatom are automatically truncated to put space for printing the heteroatom.

The required argument ⟨subslist⟩ for each of these XeTeX commands takes a general format, in which the bond modifiers listed in Table 3.2 are used. The respective modes of output are collected in Fig. 3.1.

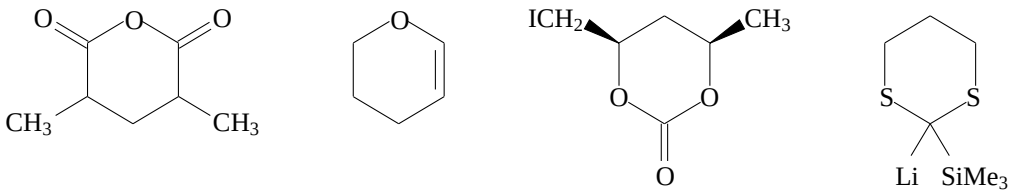
The optional argument ⟨bondlist⟩ is an character string in a pair of square brackets, where each character indicates the presence of a double bond at the edge specified by the character. The bond-specification is rather arbitrary in some cases but conforms to chemical conventions as faithfully as possible if such conventions are presence (Table 3.6). The default prints a fully saturated form and an option argument `r` or `l` can be used to prints out a mancude-ring system.

Examples for `sixheterov`:

```
\sixheterov{1==O}{2D==O;6D==O;3==CH$_{3}$;5==CH$_{3}$}\qquad
\sixheterov[b]{1==O}{}\qquad
\sixheterov{3==O;5==O}{4D==O;6B==ICH$_{2}$;2B==CH$_{3}$}\qquad
```

```
\sixheterov{3==S;5==S}{4Sa==SiMe$_{3}$;4Sb==Li}
```

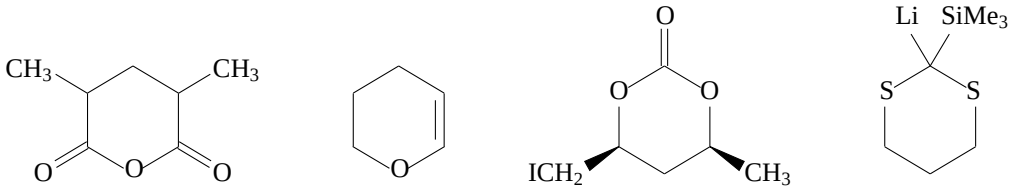
produce



Examples for `sixheterovi`:

```
\sixheterovi{1==O}{2D==O;6D==O;3==CH$_{3}$;5==CH$_{3}$}\qquad
\sixheterovi[b]{1==O}{}\qquad
\sixheterovi{3==O;5==O}{4D==O;6B==ICH$_{2}$;2B==CH$_{3}$}\qquad
\sixheterovi{3==S;5==S}{4Sa==SiMe$_{3}$;4Sb==Li}
```

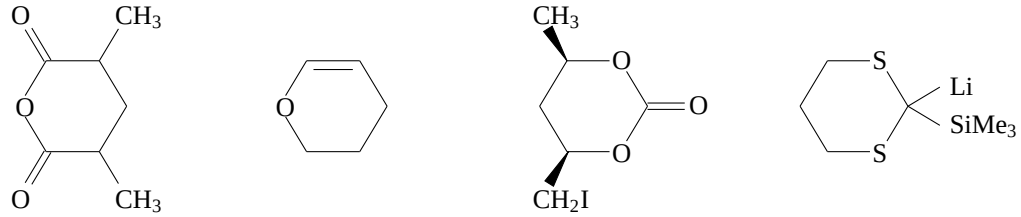
produce



Examples for `sixheteroh`:

```
\sixheteroh{1==O}{2D==O;6D==O;3==CH$_{3}$;5==CH$_{3}$}\quad
\sixheteroh[b]{1==O}{}\quad
\sixheteroh{3==O;5==O}{4D==O;6B==CH$_{2}$I;2B==CH$_{3}$}\quad
\sixheteroh{3==S;5==S}{4Sa==SiMe$_{3}$;4Sb==Li}
```

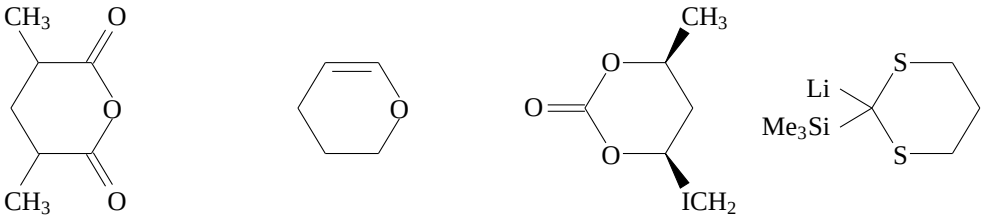
produce



Examples for `sixheterohi`:

```
\sixheterohi{1==O}{2D==O;6D==O;3==CH$_{3}$;5==CH$_{3}$}\qquad
\sixheterohi[b]{1==O}{}\qquad
\sixheterohi{3==O;5==O}{4D==O;6B==ICH$_{2}$;2B==CH$_{3}$}\qquad
\sixheterohi{3==S;5==S}{4Sa==Me$_{3}$Si;4Sb==Li}
```

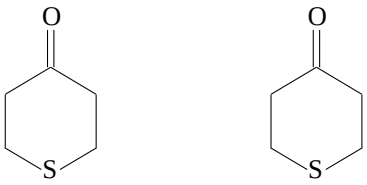
produce



The commands \sixheterov and \sixheterovi can yield the equivalent results if the modes of numbering are altered in ⟨atomlist⟩ and ⟨subslist⟩. For example, the following two statements

```
\sixheterov{4==S}{1D==O} \qquad
\sixheterovi{1==S}{4D==O}
```

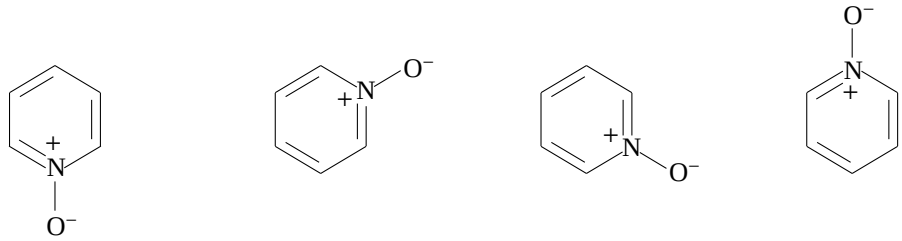
produce the same structure as follows.



However, the latter is preferred to the former because the numbering of the ring atoms conforms to the chemical nomenclature. This is the reason why we have made such macros of inverse type.

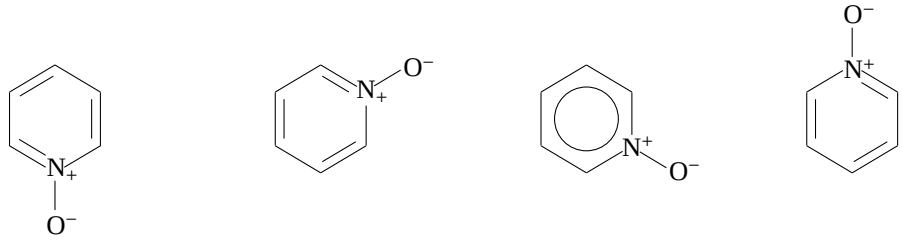
Example 3.3. The command \pyridinev (or \pyridinevi) places a nitrogen atom on a fixed position of a pyridine ring. For printing a nitrogen atom on another position, the command \sixheterov should be used as shown in the following examples of drawing different formulas of pyridine N-oxide.

```
\pyridinevi[r{1+}]{1==O$^{-}$} \qquad
\sixheterov[r{2+}]{2==N}{2==O$^{-}$} \qquad
\sixheterov[r{3+}]{3==N}{3==O$^{-}$} \qquad
\pyridinev[r{1+}]{1==O$^{-}$}
```



A charge on an inner nitrogen can be alternatively typeset by putting a charged atom in the ⟨atomlist⟩ of the \sixhetrov command.

```
\sixheterov[r]{4==N$_{+}$}{4==O$^{-}$} \qquad
\sixheterov[l]{2==N$_{+}$}{2==O$^{-}$} \qquad
\sixheterov[A]{3==N$^{+}$}{3==O$^{-}$} \qquad
\sixheterov[ace]{1==N$^{+}$}{1==O$^{-}$}
```

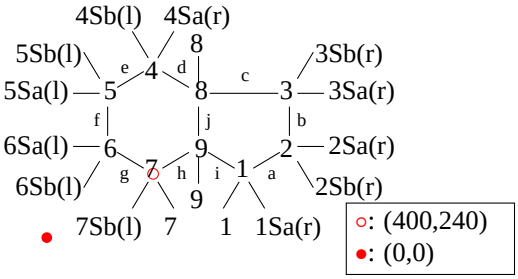


Note that the ⟨bondlist⟩ of \sixheterov is capable of taking [r], [l], or [A]. □

3.4.5 Drawing Heterocycles with Fused Six-to-Five-Membered Rings

The XeTeX commands \nonaheterov and \nonaheterovi for general use, which are defined in hetarom.sty for drawing 6-5 fused heterocycles of vertical direction, have the following formats:

(a) Output of \nonaheterov



(b) Output of \nonaheterovi

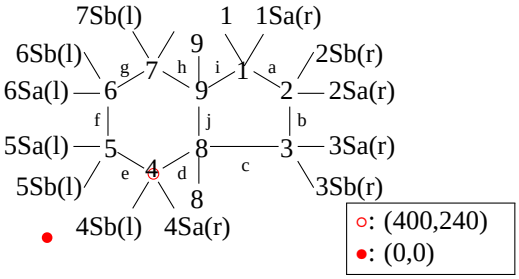
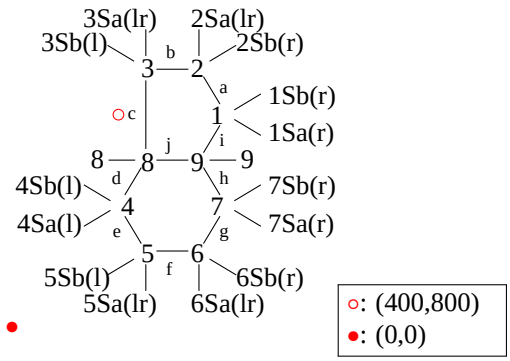


Figure 3.9. XeLaTeX commands for general use, which output 6-5 fused heterocyclic rings of vertical type. For the meanings of the symbols, see the caption of Fig. 3.2.

(a) Output of \nonaheteroh



(b) Output of \nonaheterohi

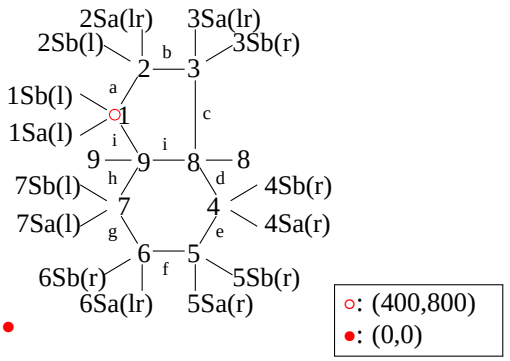


Figure 3.10. XeLaTeX commands for general use, which output 6-5 fused heterocyclic rings of horizontal type. For the meanings of the symbols, see the caption of Fig. 3.2.

```
\nonaheterov(⟨skelbdlist⟩)[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}[⟨delbdlist⟩]
\nonaheterovi(⟨skelbdlist⟩)[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}[⟨delbdlist⟩]
```

The horizontal counterparts \nonaheteroh and \nonaheterohi for general use, which are also defined in hetarom.sty for drawing 6-5 fused heterocycles, have the following formats:

```
\nonaheteroh(⟨skelbdlist⟩)[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}[⟨delbdlist⟩]
\nonaheterohi(⟨skelbdlist⟩)[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}[⟨delbdlist⟩]
```

The required arguments ⟨atomlist⟩ and ⟨subslist⟩ (cf. Section 3.2) as well as the optional arguments ⟨skelbdlist⟩, ⟨bondlist⟩, and ⟨delbdlist⟩ (cf. Section 3.3) can be declared according to the general format of \ComGen (page 32).

The locant numbers and the locant alphabets assigned to the structures depicted by these commands are shown in Figs. 3.9 and 3.10. The locant numbers (1 to 9) and the locant alphabets (a to j) are also shown in the diagrams.

The required argument ⟨atomlist⟩ has been discussed in Subsection 3.2.2. It takes a usual format with respect to heteroatoms attached to n = 1 to 7, *e.g.*, 1==N for a nitrogen atom at 1-position. Hetero atoms at 3a- and 7a-positions are represented as to be 3a==N (or 8==N) for a nitrogen at 3a-position, 7a==N (or 9==N) for at a nitrogen at 7a-position, and so on.

The required argument ⟨subslist⟩ for each of these XeLaTeX commands takes a general format except that the locant numbers 3a and 7a are replaced by 8 and 9. The bond modifiers listed in Table 3.2 are used. The respective modes of output are collected in Fig. 3.1. The handedness for each oriented or double-sided position is shown with a character set (r or l) in parentheses.

Table 3.7. Argument ⟨bondlist⟩ for commands \nonaheterov, \nonaheterovi, \nonaheteroh, and \nonaheterohi

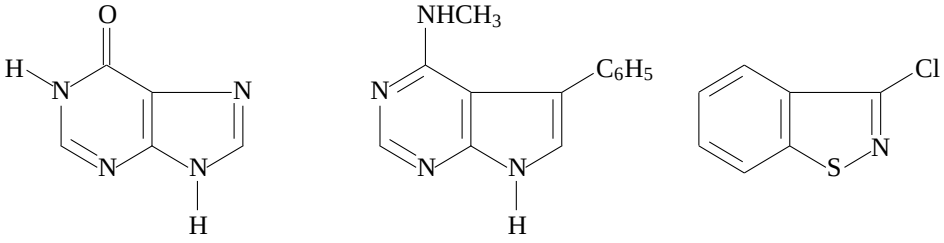
Character	Printed structure	Character	Printed structure
none or H or []	fully saturated form		
a	1,2-double bond	b	2,3-double bond
c	3,3a-double bond	d	4,3a-double bond
e	4,5-double bond	f	5,6-double bond
g	6,7-double bond	h	7,7a-double bond
i	1,7a-double bond	j	3a,4a-double bond
r	right-handed mancude ring (six-membered ring)		
A	aromatic circle (six-membered ring)		
B	aromatic circle (five-membered ring)		
{*n*+}	plus at the *n*-hetero atom (*n* = 1 to 9)		

The optional argument ⟨bondlist⟩ specifies edges with a double bond (Table 3.7).

Examples for \nonaheterov:

```
\nonaheterov[bjg]{1==N;3==N;5==N;7==N}{1==H;5==H;4D==O}
\nonaheterov[bjge]{1==N;5==N;7==N}%
 {1==H;3==C$_{6}$H$_{5}$;4==NHCH$_{3}$}
\nonaheterov[bjge]{1==S;2==N}{3==Cl}
```

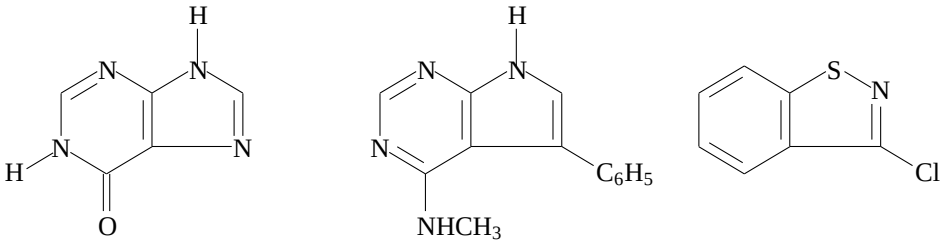
produce the following structures:



Examples for \nonaheterovi:

```
\nonaheterovi[bjg]{1==N;3==N;5==N;7==N}{1==H;5==H;4D==O}
\nonaheterovi[bjge]{1==N;5==N;7==N}%
 {1==H;3==C$_{6}$H$_{5}$;4==NHCH$_{3}$}
\nonaheterovi[bjge]{1==S;2==N}{3==Cl}
```

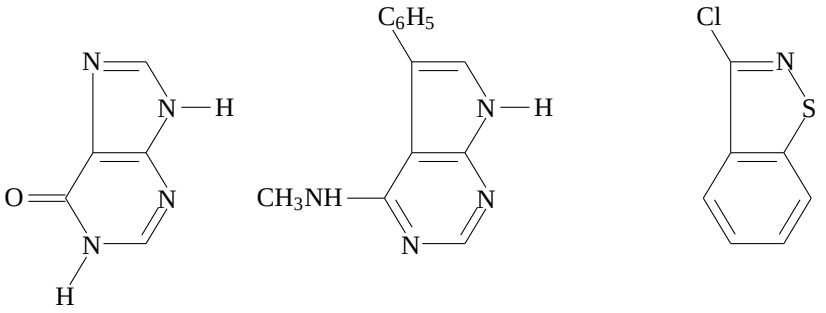
produce the following structures:



Examples for \nonaheteroh:

```
\nonaheteroh[bjg]{1==N;3==N;5==N;7==N}{1==H;5==H;4D==O}
\nonaheteroh[bjge]{1==N;5==N;7==N}%
 {1==H;3==C$_{6}$H$_{5}$;4==NHCH$_{3}$}
\nonaheteroh[bjge]{1==~S;2==N}{3==Cl}
```

produce the following structures:

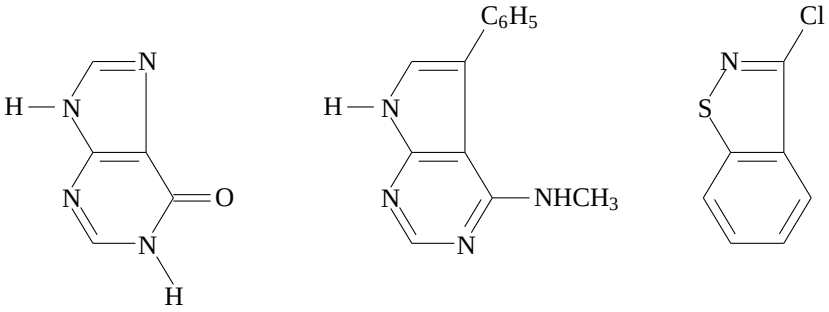


Note that the position of a sulfur atom in the last structure is adjusted by inputing `1==~S` in place of `1==S`. The width of the letter 'N' is calculated to be 7.22pt by inputting `{\setbox0=\hbox{N} \the\wd0}`, while the width of the letter 'S' is calculated to be 5.56pt by inputting `{\setbox0=\hbox{S} \the\wd0}`. The adjusted input '`~S`' has the width of 8.06pt, which is compatible to the width of 'N'.

Examples for `\nonaheterohi`:

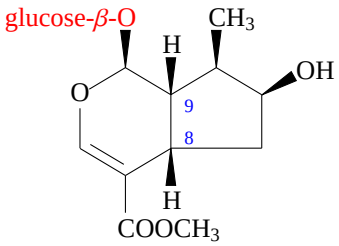
```
\nonaheterohi[bjg]{1==N;3==N;5==N;7==N}{1==H;5==H;4D==O}
\nonaheterohi[bjge]{1==N;5==N;7==N}%
 {1==H;3==C$_{6}$H$_{5}$;4==NHCH$_{3}$}
\nonaheterohi[bjge]{1==S~;2==N}{3==Cl}
```

produce the following structures:



Note that the position of a sulfur atom in the last structure is adjusted by inputing `1==S~` in place of `1==S`.

Example 3.4. A configuration at a bridgehead position can be designated by a bond modifier, which is declared in the ⟨subslist⟩ of the `\nonahetrovi` command. As exemplified by the structural formula **3-62** of loganin, the bond modifier `B` in the setting of `8B==H;9B==H` (cf. Table 3.2) produces *β*-hydrogens at the bridgehead positions of **3-62**.



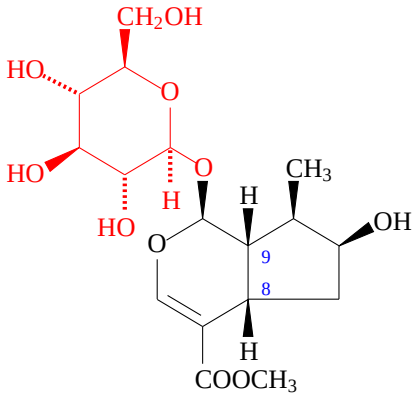
3-62

common name: loganin
XƎMTEX command:

```
\nonaheterovi[e]{6==O}%
{1B==CH$_{3}$;2B==OH;4==COOCH$_{3}$;%
7B==\lmoiety{glucose-$\beta$-O};
8B==H;9B==H}
```

In the structure **3-62**, the *β*-glucose moiety colored in red is represented by a character string "glucose-*β*-O", which is generated by `\lmoiety{glucose-$\beta$-O}`, where `\lmoiety` produces a left-handed output of the character string.

In order to print out the *β*-glucose moiety of **3-62** in the form of a full structural formula, a (yl)-function for `\sixheterov` is combined with the `\lyl` command, as found in a red-colored part of the XƎMTEXcommand in the right-hand side of the formula **3-63**.



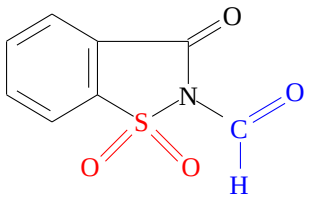
3-63

common name: loganin
XeLaTeX command:

```
\nonaheterovi[e]{6==O}%
{1B==CH$_{3}$;2B==OH;4==COOCH$_{3}$;%
7B==\lyl(8==O){3==\sixheterov{2==O}%
{3==(yl);1B==CH$_{2}$OH;3GA==H;%
4A==\lmoiety{HO};5B==HO;6A==HO}};%
8B==H;9B==H}
```

The the red-colored part is declared in the ⟨subslist⟩ of the command `\nonaheterovi` according to the substitution technique. □

Example 3.5. The structure **3-64** of N-formylsaccharin as a new formylating agent [3] is drawn below by using `\nonaheterov`.



3-64

common name: N-formylsaccharin
XeLaTeX command:

```
\nonaheterov[r]{1h==%
\dtrigonal{1==(yl);0==S;2D==O;3D==O};%
2==N}{3D==O;2==%
\Utrigonal{3==(yl);0==C;2D==O;1==H}}
```

In the ⟨atomlist⟩ of `\nonaheterov`, the code due to `\dtrigonal` is declared to output the SO_2 moiety according to the replacement technique. In the ⟨subslist⟩ of `\nonaheterov`, on the other hand, the code due to `\Utrigonal` is declared to output the formyl moiety (C(=O)H) according to the substitution technique. The declaration of `r` in the ⟨bondlist⟩ of `\nonaheterov` aims at outputting a right-handed mancude-ring system (an aromatic six-membered ring) according to Table 3.7. □

3.4.6 Drawing Heterocycles with Fused Six-to-Six-Membered Rings

The XeLaTeX commands `\decaheterov` and `\decaheterovi` for general use, which are defined in hetarom.sty for drawing 6-6 fused heterocycles of vertical direction, have the following formats:

```
\decaheterov(⟨skelbdlist⟩)[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}[⟨delbdlist⟩]
\decaheterovi(⟨skelbdlist⟩)[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}[⟨delbdlist⟩]
```

The horizontal counterparts `\decaheteroh` and `\decaheterohi` for general use, which are also defined in hetarom.sty for drawing 6-6 fused heterocycles, have the following formats:

```
\decaheteroh(⟨skelbdlist⟩)[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}[⟨delbdlist⟩]
\decaheterohi(⟨skelbdlist⟩)[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}[⟨delbdlist⟩]
```

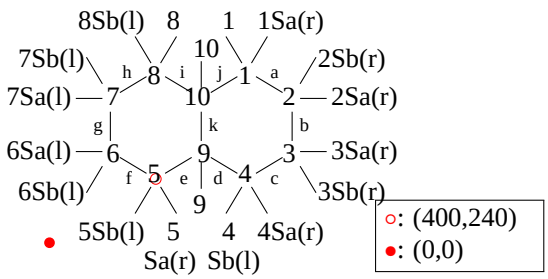
The diagonal counterparts `\decaheterovb` and `\decaheterovt` for general use, which are also defined in hetarom.sty for drawing 6-6 fused heterocycles, have the following formats:

```
\decaheterovb(⟨skelbdlist⟩)[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}[⟨delbdlist⟩]
\decaheterovt(⟨skelbdlist⟩)[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}[⟨delbdlist⟩]
```

The required arguments ⟨atomlist⟩ and ⟨subslist⟩ (cf. Section 3.2) as well as the optional arguments ⟨skelbdlist⟩, ⟨bondlist⟩, and ⟨delbdlist⟩ (cf. Section 3.3) can be declared according to the general format of `\ComGen` (page 32).

The locant numbers and the locant alphabets assigned to the structures depicted by these commands are shown in Figs. 3.11–3.13. The locant numbers (1 to 10) and the locant alphabets (`a` to `k`) are also shown in the diagrams.

(a) Output of `\decaheterov`



(b) Output of `\decaheterovi`

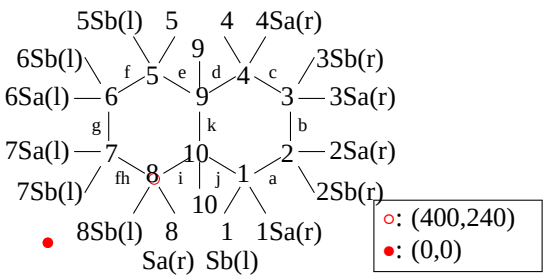
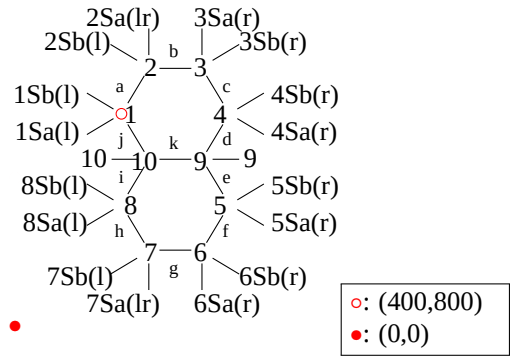


Figure 3.11. XyMTEX commands for general use, which output 6-6 fused heterocyclic rings of vertical type. For the meanings of the symbols, see the caption of Fig. 3.2.

(a) Output of `\decaheteroh`



(b) Output of `\decaheterohi`

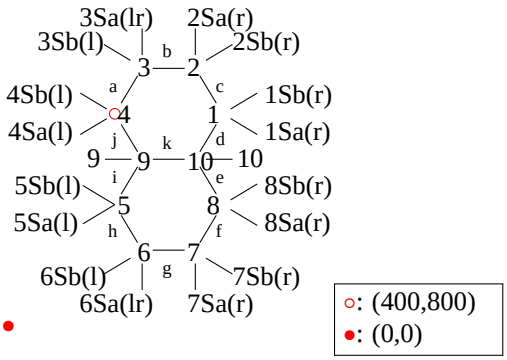
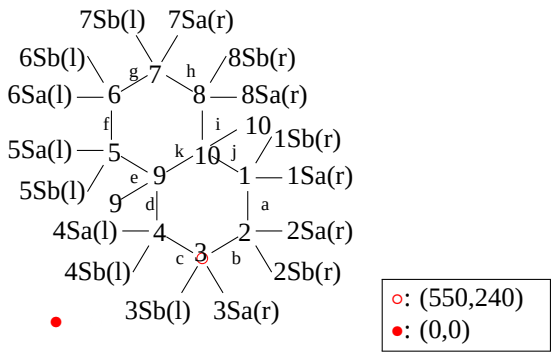


Figure 3.12. XyMTEX commands for general use, which output 6-6 fused heterocyclic rings of horizontal type. For the meanings of the symbols, see the caption of Fig. 3.2.

(a) Output of `\decaheterovb`



(b) Output of `\decaheterovt`

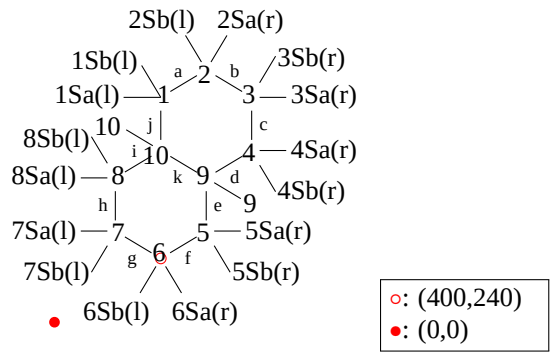


Figure 3.13. XyMTEX commands for general use, which output 6-6 fused heterocyclic rings of diagonal type. For the meanings of the symbols, see the caption of Fig. 3.2.

The required argument ⟨atomlist⟩ has been discussed in Subsection 3.2.2. It takes a usual format with respect to heteroatoms attached to n = 1 to 8, *e.g.*, `1==N` for a nitrogen atom at 1-position. A hetero-atom

Table 3.8. Argument ⟨bondlist⟩ for commands `\decaheterov`, `\decaheterovi`, `\decaheteroh`, `\decaheterohi` `\decaheterovb`, and `\decaheterovt`

Character	Printed structure	Character	Printed structure
none or [H] or []	fully saturated form		
a	1,2-double bond	b	2,3-double bond
c	4,3-double bond	d	4,4a-double bond
e	4a,5-double bond	f	5,6-double bond
g	6,7-double bond	h	7,8-double bond
i	8,8a-double bond	j	1,8a-double bond
k	4a,8a-double bond		
r	mancude-ring system (right-handed)		
A	aromatic circle in the left ring		
B	aromatic circle in the right ring		
{*n*+}	plus at the *n*-nitrogen atom (*n* = 1 to 10)		

on the 4a-position is designated to be `4a==N` or `9==N`; and a hetero-atom on the 8a-position is given as to be `8a==N` or `{{10}}==N`.

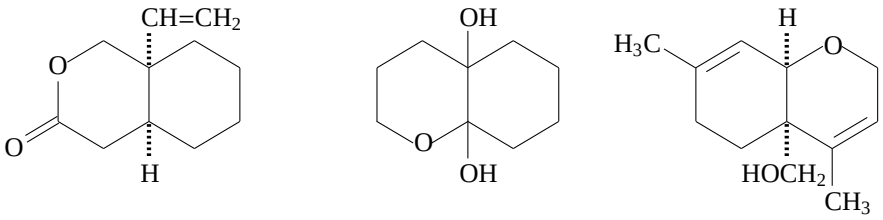
The required argument ⟨subslist⟩ for each of these XeLaTeX commands takes a general format except that the locant numbers 4a and 8a are replaced by 9 and 10. The bond modifiers listed in Table 3.2 are used. The respective modes of output are collected in Fig. 3.1. The handedness for each oriented or double-sided position is shown with a character set (r or l) in parentheses.

Each character in the optional argument ⟨bondlist⟩ specifies an inner (endocyclic) double bond as shown in Table 3.8.

Examples of `\decaheterov`:

```
\decaheterov{7==O}{6D==O;9A==H;{{10}A}==CH=CH$_{2}$}
\decaheterov{5==O}{9==OH;{{10}}==OH}
\decaheterov[ch]{1==O}{9A==\lmoiety{HOC\rlap{H$_{2}$}};{{10}A}==H;%
4==CH$_{3}$;7==H$_{3}$C}
```

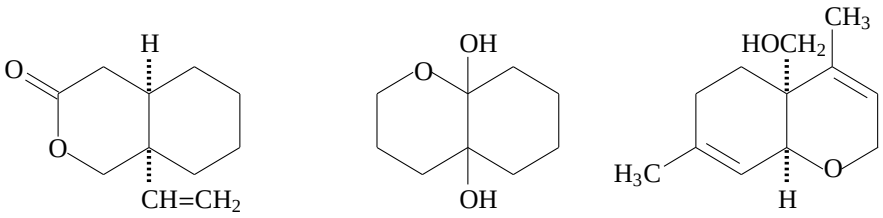
produce the following structures:



Examples of `\decaheterovi`:

```
\decaheterovi{7==O}{6D==O;9A==H;{{10}A}==CH=CH$_{2}$}
\decaheterovi{5==O}{9==OH;{{10}}==OH}
\decaheterovi[ch]{1==O}{9A==\lmoiety{HOC\rlap{H$_{2}$}};{{10}A}==H;%
4==CH$_{3}$;7==H$_{3}$C}
```

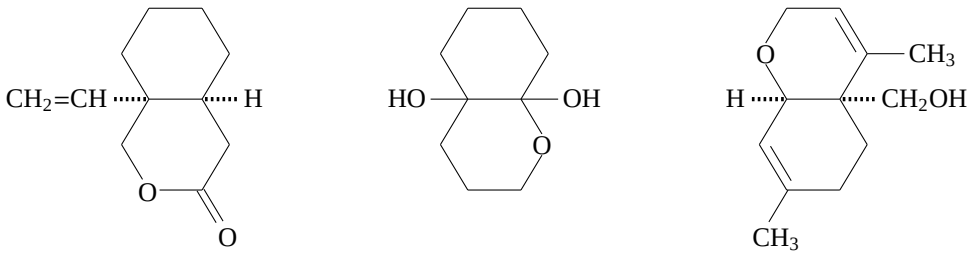
produce the following structures:



Examples of \decaheteroh:

```
\decaheteroh{7==O}{6D==O;9A==H;{{10}A}==CH$_{2}$=CH}
\decaheteroh{5==O}{9==OH;{{10}}==HO}
\decaheteroh[ch]{1==O}{9A==CH$_{2}$OH;{{10}A}==H;%
4==CH$_{3}$;7==CH$_{3}$}
```

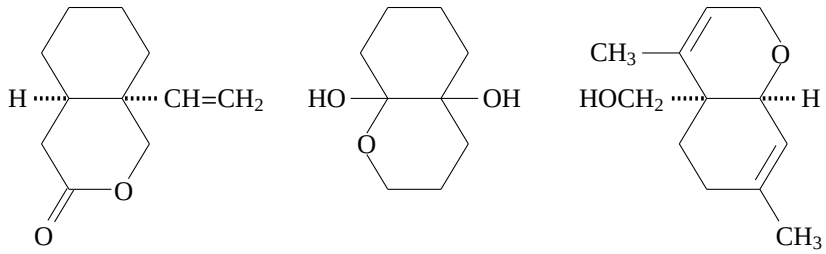
produce the following structures:



Examples of \decaheterohi:

```
\decaheterohi{7==O}{6D==O;9A==H;{{10}A}==CH=CH$_{2}$}
\decaheterohi{5==O}{9==HO;{{10}}==OH}
\decaheterohi[ch]{1==O}{9A==\lmoiety{HOCH$_{2}$};{{10}A}==H;%
4==CH$_{3}$;7==CH$_{3}$}
```

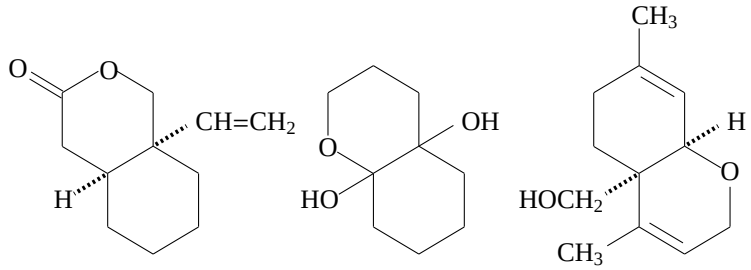
produce the following structures:



Examples for \decaheterovb:

```
\decaheterovb{7==O}{6D==O;9A==H;{{10}A}==CH=CH$_{2}$}
\decaheterovb{5==O}{9==HO;{{10}}==OH}
\decaheterovb[ch]{1==O}{9A==HOCH$_{2}$;{{10}A}==H;%
4==CH$_{3}$;7==CH$_{3}$}
```

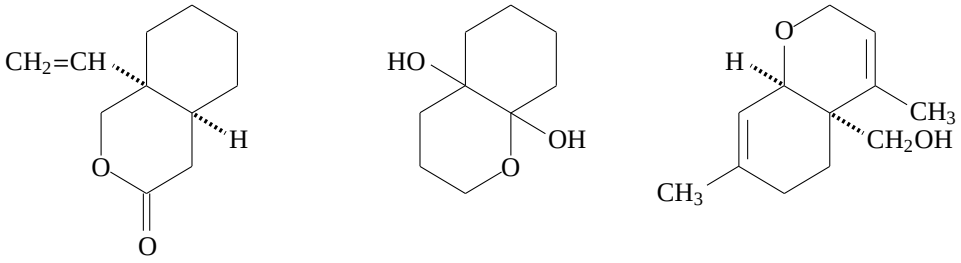
produce the following structures:



Examples for \decaheterovt:

```
\decaheterovt{7==O}{6D==O;9A==H;{{10}A}==CH$_{2}$=CH}
\decaheterovt{5==O}{9==OH;{{10}}==HO}
\decaheterovt[ch]{1==O}{9A==CH$_{2}$OH;{{10}A}==H;%
4==CH$_{3}$;7==CH$_{3}$}
```

produce the following structures:



3.5 Enhanced Functions of Commands for General Use

This section is devoted to additional examples for explaining enhanced functions of XeLaTeXcommands for general use, which mainly stem from the optional arguments added to the expanded format, i.e., ⟨skelbdlist⟩ and ⟨delbdlist⟩.

3.5.1 Simplified Format vs. Expanded Format

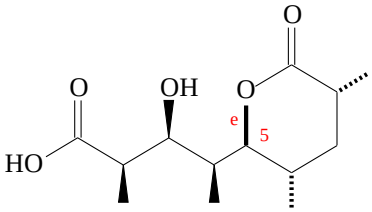
As found in the comparison between the simplified syntax of a XeLaTeX command of general use (Subsection 2.2.2 on page 17) and its expanded format (Section 3.1 on page 32), we add a top optional argument ⟨skelbdlist⟩ to treat stereochemical information (Subsection 3.3.2) as well as an end optional argument ⟨delbdlist⟩ to treat a bond-deleted skeleton (Subsection 3.3.3).

The argument ⟨skelbdlist⟩ contains pairs of two alphabets in braces, where each pair consists of a bond specifier (a lowercase letter) and an uppercase letter (A or B). The letter A represents an α (downward) bond, while B represents a β (upward) bond. For example, an ⟨skelbdlist⟩, `({aA}{cB})`, represents that bond '`a`' is an α bond in a dotted form and that bond '`c`' is a β bond in a boldfaced form. The argument ⟨delbdlist⟩ is a list of bond specifiers, each of which designates a bond to be deleted. As a matter of course, ⟨skelbdlist⟩ and ⟨delbdlist⟩ take no common bond specifiers.

3.5.2 Boldfaced and Dotted Bonds

The following example shows that the `\sixheterov` command takes `({eB})` as an optional ⟨skelbdlist⟩, which typesets a boldfaced bond at '`e`' in the resulting tetrahydropyran ring.

```
\sixheterov({eB}){6==O}{1D==O;2A==\null;4A==\null;%
5==\tetramethylenei{}{1W==HO;1D==O;2B==\null;3B==OH;4B==\null;4==(yl)}}
```



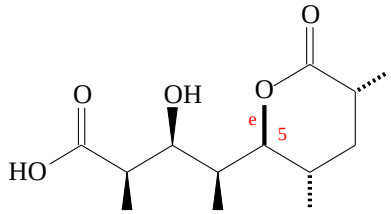
3-65

This is an example of the substitution technique (cf. Section 2.7), in which the side-chain is based on `\tetramethylenei` written in the ⟨subslist⟩ of the outer `\sixheterov` command.

The almost same structural formula can alternatively drawn by means of the replacement technique (cf. Section 2.7), in which the ⟨bondlist⟩ of the `\sixheterov` command is used for specifying the side-chain. Thus, the code,

```
\sixheterov({eB}){6==O;%
5s==\pentamethylenei{}{1W==HO;1D==O;2B==\null;3B==OH;4B==\null;5==(yl)}%
}{1D==O;2A==\null;4A==\null}
```

generates the following formula:



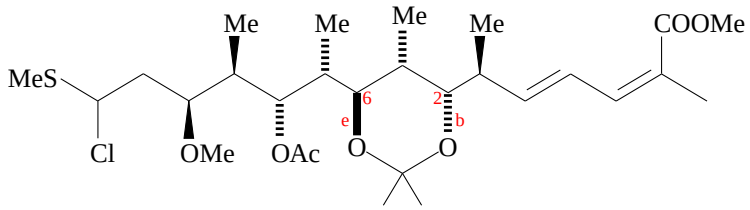
3-66

Compare between **3-65** and **3-66** with focusing on the lengths of the exocyclic bonds at the locant number 5. Then we find that the bond length of **3-65** is shorter than that of **3-66**. The bond length of **3-65** due to the substitution technique is assigned to a bond linking a skeletal position with a substituent. Note that the chain moiety generated by `\tetramethylenei` is regarded as a substituent attached to the skeletal position 5. On the other hand, the bond length of **3-66** due to the replacement technique is assigned to a skeletal bond contained in the chain drawn by `\pentamethylenei`.

Example 3.6. To clarify the difference between the substitution technique and the addition technique, we examine further examples in which the `\sixheterov` command takes an optional ⟨skelbdlist⟩. The following two examples show the comparison between the substitution and the replacement technique, giving formulas of chemically equivalence with slightly different bond lengths.

The substitution technique:

```
\def\thickLineWidth{3pt}
\sixheterov({bA}{eB}){3==O;5==O}{1A==Me;4Sa==\null;4Sb==\null;%
6==\hexamethylene{}{1W==MeS;1==Cl;3B==OMe;4B==Me;5A==OAc;6A==Me;6==(yl)};
2==\hexamethylenei[bd]{}{1==(yl);1B==Me;5==COOMe}}
```

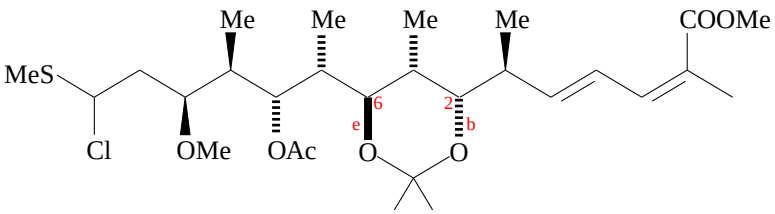


3-67

Note that the declaration of `\def\thickLineWidth{3pt}` changes the thickness of a bold bond (as well as the thickness of a dashed bond) into 3pt.

The replacement technique:

```
\def\thickLineWidth{3pt}
\sixheterov({bA}{eB}){3==O;5==O;%
6s==\heptamethylene{}{1W==MeS;1==Cl;3B==OMe;4B==Me;5A==OAc;6A==Me;7==(yl)};
2s==\heptamethylene[ce]{}{1==(yl);2B==Me;6==COOMe}%
}{1A==Me;4Sa==\null;4Sb==\null}
```

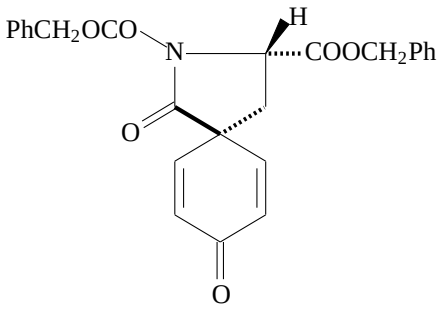


3-68

Compare again between **3-67** (due to the substitution technique) and **3-68** (due to the replacement technique) with focusing on the lengths of the exocyclic bonds at the locant number 2 and 6. For a further modification, see Example 3.15. □

Example 3.7. The following structure shows the use of ⟨skelbdlist⟩ in drawing a spiro ring.

```
\sixheterov[be]{%
1s==\fiveheterov({aA}{eB}){4==N}%
{4==PhCH$_{2}$OCO;3SB==H;3SA==COOCH$_{2}$Ph;5D==O;1==(yl)}%
}{4D==O}
```



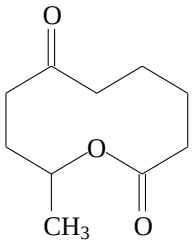
3-69

For a further modification of the skeletal bonds, see Example 3.16. □

3.5.3 Bond Deletion

The ⟨delbdlist⟩ argument of each command for general use is used to draw a large ring. The following example is a simple case in which one bond is deleted:

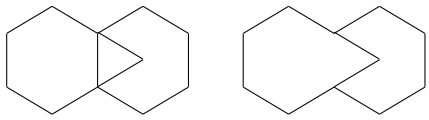
```
\decaheterov{9==O}{4D==O;8D==O;5==CH$_{3}$}[k]
```



3-70

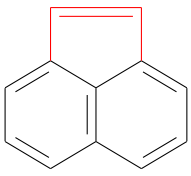
The absence and presence of the ⟨delbdlist⟩ argument give different formulas as follows.

```
\decaheterov[{k\threefuseh{}{}{b}}]{}{}
\decaheterov[{k\threefuseh{}{}{b}}]{}{}[k]
```



3-71 **3-72**

Example 3.8. Acenaphthylene (**3-73**) is drawn by the technique of ring fusion (Section 2.5), which has been once applied to the drawing **3-41**. The present case **3-73** uses `\fiveusev` in place of `\sixfusev` for drawing **3-41**.



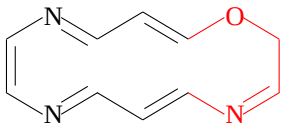
3-73

IUPAC name: acenaphthylene
XyMTEX command:

```
\decaheterov[r%
{j\fivefusev[c]{}{}{a}[e]}%
]{}{}
```

Compare **3-73** with **3-41** under focusing your attention on deleted skeletal bonds. □

Example 3.9. 1-Oxa-4,8,11-triazacyclotetradeca-3,5,5,9,11,13-hexaene [2, P25.2.2.1.2] is also drawn by the technique of ring fusion (Section 2.5) in accord with the scheme 6-6←6, where `\decaheterov` is combined with `\sixfusev`.



3-74

IUPAC name: 1-oxa-4,8,11-triazacyclotetradeca-3,5,5,9,11,13-hexaene

XyMTEX command:

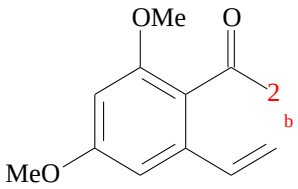
```
\decaheterov[acegi%
{b\sixfusev[c]{1==O;4==N}{}{E}}%
]{5==N;8==N}{}[bk]
```

The ⟨delbdlist⟩ of `\decaheterov` is declared to be `[bk]`, which deletes skeletal bonds at the fused positions so as to generate a peri-cyclic 14-membered ring. □

Example 3.10. A complicated case contains a ring fusion as follows. First, the code

```
\decaheterov[cegi]{2==\null}{6==MeO;8==OMe;1D==O}[b]
```

generates the following formula:

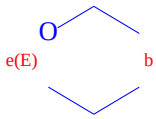


3-75

where `[b]` indicates the deletion of bond ‘b’ and `2==\null` indicates the truncation of the position 2. A similar mechanism is also available in a fusing unit, `\sixfusev`. The code,

```
\sixfusev{6==O}{}{E}[b]
```

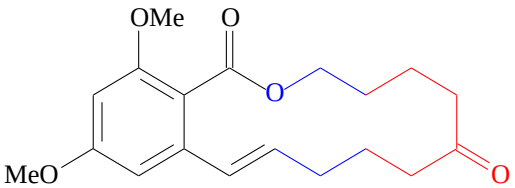
generates a formula:



3-76

where bond ‘e’ is deleted by means of the ⟨fuse⟩ argument (`E`) and bond ‘b’ is deleted by means of the ⟨delbdlist⟩ argument (`b`). Finally, we obtain the structural formula **3-77** of zearalenone:

```
\decaheterov[cegi%
{b\sixfusev[%
{b\sixfusev{}{3D==O}{E}}%
]{6==O}{}{E}[b]}%
]{2==\null%
}{6==MeO;8==OMe;1D==O}[b]
```

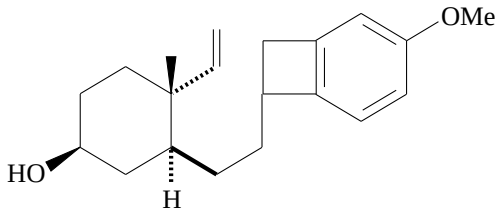


3-77

where two ring-fusion processes by the command `\sixfusev` are involved in a nested fashion (the blue and red components). □

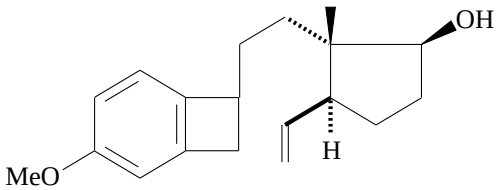
Example 3.11. Intermediates for steroid synthesis via intermolecular cycloadditions of *o*-quinodimethane derivatives (Kametani, et al. *J. Org. Chem.*, 1980, **45**, 2204; Grieco, et al. *J. Org. Chem.*, 1980, **45**, 2247) can be drawn by the bond deletion of `\decaheterov` and `\nonaheterov`.

```
\decaheterov({jA}{dB}){%
2s==\fourhetero[{b\sixfusev[ace]{}{2==OMe}{e}}]%
{}{1==(yl)}%
}{6B==HO;9A==H;{10}B==\null;1D==\null}[a]
```



3-78

```
\nonaheterov({dA}{hB}){%
6s==\fourhetero[%
{d\sixfusev[bdf]{}{5==MeO}{b}}]%
{}{3==(yl)}%
}{3B==OH;8B==\null;7D==\null;9A==H}[g]
```

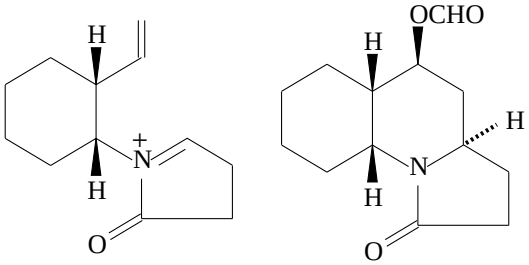


3-79

Each 6-4 fused ring in **3-78** or **3-79** is constructed by the addition technique and then attached to a 6-6 fused ring (with bond deletion) in a spiro fusion (due to the replacement technique). □

Example 3.12. A remarkable merit of using a skeleton with deleted bonds appears in drawing a starting compound with an acyclic part along with the resulting product via cyclization, since their codes are akin to each other.

```
\decaheterov[{4+}%
{c\fivefusevi[e]{5==\null}{4D==O}{E}}%
]{4==N}{1D==\null;9B==H;{10}B==H}[ab]
\hskip2cm
\decaheterov[%
{c\fivefusevi{5==\null}{4D==O}{E}}%
]{4==N}{1B==OCHO;9B==H;{10}B==H;3FA==H}
```

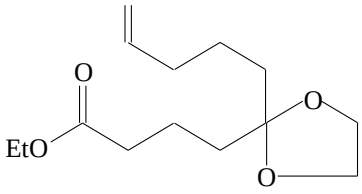


3-80 **3-81**

The latter compound was obtained by the cyclization of the former (D. J. Hart, et al., *J. Am. Chem. Soc.*, 1980, **102**, 397). □

Example 3.13. Some polymethylene chains are drawn in a folded form. The bond-deletion technique can be applied to drawing such folded formulas.

```
\sixheterov{%
3s==\fiveheterovi{1==O;4==O}{5==(yl)};%
6s==\dimethylenei{}{1D==\null;2==(yl)};%
5s==\trimethylenei{}{1W==EtO;1D==O;3==(yl)}%
}{}[e]
```

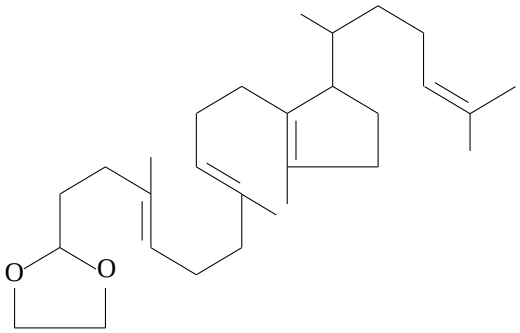


3-82

Note that the omission of '`[e]`' from the last part of the code results in the revival of a spiro ring. □

Example 3.14. The following formula, which is an intermediate for synthesizing steroid skeletons, can also been drawn by this technique.

```
\decaheterov[k%
{f\fivefusevi{2==\null;5==O}{}{A}}%
{a\sixfusev[d%
{b\fivefusevi[d%
{a\sixfusev{%
3s==\trimethylenei[a]{}{1==(yl);2==\null}%
}{6==\null}{D}[c]}%
]{}{}{D}}%
]{}{3G==\null}{D}[c]}%
]{5==O}{{10}Sb==\null;2G==\null}[ej]
```



3-83

If the bond deletion is not considered, the code is based on a nested ring fusion, which is represented schematically by 5 → 6-6 ← 6 ← 5 ← 6. □

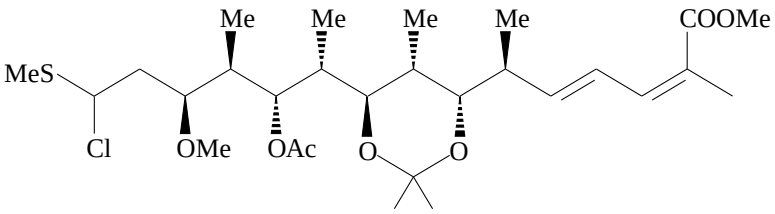
3.5.4 Combination of Bond Deletion with the Replacement Technique

The outputs of Examples 3.6 and 3.16 can be refined so as to avoid simultaneous appearance of a bold bond and a wedged bond.

Example 3.15. The bold line and bold dashed line of **3-68** can be replaced by a wedge and a hashed wedges after bond deletion by ⟨delbdlist⟩, just as **3-39** is redrawn to give **3-44** by using `\WedgeAsSubst` and `\HashWedgeAsSubst`. Hence, the code for drawing **3-68** (Example 3.6) is rewritten as follows:

```
\wedgehashedwedge
\sixheterov{3==O;5==O;%
6s==\heptamethylene{}{1W==MeS;1==Cl;3B==OMe;4B==Me;5A==OAc;6A==Me;7==(yl)};
2s==\heptamethylene[ce]{}{1==(yl);2B==Me;6==COOMe};%
6s==\WedgeAsSubst(0,0)(0,-1){150};%
2s==\HashWedgeAsSubst(0,0)(0,-1){150}%
}{1A==Me;4Sa==\null;4Sb==\null}[be]
```

Thereby, we obtain the following structural formula, where the command `\wedgehashedwedge` is declared to change the default setting.

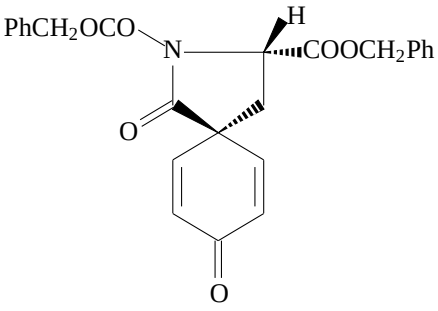


3-84

Thus, the bold skeletal bond of **3-68** is replaced by the wedge bond in **3-84**. □

Example 3.16. Along a similar line, **3-69** (Example 3.7) is converted into **3-85**, where the bold line and bold dashed line of **3-69** are replaced by a wedge and a hashed wedges after bond deletion by ⟨delbdlist⟩.

```
\wedgehashedwedge
\sixheterov[be]{%
1s==\WedgeAsSubst(0,0)(-3,2){160};%
1s==\HashWedgeAsSubst(0,0)(3,2){160};%
1s==\fiveheterov{4==N}%
{4==PhCH$_{2}$OCO;3SB==H;3SA==COOCH$_{2}$Ph;5D==O;1==(yl)}[ae]%
}{4D==O}
```



3-85

Note that `\WedgeAsSubst`, `\HashWedgeAsSubst`, and `\fiveheterov` are declared in the ⟨atomlist⟩ of the command `\sixheterov`. This means that they are based on the replacement technique. □

References

[1] S. Fujita, *Comput. Chem.*, **18**, 109–116 (1994).

[2] IUPAC Chemical Nomenclature and Structure Representation Division, *Provisional Recommendations. Nomenclature of Organic Chemistry* (2004). http://www.iupac.org/reports/provisional/abstract04/favre_310305.html.

[3] T. Cochet, V. Bellosta, A. Greiner, D. Roche, and J. Cossy, *Synlett*, 1920–1922 (2011).

Fusing Units: Syntax

In Subsection 2.5.2 (page 25), the simplified format of the commands for ring fusion (`\ComFuse`) has been discussed briefly. The full form of the syntax is discussed in this chapter, where the commands of this type (stored in the fusering package) are described in detail.

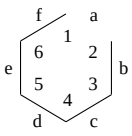
4.1 Command Names and Syntax

XeLaTeX commands for ring fusion, which are represented by `\ComFuse` in general, are designed to have a variable set of skeletal heteroatoms. Their command names are selected in accord with parent structures to be drawn, where they are based on commonly-used terms (e.g., `\sixfusev` for a six-membered fusing unit). The commands of ring fusion are suffixed with '`v`', '`vi`', '`h`' and '`hi`', just as the XeLaTeX commands for general use are suffixed with with '`v`', '`vi`', '`h`' and '`hi`'.

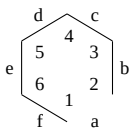
Table 4.1. XeLaTeX Commands for Ring Fusion

vertical type		horizontal type	
`\...v`	`\...vi`	`\...h`	`\...hi`
`\threefusev{}{}{}`	`\threefusevi{}{}{}`	`\threefuseh{}{}{}`	`\threefusehi{}{}{}`
`\fourfuse{}{}{}`			
`\fivefusev{}{}{}`	`\fivefusevi{}{}{}`	`\fivefuseh{}{}{}`	`\fivefusehi{}{}{}`
`\sixfusev{}{}{}`	`\sixfusevi{}{}{}`	`\sixfuseh{}{}{}`	`\sixfusehi{}{}{}`

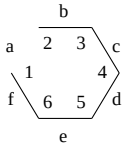
To show different outputs due to the suffixes '`v`', '`vi`', '`h`', and '`hi`', the command `\sixfusev` and the related commands are used to draw hexagonal diagrams **4-1**–**4-4**, which are characterized by the respective sets of locant numbers (for vertices) and of locant alphabets (for edges). Note that the locant alphabet '`a`' is declared in the argument ⟨fuse⟩ (see below) to delete the bond '`a`'.



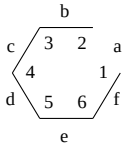
4-1
`\sixfusev{}{}{a}`



4-2
`\sixfusevi{}{}{a}`



4-3
`\sixfuseh{}{}{a}`



4-4
`\sixfusehi{}{}{a}`

The modes of numbering for fusing units are based on those of the XeLaTeX commands (e.g., `\sixheterov`) for general use described in Chapter 3. Thus, the locant numbers (alphabets) of `\sixfusev`

for vertical drawing (**4-1**) start from the top vertex and are placed in a clockwise fashion, while the locant numbers (alphabets) of `\sixfusevi` for inverse vertical drawing (**4-2**) start from the bottom vertex and are placed in an anti-clockwise fashion. On the other hand, the locant numbers (alphabets) of `\sixfuseh` for horizontal drawing (**4-3**) start from the leftmost vertex and are placed in a clockwise fashion, while the locant numbers (alphabets) of `\sixfusehi` for inverse horizontal drawing (**4-4**) start from the rightmost vertex and are placed in an anti-clockwise fashion.

The syntax of a XyMTEX command of ring fusion (Table 4.1) is represented as follows, where the symbol `\ComFuse` is used to represent each command:

Syntax:
`\ComFuse(`⟨skelbdlist⟩`)[`⟨bondlist⟩`]{`⟨atomlist⟩`}{`⟨subslist⟩`}{`⟨fuse⟩`}[`⟨delbdlist⟩`]`

Arguments:

- ⟨skelbdlist⟩ for specifying modification of skeletal bonds (option),
- ⟨bondlist⟩ for specifying unsaturation (option),
- ⟨atomlist⟩ for specifying modification of skeletal atoms (required),
- ⟨subslist⟩ for specifying substituents (required),
- ⟨fuse⟩ for specifying a fusing bond (required), and
- ⟨delbdlist⟩ for specifying deleted bonds in a skeleton (option).

Among these arguments, the required arguments ⟨atomlist⟩, ⟨subslist⟩, and ⟨fuse⟩ as well as the optional argument ⟨bondlist⟩ are frequently used in the form of a simplified format, as discussed in Subsection 2.5.2 (page 25).

4.2 Specification of Required Arguments

As found by the comparison between the syntax of `\ComFuse` and that of `\ComGen` (page 32), the former has an additional argument ⟨fuse⟩ and the remaining arguments are identical with those of the latter. For the specifications of the required arguments other than ⟨fuse⟩, see Section 3.2.

4.2.1 Substitution Lists ⟨subslist⟩

For the construction of ⟨subslist⟩, bond modifiers (Table 3.2), and values of ⟨subsvalue⟩, see Subsection 3.2.1.

4.2.2 Atom Lists ⟨atomlist⟩

For the construction of ⟨atomlist⟩, spiro modifiers, and values of ⟨atomvalue⟩ in the ⟨atomlist⟩, see Subsection 3.2.2.

4.2.3 A Fusing Bond Designated by ⟨fuse⟩

The argument ⟨fuse⟩ consists of one locant alphabet (lowercase letter) or its upper-case letter, which indicates a bond to be deleted for the purpose of ring fusion.

$\left\{ \text{a or A (b or B, } \cdots \text{)} \right\}$

As shown by the diagrams **4-5-4-10** for `\sixfusev` (Fig. 4.1), the lowercase alphabet indicates one terminal of the younger locant number as the control point `(0,0)` of the fused bond, while the uppercase alphabet indicates the other terminal of the senior locant number.

The mechanism of ring fusion has been described in terms of the addition technique in Subsection 2.5.2. For example, the structure **4-11** of a benzoxazole [1, page 469] is drawn by the addition technique, where

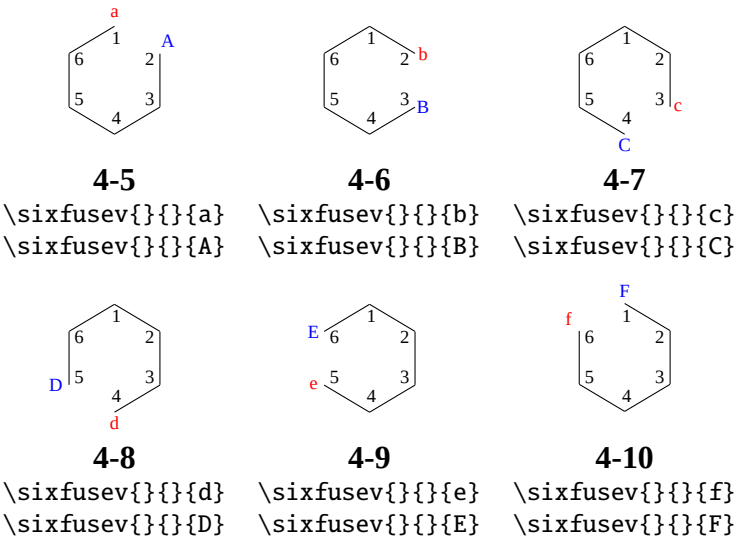
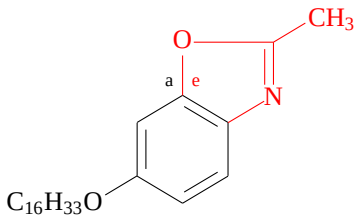


Figure 4.1. Effects of the argument ⟨fuse⟩ of the command `\sixfusev`.

a benzene nucleus generated by `\sixheterov` (the control point: the lowercase letter 'a') is regarded as a parent structure, while an oxazole ring generated by `\fivefusev` (the control point: the lowercase letter 'e') is a fusing unit. The superposition of the former 'a' onto the latter 'e' results in the ring fusion of the two rings at issue.

```
\sixheterov[ace%
{a\fivefusev[b]{2==N;4==O}{3==CH$_{3}$}{e}}]%
{}{5==C$_{16}$H$_{33}$O}
```



4-11

4.3 Specification of Optional Arguments

As found by the comparison between the syntax of `\ComFuse` and that of `\ComGen` (page 32), they have the same set of optional arguments, i.e., ⟨bondlist⟩, ⟨skelbdlist⟩, and ⟨delbdlist⟩. For the specifications of these optional arguments, see Section 3.3.

4.3.1 Bond Lists ⟨bondlist⟩

See Subsubsection 3.3.1. This argument provides a tool for adding skeletal double bonds.

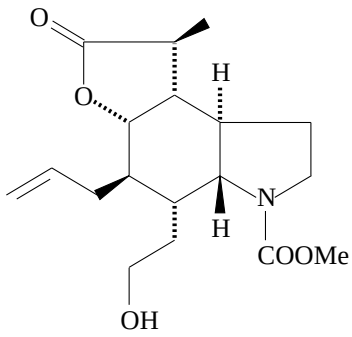
4.3.2 Skeletal Bond Lists ⟨skelbdlist⟩

See Subsection 3.3.2. This argument provides a tool for drawing boldfaced and dotted skeletal bonds for specifying stereochemical information.

The first example shows that the command `\fivefusev` with a ⟨skelbdlist⟩ generates a formula **4-12** with dotted bonds at fused positions.

```
\nonaheterov[%
{e\fivefusev({bA}{eA}){5==O}{3B==\null;4D==O}{A}}%
]{1==N}{1==COOMe;8A==H;9B==H;%
```

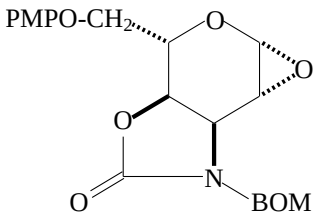
```
6B==\trimethylene[a]{}{3==(yl)};%
7A==\dimethylene{}{2==(yl);1==OH}}
```



4-12

The next example **4-13** shows the use of the ⟨skelbdlist⟩ of `\threefuseh` or `\fivefusevi` to indicate stereochemical information.

```
\sixheterov[%
{b\threefuseh({aA}{cA}){1==O}{}{B}}%
{d\fivefusevi({bB}{eB}){3==N;5==O}{3==BOM;4D==O}{A}}%
]{1==O}{6A==PMPO-CH$_{2}$}
```



4-13

4.3.3 Deleted Bond Lists ⟨delbdlist⟩

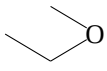
See Subsection 3.3.3. This argument provides a tool for deleting one or more skeletal bonds. In contrast, note that the bond specified by the ⟨fuse⟩ is deleted automatically.

Larger Rings from Two or More Three-Membered Rings

To draw a fused four-membered ring, we can use two `\threefuseh(i)` commands in a nested fashion. Four example, the code

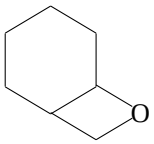
```
\threefusehi[{b\threefuseh{1==O}{}{b}}]{}{}{c}[b]%
```

generates a four-membered unit:



The resulting unit is used to draw a four-membered fused ring in **4-14**, as shown below:

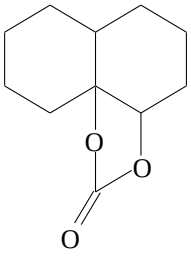
```
\sixheterov[%
{c\threefusehi[{b\threefuseh{1==O}{}{b}}%
]{}{}{c}[b]}%
]{}{}
```



4-14

In a similar way, a five-membered fusing unit can be drawn by combining three `\threefuseh(i)` commands, as shown in the following example for drawing **4-15**:

```
\decaheterov[%
{d\threefuseh[%
{a\threefusehi[%
{a\threefuseh{1==\null;3==\null}{2D==O}{c}}%
]{2==O;1==\null}{}{c}[a]}%
]{2==O}{}{C}[a]}%
]{}{}
```

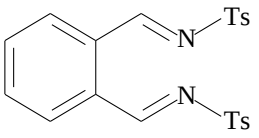


4-15

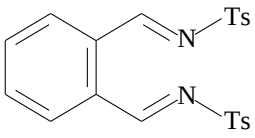
Open Chains of Specific Arrangements

An open chain is sometimes drawn by a hypothetical ring rearrangement. For example, the structure **4-16** contains two C=N-Ts groups, where C=N$\cdots$N=C is a part of a hypothetical six-membered ring generated by `\sixfusev` with the declaration of ⟨delbdlist⟩. The equivalent structure **4-17** can be drawn by using `\decaheterov` with the declaration of ⟨delbdlist⟩.

```
\sixheterov[ace%
{b\sixfusev[ac]{2==N;3==N}{2==Ts;3==Ts}{E}[b]}]{}{}
\decaheterov[acfhk]{2==N;3==N}{2==Ts;3==Ts}[b]
```



4-16



4-17

4.4 Details and Examples of Fusing Units

4.4.1 Six-membered Fusing Units

Vertical Units of Normal and Inverse Types

In X$\mathfrak{Y}$MTEX version 1.01, we can use `\sixunitv` and `\fiveunitv` as building blocks, where one or more bonds can be omitted. In X$\mathfrak{Y}$MTEX version 2.00 and later, we prepare such commands as `\sixfusev` an `\sixfusevi`, producing building blocks with only one deleted bond. These commands can be used in the ⟨bondlist⟩ of another command so as to give a fused structural formula, as described in the preceding chapter. The commands `\sixfusev` and `\sixfusevi` have formats represented by

```
\sixfusev(⟨skelbdlist⟩)[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}{⟨fuse⟩}[⟨delbdlist⟩]
\sixfusevi(⟨skelbdlist⟩)[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}{⟨fuse⟩}[⟨delbdlist⟩]
```

where the argument ⟨fuse⟩ is an alphabetical character (a–f) or the uppercase counterpart (A–F), each of which is a bond specifier representing one bond to be omitted. A lowercase character (a–f) represents the younger terminal of the omitted bond (cf. **4-5-4-10** in Fig. 4.2). The corresponding uppercase character (A–F) designates the other terminal of the bond to be omitted (cf. **4-5-4-10** in Fig. 4.2).

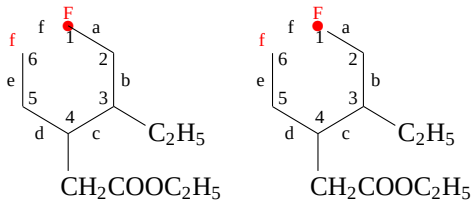
The arguments other than ⟨fuse⟩ have the same formats as described in the general conventions. See Sections 3.2 and 3.3 in Chapter 3 as well as Sections 4.2 and 4.3 in this chapter.

The locant numbers and the bond specifiers (locant alphabets) of the command `\sixfusev` correspond to those of the command `\sixheterov`, which are shown in Fig. 3.7 (cf. **4-1**). The command `\sixfusevi` is the inverse counterpart of `\sixfusev` and corresponds to the command `\sixheterovi` (cf. **4-2** and Fig. 3.7). Moreover, the ⟨bondlist⟩ is capable of accommodating the ring-fusion function due to the addition technique. the ⟨atomlist⟩ can accommodate the spiro-ring function due to the replacement technique, and the ⟨subslist⟩ serves a method producing substituents ((yl)-functions) by means of the substitution technique.

Example 4.1. For example, the last argument '`F`' of the `\sixfusev` appearing in each of the codes,

```
\sixfusev{}{3==C$_2$H$_5$;4==CH$_2$COOC$_2$H$_5$}{F}
\sixfusev{1==\null}{3==C$_2$H$_5$;4==CH$_2$COOC$_2$H$_5$}{F}
```

results in the deletion of the bond '`f`' between atom no. 6 (younger terminal) and atom no. 1 (older terminal) from a hexagon (cf. **4-10**). Note that the difference between these codes is the absence or presence of the designation in the ⟨atomlist⟩ (none or `1==\null`). Thereby, the following building blocks are obtained:

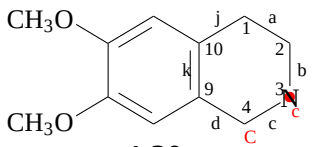


4-18 **4-19**

where the reference point (control point '`F`') for superposition in each building block (**4-18** or **4-19**) is the older terminal (i.e. atom no. 1 designated by a red solid circle) of the bond '`f`'. The code `1==\null` added in the ⟨atomlist⟩ of the second code causes truncation to assure a vacancy at the position of atom no. 1, as found in **4-19**.

On the other hand, the code `{c\put(0,0){\redx{\circle*{40}}}}` in the argument ⟨bondlist⟩ of `\decaheterov` for generating the parent structure **4-20** places a red circle • at the control point, which specifies one terminal '`c`' of the bond '`c`'. For the locant numbers and locant alphabets of `\decaheterov`, see Fig. 3.11.

```
\decaheterov[fhk%
{c\put(0,0){\redx{\circle*{40}}}}
]{3==N}{6==CH$_3$O;7==CH$_3$O}
```

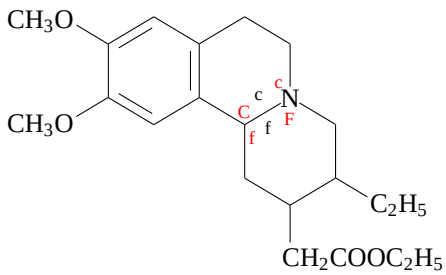


4-20

Let us replace the code `{c\put(0,0){\redx{\circle*{40}}}}` by the code of the building block **4-19** (the second one), i.e., `{c\sixfusev{1==\null}{...}{F}}`. Thus, the code of the second building block **4-19** is declared in the ⟨bondlist⟩ of the `\decaheterov` for drawing **4-20**, as shown in the code:

```
\decaheterov[fhk%
{c\sixfusev{1==\null}{3==C$_2$H$_5$;4==CH$_2$COOC$_2$H$_5$}{F}}%
]{3==N}{6==CH$_3$O;7==CH$_3$O}
```

Thereby we obtain the following structure:



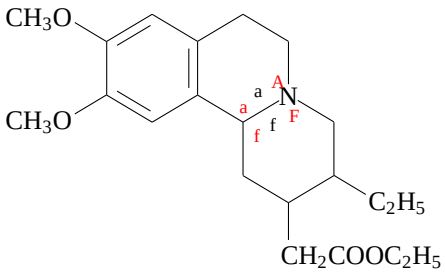
4-21

The ring fusion for generating **4-21** is based on the addition technique applied to the bond ‘c’ of `\decaheterov` (cf. **4-20**) and the bond ‘f’ of `\sixfusev` (cf. **4-19**), where the control point ‘F’ of the latter is superposed on the the control point ‘c’ of the former. If the bond descriptor ‘c’ is selected as above, the selection of ‘f’ for ⟨fuse⟩ results in an incorrect fusion between the bond c and f. If the bond descriptor ‘C’ is selected, the selection of ‘F’ for ⟨fuse⟩ results in an incorrect fusion between the bond c and f, so that the combination of ‘C’ with ‘f’ should be selected to assure a correct fusion. □

Example 4.2. Let us use `\decaheterovi` in place of `\decaheterov` for the purpose of drawing the bicyclic mother skeleton. Then the last argument ‘F’ of the `\sixfusev` can be changed into ‘f’, as found in the code:

```
\decaheterovi[fhk%
{a\sixfusev[]{1==\null}%
{3==C$_2$H$_5$;4==CH$_2$COOC$_2$H$_5$}{f}}]{2==N}{6==CH$_3$O;7==CH$_3$O}
```

Thereby, we have the following structure,



4-22

For the locant numbers and alphabets of `\decaheterovi`, see Fig. 3.11. □

As shown in page 66, the argument ⟨fuse⟩ consists of one locant alphabet (lowercase letter) or its uppercase letter, which indicates a bond to be deleted for the purpose of ring fusion. In a similar way to the diagrams **4-5**-**4-10** for `\sixfusev` (Fig. 4.1), the diagrams **4-23**-**4-28** (Fig. 4.2) show the effects of the argument ⟨fuse⟩ of `\sixfusevi`, where the lowercase alphabet indicates one terminal of the younger locant number as the control point `(0,0)` of the fused bond, while the uppercase alphabet indicates the other terminal of the senior locant number.

Example 4.3. The formula **4-29** opposite vertically to **4-21** and **4-22** can be drawn by the combination of `\sixfusevi` and `\decaheterovi` with no other changes of designation (in comparison with the first code of **4-21**), i.e.

```
\decaheterovi[fhk%
{c\sixfusevi{1==\null}%
{3==C$_2$H$_5$;4==CH$_2$COOC$_2$H$_5$}{F}}]{3==N}{6==CH$_3$O;7==CH$_3$O}
```

Thereby we have

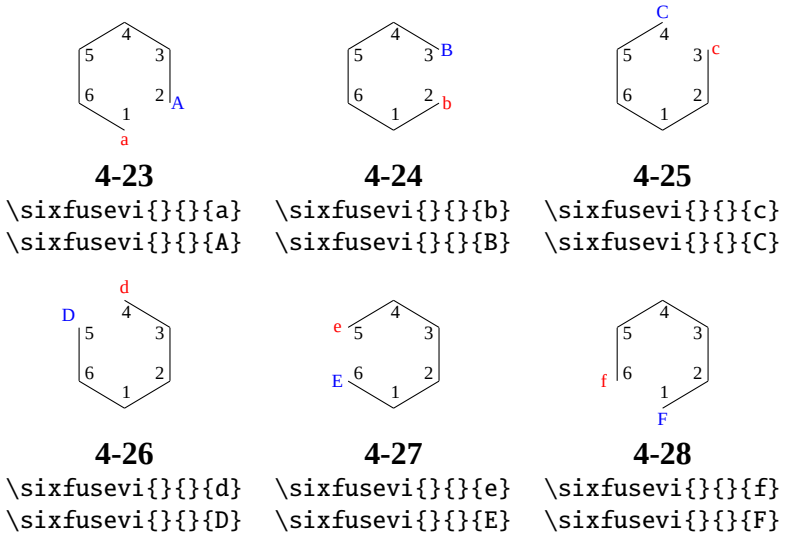
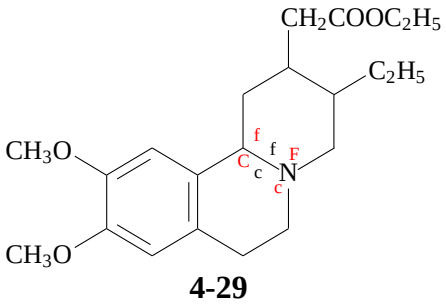


Figure 4.2. Effects of the argument ⟨fuse⟩ of the command `\sixfusevi`.



To assure correct fusions, you should select the correct combinations described above, i.e., ‘c’/‘F’ (or ‘C’/‘f’) for **4-21**; ‘a’/‘f’ (or ‘A’/‘F’) for **4-22**; and ‘c’/‘F’ (or ‘C’/‘f’) for **4-29**. In practice, if you select an incorrect combination, what you have to do is the changing of either one of bond descriptors into the uppercase or lowercase letter. □

Horizontal Units of Normal and Inverse Types

For drawing horizontal fusing units, we can use the commands `\sixfuseh` and `\sixfusehi`, which are represented by

```
\sixfuseh(⟨skelbdlist⟩)[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}{⟨fuse⟩}[⟨delbdlist⟩]
\sixfusehi(⟨skelbdlist⟩)[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}{⟨fuse⟩}[⟨delbdlist⟩]
```

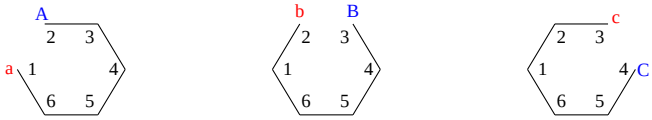
For the argument ⟨fuse⟩, see the specification of the commands `\sixfusev` and `\sixfusevi` (page 70).

The arguments other than ⟨fuse⟩ have the same formats as described in the general conventions. See Sections 3.2 and 3.3 in Chapter 3 as well as Sections 4.2 and 4.3 in this chapter.

The diagrams **4-30**-**4-35** shown in Fig. 4.3 show the effects of the argument ⟨fuse⟩ of `\sixfuseh`, where the lowercase alphabet indicates one terminal of the younger locant number as the control point `(0,0)` of the fused bond, while the uppercase alphabet indicates the other terminal of the senior locant number.

On the other hand, the diagrams **4-36**-**4-41** shown in Fig. 4.4 show the effects of the argument ⟨fuse⟩ of `\sixfusehi`, where the lowercase alphabet indicates one terminal of the younger locant number as the control point `(0,0)` of the fused bond, while the uppercase alphabet indicates the other terminal of the senior locant number.

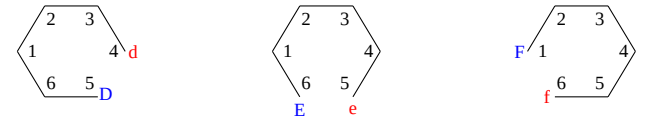
The locant numbers and the bond specifiers (locant alphabets) of the command `\sixfuseh` correspond to those of the command `\sixheteroh`, which are shown in Fig. 3.8 (cf. **4-3**). The command `\sixfusehi` is the inverse counterpart of `\sixfuseh` and corresponds to the command `\sixheterohi` (cf. **4-4** and Fig. 3.8).



4-30 `\sixfuseh{}{}{a}` `\sixfuseh{}{}{A}`

4-31 `\sixfuseh{}{}{b}` `\sixfuseh{}{}{B}`

4-32 `\sixfuseh{}{}{c}` `\sixfuseh{}{}{C}`

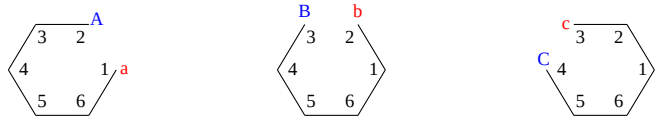


4-33 `\sixfuseh{}{}{d}` `\sixfuseh{}{}{D}`

4-34 `\sixfuseh{}{}{e}` `\sixfuseh{}{}{E}`

4-35 `\sixfuseh{}{}{f}` `\sixfuseh{}{}{F}`

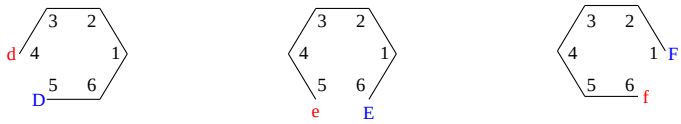
Figure 4.3. Effects of the argument ⟨fuse⟩ of the command `\sixfuseh`.



4-36 `\sixfusehi{}{}{a}` `\sixfusehi{}{}{A}`

4-37 `\sixfusehi{}{}{b}` `\sixfusehi{}{}{B}`

4-38 `\sixfusehi{}{}{c}` `\sixfusehi{}{}{C}`



4-39 `\sixfusehi{}{}{d}` `\sixfusehi{}{}{D}`

4-40 `\sixfusehi{}{}{e}` `\sixfusehi{}{}{E}`

4-41 `\sixfusehi{}{}{f}` `\sixfusehi{}{}{F}`

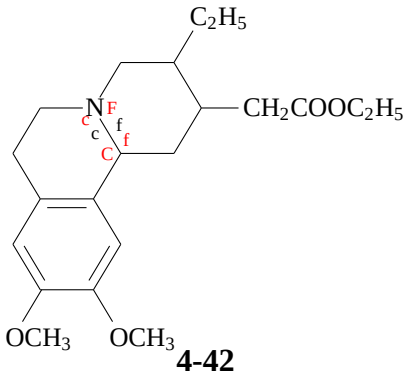
Figure 4.4. Effects of the argument ⟨fuse⟩ of the command `\sixfusehi`.

Moreover, the ⟨bondlist⟩ is capable of accommodating the ring-fusion function due to the addition technique. the ⟨atomlist⟩ can accommodate the spiro-ring function due to the replacement technique, and the ⟨subslist⟩ serves a method producing substituents ((yl)-functions) by means of the substitution technique.

Example 4.4. The horizontal formula of normal type, which are related to the tricyclic formulas **4-21**–**4-29** described in the preceding subsection, can be drawn by the combination of `\sixfuseh` and `\decaheteroh` with few changes of designation (CH_3O to OCH_3), i.e.,

```
\decaheteroh[fhk%
{c\sixfuseh{1==\null}{3==C$_2$H$_5$;4==CH$_2$COOC$_2$H$_5$}{F}}%
]{3==N}{6==OCH$_3$;7==OCH$_3$}}
```

Compare this code with the code for drawing **4-21** described above. Thus, this code typesets the following structure:



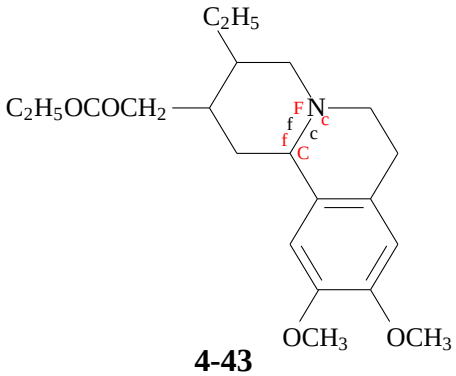
4-42

where the control point '`F`' of the fusing component (generated by `\sixfuseh`) is superposed on the control point '`c`' of the parent structure (generated by `\decaheteroh`). For the locant numbers and locant alphabets of the command `\decaheteroh`, see Fig. 3.12. □

Example 4.5. The horizontally opposite formula can be drawn by the combination of `\sixfusehi` (in place of `\sixfuseh`) and `\decaheterohi` (in place of `\decaheteroh`) with slight changes concerning the handedness of substituents. For locant numbers and locant alphabets of the command `\decaheterohi`, see Fig. 3.12.

```
\decaheterohi[fhk%
{c\sixfusehi[]{1==\null}%
{3==C$_2$H$_5$;4==C$_2$H$_5$OCOCH$_2$}{F}}]{3==N}{6==OCH$_3$;7==OCH$_3$}
```

Thereby we obtain:



4-43

To assure correct fusions, the correct combinations described above should be selected, i.e., '`c`'/'`F`' (or '`C`'/'`f`') for **4-42** and for **4-43**. □

4.4.2 Five-membered Fusing Units

Vertical Units of Normal and Inverse Types

To obtain a vertical five-membered building block, we can use `\fivefusev` and `\fivefusevi`:

```
\fivefusev(⟨skelbdlist⟩)[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}{⟨fuse⟩}[⟨delbdlist⟩]
\fivefusevi(⟨skelbdlist⟩)[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}{⟨fuse⟩}[⟨delbdlist⟩]
```

where the argument ⟨fuse⟩ is an alphabetical character (a–e) or the uppercase counterpart (A–E), each of which is a bond specifier representing one bond to be omitted.

The arguments other than ⟨fuse⟩ have the same formats as described in the general conventions. See Sections 3.2 and 3.3 in Chapter 3 as well as Sections 4.2 and 4.3 in this chapter.

The diagrams **4-44**-**4-48** listed in Fig. 4.5 show the effects of the argument ⟨fuse⟩ of `\fivefusev`, where the lowercase alphabet indicates one terminal of the younger locant number as the control point `(0,0)` of the fused bond, while the uppercase alphabet indicates the other terminal of the senior locant number.

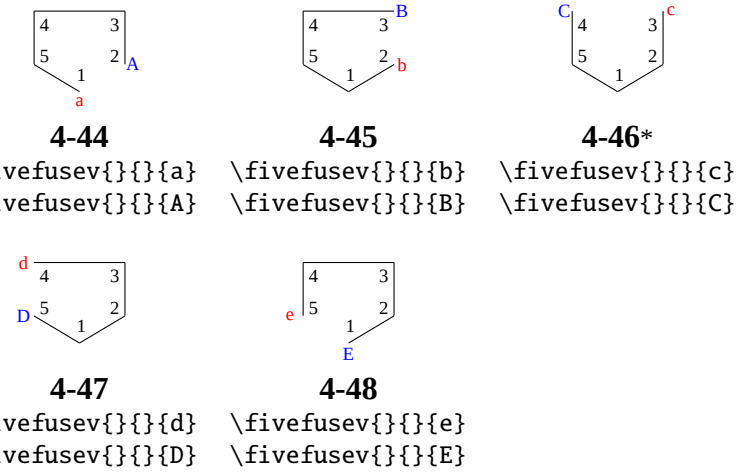


Figure 4.5. Effects of the argument ⟨fuse⟩ of the command `\fivefusev`. The symbol * indicates a forbidden ring fusion.

On the other hand, the diagrams **4-49**-**4-53** listed in Fig. 4.6 show the effects of the argument ⟨fuse⟩ of `\fivefusevi`, where the lowercase alphabet indicates one terminal of the younger locant number as the control point `(0,0)` of the fused bond, while the uppercase alphabet indicates the other terminal of the senior locant number.

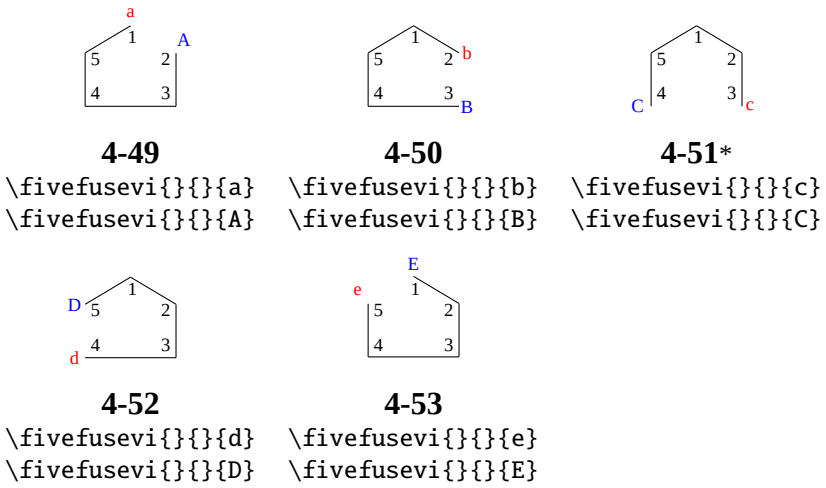


Figure 4.6. Effects of the argument ⟨fuse⟩ of the command `\fivefusevi`. The symbol * indicates a forbidden ring fusion.

Among the diagrams shown in Figs. 4.5 and 4.6, the asterisked ones **4-46** and **4-51** cannot be used in ring fusion. Although the bond corresponding to 'c' or 'C' is deleted, the adjustment of the control point (0,0) is not accomplished in the diagram **4-46** or **4-51**, so that the following XyMTEX warning is typed out in a display as well as in a log file.

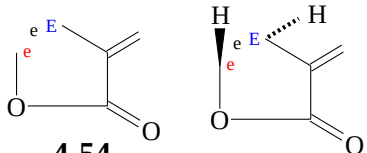
```
XyMTeX Warning: Not-used fusion at bond 'c' on input line 1497
XyMTeX Warning: Not-used fusion at bond 'C' on input line 1501
```

The locant numbers and the bond specifiers (locant alphabets) of the command `\fivefusev` correspond to those of the command `\fiveheterov`, which are shown in Fig. 3.5. The command `\fivefusevi` is the inverse counterpart of `\fivefusev` and corresponds to the command `\fiveheterovi` (cf. Fig. 3.6).

Moreover, the ⟨bondlist⟩ is capable of accommodating the ring-fusion function due to the addition technique. The ⟨atomlist⟩ can accommodate the spiro-ring function due to the replacement technique, and the ⟨subslist⟩ serves a method producing substituents ((yl)-functions) by means of the substitution technique.

Example 4.6. The following example **4-54** is derived by the use of the `\fivefusevi` command by itself (cf. **4-53**), where its ⟨subslist⟩ contains some substituents:

```
\fivefusevi{4==O}{2D==;3D==O}{E}
\fivefusevi{4==O}{1GA==H;5GB==H;2D==;3D==O}{E}
```

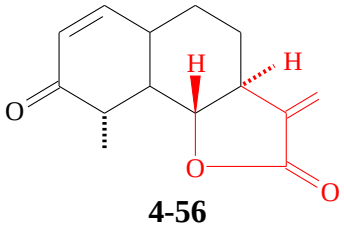


4-54 **4-55**

To show hydrogen substitution at the fused positions, we add the designation of `1GA==H;5GB==H` to the ⟨subslist⟩ of the `\fivefusevi` command, giving **4-55**. Then, the latter code is written in the ⟨bondlist⟩ of a command `\decalinev` according to the addition technique (colored in red), as found in the code:

```
\decalinev[h%
{c\fivefusevi{4==O}{1GA==H;5GB==H;2D==;3D==O}{E}}%
]{6D==O;5A==;0FB==;0GA==H}
```

Thereby, we obtain



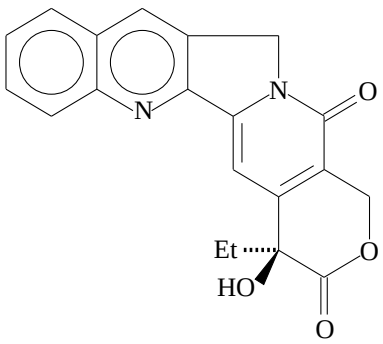
4-56

where the red-colored portion corresponds to the fusing unit represented by **4-55**. □

Example 4.7. Fusing units such as `\fivefusev` can be multiply nested in itself and in other types of fusing units. The following example shows such a triply-nested case.

```
\decaheterovi[AB%
{b\fivefusev[{a\sixfusev[ce%
{c\sixfusev{3==O}{4D==O;5SB==HO;5SA==Et}{F}}]{1==\null}{2D==O}{f}}]%
{2==N}{}{D}}]{1==N}{}
```

Thereby, we obtain **4-57**:



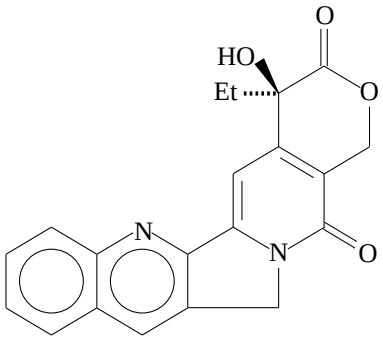
4-57

where the applied addition technique is represented by the scheme 6-6 ← 5 ← 6 ← 6. □

Example 4.8. When all of the commands in the above code are changed into the inverse counterparts with a suffix ‘`v`’ in place of ‘`vi`’ (i.e. `\decaheterovi` to `\decaheterov`; `\fivefusev` and `\fivefusevi`; and `\sixfusev` to `\sixfusevi`), the code is transformed into another code,

```
\decaheterov[AB%
{b\fivefusevi[{a\sixfusevi[ce%
{c\sixfusevi{3==O}{4D==O;5SB==HO;5SA==Et}{F}}]{1==\null}{2D==O}{f}}]%
{2==N}{}{D}}]{1==N}{}
```

Thereby, we obtain the formula of vertically inverse type:



4-58

where the applied addition technique is also represented by the scheme 6-6 ← 5 ← 6 ← 6. □

Horizontal Units of Normal and Inverse Types

Horizontal five-membered building blocks are obtained by using `\fivefuseh` and `\fivefusehi`:

```
\fivefuseh(⟨skelbdlist⟩)[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}{⟨fuse⟩}[⟨delbdlist⟩]
\fivefusehi(⟨skelbdlist⟩)[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}{⟨fuse⟩}[⟨delbdlist⟩]
```

where the argument ⟨fuse⟩ is an alphabetical character (a–e) or the uppercase counterpart (A–E), each of which is a bond specifier representing one bond to be omitted. The other specifications have the same formats as found in the preceding section.

The diagrams **4-59**-**4-63** shown in Fig. 4.7 show the effects of the argument ⟨fuse⟩ of `\fivefuseh`, where the lowercase alphabet indicates one terminal of the younger locant number as the control point `(0,0)` of the fused bond, while the uppercase alphabet indicates the other terminal of the senior locant number.

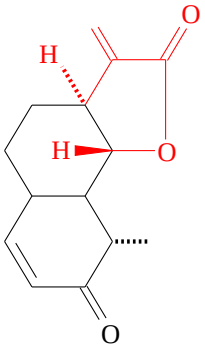
On the other hand, the diagrams **4-64**-**4-68** shown in Fig. 4.8 show the effects of the argument ⟨fuse⟩ of `\fivefusehi`, where the lowercase alphabet indicates one terminal of the younger locant number as the control point `(0,0)` of the fused bond, while the uppercase alphabet indicates the other terminal of the senior locant number.

Among the diagrams shown in Figs. 4.7 and 4.8, the asterisked ones **4-61** and **4-66** cannot be used in ring fusion. Although the bond corresponding to 'c' or 'C' is deleted, the adjustment of the control point (0,0) is not accomplished in the diagram **4-61** or **4-66**.

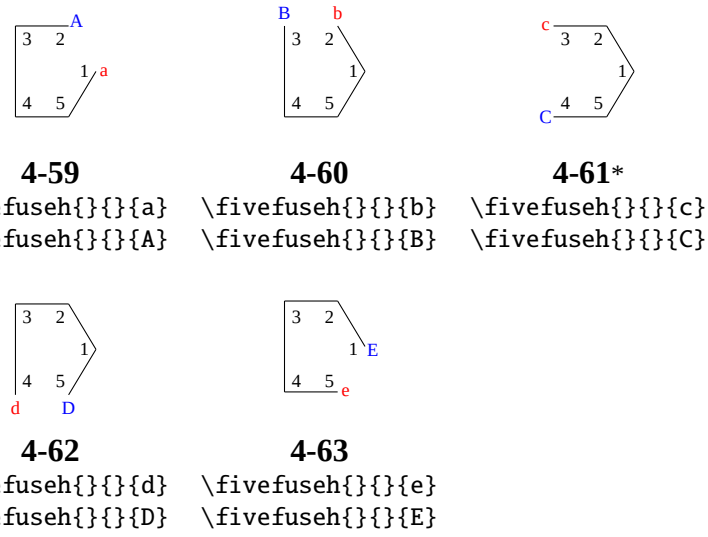
Example 4.9. The example **4-56** given for a vertical command `\fivefusevi` is changed into the one using the horizontal counterpart `\fivefusehi` as colored in red:

```
\decalineh[h%
{c\fivefusehi{4==O}{1GA==H;5GB==H;2D==;3D==O}{E}}%
]{5A==;6D==O}
```

This code generates the following structure of horizontal type:



4-69



4-59
`\fivefuseh{}{}{a}`
`\fivefuseh{}{}{A}`

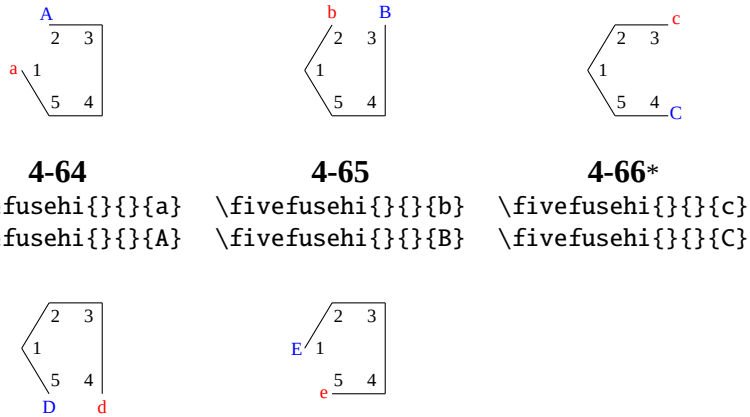
4-60
`\fivefuseh{}{}{b}`
`\fivefuseh{}{}{B}`

4-61*
`\fivefuseh{}{}{c}`
`\fivefuseh{}{}{C}`

4-62
`\fivefuseh{}{}{d}`
`\fivefuseh{}{}{D}`

4-63
`\fivefuseh{}{}{e}`
`\fivefuseh{}{}{E}`

Figure 4.7. Effects of the argument ⟨fuse⟩ of the command `\fivefuseh`. The symbol * indicates a forbidden ring fusion.



4-64
`\fivefusehi{}{}{a}`
`\fivefusehi{}{}{A}`

4-65
`\fivefusehi{}{}{b}`
`\fivefusehi{}{}{B}`

4-66*
`\fivefusehi{}{}{c}`
`\fivefusehi{}{}{C}`

4-67
`\fivefusehi{}{}{d}`
`\fivefusehi{}{}{D}`

4-68
`\fivefusehi{}{}{e}`
`\fivefusehi{}{}{E}`

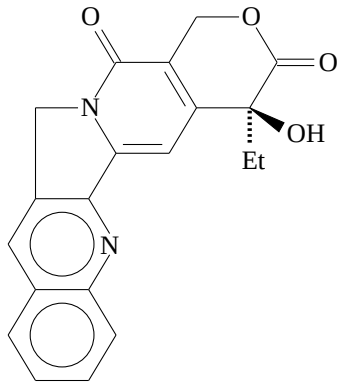
Figure 4.8. Effects of the argument ⟨fuse⟩ of the command `\fivefusehi`. The symbol * indicates a forbidden ring fusion.

where the red-colored portion is generated by the command `\fivefusehi` according to the addition technique. Note that no changes of other designation (cf. the code for drawing **4-56**) are necessary except that `\decalineh` and `\fivefusehi` are used in place of the vertical counterpart described above. □

Example 4.10. The multiply nested example **4-57** described above for drawing a structure of vertical type can be changed into the corresponding one of horizontal type, if all of the commands for drawing **4-57** are changed into horizontal types (`\decaheterovi` to `\decaheterohi`; `\fivefusev` to `\fivefuseh`; and `\sixfusev` to `\sixfuseh`).

```
\decaheterohi[AB%
{b\fivefuseh[{a\sixfuseh[ce%
{c\sixfuseh{3==O}{4D==O;5SB==OH;5SA==Et}{F}}]{1==\null}{2D==O}{f}}]%
{2==N}{}{D}}]{1==N}{}
```

This code generates the following structure of horizontal type:



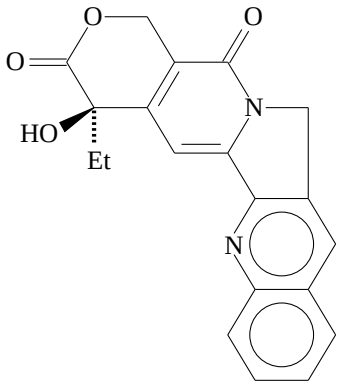
4-70

where the applied addition technique is represented by the scheme 6-6 ← 5 ← 6 ← 6. □

Example 4.11. When all the commands for drawing **4-70** in the above code are changed into the inverse counterparts (`\decaheterohi` to `\decaheteroh`; `\fivefuseh` and `\fivefusehi`; and `\sixfuseh` to `\sixfusehi`), the code is transformed into another code:

```
\decaheteroh[AB%
{b\fivefusehi[{a\sixfusehi[ce%
{c\sixfusehi{3==O}{4D==O;5SB==HO;5SA==Et}{F}}]{1==\null}{2D==O}{f}}]%
{2==N}{}{D}}]{1==N}{}
```

Thereby, we obtain the formula of horizontally inverse type.



4-71

where the applied addition technique is represented by the scheme 6-6 ← 5 ← 6 ← 6. □

4.4.3 Four-membered Fusing Units

To obtain a four-membered building block, we can use `\fourfuse`:

```
\fourfuse(⟨skelbdlist⟩)[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}{⟨fuse⟩}[⟨delbdlist⟩]
```

where the argument ⟨fuse⟩ is an alphabetical character (a–d) or the uppercase counterpart (A–D), each of which is a bond specifier representing one bond to be omitted.

The diagrams **4-72**-**4-75** shown in Fig. 4.9 show the effects of the argument ⟨fuse⟩ of `\fourfuse`, where the lowercase alphabet indicates one terminal of the younger locant number as the control point `(0,0)` of the fused bond, while the uppercase alphabet indicates the other terminal of the senior locant number.

The assignment of characters (a to d) and locants (1 to 4) for the command `\fourhetero` is applied in the same way to this case. The other specifications have the same formats as those of the command `\fourhetero`.

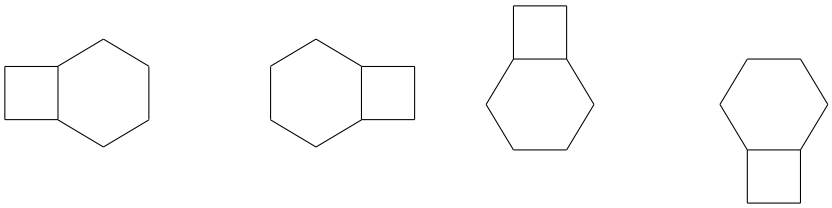
For example, the code,

4-72	**4-73**	**4-74**	**4-75**
`\fourfuse{}{}{a}`	`\fourfuse{}{}{b}`	`\fourfuse{}{}{c}`	`\fourfuse{}{}{d}`
`\fourfuse{}{}{A}`	`\fourfuse{}{}{B}`	`\fourfuse{}{}{C}`	`\fourfuse{}{}{D}`

Figure 4.9. Effects of the argument ⟨fuse⟩ of the command `\fourfuse`.

```
\sixheterov[{e\fourfuse{}{}{b}}]{}{}
\sixheterov[{b\fourfuse{}{}{d}}]{}{}
\sixheteroh[{b\fourfuse{}{}{a}}]{}{}
\sixheteroh[{e\fourfuse{}{}{c}}]{}{}
```

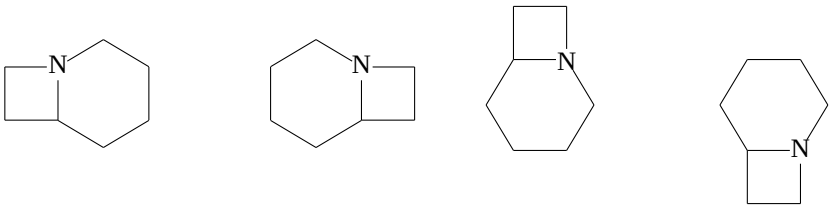
produces the following structural formulas.



A hetero atom at a fused position is designated in the ⟨atomlist⟩ of `\fourfuse`, which is associated the code `\null` in the ⟨atomlist⟩ of a command for drawing a parent structure. For example, the code

```
\sixheterov[{e\fourfuse{3==N}{}{b}}]{6==\null}{}
\sixheterov[{b\fourfuse{4==N}{}{d}}]{2==\null}{}
\sixheteroh[{b\fourfuse{2==N}{}{a}}]{3==\null}{}
\sixheteroh[{e\fourfuse{3==N}{}{c}}]{5==\null}{}
```

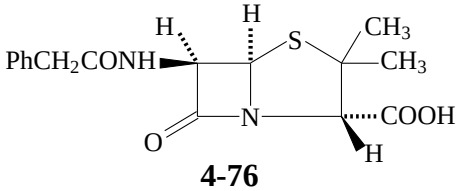
produces the following structural formulas.



Example 4.12. The structure **4-76** of penicillin G can be drawn by using the `\fourfuse` command in the code:

```
\fiveheterovi[{d\fourfuse{2==\null}{1D==O;4Su==PhCH$_{2}$CONH;4Sd==H}{b}}]%
{1==S;4==N}{2Sa==CH$_{3}$;2Sb==CH$_{3}$;3SA==COOH;3SB==H;5GA==H}
```

which typesets the following formula:



4-76

The bridgehead nitrogen corresponds to `4==N` in the ⟨atomlist⟩ of `\fiveheterovi` as well as to `2==\null` in the ⟨atomlist⟩ of `\fourfuse`. □

4.4.4 Three-membered Fusing Units

Vertical Units of Normal and Inverse Types

To obtain three-membered building blocks of vertical type, we can use `\threefusev` and `\threefusevi`:

```
\threefusev(⟨skelbdlist⟩)[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}{⟨fuse⟩}[⟨delbdlist⟩]
\threefusevi(⟨skelbdlist⟩)[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}{⟨fuse⟩}[⟨delbdlist⟩]
```

where the argument ⟨fuse⟩ is an alphabetical character (a–c) or the uppercase counterpart (A–C), each of which is a bond specifier representing one bond to be omitted.

The diagrams **4-77**-**4-79** listed in Fig. 4.10 show the effects of the argument ⟨fuse⟩ of `\threefusev`, while the diagrams **4-80**-**4-82** listed in Fig. 4.11 show the effects of the argument ⟨fuse⟩ of `\threefusevi`. Note that the lowercase alphabet indicates one terminal of the younger locant number as the control point `(0,0)` of the fused bond, while the uppercase alphabet indicates the other terminal of the senior locant number.

4-77

```
\threefusev{}{}{a}
\threefusev{}{}{A}
```

4-78

```
\threefusev{}{}{b}
\threefusev{}{}{B}
```

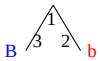
4-79

```
\threefusev{}{}{c}
\threefusev{}{}{C}
```

Figure 4.10. Effects of the argument ⟨fuse⟩ of the command `\threefusev`.

4-80

```
\threefusevi{}{}{a}
\threefusevi{}{}{A}
```



4-81

```
\threefusevi{}{}{b}
\threefusevi{}{}{B}
```

4-82

```
\threefusevi{}{}{c}
\threefusevi{}{}{C}
```

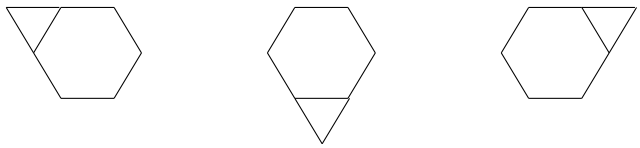
Figure 4.11. Effects of the argument ⟨fuse⟩ of the command `\threefusevi`.

The assignment of characters (a to c) and locants (1 to 3) for the command `\threeheterov` or `\threeheterovi` is applied in the same way to this case. The other specifications have the same formats as those of the command `\threeheterov` or `\threeheterovi`.

For example, the code using `\threefusev`,

```
\sixheteroh[{a\threefusev{}{}{a}}]{}{}
\sixheteroh[{e\threefusev{}{}{b}}]{}{}
\sixheteroh[{c\threefusev{}{}{c}}]{}{}
```

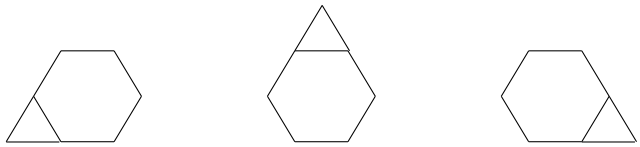
produces the following structural formulas.



The use of the inverse type is shown in the code,

```
\sixheteroh[{F\threefusevi{}{}{a}}]{}{}
\sixheteroh[{B\threefusevi{}{}{b}}]{}{}
\sixheteroh[{D\threefusevi{}{}{c}}]{}{}
```

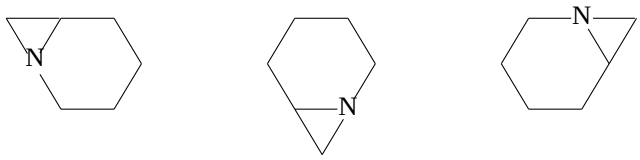
which produces the following structural formulas.



Hetero-atoms at fused positions can be typeset by designating atom lists ⟨atomlist⟩. For example, the code,

```
\sixheteroh[{a\threefusev{1==N}{}{a}}]{1==\null}{}
\sixheteroh[{e\threefusev{2==N}{}{b}}]{5==\null}{}
\sixheteroh[{c\threefusev{3==N}{}{c}}]{3==\null}{}
```

produces the following structural formulas.



Horizontal Units of Normal and Inverse Types

Three-membered building blocks of horizontal type can be obtained by using commands with a suffix ‘h’ or ‘hi’, i.e., `\threefuseh` and `\threefusehi`:

```
\threefuseh(⟨skelbdlist⟩)[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}{⟨fuse⟩}[⟨delbdlist⟩]
\threefusehi(⟨skelbdlist⟩)[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}{⟨fuse⟩}[⟨delbdlist⟩]
```

where the argument ⟨fuse⟩ is an alphabetical character (a–c) or the uppercase counterpart (A–C), each of which is a bond specifier representing one bond to be omitted.

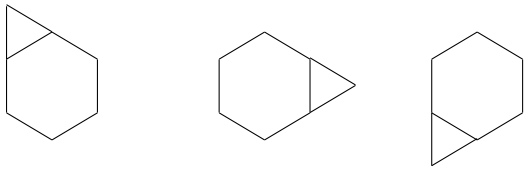
The diagrams **4-83**-**4-85** shown in Fig. 4.12 show the effects of the argument ⟨fuse⟩ of `\threefuseh`. On the other hand, the diagrams **4-86**-**4-88** shown in Fig. 4.13 show the effects of the argument ⟨fuse⟩ of `\threefusehi`. Note that the lowercase alphabet indicates one terminal of the younger locant number as the control point `(0,0)` of the fused bond, while the uppercase alphabet indicates the other terminal of the senior locant number.

The assignment of characters (a to c) and locants (1 to 3) for the command `\threeheteroh` or `\threeheterohi` is applied in the same way to this case. The other specifications have the same formats as those of the command `\threeheteroh` or `\threeheterohi`.

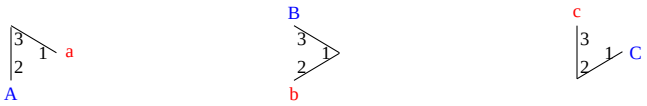
For example, the codes using `\threefuseh`,

```
\sixheterov[{F\threefuseh{}{}{a}}]{}{}
\sixheterov[{B\threefuseh{}{}{b}}]{}{}
\sixheterov[{D\threefuseh{}{}{c}}]{}{}
```

produce the following structural formulas.



The use of the inverse type is shown in the codes,

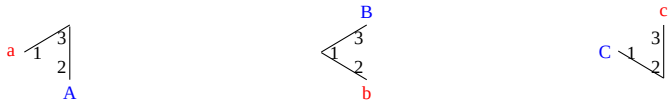


4-83
`\threefuseh{}{}{a}`
`\threefuseh{}{}{A}`

4-84
`\threefuseh{}{}{b}`
`\threefuseh{}{}{B}`

4-85
`\threefuseh{}{}{c}`
`\threefuseh{}{}{C}`

Figure 4.12. Effects of the argument ⟨fuse⟩ of the command `\threefuseh`.



4-86
`\threefusehi{}{}{a}`
`\threefusehi{}{}{A}`

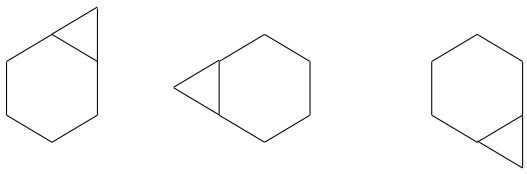
4-87
`\threefusehi{}{}{b}`
`\threefusehi{}{}{B}`

4-88
`\threefusehi{}{}{c}`
`\threefusehi{}{}{C}`

Figure 4.13. Effects of the argument ⟨fuse⟩ of the command `\threefusehi`.

```
\sixheterov[{a\threefusehi{}{}{a}}]{}{}
\sixheterov[{e\threefusehi{}{}{b}}]{}{}
\sixheterov[{c\threefusehi{}{}{c}}]{}{}
```

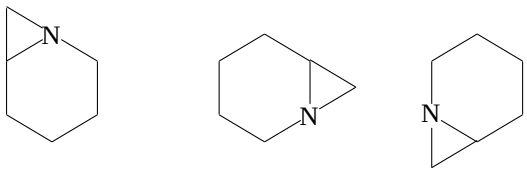
which produce the following structural formulas.



Hetero-atoms at fused positions can be typeset by designating ⟨atomlist⟩. For example, the codes,

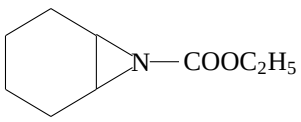
```
\sixheterov[{F\threefuseh{1==N}{}{a}}]{1==\null}{}
\sixheterov[{B\threefuseh{2==N}{}{b}}]{3==\null}{}
\sixheterov[{D\threefuseh{3==N}{}{c}}]{5==\null}{}
```

produce the following structural formulas.



Example 4.13. The structure **4-89** of an aziridine derivative [2] is drawn by the code:

```
\sixheterov[{B\threefuseh{1==N}{1==COOC$_{2}$H$_{5}$}{b}}]{}{}
```



4-89

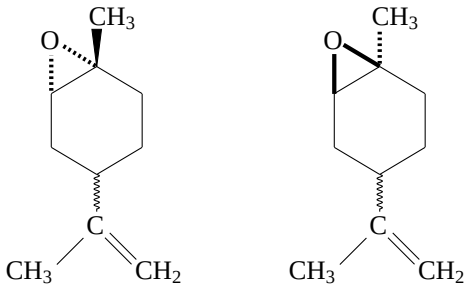
This code is based on the addition technique, where the fusing unit `\threefuseh` is declared in the ⟨bondlist⟩ of `\sixheterov`. □

The configurations of skeletal bonds can be specified by using ⟨skelbdlist⟩, as discussed in Subsection 4.3.2 (e.g., **4-12** and **4-13**).

Example 4.14. For the purpose of showing the effects of the ⟨skelbdlist⟩ of the command `\threefuseh`, the structures **4-90** and **4-91** of cyclohexene epoxides [3, page 668] are drawn by using the addition technique:

```
\cyclohexanev[%
{F\threefuseh({bA}{cA}){3==O}{}{a}}%
]{1B==CH$_{3}$;4U==\dtrigonal{0==C;1==(yl);2D==CH$_{2}$;3==CH$_{3}$$}}
\cyclohexanev[%
{F\threefuseh({bB}{cB}){3==O}{}{a}}%
]{1A==CH$_{3}$;4U==\dtrigonal{0==C;1==(yl);2D==CH$_{2}$;3==CH$_{3}$$}}
```

These codes produce the following structures:



4-90 **4-91**

The 2-propenyl substituent is depicted by the substitution technique applied to `\dtrigonal`. □

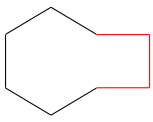
4.5 Special Effects by Optional Arguments

4.5.1 Further Rings by the Argument ⟨delbdlist⟩

A combination of the addition technique with a bond deletion is capable of depicting a large ring, as found in Examples 3.9 and 3.10. Because this method has wide applicability, several illustrative examples are added here.

Example 4.15. A six-membered ring fused by a four-membered unit gives an eight-membered ring as follows:

```
\sixheterov[%
{b\fourfuse{}{}{d}}%
]{}{}[b]
```

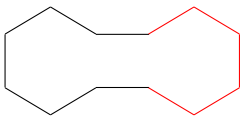


4-92

Note that the red-colored portion of **4-92** is the four-membered unit generated by `\fourfuse` (colored in red). □

Example 4.16. The bond ‘b’ of the four-membered unit in the resulting ring **4-92** is deleted and used as an acceptor ring of a six-membered fusing unit according to the addition technique. Then, we obtain a twelve-membered ring:

```
\sixheterov[{b\fourfuse[%
{b\sixfusev{}{}{e}}%
]{}{}{d}[b]}]{}{}[b]
```

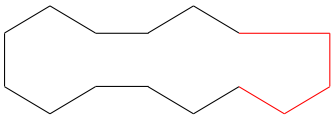


4-93

Note that the red-colored portion of **4-93** is the six-membered unit generated by `\sixfusev` (colored in red). □

Example 4.17. After applying the bond-deletion technique to the twelve-membered ring of **4-93**, this is used as an acceptor of a five-membered fusing unit. Then we obtain a fifteen-membered ring:

```
\sixheterov[{b\fourfuse[{b\sixfusev[%
{b\fivefusev{}{}{d}}%
]{}{}{e}[b]}]{}{}{d}[b]}]{}{}[b]
```

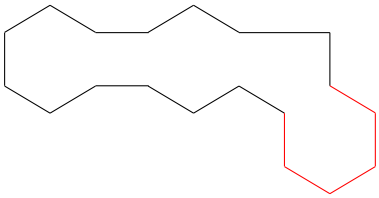


4-94

Note that the red-colored portion of **4-94** is the five-membered unit generated by `\fivefusev` (colored in red). □

Example 4.18. The fifteen-membered ring **4-94** undergoes a further fusion of a six-membered unit to give a nineteen-membered ring:

```
\sixheterov[{b\fourfuse[{b\sixfusev[%
{b\fivefusev[%
{a\sixfusev{}{}{f}}%
]{}{}{d}[a]}%
]{}{}{e}[b]}]{}{}{d}[b]}]{}{}[b]
```



4-95

Note that the red-colored portion of **4-95** is the six-membered unit generated by `\sixfusev` (colored in red). □

4.5.2 Nested Ring Fusion

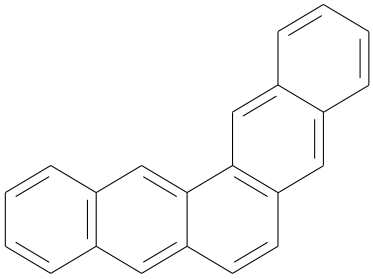
A linear propagation by the multiply-nested addition technique is capable of generating a linearly-fused structure, where the ⟨delbdlist⟩ of each fusing unit is not used.

Example 4.19. As an example of a linear propagation, a pentacyclic aromatic compound **4-96** named pentaphene can be drawn by the code:

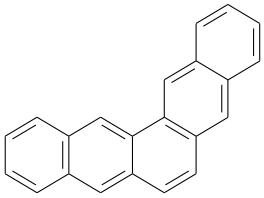
```
\hanthracenev[acehjmp%
{a\sixfusev[bf%
{a\sixfusev[bf]{}{}{D}}
]{}{}{D}}%
]{}
```

with no use of the ⟨delbdlist⟩ in each of the two fusing units.

The mode of nesting is designated by 666 ← 6 ← 6. where 666 represents an anthracene ring and ←6 represents the fusion of a six-membered unit.



4-96

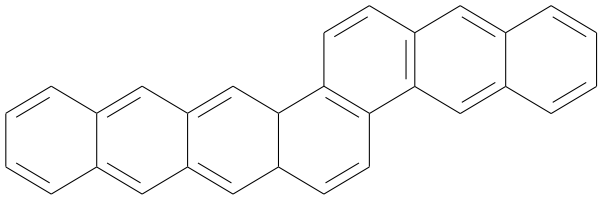


4-96′

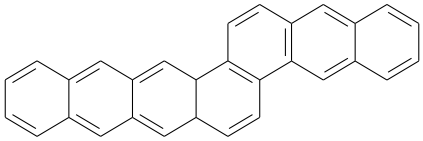
The formula **4-96** is drawn by the default unit length (0.1pt) of the XeLaTeX system. The formula **4-96′** appearing in the right-hand side is drawn under declaring `\changeunitlength{0.07pt}`. □

Example 4.20. This is another example of a linear propagation. The formula of anthra[2,1-a]nathphacene can be generated by the nesting that is represented to be $66 \leftarrow 6 \leftarrow 6 \leftarrow 6 \leftarrow 6 \leftarrow 6$.

```
\decaheterov[dfhj%
{b\sixfusev[df{b\sixfusev[ac%
{a\sixfusev[bf%
{b\sixfusev[ac{b\sixfusev[ac]{}{}{E}}]{}{}{E}}%
]{}{}{D}}%
]{}{}{E}}]{}{}{E}}%
]{}{}{}
```



4-97



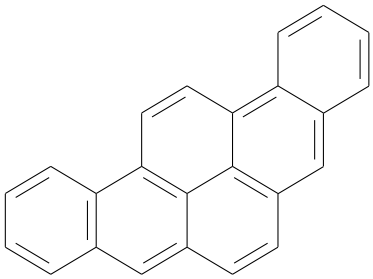
4-97′

The right formula **4-97′** is drawn under declaring `\changeunitlength{0.07pt}`. □

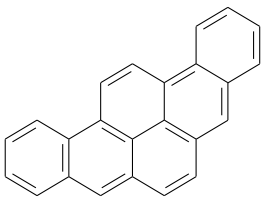
On the other hand, a non-linear propagation requires the use of the ⟨delbdlist⟩ of each fusing unit, as found in the following example.

Example 4.21. The fusion of a six-membered unit on the formula of pentaphene (**4-96**) generates benzo[*rst*]pentaphene **4-98**, which is drawn by the code:

```
\hanthracenev[acehjmp%
{a\sixfusev[bf%
{a\sixfusev[bf]{}{}{D}}%
]{}{}{D}}%
{m\sixfusev[f]{}{}{D}[bc]}%
]{}
```



4-98



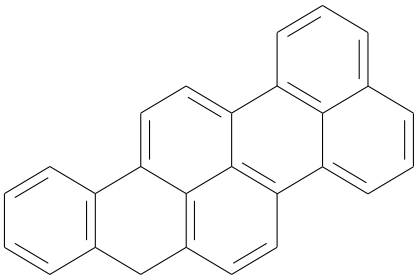
4-98′

The right formula **4-98′** is drawn under declaring `\changeunitlength{0.07pt}`.

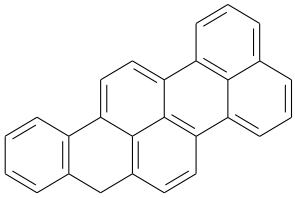
Note that the bay area represented by *rst* in pentacene corresponds to the bond 'm' of the mother skeleton `\hanthracenev`.[a] The last optical argument `[bc]` in the code `m\sixfusev[f]{}{}{D}[bc]` designates bonds to be deleted. □

Example 4.22. A further fusion generates 9*H*-dibenzo[*de,rst*]pentaphene **4-99** as follows:

```
\hanthracenev[chojp%
{a\sixfusev[d%
{a\sixfusev[bdf]{}{}{D}}
{b\sixfusev[bd]{}{}{E}[f]}
]{}{}{D}}%
{m\sixfusev[ae]{}{}{D}[bc]}%
]{}
```



4-99

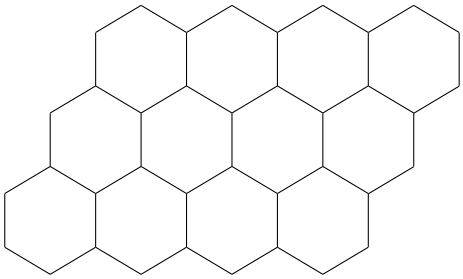


4-99′

The right formula **4-99′** is drawn under declaring `\changeunitlength{0.07pt}`. □

Example 4.23. Enumeration of Kekulé structures of dibenzo[b,n]picene by Fujita's method has been reported [4]. The structure **4-100** of dibenzo[b,n]picene with no specification of double bonds is drawn by the code:

```
\decaheterov[%
%first series
{i\sixfusev[{a\sixfusev[{b\sixfusev[%
{b\sixfusev[{b\sixfusev{}{}{E}[d]}]{}{}{E}[cd]}
]{}{}{E}[cd]}]{}{}{D}[c]}]{}{}{D}[c]}%
%second series
{a\sixfusev[{b\sixfusev[{b\sixfusev{}{}{E}[d]}
]{}{}{E}[cd]}]{}{}{D}[ce]}%
%third series
{b\sixfusev[{b\sixfusev{}{}{E}}]{}{}{E}}%
]{}{}
```



4-100

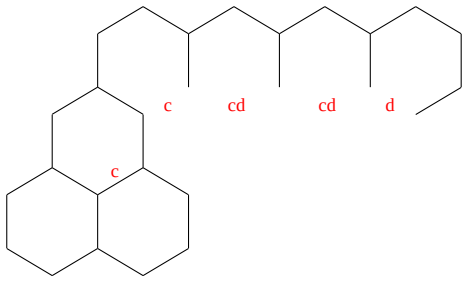
The above code contains three series of nested fusions: the first is a series starting from the edge `i` of `\decaheterov`, the second is a series starting from the edge `a`, and the third is a series starting from the

[a] Since the bond 'm' is not considered as a proper fused position under usual derivation, a XeTeX warning appears in the present drawing. However, there is no problem to draw such improper fusing.

edge b. For example, the first series of nested fusions is demonstrated by commenting out the remaining two series, as found in the code:

```
\decaheterov[%
%first series
{i\sixfusev[{a\sixfusev[{b\sixfusev[%
{b\sixfusev[{b\sixfusev{}{}{E}[d]}]{}{}{E}[cd]}
]{}{}{E}[cd]}]{}{}{D}[c]}]{}{}{D}[c]}%
%%second series
%{a\sixfusev[{b\sixfusev[{b\sixfusev{}{}{E}[d]}
%]{}{}{E}[cd]}]{}{}{D}[ce]}%
%%third series
%{b\sixfusev[{b\sixfusev{}{}{E}}]{}{}{E}}%
]{}{}
```

Thereby, we obtain the following diagram, in which unnecessary skeletal bonds are deleted by using the respective optional arguments ⟨delbdlist⟩, i.e., `[c]`, `[c]`, `[cd]`, `[cd]`, and `[d]`.



The remaining two series can be demonstrated in a similar way. □

References

[1] S. Fujita, “Organic Chemistry of Photography,” Springer-Verlag, Berlin-Heidelberg (2004).

[2] T. Hiyama, H. Koide, S. Fujita, and H. Nozaki, *Tetrahedron*, **29**, 3137–3139 (1973).

[3] F. A. Carey and R. J. Sundberg, “Advanced Organic Chemistry. Part B: Reactions and Syntheses,” 3rd ed., Prenum Press, New York-London (1990).

[4] S. Fujita, *MATCH Commun. Math. Comput. Chem.*, **69**, 333–354 (2013).

Chapter 5

Size Reduction

5.1 Historical Comments

The TEX/LATEX-compatible mode of the XƎMTEX system depends on the LATEX picture environment and the epic package. The mechanism of epic.sty for obtaining the slope of a line sometimes provides an erroneous result so that it occasionally gives a split line. For example, the commands `\drawline(0,0)(171,103)` and `\drawline(0,0)(171,-103)` of epic.sty under `\unitlength=0.08pt` give the following split lines if we encounter the wrongest situation:

This is because the XƎMTEX system version 2.00 and before has adopted the `\dottedline` command only and has not adopted the `\drawline` command of the epic package. This means that the previous versions of XƎMTEX before 2.00 have no methods of reducing the size of a structural formula into less than `\unitlength=0.1pt`, because the original picture environment of LATEX 2_ε cannot draw a short line. The XƎMTEX version 3.00 [1] has avoided the drawback of the original `\drawline` of the epic package, so that an enhanced function for reducing sizes of structural formulas (sizeredc.sty) is available, even if you use the TEX/LATEX-compatible mode.

On the other hand, the PostScript-compatible mode (supported by the XƎMTEX system 4.00 and later) as well as the PDF-compatible mode (supported by the XƎMTEX system 5.00 and later) is free from such a drawback. Hence, size reduction is freely available. if you use the PostScript- or PDF-compatible mode.

5.2 Basic Functions

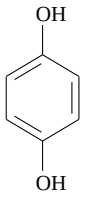
5.2.1 Changing Unit Lengths

The default unit length of the XƎMTEX system is equal to 0.1pt. This setting can be changed by the command `\changeunitlength`, which is defined in the sizeredc.sty package:

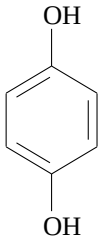
```
\changeunitlength{⟨unitlength⟩}
```

The argument ⟨unitlength⟩ denotes the unit length to be applied to the sizes of structural formulas, where its default value is decided to be 0.1pt. As shown in the following code, the setting by `\changeunitlength` can be done in the preamble of a document if the value is used in the whole document.

```
\documentclass{article}
\usepackage{xymtexpdf}%PDF mode
%\usepackage{xymtexps}%PostScript mode
%\usepackage{xymtex}%TeX/LaTeX mode
\changeunitlength{0.08pt}
\begin{document}
\bzdrv{1==OH;4==OH}
\end{document}
```



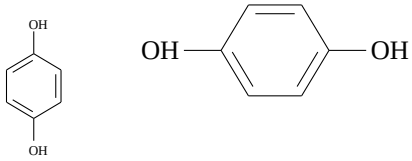
Compare this formula with the counterpart with the standard unit length (0.1pt).



The command `\changeunitlength` can be declared at any place of a document, where the setting of the command is effective after the declaration place until an alternative declaration is carried out afterward. The grouping technique can be used to limit the effect of the setting within a pair of braces. For example, the code represented by

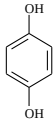
```
{%grouping by braces
\changeunitlength{0.06pt}
\bzdrv{1==OH;4==OH}}
\qquad \bzdrh{1==OH;4==OH}
```

produces a size-reduced formula as follows:



In the PDF-compatible mode of X$\mathfrak{M}$TEX Version 5.00 and later, the command `\setxymtxpdf[0.05pt]` can be also used in place of the command `\changeunitlength{0.05pt}`.

```
{%
\setxymtxpdf[0.05pt]
\bzdrv{1==OH;4==OH}
}
```



5.2.2 Size Reduction of Carbocycles

When the `\sizereductiontrue` is not declared (i.e. `\sizereductionfalse`), the original picture environment of LaTeX 2_ε works. The following example shows the comparison between cases with and without the use of sizeredc.sty. Note Version 4.00 (or later) requires the declaration of `\originalpicture`.

```
\begin{table}
\caption{With and Without \textsf{sizeredc.sty}}
```

Table 5.1. With and Without sizeredc.sty

without sizeredc.sty	with sizeredc.sty
0.08pt	
	
0.07pt	
	
0.06pt	
	

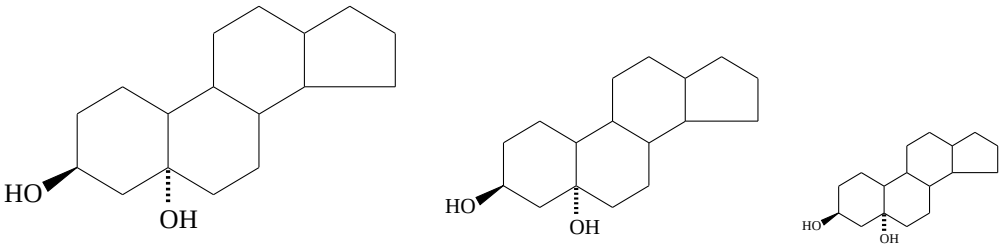
```
\label{tt:300c}
\begin{center}
\begin{tabular}{ll}
\hline
without \textsf{sizeredc.sty} & with \textsf{sizeredc.sty} \\
\hline
0.08pt &  \\
{\originalpicture\unitlength=0.08pt \bzdrv{}} &
{\changeunitlength{0.08pt}\bzdrv{}} \\
0.07pt & \\
{\originalpicture\unitlength=0.07pt\bzdrv{}} &
{\changeunitlength{0.07pt}\bzdrv{}} \\
0.06pt & \\
{\originalpicture\unitlength=0.06pt \bzdrv{}} &
{\changeunitlength{0.06pt}\bzdrv{}} \\
\hline
\end{tabular}
\end{center}
\end{table}
```

This code gives the results shown in Table 5.1. Without sizeredc.sty, the resulting formulas (0.07pt and 0.06pt in the left column) have no slanting lines (inner double bonds) in agreement with the original specification of the LaTeX 2_ε picture environment.[a] By using sizeredc.sty, the slanted lines are revived, as shown in the right column of Table 5.1.

The following examples show the application of the `\changeunitlength` command to steroid derivatives in their size reductions.

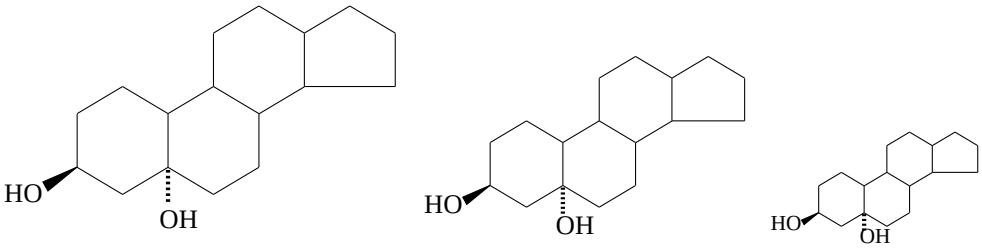
```
\steroid{3B==HO;5A==OH}%default unit length = 0.1pt
{\changeunitlength{0.08pt} \steroid{3B==HO;5A==OH}}
{\changeunitlength{0.05pt} \steroid{3B==HO;5A==OH}}
```

[a] Note that XeTeX is based on the LaTeX 2_ε picture environment without using sizeredc.sty. The slanted lines of the benzene ring are drawn by the \line command with slopes (5, 3) and (5, –3).



Note that font sizes are also changed during the size reduction. The direct change of `\unitlength` causes no change of font sizes. In this case, `\substfontsize` should be redefined (cf. Chapter 6).

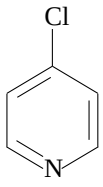
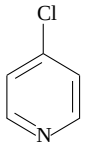
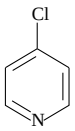
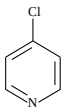
```
\steroid{3B==HO;5A==OH}%default unit length = 0.1pt
{\unitlength=0.08pt \steroid{3B==HO;5A==OH}}
{\unitlength=0.05pt \let\substfontsize=\footnotesize \steroid{3B==HO;5A==OH}}
```



5.2.3 Size Reduction of Heterocycles

Table 5.2 shows the effect of size reduction to the drawing of 4-chloropyridine, where `\unitlength` is changed from 0.1pt (default value) to 0.04pt by using `\changeunitlength`.

Table 5.2. Size Reduction of 4-Chloropyridine

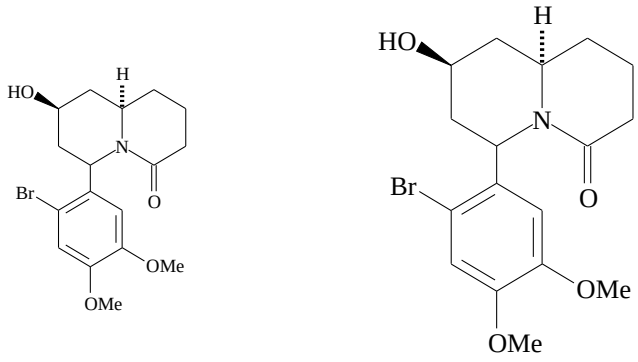
0.1pt (default)	0.08pt	0.07pt	0.06pt	0.05pt	0.04pt
					

5.2.4 Nested Substitution

Formulas by nested substitution can be totally reduced in size by the following code:

```
\changeunitlength{0.07pt}
\decaheterov[]{4a==N}{4D==O;7B==HO;{{10}A}==H;%
5==\bzdrv{3==OMe;4==OMe;6==Br;1==(yl)}}
```

This code produces the left formula shown below:



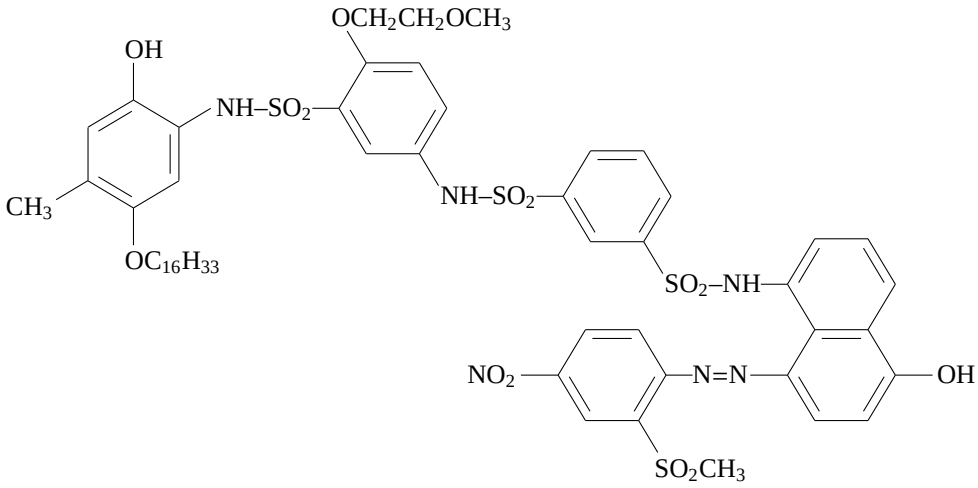
The right formula is drawn by the same code with the standard unit length (0.1pt).

A cyan dye releaser will be drawn by using two or more `\ryl` and `\lyl` commands in Section 26.3. We here discuss the size-reduction of the cyan dye releaser. First, we define `\cyandyereleaser` as being

```
\def\cyandyereleaser{%
\bzdrv{1==OH;5==CH$_{3}$;4==OC$_{16}$H$_{33}$;%
2==\ryl(4==NH--SO$_{2}$){4==\bzdrh{1==(yl);2==OCH$_{2}$CH$_{2}$OCH$_{3}$;%
5==\ryl(2==NH--SO$_{2}$){4==\bzdrh{1==(yl);%
5==\ryl(2==SO$_{2}$--NH){4==\naphdrh{1==(yl);5==OH;%
8==\lyl(4==N=N){4==\bzdrh{4==(yl);1==NO$_{2}$;5==SO$_{2}$CH$_{3}$}}}}}}}}}}
```

Then, we write down the command `\cyandyereleaser`. Thereby, we obtain a target formula:

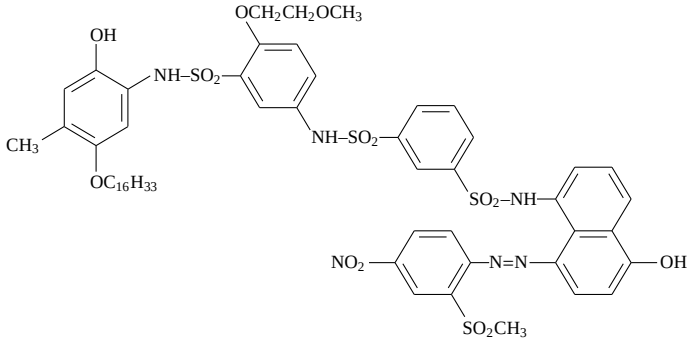
—0.1pt (default)



The size of the formula can be reduced by declaring the command `\changeunitlength`.

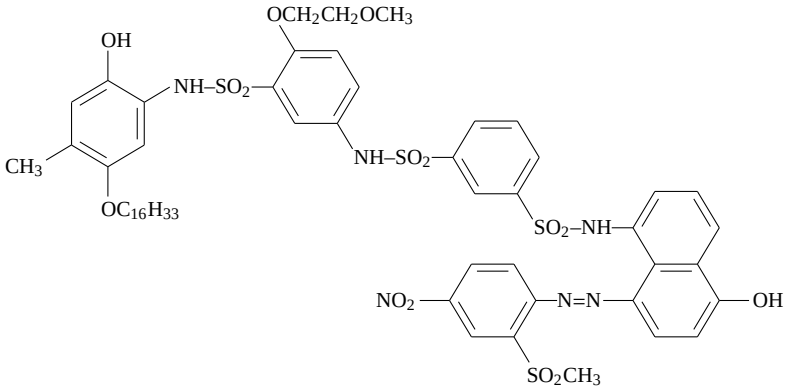
—0.07pt: (`\changeunitlength{0.07pt}`)

```
\changeunitlength{0.07pt}
\cyandyereleaser
```



—0.08pt: (\changeunitlength{0.08pt})

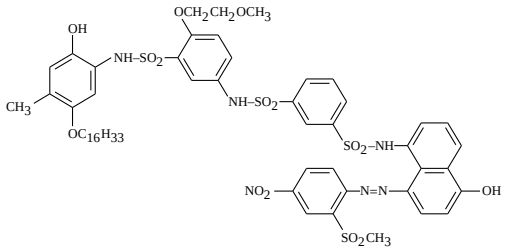
```
\changeunitlength{0.08pt}
\cyandyereleaser
```



A further reduction is possible. The following example shows the case of \unitlength=0.05pt.

—0.05pt: (\changeunitlength{0.05pt})

```
\changeunitlength{0.05pt}
\cyandyereleaser
```

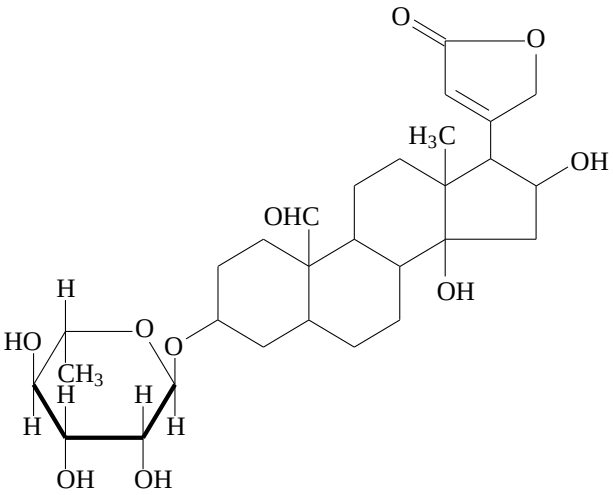


The structural formula of adonitoxin will be drawn in Section 26.3. We here discuss the size-reduction of adonitoxin, which is drawn by the code defined as follows:

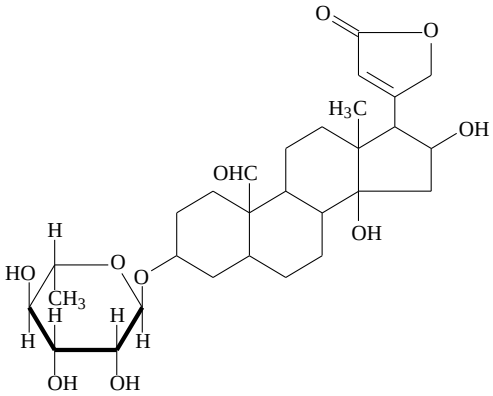
```
\def\adonitoxin{%
\steroid{{{10}}==\lmoiety{OHC};{{14}}==OH;%
{{13}}==\lmoiety{H$_{3}$C};{{16}}==OH;%
{{17}}==\fiveheterov[e]{3==O}{4D==O;1==(yl)};%
3==\lyl(3==O){8==%
\pyranose{1Sb==(yl);1Sa==H;2Sb==H;2Sa==OH;3Sb==H;3Sa==OH;4Sb==HO;%
4Sa==H;5Sb==H;5Sa==CH$_{3}$}}}}
```

Then, we write down the defined command \adonitoxin. Because it is necessary to reduce the size of a formula, the command \changeunitlength is declared.

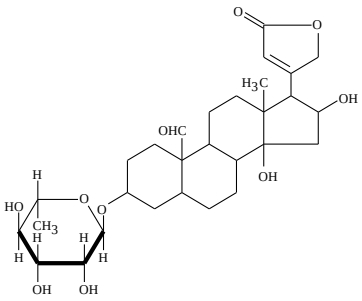
—0.1pt (default)



—0.08pt (`\changeunitlength{0.08pt}`)



—0.06pt (`\changeunitlength{0.06pt}`)



5.3 Switching to the Original Picture Environment

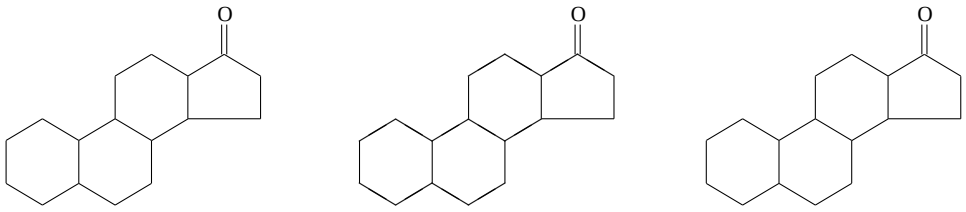
Even if the PostScript-compatible or the PDF-compatible mode is selected, the original LaTeX picture environment can be used by a switching declaration `\orignalpicture`:

```
\orignalpicture
```

which becomes effective after the declaration. For example, in the present book that has included the xymtexpdf or xymtexps package, we write down following code:

`\changeunitlength{0.08pt}`

```
\steroid{{17}D==O}
{\originalpicture
\changeunitlength{0.08pt}
\steroid{{17}D==O}}
\steroid{{17}D==O}
```



The declaration of `\orignalpicture` is effective until another switching declaration will be inputted. The above example shows that a grouping restricts the effect of `\orignalpicture` within a pair of braces, where the second formula of a steroid is typeset by virtue of the original LaTeX picture environment and the remaining two formulas are drawn by PDF (the PDF-compatible mode by using the pgf package) or PostScript (the PDF-compatible mode by using the PSTricks package).

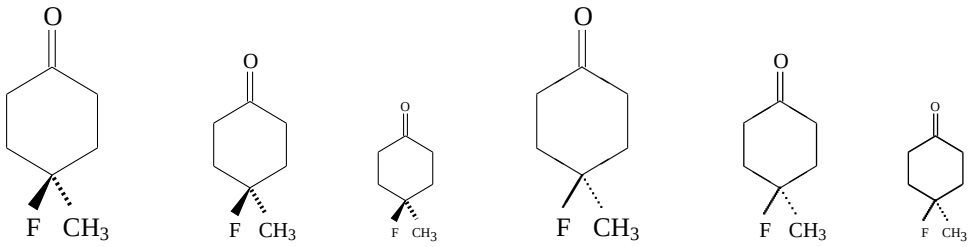
Although the original LaTeX picture environment gives an insufficient result of reducing formula sizes, the latest version of the XeTeX system gives sufficient size reduction, because it includes the sizeredc package automatically by declaring `\usepackage{xymtex}` (the original TeX/LaTeX-compatible mode), `\usepackage{xymtexps}` (the PostScript-compatible mode), or `\usepackage{xymtexpdf}` (the PDF-compatible mode). Once the sizeredc package is additionally included, the original LaTeX picture environment can be used by a switching declaration `\reducedsizepicture` in order to reduce the sizes of formulas:

```
\reducedsizepicture[⟨unitlength⟩]
```

where the optional argument ⟨unitlength⟩ represents a unit length (the default value: 0.1pt). For example, a minimal set of packages are used in the following code:

```
%400test3.tex
\documentclass[draft]{article}
\usepackage{xymtexpdf}% PDF mode
%\usepackage{xymtexps}% PostScript mode
\begin{document}
{\cyclohexanev{1D==O;4SA==CH$_{3}$;4SB==F}
\changeunitlength{0.08pt}
\cyclohexanev{1D==O;4SA==CH$_{3}$;4SB==F}
\changeunitlength{0.06pt}
\cyclohexanev{1D==O;4SA==CH$_{3}$;4SB==F}}
{\reducedsizepicture
\cyclohexanev{1D==O;4SA==CH$_{3}$;4SB==F}
\changeunitlength{0.08pt}
\cyclohexanev{1D==O;4SA==CH$_{3}$;4SB==F}
\changeunitlength{0.06pt}
\cyclohexanev{1D==O;4SA==CH$_{3}$;4SB==F}}
\end{document}
```

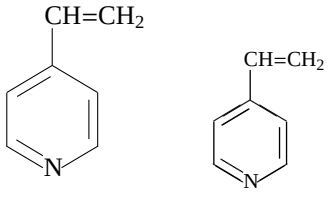
Thereby, we obtain structural formulas with various sizes. The top three formulas are drawn in PDF (or PostScript) and the remaining three are typeset within the picture environment and the epic package.



The declaration command `\reducedsizepicture` can take an optional argument, by which the unit length of the picture environment is specified.

```
%400test4.tex
\documentclass{article}
\usepackage{xymtexpdf}% PDF mode
%\usepackage{xymtexps}% PostScript mode
\begin{document}
\pyridinevi{4==CH=CH$_{2}$}
\reducedsizepicture[0.08pt]
\pyridinevi{4==CH=CH$_{2}$}
\end{document}
```

This code produces the following two formulas. The first formula is drawn in PDF or PostScript at the standard unit length of 0.1pt, while the second one is typeset in the LaTeX picture environment (plus the epic package) at the unit length of 0.08pt.



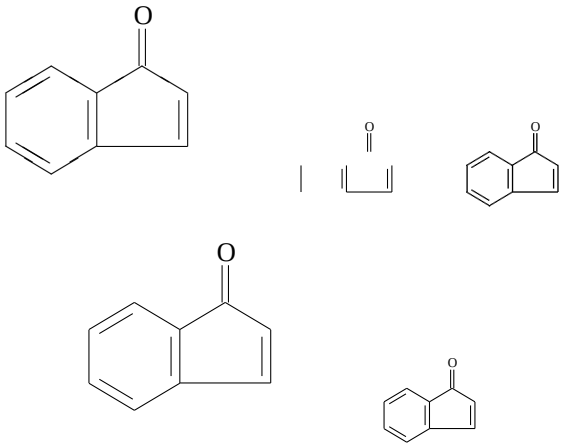
If the text mode is run under `\originalpicture`, the declaration `\setxymtxpdf` is used to return to the PDF drawing mode (or the declaration `\setxymtxps` is used to return to the PostScript drawing mode).

`\setxymtxpdf[`⟨unitlength⟩`]` (for the PDF-compatible mode)
`\setxymtxps[`⟨unitlength⟩`]` (for the PostScript-compatible mode)

```
%400test5.tex
\documentclass{article}
\usepackage{xymtexpdf}% PDF mode
%\usepackage{xymtexps}% PostScript mode
\begin{document}
\begin{center}
\originalpicture%original picture environment
\indanevi{1D==O}
\changeunitlength{0.05pt}
\indanevi{1D==O}
{\reducedsizepicture[0.05pt]
\indanevi{1D==O}} \\
\setxymtxpdf%PDF drawing
%\setxymtxps%PostScript drawing
\indanevi{1D==O}
\changeunitlength{0.05pt}
\indanevi{1D==O}
\end{center}
```

```
\end{document}
```

These codes produce the following formulas.



The first two formulas in the top row are typeset within the original LaTeX picture environment,[b] while the last one in the top row is typeset by the picture environment plus the epic package. In contrast, the two formulas in the bottom row are drawn in PDF (or PostScript).

It should be noted that the declaration:

```
\originalpicture%original picture environment
\changeunitlength{0.05pt}
```

indicates that the utilities of the original picture environment are adopted without the sizeredc package (including the modified epic package). On the other hand, the declaration:

```
\reducedsizepicture[0.05pt]
```

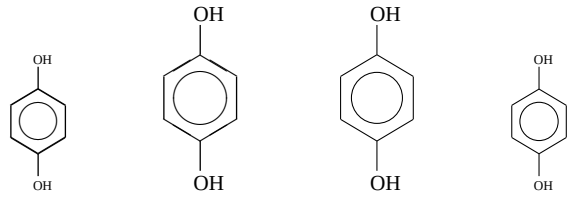
indicates that the utilities of the sizeredc package (including the modified epic package) are included along with those of the original picture environment.

The declaration `\setxymtxpdf` (or `\setxymtxps`) can take an optional argument, which specifies the unit length when returned to the PDF or PostScript drawing mode.

```
%400test6.tex
\documentclass{article}
\usepackage{xymtexpdf}% PDF mode
%\usepackage{xymtexps}% PostScript mode
\begin{document}
\reducedsizepicture[0.06pt]
\bzdrv[A]{1==OH;4==OH}
\changeunitlength{0.08pt}
\bzdrv[A]{1==OH;4==OH}
\setxymtxpdf[0.08pt]%PDF mode
%\setxymtxps[0.08pt]%PostScript mode
\bzdrv[A]{1==OH;4==OH}
\changeunitlength{0.06pt}
\bzdrv[A]{1==OH;4==OH}
\end{document}
```

The top two of the resulting formulas are typeset within the LaTeX picture environment and the epic package, while the remaining two after the declaration `\setxymtxpdf[0.08pt]` (or `\setxymtxps[0.08pt]`) are drawn in PDF (or PostScript).

[b] Note that the LaTeX picture environment is incapable of drawing short lines. Hence, the inner slanted lines disappear in the benzene ring of the second formula.

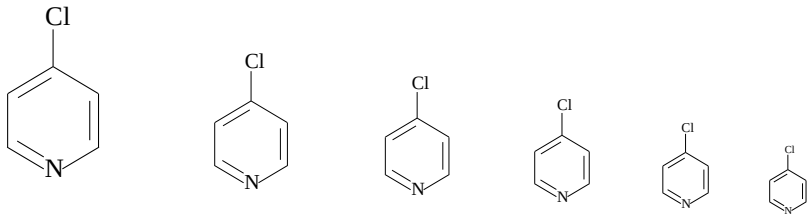


5.4 Utilities Supported by the graphicx Package

By using the graphicx package, the command `\scalebox` is available for the purpose of size reduction. After the declaration of `\usepackage{graphicx}` in the preamble, the following codes:

```
\scalebox{1}{\pyridinevi{4==Cl}}
\scalebox{0.8}{\pyridinevi{4==Cl}}
\scalebox{0.7}{\pyridinevi{4==Cl}}
\scalebox{0.6}{\pyridinevi{4==Cl}}
\scalebox{0.5}{\pyridinevi{4==Cl}}
\scalebox{0.4}{\pyridinevi{4==Cl}}
```

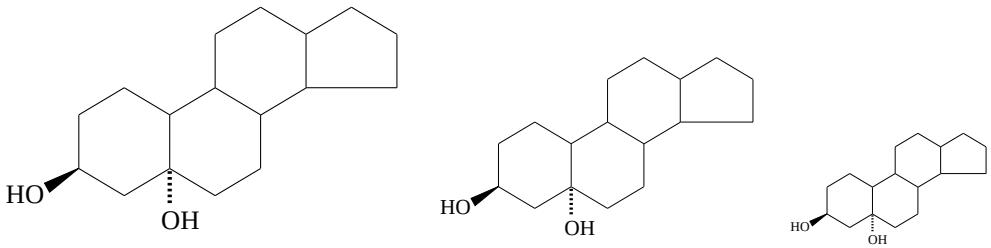
produce structural formulas of reduced sizes:



which correspond to the formulas listed in Table 5.2. Note that the sizes of characters (N and Cl) and the thicknesses of bonds are reduced in accord with the values declared in the first argument of `\scalebox`. Compare these formulas with those collected in Table 5.2, where the thickness of bond is not reduced even in the case of 0.04pt.

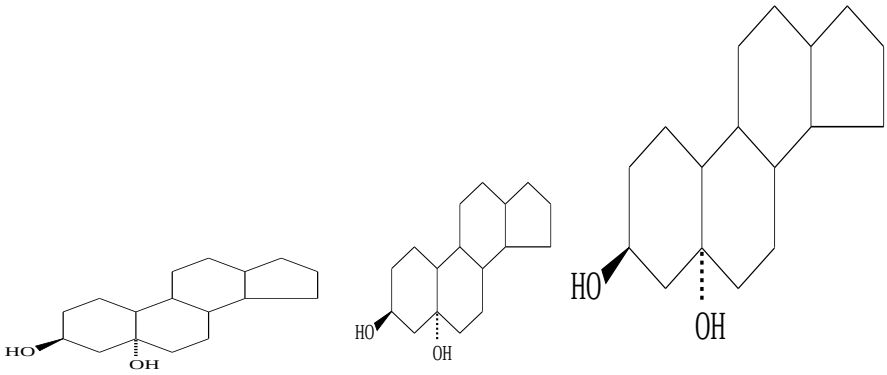
The `\scalebox` command of the graphicx package can also be used to change the sizes of structural formulas. Thus, essentially equivalent results to those of the preceding subsection can be obtained as follows:

```
\steroid{3B==HO;5A==OH}
\scalebox{0.8}{\steroid{3B==HO;5A==OH}}
\scalebox{0.5}{\steroid{3B==HO;5A==OH}}
```



The `\scalebox` command is capable of taking an optional argument, by which the aspect ratio of a structural formula can be changed, as shown in the following examples:

```
\scalebox{0.8}[0.5]{\steroid{3B==HO;5A==OH}}
\scalebox{0.5}[0.8]{\steroid{3B==HO;5A==OH}}
\scalebox{0.8}[1.5]{\steroid{3B==HO;5A==OH}}
```



References

[1] S. Fujita and N. Tanaka, *TUGboat*, **22 (4)**, 285–289 (2001).

Chapter 6

Fonts and Related Matters

6.1 Fonts and Font Sizes

The font for drawing substituents and atoms in a default mode is selected by the following setting:

```
\let\substfont=\normalfont
\let\substfontsize=\normalsize
```

According to this specification,[a] the font and its size can be changed by substituting `\substfont` and `\substfontsize`. The declaration is globally effective if the above setting is done in the preamble before `\begin{document}`, e.g.,

```
\documentclass{article}
\usepackage{xymtexpdf}%PDF mode
%\usepackage{xymtexps}%PostScript mode
\let\substfont=\sffamily
\let\substfontsize=\small
\begin{document}
(text)
\end{ducment}
```

The command `\substfont` is redefined by using `\let` or `\def`, where the three kind of properties can be changed:

- (family) `\rmfamily` (roman), `\sffamily` (san serif), and `\ttfamily` (typewriter).
- (series) `\mdseries` (medium) and `\bfseries` (boldfaced).
- (shape) `\upshape` (upright), `\itshape` (italic), `\scshape` (small capital), `\alshape` (slanted).

Note that `\normalfont` represents the combined font which stems from `\rmfamily`, `\mdseries`, and `\upshape`.

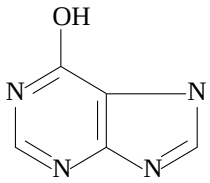
The command `\substfontsize` is redefined by using `\let` or `\def`, where the font size is selected from `\tiny`, `\scriptsize`, `\footnotesize`, `\small`, `\normalsize`, `\large`, `\Large`, `\LARGE`, `\huge`, and `\Huge`.

For example, the following modes of setting are typical, where the declaration is local for the sake of convenience.

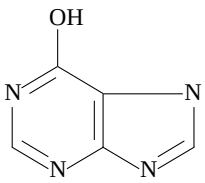
[a] This specification is different from that of the previous versions (version 3.00 and the older versions).

- \nomalfont (default):

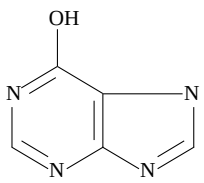
```
\purinev{4==OH}
{\let\substfontsize=\small
\purinev{4==OH}}
{\let\substfontsize=\footnotesize
\purinev{4==OH}}
```



(\normalsize)



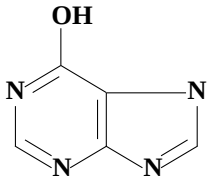
\small



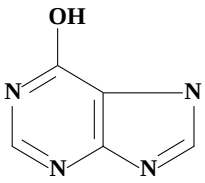
\footnotesize

- \bfseries:

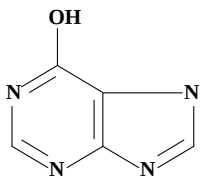
```
{\let\substfont=\bfseries
\purinev{4==OH}
{\let\substfontsize=\small
\purinev{4==OH}}
{\let\substfontsize=\footnotesize
\purinev{4==OH}}
}
```



(\normalsize)



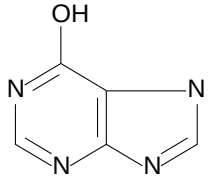
\small



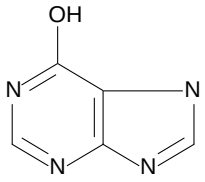
\footnotesize

- \sffamily:

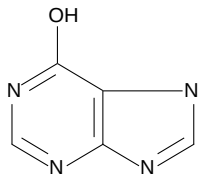
```
{\let\substfont=\sffamily
\purinev{4==OH}
{\let\substfontsize=\small
\purinev{4==OH}}
{\let\substfontsize=\footnotesize
\purinev{4==OH}}
}
```



(\normalsize)



\small

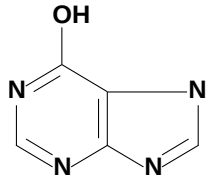


\footnotesize

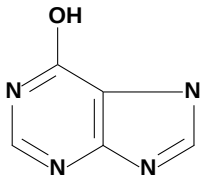
- \sffamily and \bfseries:

```
{\def\substfont{\sffamily\bfseries}
\purinev{4==OH}
{\let\substfontsize=\small
\purinev{4==OH}}
{\let\substfontsize=\footnotesize
\purinev{4==OH}}
```

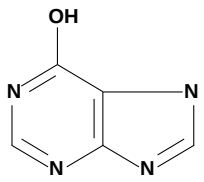
```
}
```



(\normalsize)



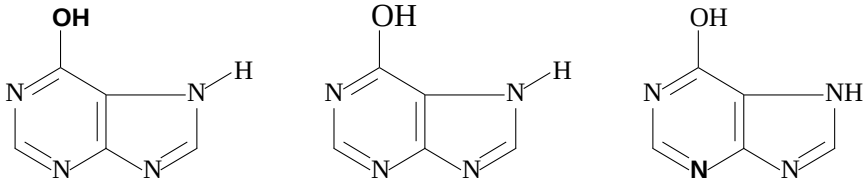
\small



\footnotesize

The declaration of fonts and font sizes is local if it is surrounded by a pair of braces or involved by an appropriate environment (e.g., the `center` environment). A more local setting is available as shown in the following codes:

```
\purinev{4=={\sffamily\bfseries OH};3==H}
\purinev{4=={\large OH};3==H}
\nonaheterov[aegj]{1==N;3==NH;5==N;7=={\sffamily\bfseries N}}{4==OH}
```



6.2 Bond Thickness

The thickness of bonds in a default mode is selected by the following setting:

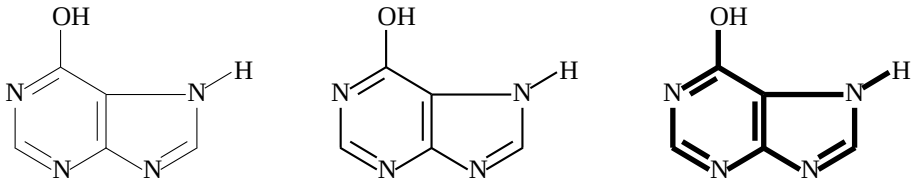
```
\def\thickLineWidth{1.6pt}
\def\thinLineWidth{0.4pt}
```

According to this specification, the thickness of bonds can be changed by redefining these commands. The declaration is globally effective if the above setting is done in the preamble before `\begin{document}`, e.g.,

```
\documentclass{article}
\usepackage{xymtexpdf}%PDF mode
%\usepackage{xymtexps}%PostScript mode
\def\thickLineWidth{2.8pt}
\def\thinLineWidth{0.8pt}
\begin{document}
(text)
\end{ducment}
```

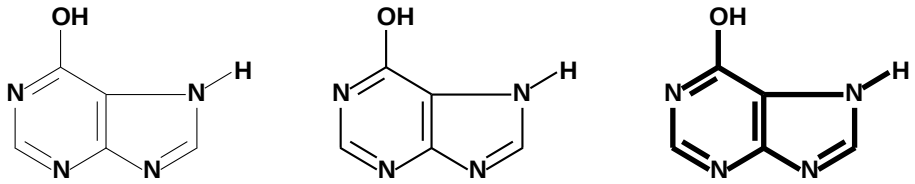
The following example shows the changing `\thinLineWidth`.

```
\purinev{4==OH;3==H}
{\def\thinLineWidth{0.8pt}
\purinev{4==OH;3==H}}
{\def\thinLineWidth{2pt}
\purinev{4==OH;3==H}}
```



The following example shows the changing of `\thinLineWidth` along with the changing of fonts.

```
{\def\substfont{\sffamily\bfseries}
\purinev{4==OH;3==H}
{\def\thinLineWidth{0.8pt}
\purinev{4==OH;3==H}}
{\def\thinLineWidth{2pt}
\purinev{4==OH;3==H}}}
```

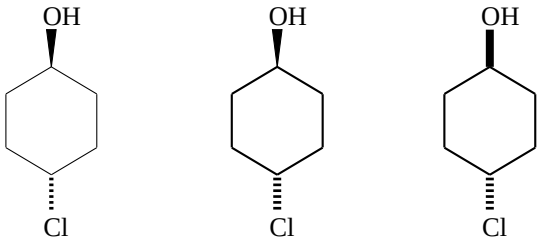


The declaration of bond thickness is local if it is surrounded by a pair of braces or involved by an appropriate environment (e.g., the `center` environment.

An absolute configuration is represented by a pair of wedges and hashed-dashed bonds (the default setting of the XeLaTeX system: `\wedgehasheddash`), a pair of dashes and hashed-dashed bonds (`\dashhasheddash`), or other combinations (cf. Chapter 29). The thicknesses of dashes and hashed-dashed bonds can be changed by redefining `\thickLineWidth`. Thus the codes:

```
\cyclohexanev{1B==OH;4A==Cl}
{\def\thinLineWidth{0.8pt}
\def\thickLineWidth{3pt}
\cyclohexanev{1B==OH;4A==Cl}
{\dashhasheddash
\cyclohexanev{1B==OH;4A==Cl}}}
```

generate the following results:



Part II

Carbocyclic Compounds

Six-Membered Carbocycles. Commands for Specific Use

XeLaTeX commands for specific use `ComSpec` are short-cut commands of those for general use `ComGen`, where appropriate arguments are selected from the required and optional arguments of the latter (cf. Section 3.1 for the syntax). This chapter is devoted to introduce commands for drawing benzene derivatives as well as cyclohexane derivatives. These commands are short-cut commands of `\sixheterov` etc. for general use.

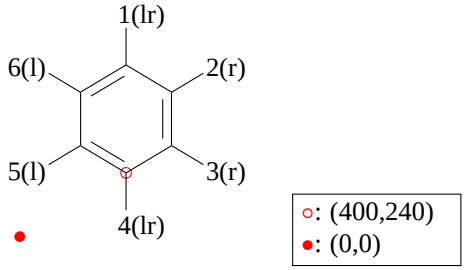
7.1 Drawing Benzene Derivatives

7.1.1 Vertical Forms of Benzene Derivatives

The XeLaTeX command `\bzdrv` (or synonymously `\benzenev`) for specific use is used to draw benzene derivatives of vertical type (carom.sty). The format of this command is defined as follows:

```
\bzdrv[⟨bondlist⟩]{⟨subslist⟩}
\benzenev[⟨bondlist⟩]{⟨subslist⟩}
```

The name and arguments of this command conform to the general conventions described in Section 3.1. Thus, the suffix '`v`' indicates that this macro produces a vertical-type structural formula. Locant numbers for designating substitution positions in the ⟨subslist⟩ are represented by the following diagram:



in which a character set in a pair of parentheses represent the handedness of each position. In accord with the default definitions of the macro `\bzdrv` (`\benzenev`), each of the right-handed positions (2 and 3) is designed to take only a right-handed substituent, while each of the left-handed positions (5 and 6) is to take only a left-handed substituent. Such positions (designated with the letter 'r' or 'l') are referred to as 'oriented' positions in this manual. In contrast, the top (and also the bottom) position of a benzene ring (designated with the string 'lr') can accommodate a substituent of both handedness, where the position is referred to as a 'double-sided' position in this manual. Although the default definition is to put a right-handed moiety, a left-handed substituent can be printed by means of the macro `\lmoiety`.

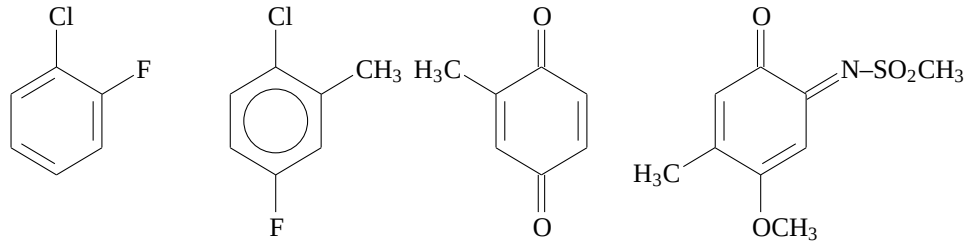
The symbols • and ○ in the diagram respectively represent the reference point and the inner origin of the macro. Since we select `\unitlength` to be equal to 0.1pt as a default value, the value 400, for example, corresponds to 40pt.

Although the syntax of bond lists ⟨bondlist⟩ principally follows the specification described in Subsection 3.3.1, the specification of a bond pattern is permissible as an alternative mode of setting. The optional argument ⟨bondlist⟩ specifying a bond pattern is shown in Table 7.1.[a] Thereby, a wide variety of bond patterns (such as two patterns of benzene double bonds as well as an aromatic circle) can be depicted, as illustrated in Figure 7.2.

The argument ⟨subslist⟩ is used to specify each substituent with a locant number and a bond modifier shown in Table 3.2 in which *n* is an Arabic numeral between 1 and 6. For the syntax of substitution lists ⟨subslist⟩, see Subsection 3.2.1. For example, the statements,

```
\bzdrv{1==Cl;2==F}
\bzdrv[c]{1==Cl;4==F;2==CH$_{3}$}\qquad
\bzdrv[pa]{1D==O;4D==O;6==H$_{3}$C}
\bzdrv[oa]{1D==O;2D==N--SO$_{2}$CH$_{3}$;4==OCH$_{3}$;5==H$_{3}$C}
```

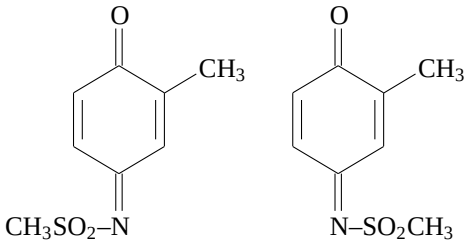
produce the following structures:



In order to designate the handedness of a substituent explicitly, you can use `\rmoiety` or `\lmoiety` commands. Thus, the statements,

```
\bzdrv[pa]{1D==O;4D==\lmoiety{CH$_{3}$SO$_{2}$--N};2==CH$_{3}$}
\bzdrv[pa]{1D==\rmoiety{O};4D==\rmoiety{N--SO$_{2}$CH$_{3}$};2==CH$_{3}$}
```

produce the following structures with left-handed and right-handed methanesulfonimido groups.



The macro `bzdrv` is used also to draw benzoquinone monoacetals and diacetals. The handedness of a substituent attached at such a tetrahedral position is determined in the light of chemical conventions. For example,

```
\bzdrv[pa]{1D==O;4Sb==CH$_{3}$O;4Sa==OCH$_{3}$;2==NH--SO$_{2}$CH$_{3}$}
\qquad \qquad
\bzdrv[pa]{1Sb==CH$_{3}$O;1Sa==OCH$_{3}$;4Sb==CH$_{3}$O;4Sa==OCH$_{3}$}
```

produce the following structures.

[a] When the optional argument ⟨bondlist⟩ specifies a bond pattern (not locant alphabets), the mechanism of ring fusion (the addition technique) is not permitted.

Table 7.1. Bond Patterns Due to the Optional Argument ⟨bondlist⟩ for Commands \bzdrv (\benzenev) and \bzdrh (\benzeneh)

Character	Printed structure (Bond pattern)
none or r	right-handed set of double bonds
l	left-handed set of double bonds
c	aromatic circle
p or pa	*p*-benzoquinone (A) (Oxygen atoms at 1,4-positions)
pb	*p*-benzoquinone (B) (Oxygen atoms at 2,5-positions)
pc	*p*-benzoquinone (C) (Oxygen atoms at 3,6-positions)
o or oa	*o*-benzoquinone (A) (Oxygen atoms at 1,2-positions)
ob	*o*-benzoquinone (B) (Oxygen atoms at 2,3-positions)
oc	*o*-benzoquinone (C) (Oxygen atoms at 3,4-positions)
od	*o*-benzoquinone (D) (Oxygen atoms at 4,5-positions)
oe	*o*-benzoquinone (E) (Oxygen atoms at 5,6-positions)
of	*o*-benzoquinone (F) (Oxygen atoms at 1,6-positions)

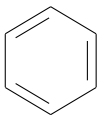
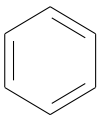
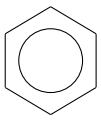
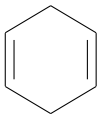
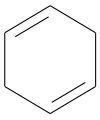
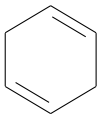
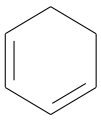
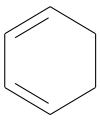
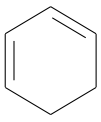
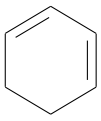
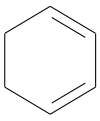
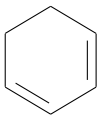
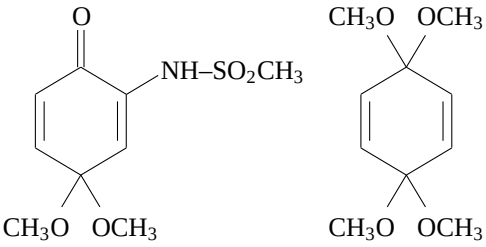
Mancude-ring systems			
	\bzdrv[r]{} \benzenev[r]{}	\bzdrv[l]{} \benzenev[l]{}	\bzdrv[c]{} \benzenev[c]{}
Para-quinones			
	\bzdrv[pa]{} \benzenev[pa]{}	\bzdrv[pb]{} \benzenev[pb]{}	\bzdrv[pc]{} \benzenv[pc]{}
Ortho-quinones			
	\bzdrv[oa]{} \benzenev[oa]{}	\bzdrv[ob]{} \benzenev[ob]{}	\bzdrv[oc]{} \benzenev[oc]{}
			
	\bzdrv[od]{} \benzenev[od]{}	\bzdrv[oe]{} \benzenev[oe]{}	\bzdrv[of]{} \benzenev[of]{}

Table 7.2. Endocylic bond patterns by the ⟨bondlist⟩ argument of \bzdrv (\benzenev)



In place of the bond patterns collected in Table 7.1, the command `\bzdrv` (`\benzenev`) can take locant alphabets to show the unsaturation of skeletal bonds. Because the letter '`c`' is used to print out an aromatic circle, the unsaturation of the 2,3-bond (locant alphabet `c`) is specified by inputting `[@c]`, where a dummy letter '`@`' is added at the top of ⟨bondlist⟩. For example, compare the following codes:

```
\benzenev[c]{}
\benzenev[@c]{}
\benzenev[@ce]{}
\benzenev[ec]{}
```

These codes produce:

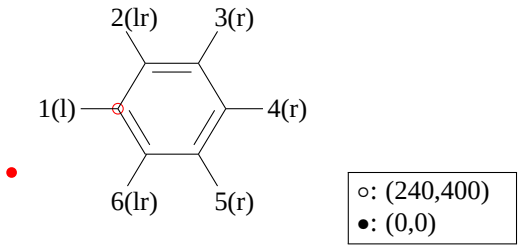
7.1.2 Horizontal Forms of Benzene Derivatives

You can use the XeTeX command `\bzdrh` (or synonymously `\benzeneh`) to draw benzene derivatives of horizontal type (carom.sty). The format of this command is as follows:

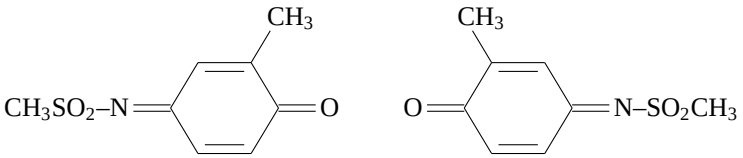
```
\bzdrh[⟨bondlist⟩]{⟨subslist⟩}
\benzeneh[⟨bondlist⟩]{⟨subslist⟩}
```

The name and arguments of this command conform to the general conventions described in Section 3.1. Thus, the suffix '`h`' indicates that this macro produces a horizontal-type structural formula.

The locant numbering and the handedness of substitution are designed as follows:



For example, the diagrams:



are typeset by inputting the statements:

```
\bzdrh[pa]{4D==O;1D==CH$_{3}$SO$_{2}$--N;3==CH$_{3}$} \qquad
\bzdrh[pa]{1D==O;4D==N--SO$_{2}$CH$_{3}$;2==CH$_{3}$}
```

It should be noted the the commands \bzdrv (\benzenev) and \bzdrh (\benzenev) are based respectively on the commands \cyclohexanev and \cyclohexaneh that will be described in the next section. Hence, structures drawn with the former set of commands can be also drawn with the latter set of commands (see Figs. 7.2 and 7.1).

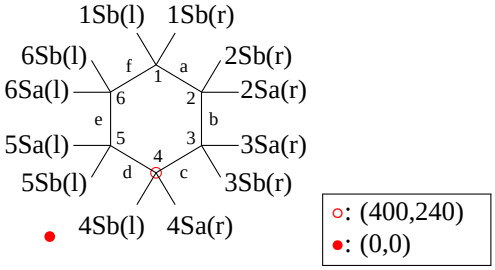
7.2 Drawing Cyclohexane Derivatives

7.2.1 Vertical Forms of Cyclohexane Derivatives

The macro \cyclohexanev is used to draw cyclohexane derivatives of vertical type (carom.sty). The format of this command is as follows:

```
\cyclohexanev[⟨bondlist⟩]{⟨subslist⟩}
```

Locant numbers (1–6) for designating substitution positions and characters (a–f) for showing bonds to be doubled are represented by the following diagram:



Each character set in parentheses represents the handedness of the corresponding position, which is fixed in this type of macros.

The option argument ⟨bondlist⟩ is an character string in a pair of brackets, where each character indicates the presence of a double bond at the edge corresponding to the character. The bond-correspondence is rather arbitrary in some cases but conforms to chemical conventions as faithfully as possible if such conventions are presence (Table 7.3). Several examples for drawing endocyclic double bonds are listed in Fig. 7.1. Note that Fig. 7.1 provides alternative ways for designating endocyclic double bonds for \bzdrv (\benzenev). Compare this with the results collected in Fig. 7.2.

The argument ⟨subslist⟩ for this macro takes a general format, in which the modifiers listed in Table 3.2 are used. Suppose you input the commands:

```
\cyclohexanev{2D==O;1Sb==H$_{3}$C;1Sa==CH$_{3}$;%
3Sb==CH$_{3}$;3Sa==CH$_{3}$} \qquad\qquad
\cyclohexanev[b]{1D==O;5Sb==CH$_{3}$;5Sa==CH$_{3}$}
```

The first example illustrates the case that \cyclohexanev accompanies no optional argument. On the other hand, the second one take [b] as an optional ⟨bondlist⟩, which prints an inner bond between 2 and 3 positions. Thus, you can obtain the following diagrams:

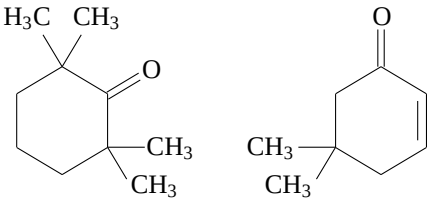
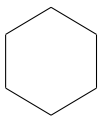
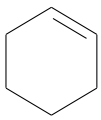


Table 7.3. Argument ⟨bondlist⟩ for Commands \cyclohexanev and \cyclohexaneh

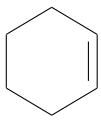
Character	Printed structure
none	cyclohexane
a	1,2-double bond
b	2,3-double bond
c	4,3-double bond
d	4,5-double bond
e	5,6-double bond
f	6,1-double bond
A	aromatic circle



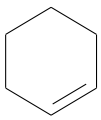
\cyclohexanev{}



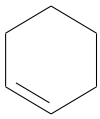
\cyclohexanev[a]{}



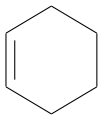
\cyclohexanev[b]{}



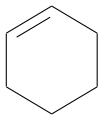
\cyclohexanev[c]{}



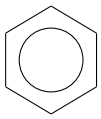
\cyclohexanev[d]{}



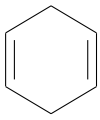
\cyclohexanev[e]{}



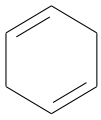
\cyclohexanev[f]{}



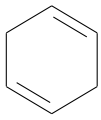
\cyclohexanev[A]{}



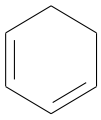
\cyclohexanev[be]{}



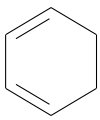
\cyclohexanev[cf]{}



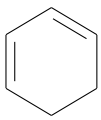
\cyclohexanev[ad]{}



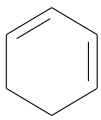
\cyclohexanev[ce]{}



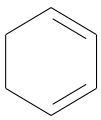
\cyclohexanev[df]{}



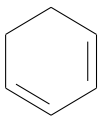
\cyclohexanev[ae]{}



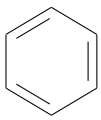
\cyclohexanev[bf]{}



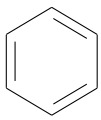
\cyclohexanev[ae]{}



\cyclohexanev[bd]{}



\cyclohexanev[bdf]{}



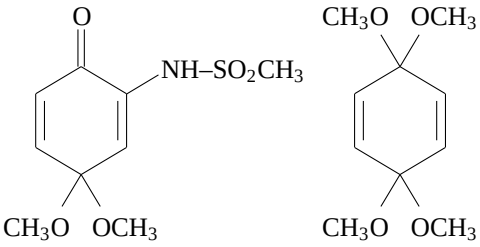
\cyclohexanev[ace]{}

Figure 7.1. Endocylic bonds by the ⟨bondlist⟩ argument of \cyclohexanev. For locant alphabets, see Table 7.3.

Since the macro `\cyclohexanev` is the basis of the macro `\bzdrv` (`\benzenev`), structural formulas depicted with the latter command can also be written by the former one. For example, the quinone acetals described above are also typeset by the following statements.

```
\cyclohexanev[be]{1D==O;4Sb==CH$_{3}$O;4Sa==OCH$_{3}$;2==NH--SO$_{2}$CH$_{3}$}
\qquad \qquad
\cyclohexanev[be]{1Sb==CH$_{3}$O;1Sa==OCH$_{3}$;4Sb==CH$_{3}$O;4Sa==OCH$_{3}$}
```

These commands are completely equivalent to those describe above and produce the following structures.

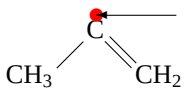


For the purpose of depicting the stereochemistry of a cyclohexane ring, input the following:

```
\cyclohexanev{2B==CH$_{3}$;3B==CH$_{3}$}\qquad\qquad
\cyclohexanev{2B==CH$_{3}$;3A==CH$_{3}$}
```

Thereby, you can obtain:

Example 7.1. Let us draw the structural formula of limonene, the IUPAC name of which is 1-methyl-4-(prop-1-en-2-yl)cyclohexene. The prop-1-en-2-yl group is generated by a (yl)-function. For example, the `\dtrigonal` command for drawing a trigonal skeleton generates the prop-1-en-2-yl group (**7-1**) by using a (yl)-function in the command `\dtrigonal`.

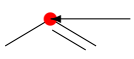


7-1

IUPAC name: prop-1-en-2-yl
XeLaTeX command:

```
\dtrigonal{1==(yl);%
0==C;2D==CH$_{2}$;3==CH$_{3}$}
```

An alternative skeletal expression (**7-2**) can be drawn by declaring a (yl)-function in the command `\trimethylene`.



7-2

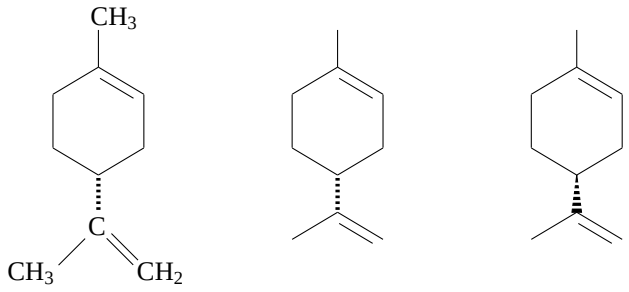
IUPAC name: prop-1-en-2-yl
XeLaTeX command:

```
\trimethylene[b]{}{2==(yl)}
```

Then, the substitution technique (cf. Section 2.7) is applied to either of these expressions.

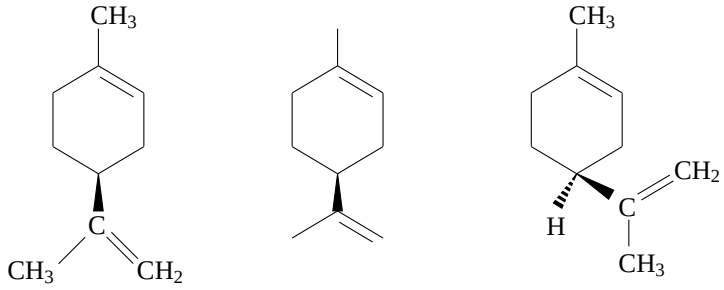
First, D-limonene (IUPAC name: (4*R*)-1-methyl-4-(prop-1-en-2-yl)cyclohexene) is drawn as follows:

```
\cyclohexanev[a]{1==CH$_{3}$;4A==\dtrigonal{1==(yl);%
0==C;2D==CH$_{2}$;3==CH$_{3}$}} \quad
\cyclohexanev[a]{1==\null;4A==\trimethylene[b]{}{2==(yl)}} \quad
{\wedgehashedwedge
\cyclohexanev[a]{1==\null;4A==\trimethylene[b]{}{2==(yl)}}}
```



Second, L-limonene (IUPAC name: (4*S*)-1-methyl-4-(prop-1-en-2-yl)cyclohexene) is drawn as follows:

```
\cyclohexanev[a]{1==CH$_{3}$;4B==\dtrigonal{1==(yl);%
0==C;2D==CH$_{2}$;3==CH$_{3}$}} \quad
\cyclohexanev[a]{1==\null;4B==\trimethylene[b]{}{2==(yl)}} \quad
{\wedgehashedwedge
\cyclohexanev[a]{1==CH$_{3}$;4Sd==H;4FB==\Utrigonal{3==(yl);%
0==C;2D==CH$_{2}$;1==CH$_{3}$}}}
```

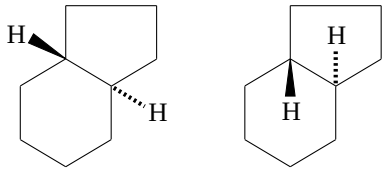


The last example adopts the `\Utrigonal` command to generate a prop-1-en-2-yl group. For the bond modifiers `Sd` and `FB`, see Table 3.2 and Fig. 3.1. □

Example 7.2. The command `\cyclohexanev` serves as a parent structure for the addition technique, where its ⟨bondlist⟩ accommodates a fusing unit. For example, the codes:

```
\begin{XyMcompd}(500,650)(250,250){}{}
\cyclohexanev[{a\fivefusev{}{}{e}}]{1FB==H;2GA==H}
\end{XyMcompd}
\qquad
\begin{XyMcompd}(500,650)(250,250){}{}
\cyclohexanev[{a\fivefusev{}{5FB==H}{e}}]{2FA==H}
\end{XyMcompd}
```

generate the following formulas with a six-to-five fused ring:



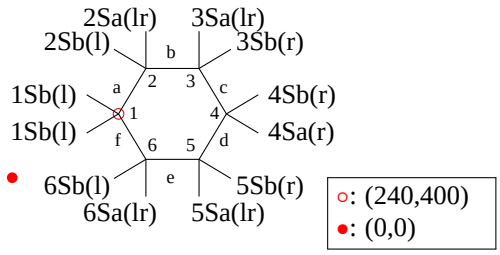
Note that the absolute configurations at bridgehead positions are designated in two ways. □

7.2.2 Horizontal Forms of Cyclohexane Derivatives

The macro `\cyclohexaneh` is used to draw cyclohexane derivatives of horizontal type (carom.sty). The format of this command is as follows:

```
\cyclohexaneh[⟨bondlist⟩]{⟨subslist⟩}
```

Locant numbers for designating substitution positions are represented by the following diagram:



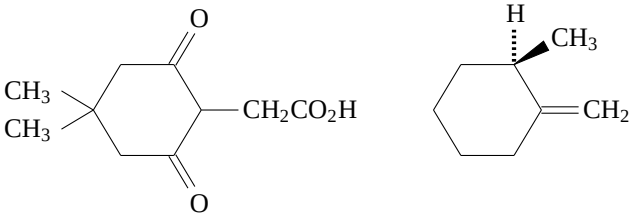
Each character set in parentheses represents the handedness of the corresponding position, which is fixed in this type of macros. The ⟨subslist⟩ and the ⟨bondlist⟩ format are shown in Table 3.2 and 7.3, respectively. Several examples for designating ⟨bondlist⟩ (Table 7.3) are collected in Fig. 7.2. Note that this figure is obtained by the slight modification of Figure 7.1, where the suffix 'v' of the command `\cyclohexanev` is changed into 'h' to input the command `\cyclohexaneh`.

The following examples show the designation of ⟨sublist⟩ and ⟨bondlist⟩.

Example:

```
\cyclohexaneh{3D==O;5D==O;1Sb==CH$_{3}$;1Sa==CH$_{3}$;%
4==CH$_{2}$CO$_{2}$H}\qquad\qquad
\cyclohexaneh{4D==CH$_{2}$;3SB==CH$_{3}$;3SA==H}
```

These commands produce:



7.3 Illustrative Examples of Drawing Six-Membered Carbocycles

7.3.1 Generation of Substituents by (yl)-Functions

The XyMTEX commands described in this chapter are able to generate substituents by using the (yl)-function technique.

Example 7.3. For example, a *p*-tolyl group is generated by `\benzeneh{1==(yl);4==CH$_{3}$}` and a cyclohexyl group (or a cyclohexylidene group) is generated by `\cyclohexaneh{1==(yl)}`. They are declared in the ⟨subslist⟩ of `\benzeneh` or `\cyclohexaneh` according to the substitution technique:

```
\begin{XyMcompd}(1150,400)(300,200){}{}
\benzeneh{4==\benzeneh{1==(yl);4==CH$_{3}$}}
\end{XyMcompd}
\qquad
\begin{XyMcompd}(850,400)(300,200){}{}
\benzeneh{4==\cyclohexaneh{1==(yl)}}
\end{XyMcompd}
\qquad
\begin{XyMcompd}(850,400)(300,200){}{}
\cyclohexaneh{4D==\cyclohexaneh{1==(yl)}}
\end{XyMcompd}
```

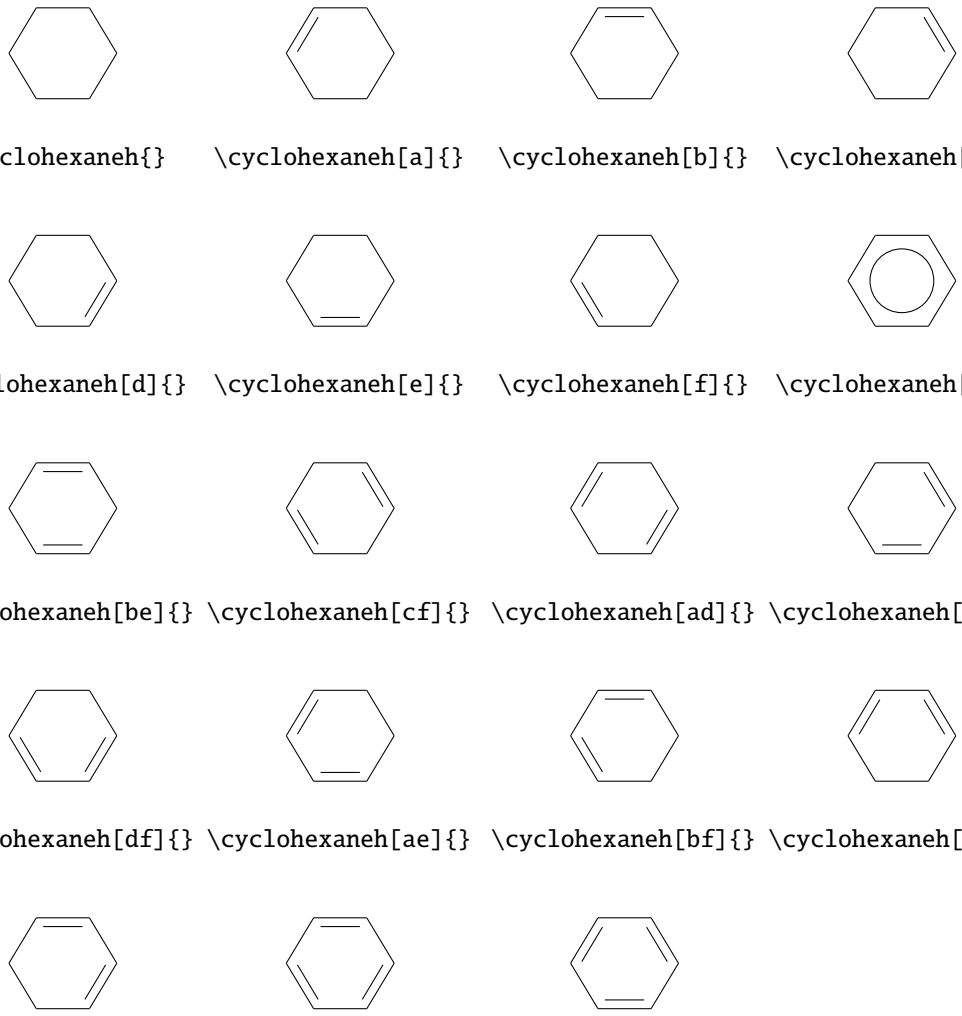
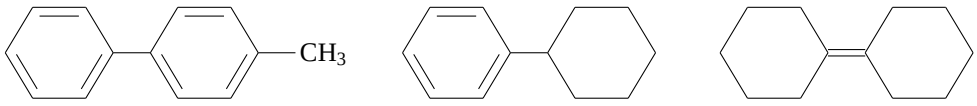


Figure 7.2. Endocylic bonds by the ⟨bondlist⟩ argument of `\cyclohexaneh`.

Thereby, the following structural formulas are obtained:

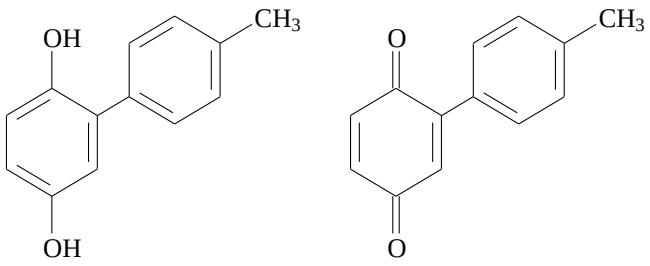


Note that a substituent produced by a (yl)-function is size-less (with no dimension), so that the resulting structure occupies no correct domain. In the above codes, the `XyMcompd` environment is used to estimate the size of such a substituent due to a (yl)-function so as to assure the correct domain of each structure with the substituent. □

Example 7.4. p-Tolylhydroquinone as an auxiliary developer in instant color photography [1, page 376] and its oxidized form are drawn in a similar way:

```
\begin{XyMcompd}(950,950)(300,0){}{}
\benzenev{1==OH;4==OH;2==\benzenev{5==(yl);2==CH$_{3}$}}
\end{XyMcompd}
\qquad
\begin{XyMcompd}(950,950)(300,0){}{}
\benzenev[pa]{1D==O;4D==O;2==\benzenev{5==(yl);2==CH$_{3}$}}
```

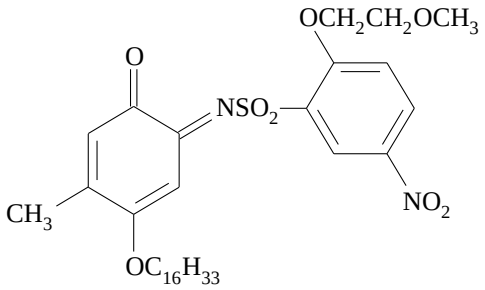
```
\end{XyMcompd}
```



□

Example 7.5. An *o*-sulfonamidophenol is oxidized to give the following *o*-quinone monoimide [1, page 465], the structural formula of which is drawn by the substitution technique using a (yl)-function and the `\ryl` command.

```
\begin{XyMcompd}(1800,1100)(0,0){}{}
\benzenev[oa]{1D==O;4==\ChemForm{OC_{16}H_{33}};5==\ChemForm{CH_3};%
2D==\ryl(5==\ChemForm{NSO_2}){4==\benzeneh{1==(yl);%
2==\ChemForm{OCH_2CH_2OCH_3};5==\ChemForm{NO_2}}}}
\end{XyMcompd}
```

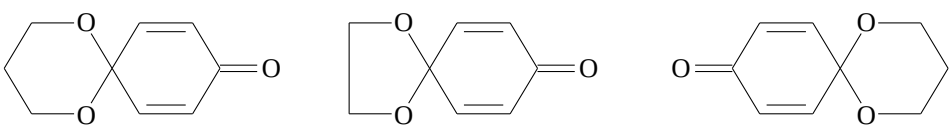


The code `\ChemForm{OC_{16}H_{33}}` etc. is declared in place of a usual code `OC$_{16}$H$_{33}$` etc., where a roman alphabet with a subscript is automatically printed out by using `\ChemForm`. □

Example 7.6. Substituents generated by the (yl)-function technique can be used in spiro fusion (cf. page 37), as found in the following codes:

```
\begin{XyMcompd}(1000,450)(250,200){}{}
\sixheteroh{3==O;5==O;4s==\benzeneh[pa]{1==(yl);4D==O}}{}
\end{XyMcompd}
\qquad
\begin{XyMcompd}(800,450)(400,200){}{}
\fiveheteroh{2==O;5==O;1s==\cyclohexaneh[be]{1==(yl);4D==O}}{}
\end{XyMcompd}
\qquad
\begin{XyMcompd}(1000,450)(0,200){}{}
\sixheteroh[be]{4s==\sixheteroh{2==O;6==O}{1==(yl)}}{1D==O;}
\end{XyMcompd}
```

These codes produce:

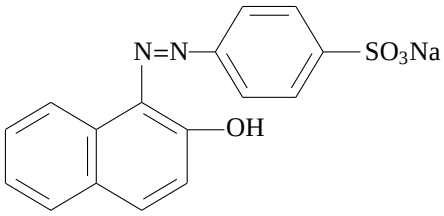


The last example is drawn by two `\sixheteroh` commands declared in a nested fashion. □

Example 7.7. A moiety generated by a (yl)-function can be declared in the `\ryl` command to insert a linking divalent unit, e.g., -N=N- (azo group). The following diagram shows an example for drawing an azo dye of 2-naphthol.

```
\begin{XyMcompd}(1500,750)(300,250){}{}
\naphthalenev{1==\ryl(8==N=N){4==\benzeneh{1==(yl);4==SO$_{3}$Na}};2Sa==OH}
\end{XyMcompd}
```

This code produces:

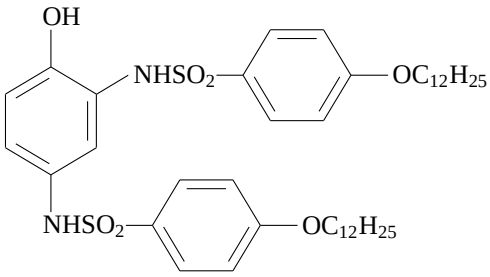


□

Example 7.8. A scavenger for color photography reduces an excess of oxidized color developer. The following structural formula represents such a scavenger incorporated in a multilayer structure of a color photographic film [1, page 19]. The structural formula is drawn by the substitution technique, where a (yl) function and the `\ryl` command are used to draw each of the sulfonamido substituents.

```
\begin{XyMcompd}(1650,1000)(300,-100){}{}
\benzenev{1==OH;%
2==\ryl(4==NHSO$_{2}$){4==\benzeneh{1==(yl);4==OC$_{12}$H$_{25}$}};%
4==\ryl(0==NHSO$_{2}$){4==\benzeneh{1==(yl);4==OC$_{12}$H$_{25}$}}}
\end{XyMcompd}
```

This code produces:

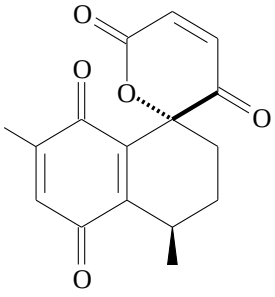


□

7.3.2 As Parent Structures for Ring Fusion

Structures which are drawn by the XyMTEX commands described in this chapter are able to participate in ring fusion as parent structures, where attached structures are generated by the XyMTEX commands for ring fusion (cf. Subsection 2.5.2).

Example 7.9. For example, Spirostomin A separated as a defence toxin from *Spirostomum teres* (a kind of ciliate) [2] is drawn by a ring-fusion scheme 6← 6 ← (spiro) 6 as follows:

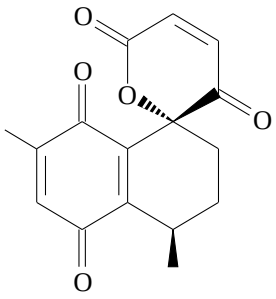


7-3

common name: spirostomin A
XyMTEX command:

```
\cyclohexanev[be%
{b\sixfusev{1s==%
\sixheterov({cB}{dA})[a]{5==O}{4==(yl);3D==O;6D==O}%
}{4B==\null}{E}}%
]{1D==O;4D==O;6==\null}
```

The configurations of the skeletal bonds in the spiro component are drawn by setting `({cB}{dA})` in the ⟨skelbdlist⟩ of `\sixheterov`, where the bonds are expressed by a bold line and a bold dashed line. These bonds can be changed by using `\WedgeAsSubst` and `\HashWedgeAsSubst`, as shown below:



7-4

common name: spirostomin A
XƎMTEX command:

```
\cyclohexanev[be%
{b\sixfusev{1s==\sixheterov[a]{5==O;%
4s==\WedgeAsSubst(0,0)(3,2){165};%
4s==\HashWedgeAsSubst(0,0)(-3,2){120}%
}{4==(yl);3D==O;6D==O}[cd]%
}{4B==\null}{E}}%
]{1D==O;4D==O;6==\null}
```

□

References

[1] S. Fujita, “Organic Chemistry of Photography,” Springer-Verlag, Berlin-Heidelberg (2004).

[2] Y. Uruma, Y. Sera, Y. Usuki, and H. Iio, *Yuki Gosei Kagaku Kyokai-Shi*, **71**, 207–215 (2013).

Chapter 8

Five- or Lower-Membered Carbocycles. Commands for Specific Use

This chapter is devoted to introduce commands for drawing 5- to 3-membered rings as embodiments of XyMTEX commands `ComSpec` for specific use (cf. Section 3.1 for the syntax). These commands are short-cut commands of `\fiveheterov` etc. (the embodiments of `ComGen` for general use).

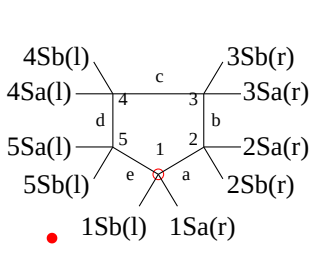
8.1 Drawing Five-Membered Carbocycles

8.1.1 Vertical Forms

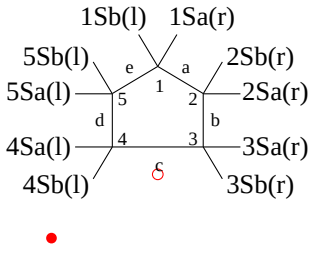
The XyMTEX command `\cyclopentanev` and the corresponding inverse macro are used to draw five-membered carbocyclic compounds of vertical type. They are defined in the lowcycle package of the XyMTEX system. The formats of these commands are as follows:

```
\cyclopentanev[⟨bondlist⟩]{⟨subslist⟩}
\cyclopentanevi[⟨bondlist⟩]{⟨subslist⟩}
```

The following diagrams show the numbering of the commands for designating substitution positions (1–5) and bond descriptors (a–e):



○: (400,240)
●: (0,0)



○: (400,240)
●: (0,0)

The optional argument ⟨bondlist⟩ shows bonds to be doubled as shown in Table 8.1. The default structure is a fully saturated form.

The argument ⟨subslist⟩ is used to specify each substituent with a locant number and a bond modifier shown in Table 3.2, in which *n* is an Arabic numeral between 1 and 5.

Examples for `\cyclopentanev` and `\cyclopentanevi`:

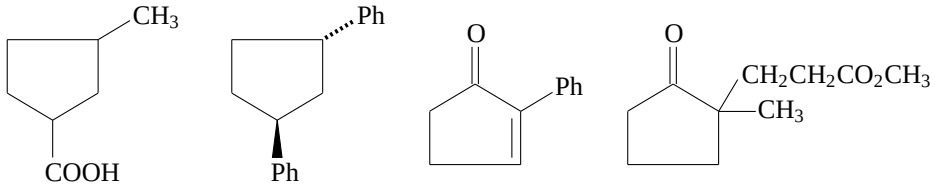
```
\begin{XyMcompd}(600,650)(250,30){}{}
\cyclopentanev{1==COOH;3==CH$_{3}$}
\end{XyMcompd}
```

Table 8.1. Argument ⟨bondlist⟩ for Commands \cyclopentanev, \cyclopentaneh, and Their Inverse Macros

Character	Printed structure
none	mother nucleus
a	1,2-double bond
b	2,3-double bond
c	4,3-double bond
d	4,5-double bond
e	5,1-double bond
A	aromatic circle
{*n*+}	plus at the *n*-nitrogen atom (*n* = 1 to 5)
{0+}	plus (or minus) at the center

```
\quad
\begin{XyMcompd}(500,650)(250,30){}{}
\cyclopentanev{1B==Ph;3A==Ph}
\end{XyMcompd}
\quad
\begin{XyMcompd}(500,550)(250,350){}{}
\cyclopentanevi[b]{1D==O;2==Ph}
\end{XyMcompd}
\quad
\begin{XyMcompd}(1050,550)(250,350){}{}
\cyclopentanevi{1D==O;2Sa==CH$_{3}$;2Sb==CH$_{2}$CH$_{2}$CO$_{2}$CH$_{3}$}
\end{XyMcompd}
```

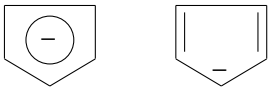
These statements produce the following structures:



The command is capable of typesetting a delocalized and a localized form of cyclopentadienyl anion as follows:

```
\begin{XyMcompd}(300,350)(250,250){}{}
\cyclopentanev[A{0{$-$}}]{}
\end{XyMcompd}
\qquad
\begin{XyMcompd}(300,350)(250,250){}{}
\cyclopentanev[bd{1{\lower1.2ex\hbox{$-$}}}]{}
\end{XyMcompd}
```

where the charges are designated in terms of the ⟨bondlist⟩ (Table 8.1). These statements produce

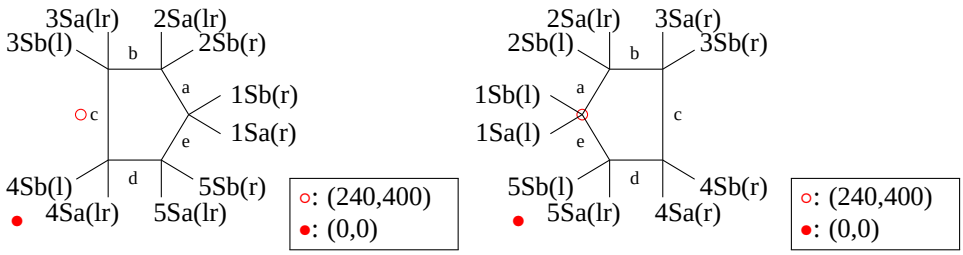


8.1.2 Horizontal Forms

The macros \cyclopentaneh and \cyclopentanehi are used to draw five-membered carbocyclic compounds of horizontal type. They are defined in the lowcycle package of the XYMTEX system. Their formats are as follows:

```
\cyclopentaneh[⟨bondlist⟩]{⟨subslist⟩}
\cyclopentanehi[⟨bondlist⟩]{⟨subslist⟩}
```

The following diagrams show locant numbers for designating substitution positions as well as bond descriptors for showing double bonds:

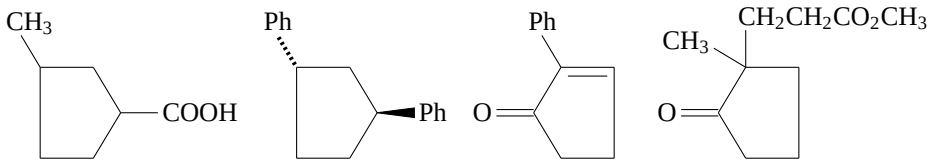


in which the same macro is used to typeset both saturated and unsaturated derivatives. For ⟨bondlist⟩, see Table 8.1.

Examples for `\cyclopentaneh` and `\cyclopentanehi`:

```
\begin{XyMcompd}(750,550)(250,250){}{}
\cyclopentaneh{1==COOH;3==CH$_{3}$}
\end{XyMcompd}
\quad
\begin{XyMcompd}(550,550)(280,250){}{}
\cyclopentaneh{1B==Ph;3A==Ph}
\end{XyMcompd}
\quad
\begin{XyMcompd}(450,550)(80,250){}{}
\cyclopentanehi[b]{1D==O;2==Ph}
\end{XyMcompd}
\quad
\begin{XyMcompd}(850,550)(80,250){}{}
\cyclopentanehi{1D==O;2Sb==CH$_{3}$;2Sa==CH$_{2}$CH$_{2}$CO$_{2}$CH$_{3}$}
\end{XyMcompd}
```

These statements produce the following structures:

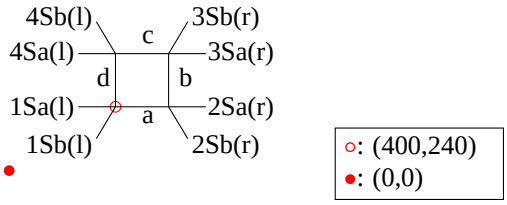


8.2 Drawing Four-Membered Carbocycles

The macro `\cyclobutane` is a command for drawing four-membered carbocycles by using the following format (lowcycle.sty).

```
\cyclobutane[⟨bondlist⟩]{⟨subslist⟩}
```

Locant numbers (1–4) and bond descriptors (a–d) are shown in the following diagram:



The handedness for each oriented position is shown with a character set in parentheses. The optional argument ⟨bondlist⟩ specifies double bonds as shown in Table 8.2.

Table 8.2. Argument ⟨bondlist⟩ for Command `\cyclobutane`

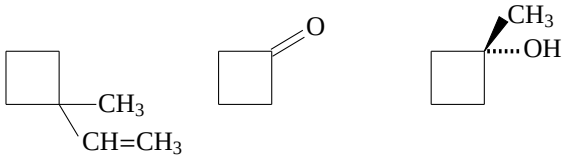
Character	Printed structure	Character	Printed structure
none	mother skeleton (fully saturated)		
a	1,2-double bond	b	2,3-double bond
c	3,4-double bond	d	4,1-double bond
{*n*+}	plus at the *n*-nitrogen atom (*n* = 1 to 4)		

The argument ⟨subslist⟩ is filled in to specify each substituent with a locant number and a bond modifier shown in Table 3.2, in which *n* is an Arabic numeral between 1 and 4.

Examples for `\cyclobutane`:

```
\cyclobutane{2Sa==CH$_{3}$;2Sb==CH=CH$_{3}$}
\cyclobutane{3D==O}
\cyclobutane{3SA==OH;3SB==CH$_{3}$}
```

produce the following structures:



8.3 Drawing Three-Membered Carbocycles

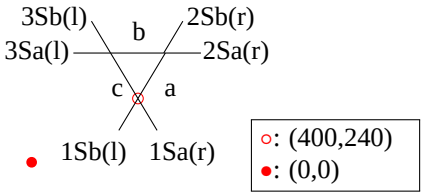
8.3.1 Vertical Forms

The X$\mathfrak{M}$TEX command `\cyclopropanev` (the same as `\cyclopropane`) and its inverse counterpart `\cyclopropanevi` (the same as `\cyclopropanei`), which are defined in lowcyclo.sty for drawing three-membered carbocycles, have the following formats.

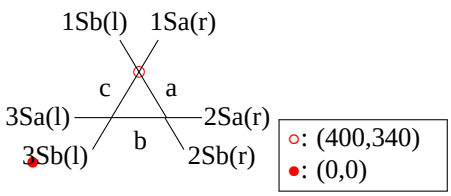
```
\cyclopropanev[⟨bondlist⟩]{⟨subslist⟩}
\cyclopropanevi[⟨bondlist⟩]{⟨subslist⟩}
```

Thus, the locant numbering (1–3) and the bond description (a–c) are common as shown in the following diagrams:

(a) Output of `\cyclopropanev`



(b) Output of `\cyclopropanevi`



The handedness for each oriented position is shown with a character set in parentheses. The optional argument ⟨bondlist⟩ is written down to specify double bonds as shown in Table 8.3.

Table 8.3. Argument ⟨bondlist⟩ for Commands `\cyclopropanev`, `\cyclopropanevi`, `\cyclopropaneh`, and `\cyclopropanehi`

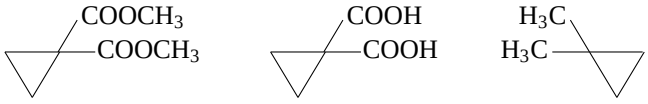
Character	Printed structure
none	saturated
a	1,2-double bond
b	2,3-double bond
c	3,1-double bond
A	aromatic circle
{*n*+}	plus at the n-hetero atom (n = 1 to 3)
	n = 4 – outer plus at 1 position
	n = 5 – outer plus at 2 position
	n = 6 – outer plus at 3 position
{0+}	plus at the center of a cyclopropane ring

The argument ⟨subslist⟩ is entered to specify each substituent with a locant number and a bond modifier shown in Table 3.2, in which *n* is an Arabic numeral between 1 and 3.

Examples for `\cyclopropanev`:

```
\cyclopropanev{2Sa==COOCH$_{3}$;2Sb==COOCH$_{3}$}\qquad
\cyclopropanev{2Sa==COOH;2Sb==COOH}\qquad\qquad
\cyclopropanev{3Sa==H$_{3}$C;3Sb==H$_{3}$C}
```

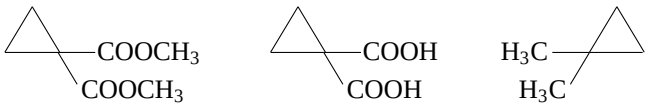
produce the following structures:



Examples for `\cyclopropanevi`:

```
\cyclopropanevi{2Sa==COOCH$_{3}$;2Sb==COOCH$_{3}$}\qquad
\cyclopropanevi{2Sa==COOH;2Sb==COOH}\qquad\qquad
\cyclopropanevi{3Sa==H$_{3}$C;3Sb==H$_{3}$C}
```

produce the following structures:

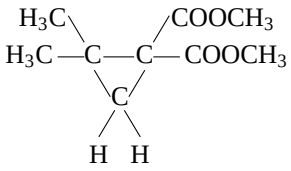


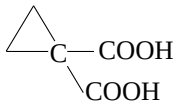
These macros are based on the macros `\threeheterov` and `\threeheterovi` in which the ⟨atomlist⟩ of the latter commands are set beforehand. In order to draw a carbon atom on a cyclopropane ring, you can use the command `\threeheterov` (or `\threeheterovi`) instead of `\cyclopropanev` (or `\cyclopropanevi`).

Examples for `\threeheterov` and `\threeheterovi`:

```
\threeheterov{1==C;2==C;3==C}%
 {1Sa==H;1Sb==H;2Sa==COOCH$_{3}$;2Sb==COOCH$_{3}$;%
  3Sa==H$_{3}$C;3Sb==H$_{3}$C}\qquad\qquad\qquad
\threeheterovi{2==C}{2Sa==COOH;2Sb==COOH}
```

produce the following structures:





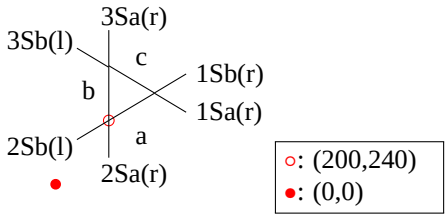
8.3.2 Horizontal Forms

The XeLaTeX command `\cyclopropaneh` and its inverse counterpart `\cyclopropanehi` for drawing three-membered carbocycles of horizontal type have the following formats (lowcycle.sty).

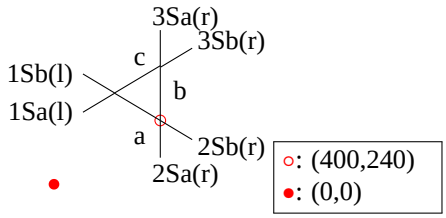
```
\cyclopropaneh[⟨bondlist⟩]{⟨subslist⟩}
\cyclopropanehi[⟨bondlist⟩]{⟨subslist⟩}
```

The locant numbering (1–3) and the bond description (a–c) are common as shown in the following diagrams:

(a) Output of `\cyclopropaneh`



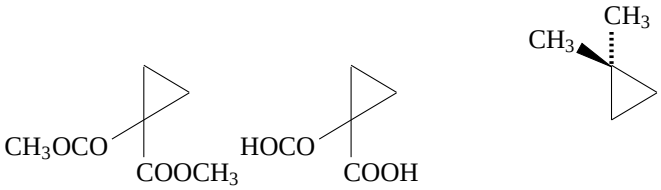
(b) Output of `\cyclopropanehi`



The handedness for each oriented position is shown with a character set in parentheses. The optional argument ⟨bondlist⟩ is written down to specify double bonds as shown in Table 8.3. The argument ⟨subslist⟩ is entered to specify each substituent with a locant number and a bond modifier shown in Table 3.2, in which *n* is an Arabic numeral between 1 and 3.
Examples for `\cyclopropaneh`:

```
\cyclopropaneh{2Sa==COOCH$_{3}$;2Sb==CH$_{3}$OCO}\qquad
\cyclopropaneh{2Sa==COOH;2Sb==HOCO}\qquad\qquad
\cyclopropaneh{3SA==CH$_{3}$;3SB==CH$_{3}$}
```

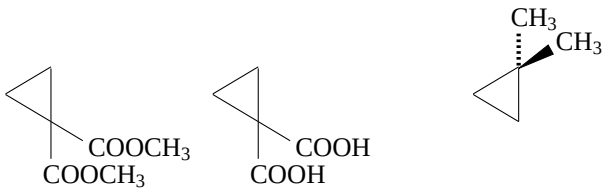
produce the following structures:



Examples for `\cyclopropanehi`:

```
\cyclopropanehi{2Sa==COOCH$_{3}$;2Sb==COOCH$_{3}$}\qquad
\cyclopropanehi{2Sa==COOH;2Sb==COOH}\qquad\qquad
\cyclopropanehi{3SA==CH$_{3}$;3SB==CH$_{3}$}
```

produce the following structures:



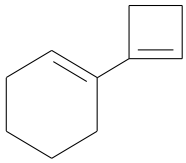
8.4 Illustrative Examples of Drawing Five- or Smaller-Membered Carbocycles

8.4.1 Generation of Substituents by (yl)-Functions

The XMTEX commands described in this chapter are able to generate substituents by using the (yl)-function technique. The resulting substituents can participate in substitution due to the substitution technique.

Example 8.1. For example, a conjugate diene **8-1** which extends between two rings [1, page 605] is drawn by the substitution technique, where a (yl)-function is declared in the command `\cyclobutane` to give a cyclobut-1-enyl group. This substituent is declared in the ⟨subslist⟩ of the outer command `\cyclohexanev` to give 1-(cyclobut-1-enyl)cyclohexene.

```
\cyclohexanev[a]{2==\cyclobutane[a]{1==(yl)}}
```

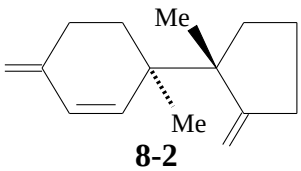


8-1

□

Example 8.2. The structure **8-2** of a conjugate diene [2, page 395] is drawn by the replacement technique, where the command `\BiFunc` is used to draw a parent structure and the two commands `\cyclohexaneh` and `\cyclopentanehi` are used after declaring (yl)-functions.

```
\BiFunc(1,0){250}
{\cyclohexaneh[e]{4==(yl);1D==\null;4GA==Me}}
{\cyclopentanehi{1==(yl);5D==\null;1GB==Me}}
```

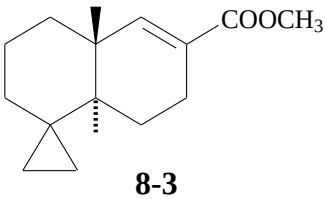


8-2

□

Example 8.3. The following structure **8-3** of a spiro compound is drawn by the replacement technique, where the command `\decaheterov` is used to give a parent structure and the command `\cyclopropanevi` is used to give an attached component by declaring a (yl)-function.

```
\decaheterov[a]{5s==\cyclopropanevi{1==(yl)}}%
{{10}B==\null;9A==\null;2==COOCH$_{3}$}
```

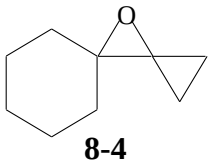


8-3

□

Example 8.4. The structure **8-4** of a double spiro compound [2, page674] is drawn by the replacement technique, where the command `\threeheterovi` is used to draw a central parent structure and the two commands `\cyclopropanev` and `\cyclohexanev` are used after declaring (yl)-functions to draw the right-hand and left-hand attached components.

```
\threeheterovi{1==O;%
2s==\cyclopropanev{3==(yl)};%
3s==\cyclohexanev{2==(yl)}%
}{}
```

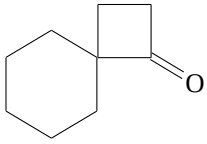


8-4

□

Example 8.5. The structure **8-5** of a spiro compound having a cyclobutanone moiety [2, page674] is drawn by the replacement technique, where the command `\sixheterov` is used to draw a parent structure and the command `\cyclobutane` is used after declaring a (yl)-function to draw the attached four-membered component.

```
\sixheterov{2s==\cyclobutane{1==(yl);2D==O}}{}
```

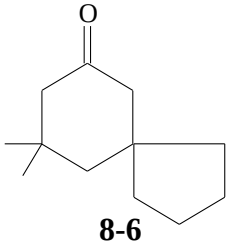


8-5

□

Example 8.6. The structure **8-6** of a spiro ketone is drawn by the replacement technique, where the command `\sixheterov` is used to draw a parent structure and the command `\cyclopentanev` is used after declaring a (yl)-function to give the attached five-membered component.

```
\sixheterov{3s==\cyclopentanev{4==(yl)}}
{1D==O;5Sa==\null;5Sb==\null}
```



8-6

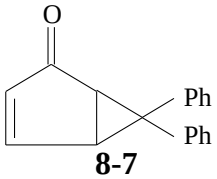
□

8.4.2 As Parent Structures for Ring Fusion

The XyMTEX commands described in this chapter are able to serve as parent structures for ring fusion in the addition technique.

Example 8.7. A photorearrangement of 4,4-diphenylcyclohexa-2,5-dienone gives 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one [1, page 1037], the structure **8-7** of which is drawn by the addition technique for ring fusion, where the command `\cyclopropaneh` is used to draw a parent structure and the command `\fivefusevi` is used to draw an attached component.

```
\cyclopropaneh[%
{b\fivefusevi[d]{}{1D==O}{B}}%
]{1Sa==Ph;1Sb==Ph}
```

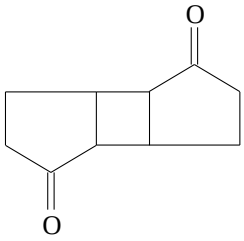


8-7

□

Example 8.8. The product **8-8** of photodimerization [1, page 1035] is drawn by the addition technique for ring fusion, where the command `\cyclobutane` is used to draw a parent structure and the two command `\fivefusevi` is used to draw two attached components.

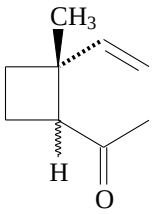
```
\cyclobutane[%
{b\fivefusevi{}{1D==O}{d}}%
{d\fivefusev{}{1D==O}{B}}%
]{}
```



8-8 □

Example 8.9. The structure **8-9** of a product of photocycloaddition [1, page 1034] is drawn by the addition technique for ring fusion, where the command `\cyclobutane` is used to draw a parent structure and the command `\sixfusev` is used to draw an attached component. As for the command `\sixfusev`, the skeletal bond of the attached component at the locant alphabet 'b' is deleted by declaring the optional argument `[b]` in its ⟨delbdlist⟩ and the skeletal bond 'f' is changed into a dashed line by declaring the optional argument `({fA})` in in its ⟨skelbdlist⟩.

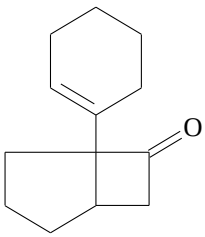
```
\cyclobutane[%
{b\sixfusev({fA})[a]{}{6GB==CH$_{3}$;5FU==H;4D==O}{e}[b]}
]{}
```



8-9 □

Example 8.10. The structure **8-10** of a 5-4 ring-fusion system [2, page 981] is drawn by the addition technique and the substitution technique. The `\cyclobutane` draws a four-membered ring which serves as a parent structure. The command `\fivefusev` is used to draw a five-membered attached component by the replacement technique, where the inner substitution technique is applied to draw a cyclohex-1-enyl group by declaring a (yl)-function in the command `\cyclohexanev`.

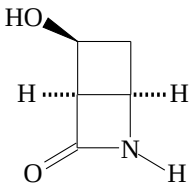
```
\cyclobutane[%
{d\fivefusev{}{3F==\cyclohexanev[d]{4==(yl)}}{B}}%
]{3D==O}
```



8-10 □

Example 8.11. The structure **8-11** of an interesting and useful β-lactam [2, page 994] is drawn by the addition technique for ring fusion, where the command `\cyclobutane` is used to draw a parent structure and the command `\fourfuse` is used to draw an attached component.

```
\cyclobutane[%
{a\fourfuse{2==N}{1D==O;2==H}{C}}%
]{1SA==H;2SA==H;4B==HO}
```



8-11

References

[1] S. H. Pine, “Organic Chemistry,” 5th ed., McGraw-Hill, New York (1987).

[2] M. B. Smith, “Organic Synthesis,” 2nd ed., McGraw-Hill, New York (2002).

Chapter 9

Carbocycles with Fused Six-to-Six-Membered Rings. Commands for Specific Use

This chapter is devoted to introduce commands for drawing naphthalene derivatives and related compounds. These commands are short-cut commands of `\decaheterov` etc. for general use (cf. Section 3.1 for the syntax).

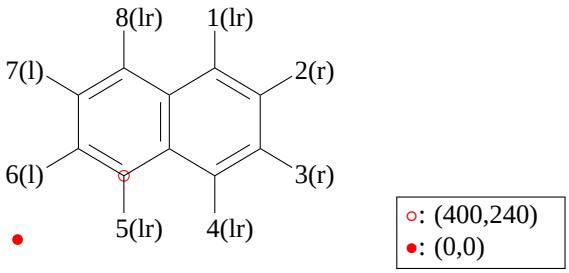
9.1 Drawing Naphthalene Derivatives

9.1.1 Vertical Forms of Naphthalene Derivatives

The macro `\naphdrv` (or synonymously `\naphthalenev`) is used to draw naphthalene derivatives of vertical type (carom.sty) as well as various naphthoquinone derivatives. The format of this command is as follows:

```
\naphdrv[⟨bondlist⟩]{⟨subslist⟩}
\naphthlenev[⟨bondlist⟩]{⟨subslist⟩}
```

Locant numbers for designating substitution positions are represented by the following diagram:



The handedness for each oriented or double-sided position is shown with a character set in parentheses. The optional argument ⟨bondlist⟩ is used to specify a bond pattern as shown in Table 9.1.[a]

Several endcyclic bond patterns typeset by the ⟨bondlist⟩ argument of the `\naphdrv` (or `naphthalenev`) command (Table 9.1) are shown in Figs. 9.1 and 9.2.

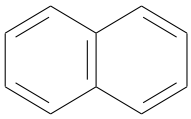
The argument ⟨subslist⟩ is used to specify each substituent with a locant number and a bond modifier shown in Table 3.2, in which *n* is an Arabic numeral between 1 and 8.

Examples for `\naphdrv`:

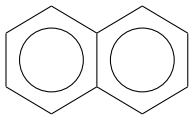
[a] When the optional argument ⟨bondlist⟩ specifies a bond pattern (not locant alphabets), the mechanism of ring fusion is not permitted.

Table 9.1. Argument ⟨bondlist⟩ for commands \naphdrv (\naphthalenev) and \naphdrh (\naphthaleneh)

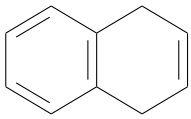
Character	Printed structure
none	naphthalene (mancude-ring system)
A	aromatic circle
p or pa	1,4-quinone (A) left aromatic, right quinone
pb	1,4-quinone (B) right aromatic, left quinone
o or oa	*o*-quinone (A) (Oxygen atoms at 1,2-positions)
ob	*o*-quinone (B) (Oxygen atoms at 2,3-positions)
oc	*o*-quinone (C) (Oxygen atoms at 3,4-positions)
od	*o*-quinone (D) (Oxygen atoms at 4,5-positions)
oe	*o*-quinone (E) (Oxygen atoms at 5,6-positions)
of	*o*-quinone (F) (Oxygen atoms at 1,6-positions)
q or qa	2,6-quinone (A)
qb	2,6-quinone (B) (actually 3,7-positions)
qc	1,5-quinone (C)
qd	1,5-quinone (D) (actually 4,8-positions)
qe	1,7-quinone (E)
qf	1,7-quinone (F) (actually 2,8-positions)
qg	1,7-quinone (G) (actually 4,6-positions)
qh	1,7-quinone (H) (actually 3,5-positions)
P or Pa	: 1,4,5,8-quinone (A)
Pb	1,2,5,8-quinone (B)
Q	1,2,3,4-quinone
O or Oa	1,2,5,6-quinone (A)
Ob	1,2,7,8-quinone (B)
Oc	1,2,3,5-quinone (C)
Od	1,2,3,7-quinone (D)



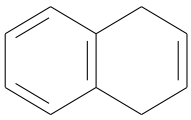
\naphdrv{}
\naphthalenev{}



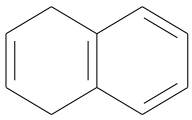
\naphdrv[A]{}
\naphthalenev[A]{}



\naphdrv[p]{}
\naphthalenev[p]{}



\naphdrv[pa]{}
\naphthalenev[pa]{}

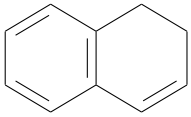


\naphdrv[pb]{}
\naphthalenev[pb]{}

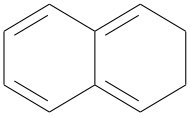
Figure 9.1. Endocyclic bond patterns by the ⟨bondlist⟩ argument of the command \naphdrv (\naphthalenev).

```
\naphdrv{1==CH$_{2}$CH=CH$_{2}$;2==OH} \qquad
\naphdrv{6==H$_{3}$C;2==COCH$_{2}$CH$_{2}$COOH} \hskip1.5cm
\naphdrv[o]{1Sb==Cl;1Sa==Cl;2D==O} \\
\naphthalenev{1==\ChemForm{CH_2CH\mbox{=}CH_2};2==OH} \qquad
\naphthalenev{6==\ChemForm{H_3C};2==\ChemForm{COCH_2CH_2COOH}} \hskip1.5cm
\naphthalenev[o]{1Sb==Cl;1Sa==Cl;2D==O}
```

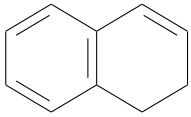
These commands produce:



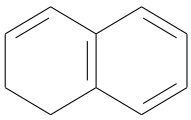
`\naphdrv[oa]{}`
`\naphthalenev[oa]{}`



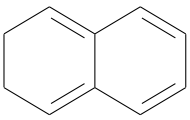
`\naphdrv[ob]{}`
`\naphthalenev[ob]{}`



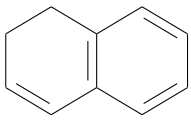
`\naphdrv[oc]{}`
`\naphthalenev[oc]{}`



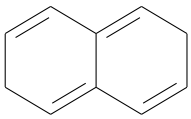
`\naphdrv[od]{}`
`\naphthalenev[od]{}`



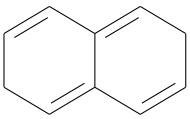
`\naphdrv[oe]{}`
`\naphthalenev[oe]{}`



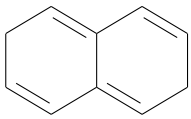
`\naphdrv[of]{}`
`\naphthalenev[of]{}`



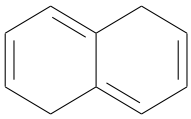
`\naphdrv[q]{}`
`\naphthalenev[q]{}`



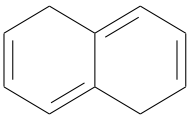
`\naphdrv[qa]{}`
`\naphthalenev[qa]{}`



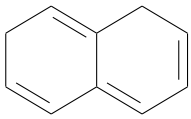
`\naphdrv[qb]{}`
`\naphthalenev[qb]{}`



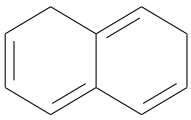
`\naphdrv[qc]{}`
`\naphthalenev[qc]{}`



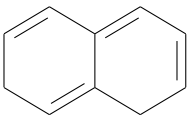
`\naphdrv[qd]{}`
`\naphthalenev[qd]{}`



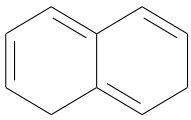
`\naphdrv[qe]{}`
`\naphthalenev[qe]{}`



`\naphdrv[qf]{}`
`\naphthalenev[qf]{}`

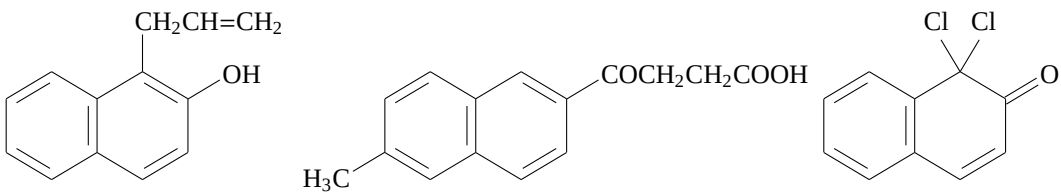


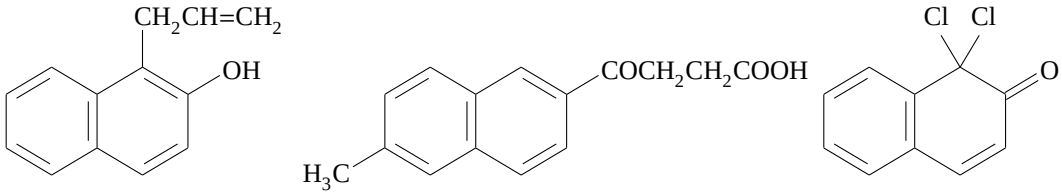
`\naphdrv[qg]{}`
`\naphthalenev[qg]{}`



`\naphdrv[qh]{}`
`\naphthalenev[qh]{}`

Figure 9.2. Endocyclic bond patterns by the ⟨bondlist⟩ argument of the command `\naphdrv` (`\naphthalenev`). (continued)





The top three outputs are based on usual TEX/LATEX-modes of giving suffixes, while the bottom three outputs are based on the command `\ChemForm` of the XETEX system. The input `\mbox{=}` of `\ChemForm{CH_2CH\mbox{=}CH_2}` prevents mathematical spaces before and after the equality symbol. Compare this input with `CH$_{2}$CH=CH$_{2}$`.

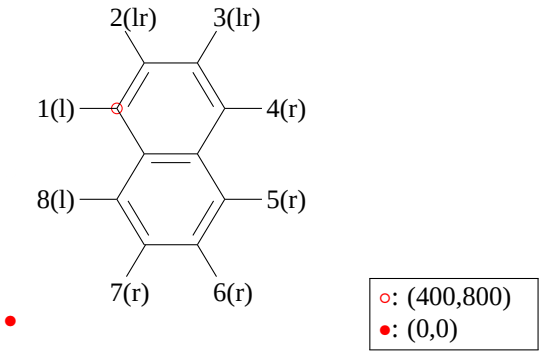
9.1.2 Horizontal Forms of Naphthalene Derivatives

The macro `\naphdrh` (or synonymously `\naphthaleneh`) is used to draw naphthalene derivatives of horizontal type (carom.sty) as well as various naphthoquinone derivatives. The format of this command is as follows:

```
\naphdrh[⟨bondlist⟩]{⟨subslist⟩}
\naphthleneh[⟨bondlist⟩]{⟨subslist⟩}
```

The format of the argument ⟨bondlist⟩ is the same as that of `\naphdrv` (Tables 9.1).

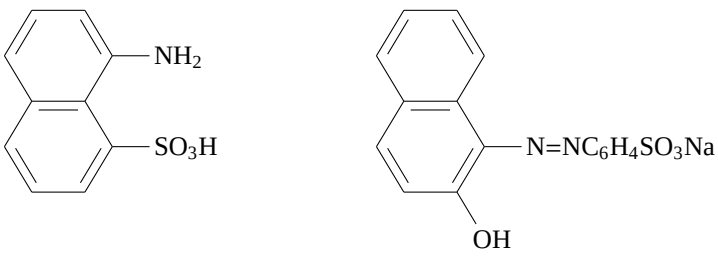
The format of the argument ⟨subslist⟩ is the same as collected in Table 3.2, in which *n* is an Arabic numeral between 1 and 8. The locant numbering and the handedness of substitution are designed as follows:



Examples for `\naphdrh`:

```
\naphdrh{4==NH$_{2}$;5==SO$_{3}$H}\qquad
\naphdrh{5==N=NC$_{6}$H$_{4}$SO$_{3}$Na;6==OH}
```

These commands produce:



9.1.3 Diagonal Forms of Naphthalene Derivatives

The XeLaTeX command \naphdrvb (or synonymously \naphthalenevb) is used to draw naphthalene derivatives of diagonal type (carom.sty) as well as various naphthoquinone derivatives, where two six-membered rings are aligned in a right- and downward direction. The format of this command is as follows:

```
\naphdrvb[⟨bondlist⟩]{⟨subslist⟩}
\naphthlenevb[⟨bondlist⟩]{⟨subslist⟩}
```

On the other hand, the XeLaTeX command \naphdrvt (or synonymously \naphthalenevt) is used to draw naphthalene derivatives of another diagonal type (carom.sty) as well as various naphthoquinone derivatives, where two six-membered rings are aligned in a right- and upward direction. The format of this command is as follows:

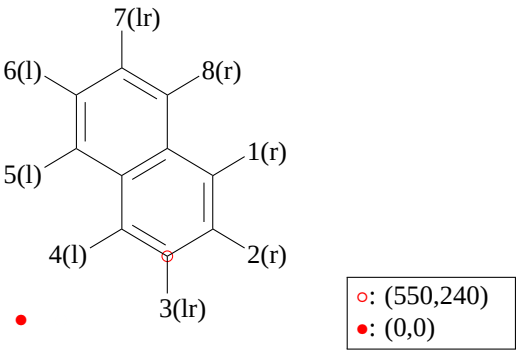
```
\naphdrvt[⟨bondlist⟩]{⟨subslist⟩}
\naphthlenevt[⟨bondlist⟩]{⟨subslist⟩}
```

The format of the argument ⟨bondlist⟩ in each command is the same as that of \naphdrv (Tables 9.1).

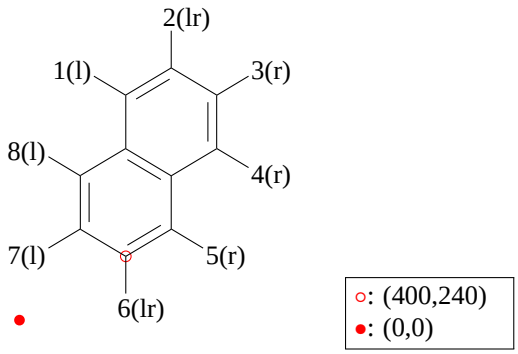
The format of the argument ⟨subslist⟩ in each command is the same as collected in Table 3.2, in which *n* is an Arabic numeral between 1 and 8.

The locant numbering and the handedness of substitution are designed as follows:

(a) Output of \naphdrvb (\naphthalenevb)



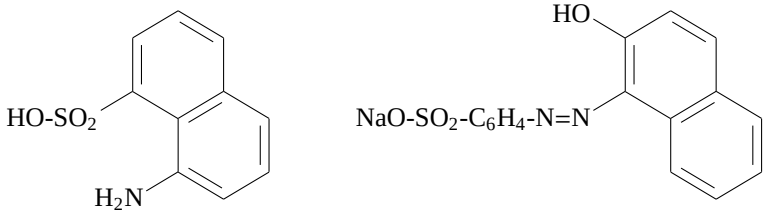
(b) Output of \naphdrvt (\naphthalenevt)



Examples for \naphdrvb:

```
\naphdrvb{4==H$_{2}$N;5==HO-SO$_{2}$}\hskip3cm
\naphdrvb{5==NaO-SO$_{2}$-C$_{6}$H$_{4}$-N=N;6==HO}
```

These commands produce:

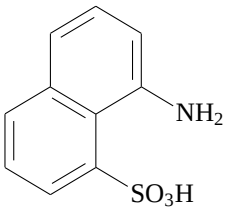


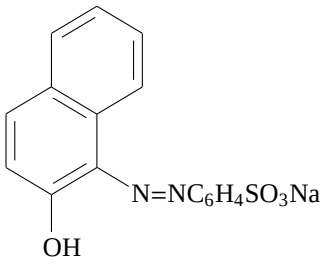
Examples for \naphdrvt:

```
\naphdrvt{4==NH$_{2}$;5==SO$_{3}$H}\qquad
```

```
\naphdrvt{5==N=NC$_{6}$H$_{4}$SO$_{3}$Na;6==OH}
```

These commands produce:





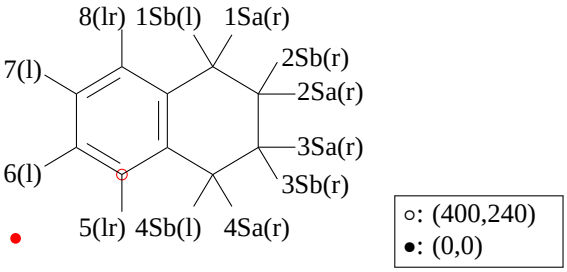
9.2 Drawing Tetraline Derivatives

9.2.1 Vertical Forms of Tetraline Derivatives

The macro `\tetralinev` is used to draw tetraline derivatives of vertical type (carom.sty) as well as various naphthoquinone derivatives. The format of this command is as follows:

```
\tetralinev[⟨bondlist⟩]{⟨subslist⟩}
```

Locant numbers for designating substitution positions are represented by the following diagram:



The handedness for each oriented or double-sided position is shown with a character set in parentheses. The optional argument ⟨bondlist⟩ is used to specify a bond pattern as shown in Table 9.2.[b] The locant alphabets `a`–`k` are not recommended, so that `decalinev` etc. should be used to specify such locant alphabets. also permissible.

Table 9.2. Argument ⟨bondlist⟩ for commands `\tetralinev` and `\tetralineh`

Character	Printed structure
none	tetraline
A	aromatic circle
e or ea	1,2-double bond
eb	2,3-double bond
ec	3,4-double bond

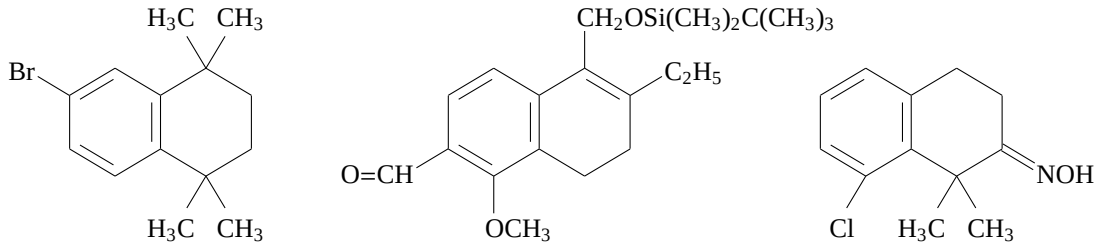
A bond modifier in the argument ⟨subslist⟩ for $n = 1$ to 4 can be one of the bond modifiers shown in Table 3.2, which allows α- or β-orientation. On the other hand a bond modifier in the argument ⟨subslist⟩ for $n = 5$ to 8 should be vacant. If there appears the overcrowding between 1- and 8-substituent or between 4- and 5-substituent, the bond modifier '`5Sb`' or '`8Sb`' is allowed to avoid such overcrowding.

Examples for `\tetralinev`:

[b] When the optional argument ⟨bondlist⟩ specifies a bond pattern (not locant alphabets), the mechanism of ring fusion is not permitted.

```
\tetralinev{1Sb==H$_{3}$C;1Sa==CH$_{3}$;%
4Sb==H$_{3}$C;4Sa==CH$_{3}$;7==Br}\qquad
\tetralinev[ea]{1==CH$_{2}$OSi(CH$_{3}$)$_{2}$C(CH$_{3}$)$_{3}$;
2==C$_{2}$H$_{5}$;5==OCH$_{3}$;6==O=CH}\qquad
\tetralinev{3D==NOH;4Sb==H$_{3}$C;4Sa==CH$_{3}$;5Sb==Cl}
```

These commands produce:

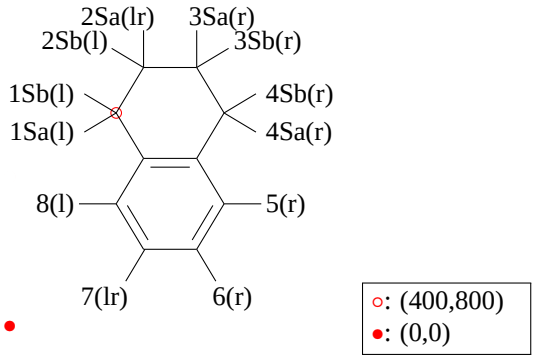


9.2.2 Horizontal Forms of Tetraline Derivatives

The `\tetralineh` is the horizontal counterpart of the command `\tetralinev`:

```
\tetralineh[⟨bondlist⟩]{⟨subslist⟩}
```

Locant numbers for designating substitution positions are represented by the following diagram:

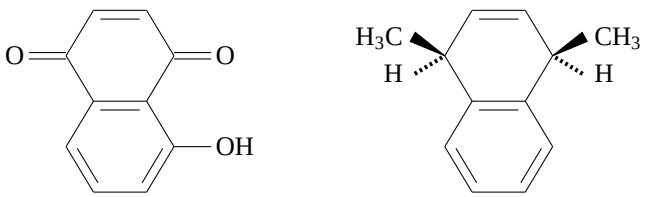


The handedness for each oriented or double-sided position is shown with a character set in parentheses. The optional argument ⟨bondlist⟩ is used to specify a bond pattern as shown in Table 9.2. The argument ⟨subslist⟩ is the same as that of `\tetralinev`.

Examples for `\tetralineh`:

```
\tetralineh[eb]{1D==O;4D==O;5==OH} \qquad
\tetralineh[eb]{1SB==H$_{3}$C;1SA==H;4SB==CH$_{3}$;4SA==H}
```

These commands produce:



9.2.3 Diagonal Forms of Tetraline Derivatives

The XƎMTEX command `\tetralinevb` is used to draw tetraline derivatives of diagonal type (carom.sty), where two six-membered rings are aligned in a right- and downward direction. The format of this command is as follows:

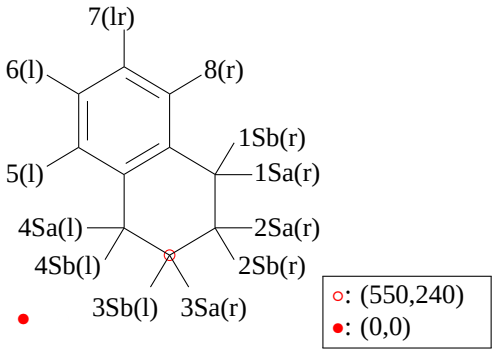
```
\tetralinevb[⟨bondlist⟩]{⟨subslist⟩}
```

On the other hand, the XƎMTEX command `\tetralinevt` is used to draw tetraline derivatives of another diagonal type (carom.sty), where two six-membered rings are aligned in a right- and upward direction. The format of this command is as follows:

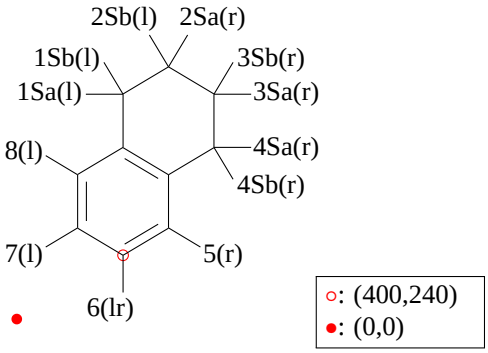
```
\tetralinevt[⟨bondlist⟩]{⟨subslist⟩}
```

Locant numbers for designating substitution positions are represented by the following diagrams:

(a) Output of `\tetralinevb`



(b) Output of `\tetralinevt`

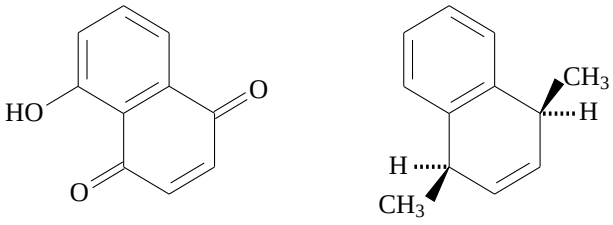


The handedness for each oriented or double-sided position is shown with a character set in parentheses. The optional argument ⟨bondlist⟩ is used to specify a bond pattern as shown in Table 9.2. The argument ⟨subslist⟩ is the same as that of `\tetralinev`.

Examples for `\tetralinevb`:

```
\tetralinevb[eb]{1D==O;4D==O;5==HO} \qquad
\tetralinevb[eb]{1SB==CH$_{3}$;1SA==H;4SB==CH$_{3}$;4SA==H}
```

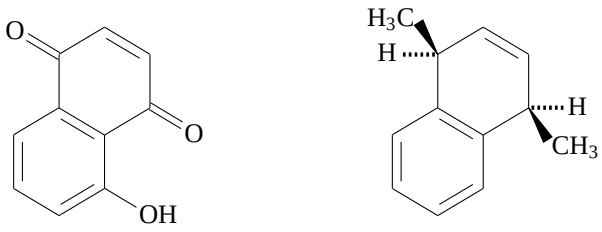
These commands produce:



Examples for `\tetralinevt`:

```
\tetralinevt[eb]{1D==O;4D==O;5==OH} \qquad
\tetralinevt[eb]{1SB==H$_{3}$C;1SA==H;4SB==CH$_{3}$;4SA==H}
```

These commands produce:



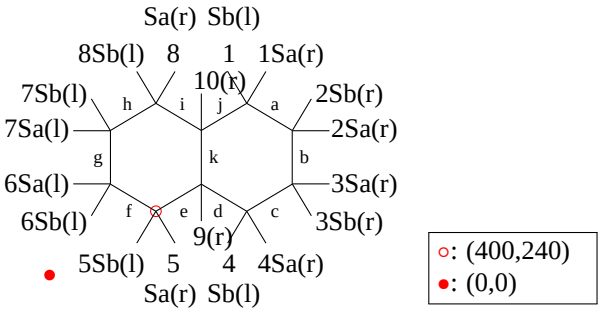
9.3 Drawing Decaline Derivatives

9.3.1 Vertical Forms of Decaline Derivatives

The macro `\decalinev` is used to draw decaline derivatives of vertical type (carom.sty). The format of this command is as follows:

```
\decalinev[⟨bondlist⟩]{⟨subslist⟩}
```

Locant numbers for designating substitution positions and characters for showing bonds to be doubled are represented by the following diagram:



The handedness for each oriented or double-sided position is shown with a character set in parentheses. The option argument ⟨bondlist⟩ is based on the assignment of characters (‘a’–‘k’) to respective bonds as shown in the above diagram. A bond modifier in the argument ⟨subslist⟩ for n = 1–8 can be one of bond modifiers shown in Table 3.2. The substitution at the bridgehead positions is designated as shown in Table 9.3.

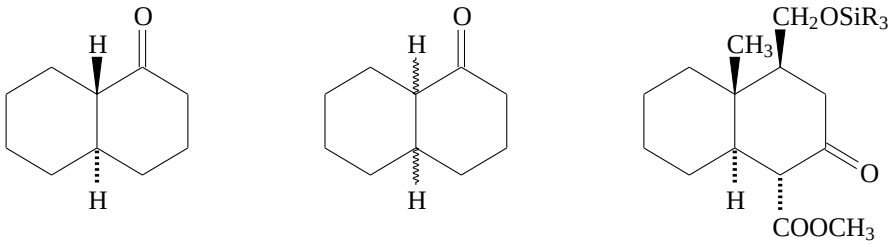
Table 9.3. Bond Modifiers of ⟨subslist⟩ for Bridgehead Positions in `\decalinev` and `\decalineh`

Character	Printed structure
{10}A	alpha single bond at 8a
{10}B	beta single bond at 8a
{10}U	unspecified single bond at 8a
9A	alpha single bond at 4a
9B	beta single bond at 4a
9U	unspecified single bond at 4a

Example for `\decalinev`:

```
\decalinev{1D==O;9A==H;{10}B==H}
\decalinev{1D==O;9U==H;{10}U==H}
\decalinev{1B==CH$_{2}$OSiR$_{3}$;3D==O;4A==COOCH$_{3}$;%
9A==H;{10}B==CH$_{3}$}
```

These commands produce:

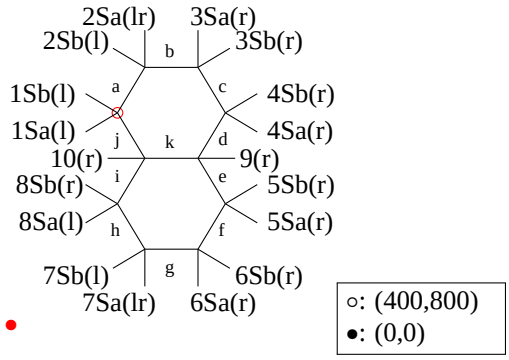


9.3.2 Horizontal Forms of Decaline Derivatives

The macro `\decalineh` (carom.sty) is the horizontal counterpart of `\decalinev`. The format and the assignment of ⟨bondlist⟩ and ⟨subslist⟩ of the former macro are the same as the latter (see Tables 3.2 and 9.3).

```
\decalineh[⟨bondlist⟩]{⟨subslist⟩}
```

Locant numbers for designating substitution positions are represented by the following diagram:

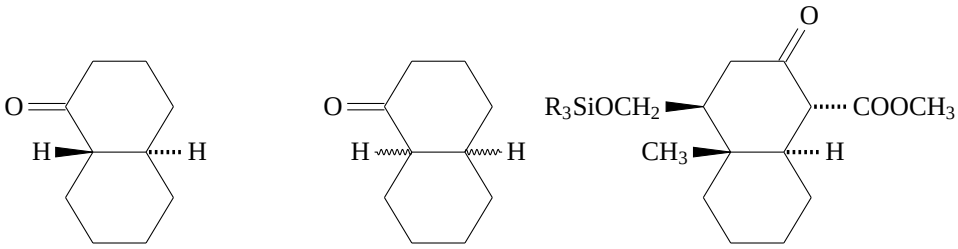


The handedness for each oriented or double-sided position is shown with a character set in parentheses.

Example for `\decalineh`:

```
\decalineh{1D==O;9A==H;{10}B==H}
\decalineh{1D==O;9U==H;{10}U==H}
\decalineh{1B==R$_{3}$SiOCH$_{2}$;3D==O;4A==COOCH$_{3}$;%
9A==H;{10}B==CH$_{3}$}
```

These commands produce:



9.3.3 Diagonal Forms of Decaline Derivatives

The XeLaTeX command `\decalinevb` is used to draw decaline derivatives of diagonal type (carom.sty), where two six-membered rings are aligned in a right- and downward direction. The format of this command is as follows:

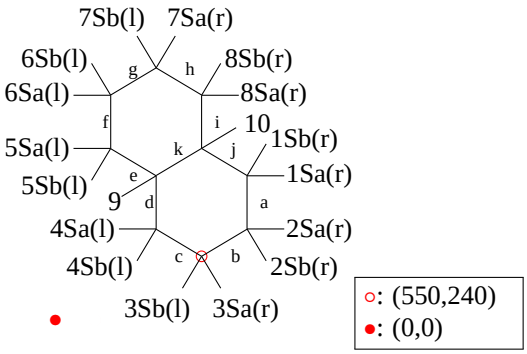
```
\decalinevb[⟨bondlist⟩]{⟨subslist⟩}
```

On the other hand, the XeLaTeX command `\decalinevt` is used to draw decaline derivatives of another diagonal type (carom.sty), where two six-membered rings are aligned in a right- and upward direction. The format of this command is as follows:

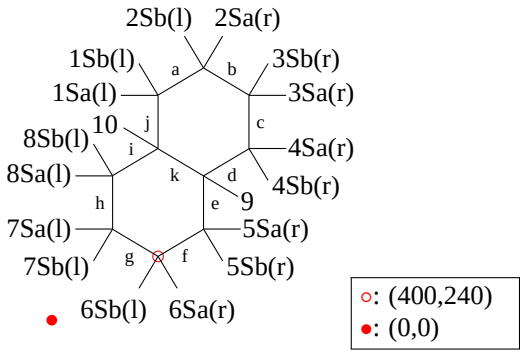
```
\decalinevt[⟨bondlist⟩]{⟨subslist⟩}
```

Locant numbers for designating substitution positions are represented by the following diagrams:

(a) Output of `\decalinevb`



(b) Output of `\decalinevt`

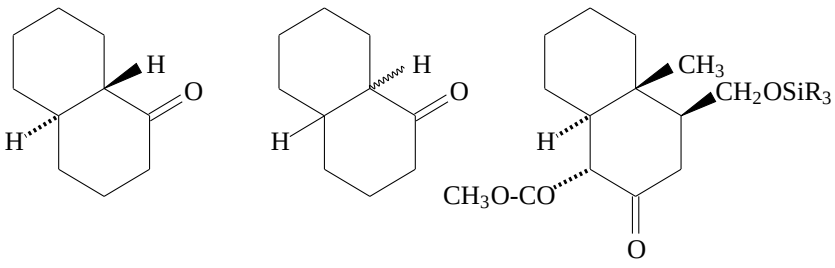


The handedness for each oriented or double-sided position is shown with a character set in parentheses. The assignment of ⟨bondlist⟩ and ⟨subslist⟩ are the same as those of `\decalinev` (see Tables 3.2 and 9.3).

Example for `\decalinevb`:

```
\decalinevb{1D==O;9A==H;{10}B==H}
\decalinevb{1D==O;9U==H;{10}U==H}
\decalinevb{1B==CH$_{2}$OSiR$_{3}$;3D==O;4A==CH$_{3}$O-CO;%
9A==H;{10}B==CH$_{3}$}
```

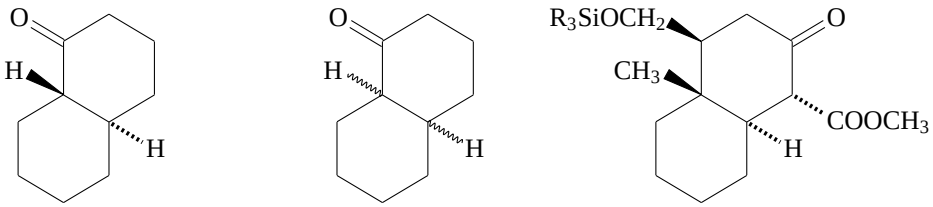
These commands produce:



Example for `\decalinevt`:

```
\decalinevt{1D==O;9A==H;{10}B==H}
\decalinevt{1D==O;9U==H;{10}U==H}
\decalinevt{1B==R$_{3}$SiOCH$_{2}$;3D==O;4A==COOCH$_{3}$;%
9A==H;{10}B==CH$_{3}$}
```

These commands produce:

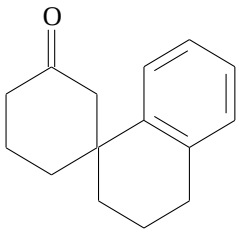


9.4 Illustrative Examples of Drawing 6-6 Fused Derivatives

9.4.1 Substituents Derived by (yl)-Functions

A (yl)-function declared in the ⟨subslist⟩ of `\decalinev` or the related commands generates a substituent which is capable of participating in the substitution technique as well as the replacement technique.

Example 9.1. Spiroannelation via organobis(cuprates) is a versatile method for synthesizing spiroketone derivatives [1]. The list of products contains 2′*H*,3′*H*,4′*H*-spiro[cyclohexan-3-one-1,1′-naphthalene] (**9-1**), the structural formula of which can be drawn by the replacement technique for spiro fusion.



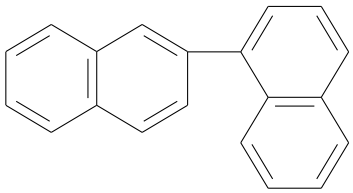
9-1

IUPAC name: 2′*H*,3′*H*,4′*H*-spiro[cyclohexan-3-one-1,1′-naphthalene]
XeLaTeX command:

```
\sixheterov{3s==\decalinevt[acK]{8==(yl)}}{1D==O}
```

□

Example 9.2. The command `\BiFunc(1,0){200}{A}{B}` generates a linking bond of the *x*-length of 200 unit lengths and the slop `(1,0)` (the horizontal direction) between A and B. The linking bond is regarded as a parent structure, the two endpoints of which accommodate the moieties A and B. When A and B is substituents derived by applying (yl)-functions to `naphthalenev` etc., the command `\BiFunc` is capable of supporting the replacement technique. Thereby, the structural formula **9-2** of 1,2′-binaphthalene [2, P-28.2.1] is drawn as follows:



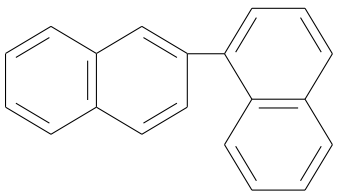
9-2

IUPAC name: 1,2′-binaphthalene (PIN)
XeLaTeX command:

```
\BiFunc(1,0){200}%
{\naphthalenev{2==(yl)}}%
{\naphthaleneh{1==(yl)}}
```

The above construction is consistent with the construction of the IUPAC name, 1,2′-binaphthalene, which is regarded as a PIN (preferred IUPAC name) [2, P-28.2.1].

If we obey another IUPAC name, 1-(naphth-2-yl)naphthalene (not a PIN), we are able to draw another diagram **9-3** by following the substitution technique:



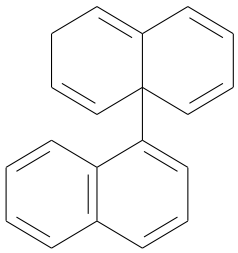
9-3

IUPAC name: 1-(naphth-2-yl)naphthalene
XeLaTeX command:

```
\naphthaleneh{1==\naphthalenev{2==(yl)}}
```

Compare **9-2** with **9-3** under focusing attention on the bond lengths linking two naphthyl groups. □

Example 9.3. The structural formula **9-4** of 1,4′a(2′*H*)-binaphthalene (PIN) [2, P-28.4.2] is drawn by following the replacement technique.

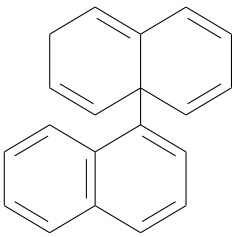


9-4

IUPAC name: 1,4′a(2′*H*)-binaphthalene (PIN)
XeLaTeX command:

```
\BiFunc(0,1){200}%
{\naphthalenev{1==(yl)}}%
{\decalinev[acfi]{9==(yl)}}
```

If we obey another IUPAC name, 2*H*-4a-(naphth-1-yl)naphthalene (not a PIN), we are able to draw another diagram **9-5** by following the substitution technique:



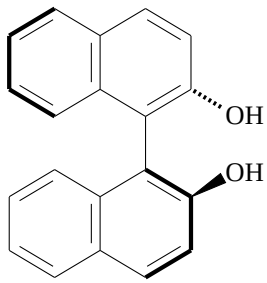
9-5

IUPAC name: 2*H*-4a-(naphth-1-yl)naphthalene
XeLaTeX command:

```
\decalinev[acfi]{9==\naphthalenev{1==(yl)}}
```

Compare **9-4** with **9-5** under focusing attention on the bond lengths linking two naphthyl groups. □

Example 9.4. Enantiomerically pure binaphthol **9-6** is used as a chiral auxiliary to generate chiral aluminum hydride reducing agents [3], as reviewed [4]. The structural formula of **9-6** is drawn by applying the replacement technique. Because the argument ⟨skelbdlist⟩ is necessary to draw bold-lined skeletal bonds, the XeLaTeX commands `\decaheterov` and `\decaheterovi` for general use are used as shown below:



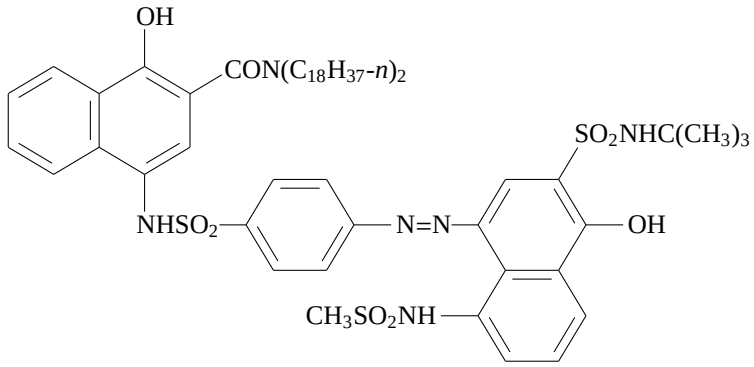
9-6

IUPAC name: 1,1′-binaphth-2-ol
XeLaTeX command:

```
\BiFunc(0,1){200}%
{\decaheterov({aB}{bB}{cB})[acfhk]%
{}{1==(yl);2B==OH}}
{\decaheterovi({fB}{gB}{hB})[acfhk]%
{}{1==(yl);2A==OH}}
```

□

Example 9.5. An azo-dye releaser **9-7** is capable of releasing a diffusible magenta dye after oxidation, so that it is used in instant color photography [5, page 428]. The structural formula of **9-7** is drawn by the multiple usage of (yl)-functions and `\ryl` commands. Thus, the substitution technique can be multiply applied in a nested fashion: i.e., `\ryl` ← (yl) ← `\ryl` ← (yl).



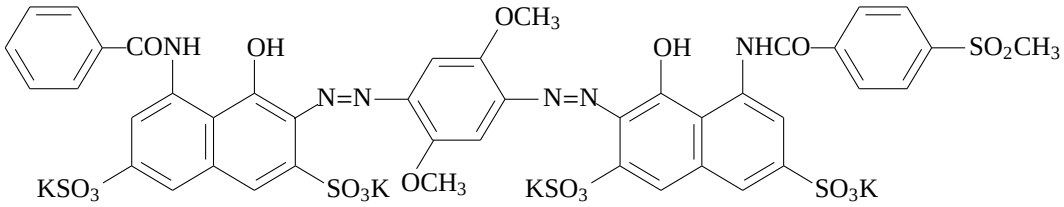
9-7

XeLaTeX command:

```
\naphthalenev{1==OH;2==CON(C$_{18}$H$_{37}$-$n$)$_{2}$;%
4==\ryl(0==NHSO$_2$){4==\benzeneh{1==(yl);%
4==\ryl(4==N=N){4==\naphthaleneh{1==(yl);4==OH;%
3==SO$_{2}$NHC(CH$_{3}$)$_{3}$;%
8==CH$_{3}$SO$_{2}$NH}}}}}
```

□

Example 9.6. A cyan bisazo dye for silver dye bleach photography has the structural formula **9-8** [5, page 550], which is drawn by the multiple application of the substitution technique. The central phenylene group of **9-8** is regarded as a parent structure, which is attached leftwards by a substituent generated by the scheme [phenylene]`\lyl` ← (yl) ← `\lyl` ← (yl)[phenyl] and rightwards by a substituent generated by the scheme [phenylene]`\ryl` ← (yl) ← `\ryl` ← (yl)[phenyl].



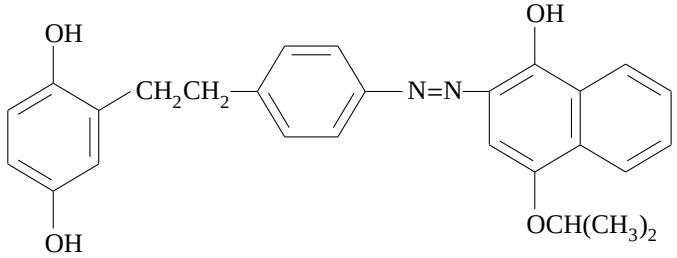
9-8

XeLaTeX command:

```
\changeunitlength{0.09pt}
\benzeneh{3==OCH$_{3}$;6==OCH$_{3}$;%
1==\lyl(4==N=N){5==\naphthalenev{2==(yl);1==OH;3==SO$_{3}$K;6==KSO$_{3}$;%
8==\lyl(8==CON\rlap{H}){4==\benzeneh{4==(yl)}}}};%
4==\ryl(4==N=N){5==\naphthalenev{7==(yl);8==OH;3==SO$_{3}$K;6==KSO$_{3}$;%
1==\ryl(8==NHCO){4==\benzeneh{1==(yl);4==SO$_{2}$CH$_{3}$}}}}}
```

□

Example 9.7. A magenta dye developer for instant color photography has the structural formula **9-9** [5, page 380], which is drawn by the multiple application of the substitution technique. The left-hand hydroquinone residue is regarded as a parent structure, which is attached rightwards by a substituent generated by the scheme `\ryl` ← (yl) ← `\ryl` ← (yl) in a nested fashion.



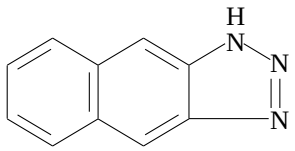
9-9

XeLaTeX command:
```
\benzenev{1==OH;4==OH;%
2==\ryl(4==\ChemForm{CH_2CH_2}){4==\benzeneh{1==(yl);%
4==\ryl(4==N=N){4==\naphthalenev{7==(yl);8==OH;5==\ChemForm{OCH(CH_3)_2}}}}}}
```
□

9.4.2 As Parent Structures for Ring Fusion

The argument ⟨bondlist⟩ of `\decalinev` or related commands is capable of setting ring fusion due to the addition technique.

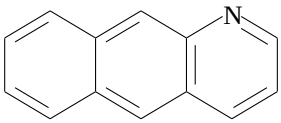
Example 9.8. For example, the structural formula of 1′*H*-naphtho[2,3-*d*][1,2,3]triazole (**9-10**) [2, P-25.3.8.1] is drawn by declaring `\fivefusevi` in the ⟨bondlist⟩ of `\decalinev` as follows:



9-10

IUPAC name: 1′*H*-naphtho[2,3-*d*][1,2,3]triazole
XeLaTeX command:
```
\decalinev[acfhk%
{b\fivefusevi[b]{1==\upnobond{N}{H};2==N;3==N}{}{D}}
]{}
```
□

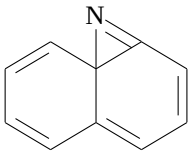
Example 9.9. By setting `\sixfusev` in the ⟨bondlist⟩ of `\decalinev`, we are able to benzo[*g*]quinoline (**9-11**) [2, P-25.3.8.1] as follows:



9-11

IUPAC name: benzo[*g*]quinoline
XeLaTeX command:
```
\decalinev[dfhj%
{b\sixfusev[ace]{1==N}{}{E}}]{}
```
□

Example 9.10. As an additional example of the addition technique, the structural formula of naphtho[1,8a]azirine (**9-12**) [2, P-25.3.8.4] is drawn by declaring `\threefuseh` in the ⟨bondlist⟩ of `\decalinev` as follows:

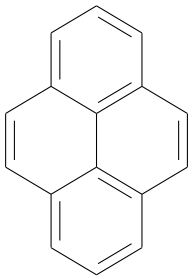


9-12

IUPAC name: naphtho[1,8a]azirine
XeLaTeX command:
```
\decalinev[bdfh%
{j\threefuseh[c]{3==N}{}{A}}%
]{}{}
```
□

Example 9.11. The restricted-subduced-cycle-index (RSCI) method for enumerating Kekulé structures (or equivalently perfect matchings of a graph) [6] has been developed as a specialized application of the USCI approach [7]. To show the versatility of the RSCI method, the number of Kekulé structures for pyrene is calculated by the RSCI method. One of such Kekulé structures is depicted as follows:

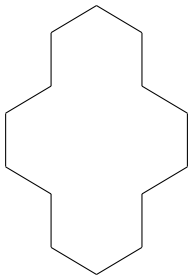
```
\begin{XyMcompd}(650,1100)(250,-80){}{}
\decaheterov[bg%
{i\sixfusev[ace]{}{}{D}[cd]}%
{d\sixfusev[ace]{}{}{A}[af]}%
]{}{}
\end{XyMcompd}
```



9-13

By starting from the above code for drawing the structure **9-13** of pyrene, all of the double bonds are changed into single bonds and the inner bonds are deleted (the ⟨delbdlist⟩: `[deijk]`). Thereby, a pericyclic skeleton remains to give a 14-membered ring.

```
\begin{XyMcompd}(650,1100)(250,-80){}{}
\decaheterov[%
{i\sixfusev{}{}{D}[cd]}%
{d\sixfusev{}{}{A}[af]}%
]{}{}[deijk]
\end{XyMcompd}
```



□

References

[1] P. A. Wender, A. W. White, and F. E. McDonald, in “Organic Syntheses,” ed. by A. I. Meyers, Organic Syntheses Inc. (1991) Vol. 70 pp 204–214.

[2] IUPAC Chemical Nomenclature and Structure Representation Division, *Provisional Recommendations. Nomenclature of Organic Chemistry* (2004). http://www.iupac.org/reports/provisional/abstract04/favre_310305.html.

[3] R. Noyori, I. Tomino, Y. Tanimoto, and M. Nisizawa, *J. Am. Chem. Soc*, **106**, (1984).

[4] S. Miyano and H. Hashimoto, *Yuki Gosei Kagaku Kyokanishi*, **44**, 713 (1986).

[5] S. Fujita, “Organic Chemistry of Photography,” Springer-Verlag, Berlin-Heidelberg (2004).

[6] S. Fujita, *MATCH Commun. Math. Comput. Chem.*, **69**, 333–354 (2013).

[7] S. Fujita, “Symmetry and Combinatorial Enumeration in Chemistry,” Springer-Verlag, Berlin-Heidelberg (1991).

Chapter 10

Carbocycles with Fused Six-to-Five-Membered Rings. Commands for Specific Use

This chapter is devoted to introduce commands for drawing indane derivatives and related compounds. These commands are short-cut commands of `\nonaheterov` etc. for general use (cf. Section 3.1 for the syntax).

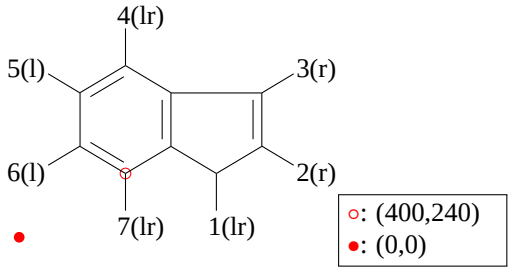
10.1 Drawing Indane Derivatives

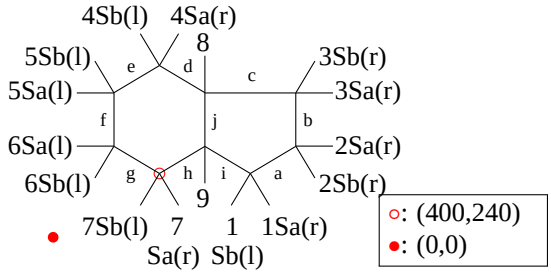
10.1.1 Vertical Forms of Indanes

The XeLaTeX commands `\indanev` and `\indanevi`, which are included in the package file 'lowcycle.sty', are applied to draw indane derivatives. The format of `\indanev` is:

```
\indanev[⟨bondlist⟩]{⟨subslist⟩}
```

The locant numbering (1–9) and the bond description (a–j) have a common format as shown in the following diagrams:





The handedness for each oriented or double-sided position is shown with a character set in parentheses. Each character in the optional argument ⟨bondlist⟩ indicates a specific double bond as shown in Table 10.1. The default setting of ⟨bondlist⟩ produces a fully unsaturated structure, when the option ⟨bondlist⟩ is omitted. If you want to draw a fully saturated structure, you should write down a null option (`[]`) or `[H]`. because the command `\indanev` adopts a mancude-ring system as a default setting.

The argument ⟨subslist⟩ is used to specify each substituent with a locant number and a bond modifier shown in Table 3.2 (cf. Fig. 3.1), in which *n* is an Arabic numeral between 1 and 7. Substitution on 8 (3a position) or 9 (7a position) can be assigned in the same way.

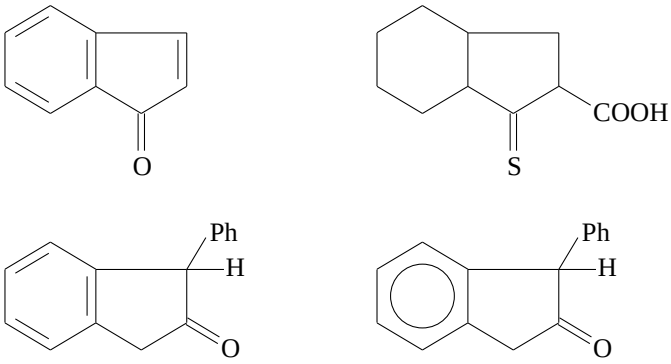
Examples for `\indanev`:

Table 10.1. Argument ⟨bondlist⟩ for Commands `\indolev` and Related Commands

Character	Printed structure	Character	Printed structure
none or r	aromatic six-membered ring	H or []	fully saturated form
a	1,2-double bond	b	2,3-double bond
c	3,3a-double bond	d	4,3a-double bond
e	4,5-double bond	f	5,6-double bond
g	6,7-double bond	h	7,7a-double bond
i	1,7a-double bond	j	3a,4a-double bond
A	aromatic circle (six-membered ring)		
B	aromatic circle (five-membered ring)		
{*n*+}	plus at the *n*-nitrogen atom (*n* = 1 to 9)		

```
\indanev{1D==O} \qquad
\indanev[H]{1D==S;2==COOH}\par
\indanev[egj]{2D==O;3Sa==H;3Sb==Ph}\qquad
\indanev[A]{2D==O;3Sa==H;3Sb==Ph}
```

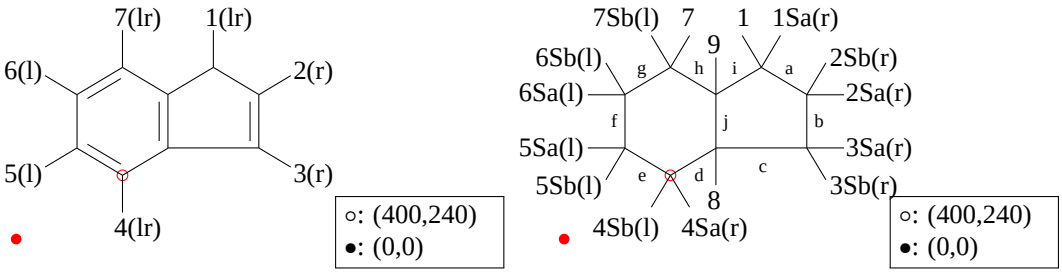
produce the following structures:



The macro `\indanevi` for drawing indane derivatives of inverse vertical type has the following format (lowcycle.sty).

```
\indanevi[⟨bondlist⟩]{⟨subslist⟩}
```

The locant numbering and the bond description are common with the vertical counterpart as shown in the following diagrams:

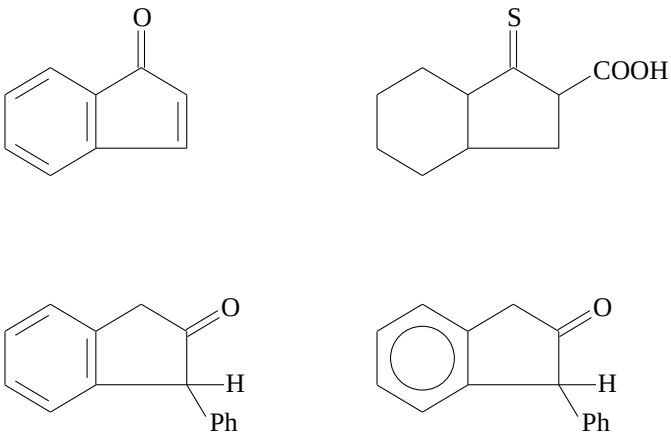


The handedness for each oriented or double-sided position is shown with a character set in parentheses; this is however omitted in the overcrowded position (between 7 and 1). The optional argument ⟨bondlist⟩ specifies bonds to be doubled as shown in Table 10.1

Examples for \indanevi:

```
\indanevi{1D==O} \qquad
\indanevi[H]{1D==S;2==COOH}\par
\indanevi[egj]{2D==O;3Sa==H;3Sb==Ph}\qquad
\indanevi[A]{2D==O;3Sa==H;3Sb==Ph}
```

produce the following structures:

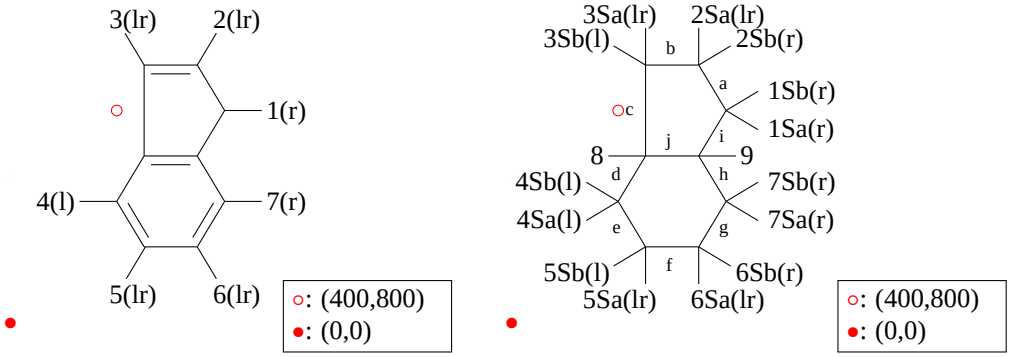


10.1.2 Horizontal Forms of Indanes

The macro \indaneh for drawing indane derivatives of horizontal type is defined in lowcycle.sty to have the following format.

```
\indaneh[⟨bondlist⟩]{⟨subslist⟩}
```

Locant numbers (1–9) for designating substitution positions and bond descriptors (a–j) are represented by the following diagram:



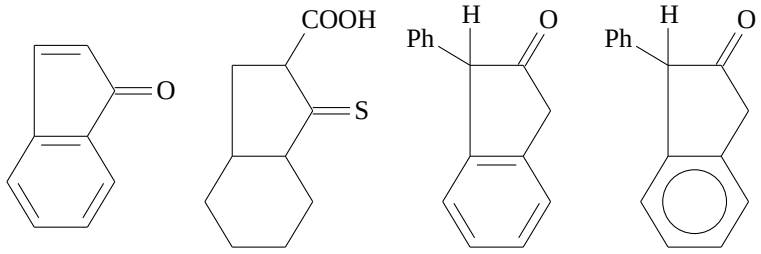
The handedness for each oriented or double-sided position is shown with a character set in parentheses. The optional argument ⟨bondlist⟩ gives the description of double bonds as shown in Table 10.1

Examples for \indaneh:

```
\begin{XyMcompd}(500,750)(450,300){}{}
   \indaneh{1D==O}
\end{XyMcompd}
\quad
\begin{XyMcompd}(500,900)(450,300){}{}
   \indaneh[H]{1D==S;2==COOH}
\end{XyMcompd}
```

```
\quad
\begin{XyMcompd}(500,900)(300,300){}{}
   \indaneh[egj]{2D==O;3Sa==H;3Sb==Ph}
\end{XyMcompd}
\quad
\begin{XyMcompd}(500,900)(300,300){}{}
   \indaneh[A]{2D==O;3Sa==H;3Sb==Ph}
\end{XyMcompd}
```

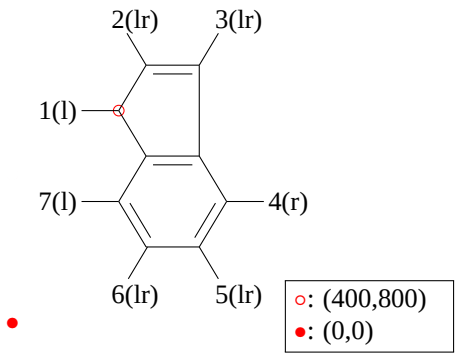
produce the following structures:

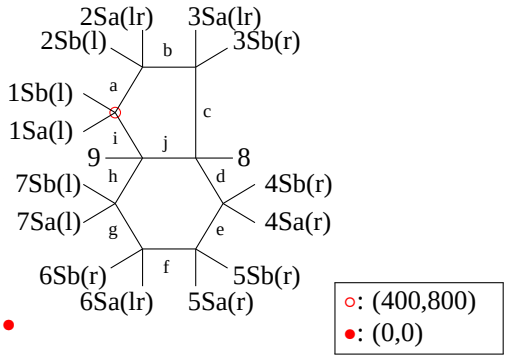


The macro `\indanehi` is the inverse counterpart of `\indaneh`, which aims at drawing indane derivatives of inverse horizontal type (lowcycle.sty).

`\indanehi[⟨bondlist⟩]{⟨subslist⟩}`

Locant numbers (1–9) for designating substitution positions and characters (a–j) for describing double bonds are shown in the following diagram:

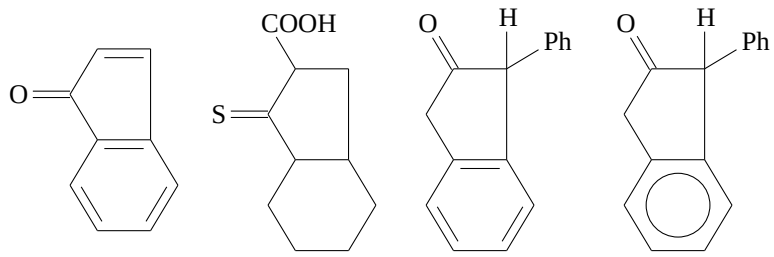




Examples for `\indanehi`:

```
\begin{XyMcompd}(500,750)(250,300){}{}
   \indanehi{1D==O}
\end{XyMcompd}
\quad
\begin{XyMcompd}(500,900)(250,300){}{}
   \indanehi[H]{1D==S;2==COOH}
\end{XyMcompd}
\quad
\begin{XyMcompd}(500,900)(400,300){}{}
   \indanehi[egj]{2D==O;3Sa==H;3Sb==Ph}
\end{XyMcompd}
\quad
\begin{XyMcompd}(500,900)(400,300){}{}
   \indanehi[A]{2D==O;3Sa==H;3Sb==Ph}
\end{XyMcompd}
```

produce the following structures:

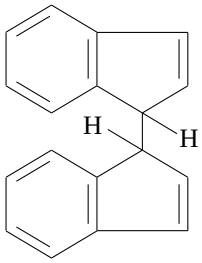


10.2 Illustrative Examples of Drawing Indane Derivatives

10.2.1 Substituents Derived by (yl)-Functions

A (yl)-function declared in the ⟨subslist⟩ of `\indanev` or the related commands generates a substituent which is capable of participating in the substitution technique as well as the replacement technique.

Example 10.1. The structural formula **10-1** of 1*H*,1′*H*,1,1′-biindene [1, P-28.4.1] is drawn by the substitution technique.

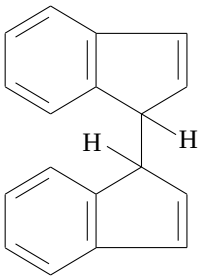


10-1

IUPAC name: 1*H*,1′*H*,1,1′-biindene
XeLaTeX command:

```
\indanev{1==\indanevi{1==(yl);1F==H};1F==H}
```

The command `\BiFunc(0,1){200}{A}{B}` generates a linking bond of the *x*-length of 200 unit lengths and the slop `(0,1)` (the vertical direction). The linking bond is regarded as a parent structure, the two endpoints of which accommodate the moieties A and B, so that it supports the replacement technique. The two moieties may be substituents generated by (yl)-functions, as found in an alternative drawing of the biindene. Thus, the following construction of the structural formula **10-2** is based on the replacement technique.



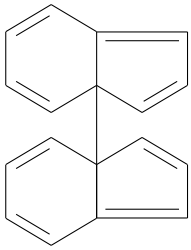
10-2

IUPAC name: 1*H*,1′*H*,1,1′-biindene
XeLaTeX command:

```
\BiFunc(0,1){200}%
{\indanevi{1==(yl);1F==H}}%
{\indanev{1==(yl);1F==H}}
```

□

Example 10.2. Another example of the replacement technique applied to `\BiFunc` gives the structural formula **10-3** of 3a,3′a-biindene [1, P-28.4.1].



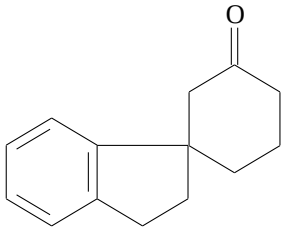
10-3

IUPAC name: 3a,3′a-biindene
XeLaTeX command:

```
\BiFunc(0,1){500}%
{\indanevi[aceg]{8==(yl)}}%
{\indanev[aceg]{9==(yl)}}
```

□

Example 10.3. Spiroannelation via organobis(cuprates) is a versatile method for synthesizing spiroketone derivatives [2]. The list of products contains 2′*H*,3′*H*-spiro[cyclohexan-3-one-1,1′-indene] (**10-4**), the structural formula of which can be drawn by the replacement technique.



10-4

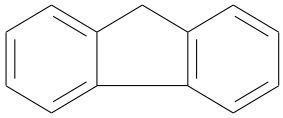
IUPAC name: 2′*H*,3′*H*-spiro[cyclohexan-3-one-1,1′-indene]
XƒMTEX command:
```
\sixheterov{5s==\indanev[egj]{3==(yl)}}{1D==O}
```

□

10.2.2 Indanes as Parent Structures for Ring Fusion

The argument ⟨bondlist⟩ of `\indanev` and related commands serves as parent components for ring fusion.

Example 10.4. For example, the structural formula **10-5** of 9*H*-fluorene [1, P-25.1.1] is drawn by applying the addition technique to the command `\indanv` (cf. Section 2.7), where `\sixfusev` is used as an attached component.



10-5

IUPAC name: 9*H*-fluorene
XƒMTEX command:
```
\indanevi[dfh%
{b\sixfusev[ace]{}{}{E}}]{}
```

□

References

[1] IUPAC Chemical Nomenclature and Structure Representation Division, *Provisional Recommendations. Nomenclature of Organic Chemistry* (2004). http://www.iupac.org/reports/provisional/abstract04/favre_310305.html.

[2] P. A. Wender, A. W. White, and F. E. McDonald, in “Organic Syntheses,” ed. by A. I. Meyers, Organic Syntheses Inc. (1991) Vol. 70 pp 204–214.

Fused Tricyclic Carbocycles. Commands for Specific Use

This chapter is devoted to introduce commands for drawing anthracene derivatives and related compounds. Because there are no general commands which correspond to the commands described in this chapter, they should be constructed by applying the addition technique to a 6-6 fused ring and a 6-membered fusing unit if necessary.

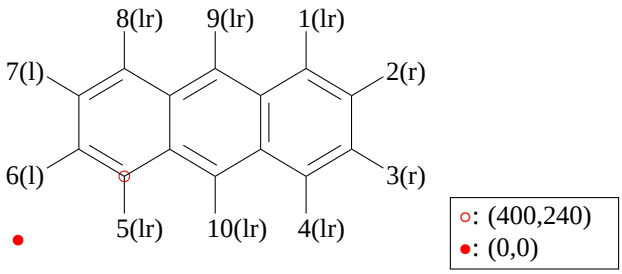
11.1 Anthracene and Perhydroanthracene Derivatives

11.1.1 Drawing Anthracene Derivatives

The macro `\anthracenev` is used to draw anthracene derivatives of vertical type (carom.sty) as well as various quinone derivatives. The format of this command is as follows:

```
\anthracenev[⟨bondlist⟩]{⟨subslist⟩}
```

Locant numbers for designating substitution positions are represented by the following diagram:



The handedness for each oriented or double-sided position is shown with a character set in parentheses. The optional argument ⟨bondlist⟩ is used to specify a bond pattern as shown in Table 11.1.[a] Thereby, we obtain the skeletal structures collected in Fig. 11.1.

The argument ⟨subslist⟩ is used to specify each substituent with a locant number and a bond modifier shown in Table 3.2, in which *n* is an Arabic numeral between 1 and 10.

Examples for `\anthracenev`:

```
\anthracenev[pa]{9D==O;{{10}D}==O;2==COOH}\hskip1.5cm
```

[a] When the optional argument ⟨bondlist⟩ specifies a bond pattern (not locant alphabets), the mechanism of ring fusion is not permitted.

Table 11.1. Argument ⟨bondlist⟩ for Command \anthracenev

Character	Printed structure
none or r	right-handed mancude-ring system
l	left-handed mancude-ring system
A	aromatic circle
p or pa	9,10-anthraquinone (A)
pA	9,10-anthraquinone (circle type)
o	1,2-anthraquinone (A)
oa	1,2-anthraquinone (A')
oA	1,2-anthraquinone (circle type)
ob	2,3-anthraquinone (B)
oc	1,2-anthraquinone (C)
q	1,4-anthraquinone (A)
qa	1,4-anthraquinone (A')
qA	1,4-anthraquinone (circle type)

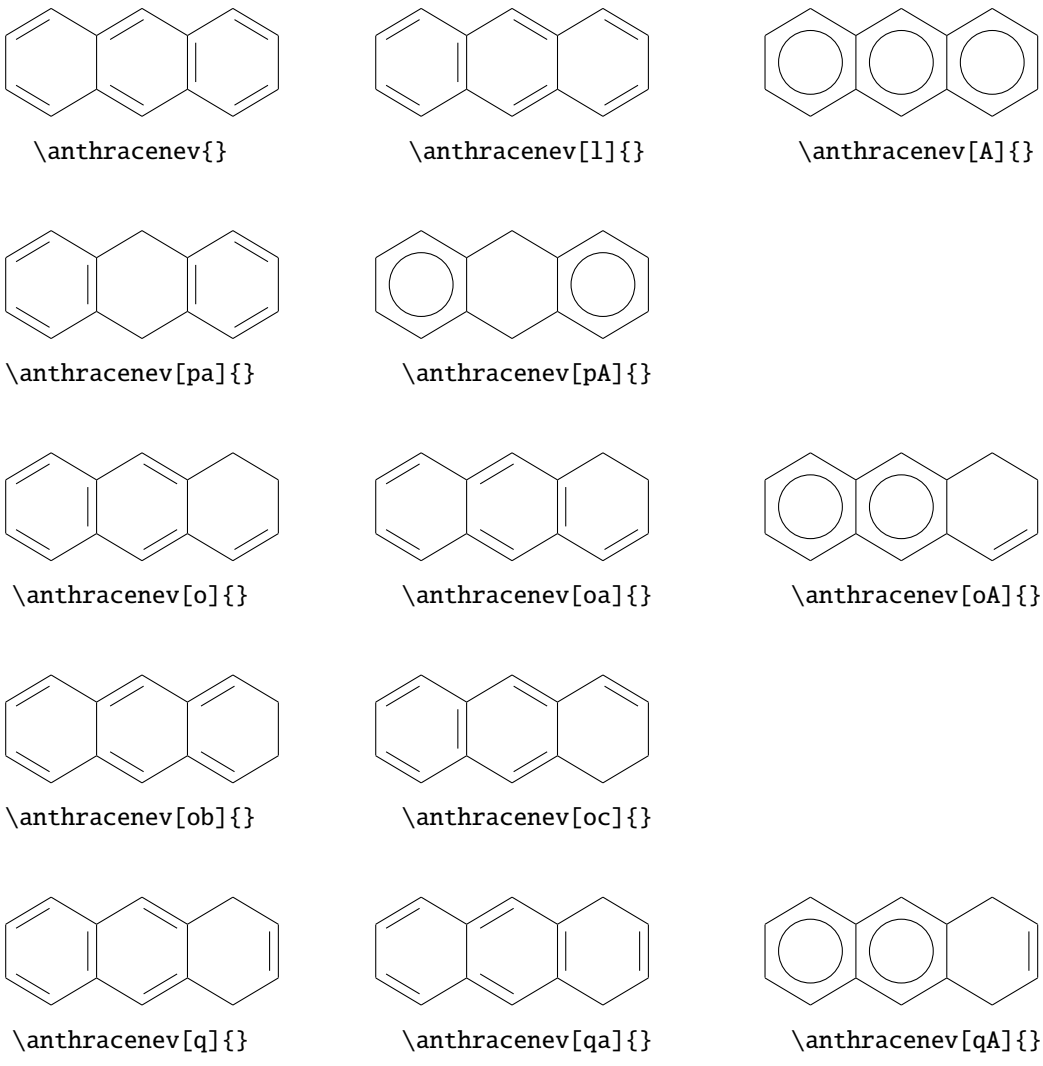
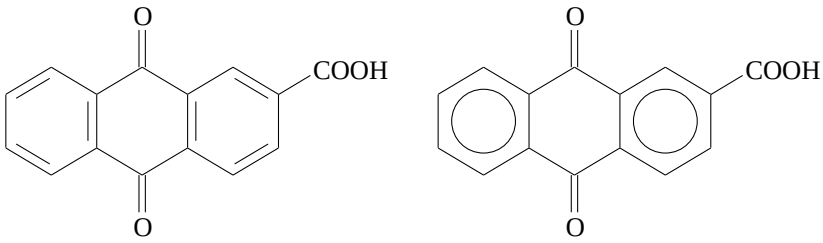


Figure 11.1. Endocyclic bond patterns by the ⟨bondlist⟩ argument of command \anthracenev.

```
\anthracenev[pA]{9D==O;{{10}D}==O;2==COOH}
```

These commands produce:

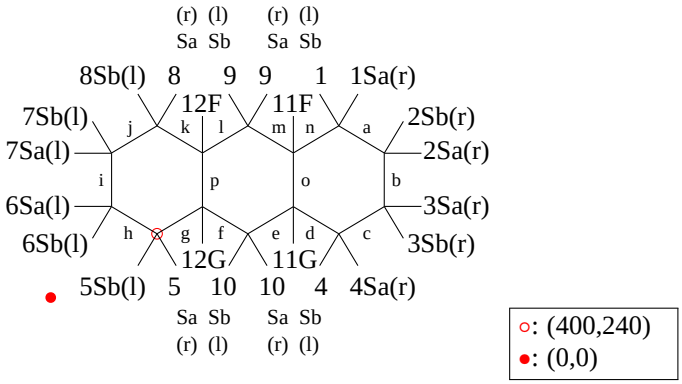


11.1.2 Drawing Perhydroanthracene Derivatives

The macro `\hanthracenev` (carom.sty) is a more general macro than `anthracenev`, where the latter is actually a short-cut command of the former. The `\hanthracenev` command takes the following format:

```
\hanthracenev[⟨bondlist⟩]{⟨subslist⟩}
```

Locant numbers (1–12) for designating substitution positions and bond descriptors (a–p) are represented by the following diagram:



The handedness for each oriented or double-sided position is shown with a character set in parentheses. The option argument ⟨bondlist⟩ is based on the assignment of characters (a–p) to respective bonds as shown in the above diagram and Table 11.2.

Table 11.2. Argument ⟨bondlist⟩ for Command `\hanthracenev`

Character	Printed structure	Character	Printed structure
none	perhydro-anthracene		
a	1,2-double bond	b	2,3-double bond
c	3,4-double bond	d	4,4a-double bond
e	10,4a-double bond	f	10,10a-double bond
g	5,10a-double bond	h	5,6-double bond
i	6,7-double bond	j	8,7-double bond
k	8,8a-double bond	l	9,8a-double bond
m	9,9a-double bond	n	1,9a-double bond
o	4a,9a-double bond	p	10a,8a-double bond
A	right aromatic circle	B	central aromatic circle
C	left aromatic circle		

A bond modifier in the argument ⟨subslist⟩ for n = 1–10 is selected from those shown in Table 3.2. The substitution at the bridgehead positions is designated as shown in Table 11.3.

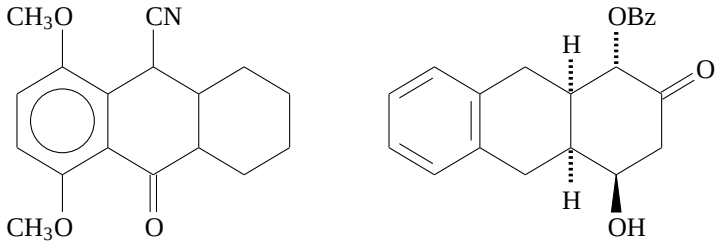
Examples for `\hanthracenev`:

Table 11.3. Bond Modifiers of ⟨subslist⟩ for Bridgehead Positions in \hanthracenev

Character	Printed structure
11FA	alpha single bond at 9a
11FB	beta single bond at 9a
11FU	unspecified single bond at 9a
11GA	alpha single bond at 4a
11GB	beta single bond at 4a
11GU	unspecified single bond at 4a
12FA	alpha single bond at 8a
12FB	beta single bond at 8a
12FU	unspecified single bond at 8a
12GA	alpha single bond at 10a
12GB	beta single bond at 10a
12GU	unspecified single bond at 10a

```
\hanthracenev[C]{5==\lmoiety{CH$_{3}$O};%
8==\lmoiety{CH$_{3}$O};9==CN;{{10}D}==O}\qquad
\hanthracenev[hjp]{{{11}FA}==H;{{11}GA}==H;1A==OBz;4B==OH;2D==O}
```

These commands produce:



11.2 Phenanthrene and Perhydrophenanthrene Derivatives

11.2.1 Drawing Phenanthrene Derivatives

The macro \phenanthrenev is used to draw phenanthrene derivatives of vertical type (carom.sty) as well as various quinone derivatives. The format of this command is as follows:

```
\phenanthrenev[⟨bondlist⟩]{⟨subslist⟩}
```

Locant numbers for designating substitution positions are represented by the following diagram:

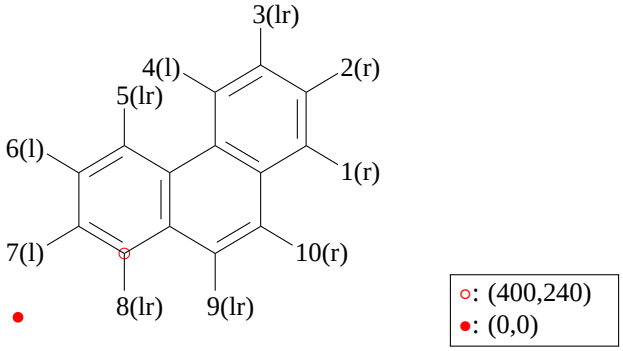


Table 11.4. Argument ⟨bondlist⟩ for Command \phenanthrenev

Character	Printed structure
none or r	right-handed double bonds
A	aromatic circle
p or pa	1,4-quinone (A)
pA	1,4-quinone (circle type)
o or oa	1,2-quinone (A)
oA	1,2-quinone (circle type)
ob	2,3-quinone (B)
oc	3,4-anthraquinone (C)
q or qa	9,10-quinone
qA	9,10-quinone (circle type)

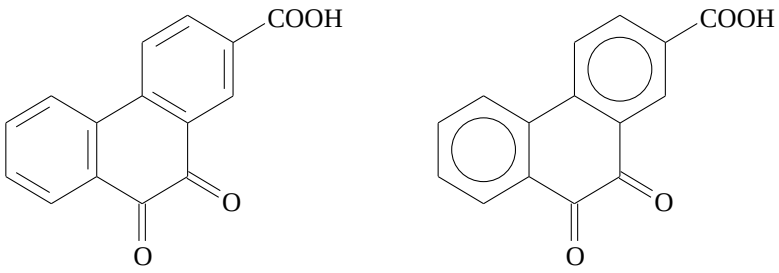
The handedness for each oriented or double-sided position is shown with a character set in parentheses. The optional argument ⟨bondlist⟩ is used to specify a bond pattern as shown in Table 11.4.[b]

The argument ⟨subslist⟩ is employed to specify each substituent with a locant number and a bond modifier shown in Table 3.2, in which *n* is selected to be an Arabic numeral between 1 and 10.

Examples for \phenanthrenev:

```
\phenanthrenev[q]{9D==O;{{10}D}==O;2==COOH}\hskip1.5cm
\phenanthrenev[qA]{9D==O;{{10}D}==O;2==COOH}
```

These commands produce:



11.2.2 Drawing Perhydrophenanthrene Derivatives

The macro \hphenantherev (carom.sty) is a more general macro than phenanthrenev, where the latter is a short-cut command based on the former. The format of the \hphenantherev command is as follows:

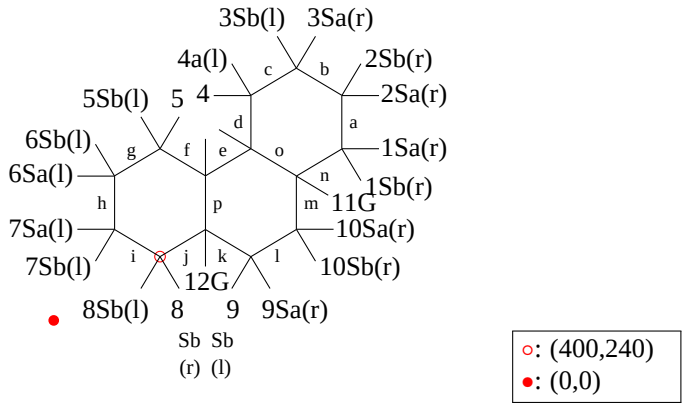
```
\hphenanthrenev[⟨bondlist⟩]{⟨subslist⟩}
```

Locant numbers (1–12) for designating substitution positions and bond descriptors (a–p) are represented by the following diagram:

[b] When the optional argument ⟨bondlist⟩ specifies a bond pattern (not locant alphabets), the mechanism of ring fusion is not permitted.

Table 11.5. Argument ⟨bondlist⟩ for Command \hphenanthrenev

Character	Printed structure	Character	Printed structure
none	perhydro-phenanthrene		
a	1,2-double bond	b	2,3-double bond
c	3,4-double bond	d	4,4a-double bond
e	4a,4b-double bond	f	4b,5-double bond
g	5,6-double bond	h	6,7-double bond
i	7,8-double bond	j	8,8a-double bond
k	8a,9-double bond	l	9,10-double bond
m	10,10a-double bond	n	1,10a-double bond
o	4a,10a-double bond	p	4b,8a-double bond
A	right aromatic circle	B	central aromatic circle
C	left aromatic circle		



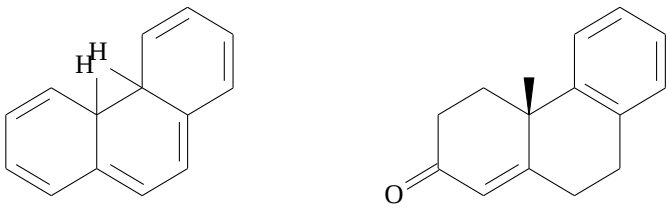
The handedness for each oriented or double-sided position is shown with a character set in parentheses, where the designation of overcrowded positions is abbreviated.

The option argument ⟨bondlist⟩ is based on the assignment of characters (a–p) to respective bonds as shown in the above diagram and Table 11.5. A bond modifier in the argument ⟨subslist⟩ for n = 1–10 can be one of bond modifiers shown in Table 3.2. The substitution at the bridgehead positions is similar to that designated in Table 11.3 for \hanthracenev.

Examples for \hphenanthrenev:

```
\hphenanthrenev[acgikm]{{{11}F}=={\kern-3em\raise1ex\hbox{H}};%
{{12}F}==\lmoiety{H˜˜}}\hskip1.5cm
\hphenanthrenev[acoj]{7D==O;{{12}FB}==}
```

These commands produce:

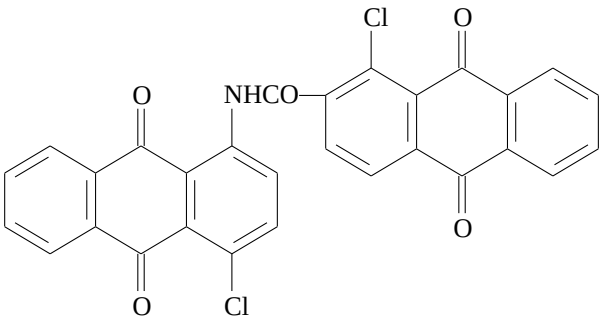


11.3 Illustrative Examples of Drawing Tricyclic Carbocycles

11.3.1 Generation of Substituents by (yl)-Functions

The command `\anthracenev` is capable of generating the corresponding substituent by declaring a (yl)-function.

Example 11.1. A red vat dye derived from 1-amino-4-chloroanthraquinone and 1-chloro-2-chloroanthraquinonecarboxylic acid chloride [Beyer, BP762888 (1956), *Chem. Abstr.*, **52**, 7719 (1958)] has the structural formula **11-1**, which is drawn by the substitution technique. An inner substituent is generated by declaring a (yl)-function in the ⟨subslist⟩ of `\anthracenev`. It is further included in the `\ryl` command to add a linking divalent unit (NHCO). Then, the resulting substituent is declared in the ⟨subslist⟩ of another `\anthracenev`.



11-1

XƎMTEX command:

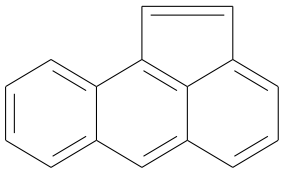
```
\anthracenev[pa]{9D==O;{10}D==O;4==Cl;%
1==\ryl(8==NHCO){4==\anthracenev[pa]%
{7==(yl);9D==O;{10}D==O;8==Cl}}}
```

□

11.3.2 As Parent Structures for Ring Fusion

The argument ⟨bondlist⟩ of `\hanthracenev` is capable of setting ring fusion.

Example 11.2. For example, the structural formula of aceanthrylene (**11-2**) is drawn by declaring `\fivefusev` in the ⟨bondlist⟩ of `\hanthracenev` as follows:



11-2

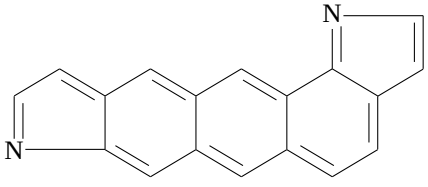
IUPAC name: aceanthrylene

XƎMTEX command:

```
\hanthracenev[acegikm%
{n\fivefusev[c]{}{}{a}[e]}%
]{}
```

□

Example 11.3. The structural formula of benzo[1,2-*f*:4,5-*g*′]diindole (**11-3**) is drawn by double ring fusion of five-membered units due to `\fiveheterov` and `\fiveheterovi`, which are declared in the ⟨bondlist⟩ of `\hanthracenev` as follows:



11-3

IUPAC name: benzo[1,2-*f*:4,5-*g*′]diindole

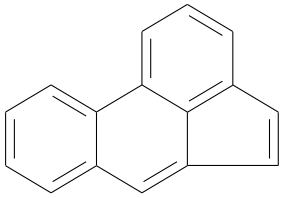
XƎMTEX command:

```
\hanthracenev[bdfhkm%
{a\fivefusev[bd]{4==N}{}{e}};%
{i\fivefusevi[ad]{4==N}{}{B}};%
]{}
```

□

The argument ⟨bondlist⟩ of `\hphenanthrenev` is capable of setting ring fusion.

Example 11.4. For example, the structural formula of acephenanthrylene (**11-4**) is drawn by declaring `\fivefusevi` in the ⟨bondlist⟩ of `\hphenanthrenev` as follows:



11-4

IUPAC name: acephenanthrylene
XꝶMTEX command:

```
\hphenanthrenev[bdfhjln%
{n\fivefusevi[b]{}{}{E}[d]}%
]{}
```

□

Chair Forms and Further Carbocyclic Compounds. Commands for Specific Use

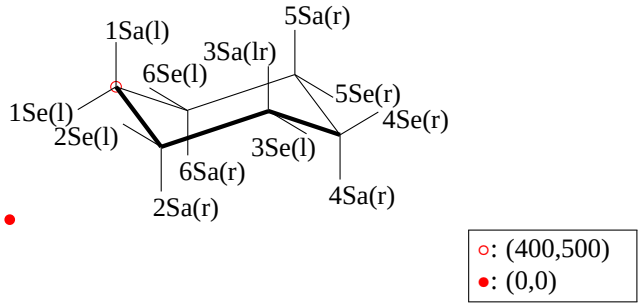
12.1 Drawing Chair Form of Cyclohexane

12.1.1 Standard formula

The XeLaTeX command `\chair` for specific use is defined to draw cyclohexane derivatives of chair-form (ccycle.sty). The format of this command is as follows:

```
\chair[⟨bondlist⟩]{⟨subslist⟩}
```

Locant numbers for designating substitution positions are represented by the following diagram:



Each character set in parentheses represents the handedness of the corresponding position, which is fixed in this type of macros.

The optional argument ⟨bondlist⟩ is an character string in a pair of brackets, where each character indicates the presence of a double bond at the edge corresponding to the character. The bond-correspondence is rather arbitrary in some cases but conforms to chemical conventions as faithfully as possible if such conventions are presence (Table 12.1).

The argument ⟨subslist⟩ for this macro takes a general format, except that modifiers are selected from '`Sa`' for an axial substituent, '`Se`' for an equatorial substituent, '`U`' for an unknown configuration, and '`D`' for a substituent through an double bond.

Examples of `\chair`:

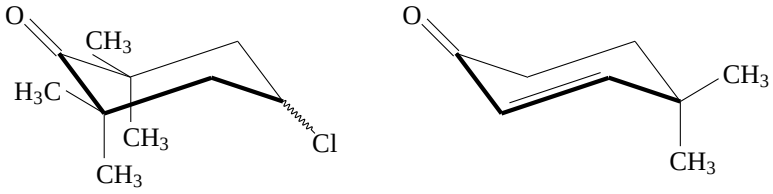
```
\begin{XyMcompd}(1150,700)(230,0){}{}
\chair{1D==O;2Se==H$_{3}$C;2Sa==CH$_{3}$;%
6Se==CH$_{3}$;6Sa==CH$_{3}$;4U==Cl}
\end{XyMcompd}
```

Table 12.1. Argument ⟨bondlist⟩ for the Commands `\chair` and `\chairi`

Character	Printed structure
none	cyclohexane
a	1,2-double bond
b	2,3-double bond
c	4,3-double bond
d	4,5-double bond
e	5,6-double bond
f	6,1-double bond

```
\qquad
\begin{XyMcompd}(1250,700)(230,0){}{}
\chair[b]{1D==O;4Se==CH$_{3}$;4Sa==CH$_{3}$}
\end{XyMcompd}
```

produce the following diagrams:

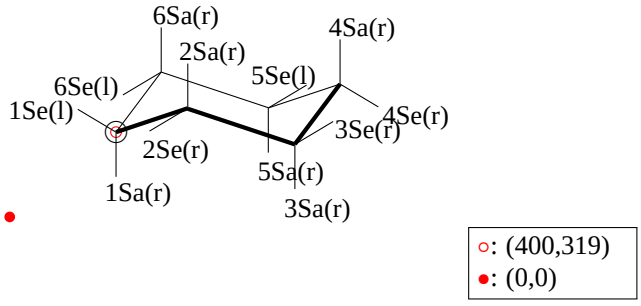


12.1.2 Inverse formula

The XeLaTeX command `\chairi` for specific use is used to draw cyclohexane derivatives of inverse chair-form (ccycle.sty). The format of this command is as follows:

```
\chairi[⟨bondlist⟩]{⟨subslist⟩}
```

Locant numbers for designating substitution positions are represented by the following diagram:



Each character set in parentheses represents the handedness of the corresponding position, which is fixed in this type of macros.

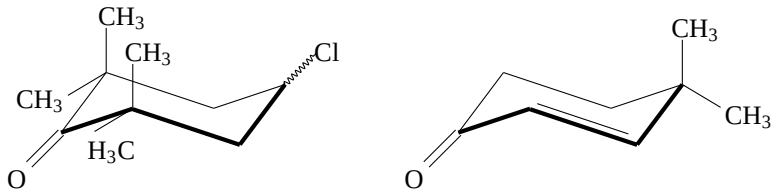
The optional argument ⟨bondlist⟩ has the same meaning as the counterpart of the `\chair` command (Table 12.1). The argument ⟨subslist⟩ for this macro takes the same format as described in the `\chair` macro, i.e., 'Sa', 'Se', 'U' and 'D'.

Examples for `\chairi`:

```
\begin{XyMcompd}(1150,700)(230,100){}{}
\chairi{1D==O;2Se==H$_{3}$C;2Sa==CH$_{3}$;%
6Se==CH$_{3}$;6Sa==CH$_{3}$;4U==Cl}
\end{XyMcompd}
\qquad
\begin{XyMcompd}(1250,700)(230,100){}{}
```

```
\chairi[b]{1D==O;4Se==CH$_{3}$;4Sa==CH$_{3}$}
\end{XyMcompd}
```

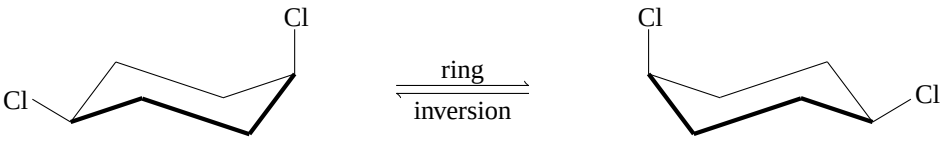
produce the following diagrams:



Example 12.1. The following example shows the ring flipping of two chair forms, which are drawn with the macros `\chair` and `\chairi`.

```
\begin{quotation}
Let us consider \emph{cis\/}-1,4-dichlorocyclohexane (\cref{cf:chair-06})
as an example. This derivative is generated by putting chlorine atoms on
the 1- and 4-positions. Thus, we take account of the following pair
of conformers (\cref{cf:chair-06a} and of \cref{cf:chair-06b}):
\end{quotation}
\begin{center}
\nocompd\label{cf:chair-06}
\cdtwocell{0pt}{160pt}{\chairi{1Se==Cl;4Sa==Cl}\vspace*{-25pt}}%
 {Conformer A (\derivlabel{cf:chair-06a})}
\reacteqarrow{0pt}{50pt}{ring}{inversion}
\cdtwocell{0pt}{160pt}{\chair{1Sa==Cl;4Se==Cl}\vspace*{-25pt}}%
 {Conformer B (\derivlabel{cf:chair-06b})}
\end{center}
```

> Let us consider *cis*-1,4-dichlorocyclohexane (**12-1**) as an example. This derivative is generated by putting chlorine atoms on the 1- and 4-positions. Thus, we take account of the following pair of conformers (**12-1a** and of **12-1b**):



Conformer A (**12-1a**) Conformer B (**12-1b**)

In this code, we use the counters *compd* and *deriv* which are available from the commands `\nocompd` and `\derivlabel` of the package chemist.sty. The counters can be referred to by using the command `\cref` defined in the package chemist.sty. The command `\cdtwocell{0pt}{160pt}{A}{B}` is to generate a box with the width of 160pt and the vertical adjustment 0pt (no shift), which accommodates A and B in a vertical alignment. The command `\reacteqarrow{0pt}{50pt}{A}{B}` is to generate an equivalent arrow of length 50pt and the vertical adjustment 0pt (no shift), which is accompanied by an upper comment A and a lower comment B. □

12.2 Drawing Bicyclo[2.2.1]heptane

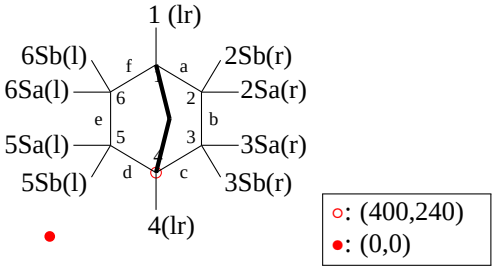
The XeLaTeX command `\bicychepv` for specific use is used to draw bicyclo[2.2.1]heptane derivatives of vertical type in a flat fashion. The format of this command is as follows:

```
\bicychepv[⟨bondlist⟩]{⟨subslist⟩}
```

Locant numbers for designating substitution positions and bond descriptors for assigning double bonds are shown in the following diagram:

Table 12.2. Argument ⟨bondlist⟩ for Commands `\bicychepv` and `\bicycheph`

Character	Printed structure
none	bicyclo[2.2.1]heptane
a	1,2-double bond
b	2,3-double bond
c	4,3-double bond
d	4,5-double bond
e	5,6-double bond
f	6,1-double bond
A	aromatic circle
7	7,7-dimethyl



Each character set in parentheses represents the handedness of the corresponding position, which is fixed in this type of macros.

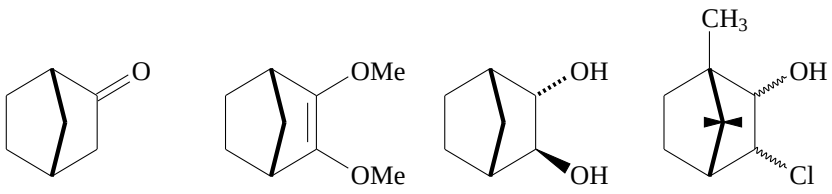
The optional argument ⟨bondlist⟩ is an character string in a pair of brackets, where each character indicates the presence of a double bond at the edge corresponding to the character (Table 12.2).

The argument ⟨subslist⟩ for this macro takes a general format, in which the modifiers listed in Table 3.2 are used.

Examples of `\bicychepv`:

```
\bicychepv{2D==O}
\bicychepv[b]{2==OMe;3==OMe}
\bicychepv{3B==OH;2A==OH}
\bicychepv[7]{1==CH$_{3}$;2U==OH;3U==Cl}
```

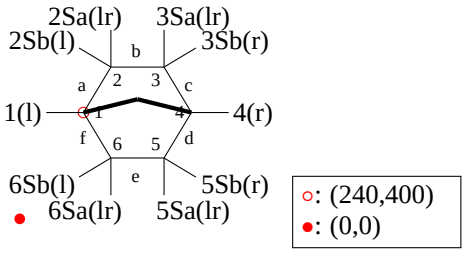
produce the following diagrams:



The XeLaTeX command `\bicycheph` for specific use is used to draw bicyclo[2.2.1]heptane derivatives of horizontal type in a flat fashion. The format of this command is as follows:

```
\bicycheph[⟨bondlist⟩]{⟨subslist⟩}
```

Locant numbers for designating substitution positions along with bond descriptors are found in the following diagram:

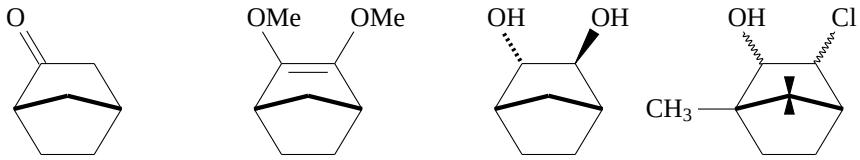


Each character set in parentheses represents the handedness of the corresponding position, which is fixed in this type of macros. For the ⟨subslist⟩ and the ⟨bondlist⟩, see Table 3.2 and 12.2. .

Examples of `\bicycheph`:

```
\bicycheph{2D==O}
\bicycheph[b]{2==OMe;3==OMe}
\bicycheph{3B==OH;2A==OH}
\bicycheph[7]{1==CH$_{3}$;2U==OH;3U==Cl}
```

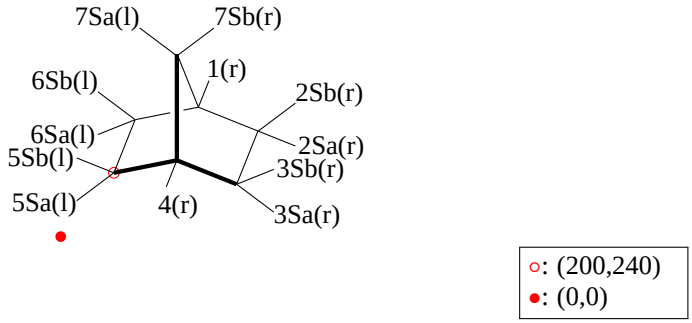
produce the following diagrams:



For the purpose of depicting the stereochemistry of bicyclo[2.2.1]heptane derivatives, you can use the command `\bornane` instead of the commands `\bicychepv` and `\bicycheph`. The format of this command is as follows:

```
\bornane[⟨bondlist⟩]{⟨subslist⟩}
```

Locant numbers for designating substitution positions are represented by the following diagram:



Each character set in parentheses represents the handedness of the corresponding position, which is fixed in this type of macros.

The option argument ⟨bondlist⟩ is an character string in a pair of brackets, where each character indicates the presence of a double bond at the edge corresponding to the character (Table 12.3). The ⟨subslist⟩ format is shown in Table 3.2.

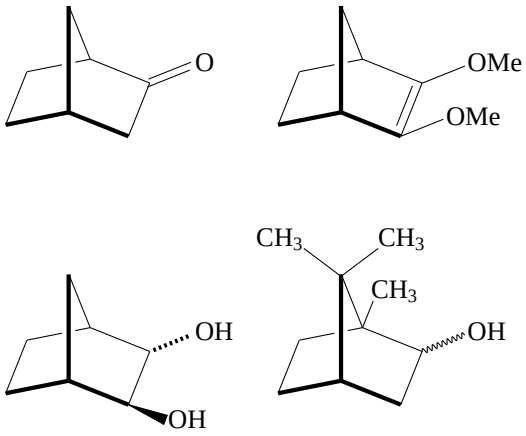
Examples of `\bornane`:

```
\bornane{2D==O}
\bornane[b]{2==OMe;3==OMe}\par
\bornane{3B==OH;2A==OH}
\bornane{7Sa==CH$_{3}$;7Sb==CH$_{3}$;1==CH$_{3}$;2U==OH}
```

Table 12.3. Argument ⟨bondlist⟩ for Commands \bornane

Character	Printed structure
none	bornane
a	1,2-double bond
b	2,3-double bond
c	4,3-double bond
d	4,5-double bond
e	5,6-double bond
f	6,1-double bond
g	1,7-double bond
h	4,7-double bond

produce the following diagrams:



12.3 Drawing Adamantane Derivatives

The XeLaTeX command \adamantane for specific use prints adamantane derivatives (vertical formulas) by means of the following format:

```
\adamantane[⟨bondlist⟩]{⟨subslist⟩}
```

where ⟨bondlist⟩ is not effective in the present specification.

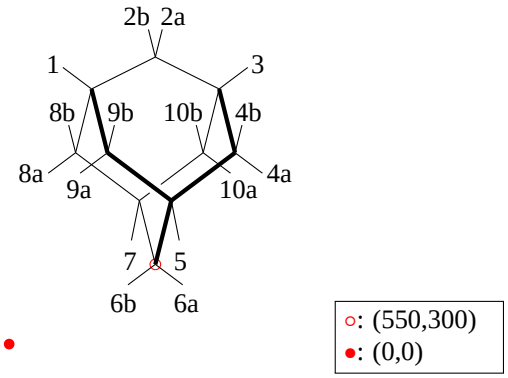


Table 12.4. Argument ⟨subslist⟩ for Commands \adamantane and \hadamantane

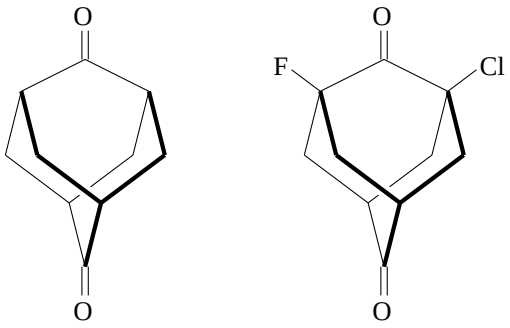
Character	Printed structure
for n = 1, 3, 5, and 7 (bridgeheads)	
n or na	exocyclic single bond at n-atom
for n = 2, 4, 6, 8, 9, and 10 (bridges)	
na	exocyclic single bond at n-atom (axial)
nb	exocyclic single bond at n-atom (equatorial)
nD	exocyclic double bond at n-atom (2 and 6)

The argument ⟨subslist⟩ is slightly different from general conventions, as shown in Table 12.4.

Examples of \adamantane:

```
\adamantane{2D==O;6D==O}
\adamantane{2D==O;6D==O;1==F;3==Cl}
```

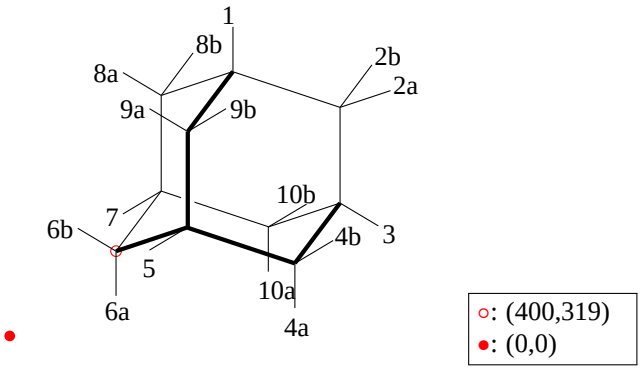
produce the following diagrams:



The X$\mathrm{\tilde{E}}$TEX command \hadamantane for specific use prints adamantane derivatives (horizontal formulas) by means of the following format:

```
\hadamantane[⟨bondlist⟩]{⟨subslist⟩}
```

where ⟨bondlist⟩ is not effective in the present specification.

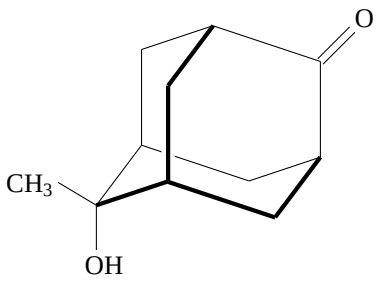


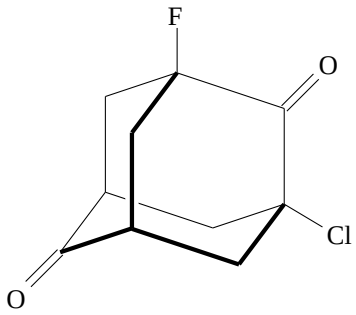
The argument ⟨subslist⟩ has the same meanings as that of \adamantane, as shown in Table 12.4.

Examples of \hadamantane:

```
\hadamantane{2D==O;6a==OH;6b==CH$_{3}$}
\hadamantane{2D==O;6D==O;1==F;3==Cl}
```

produce the following diagrams:


O
CH3
OH

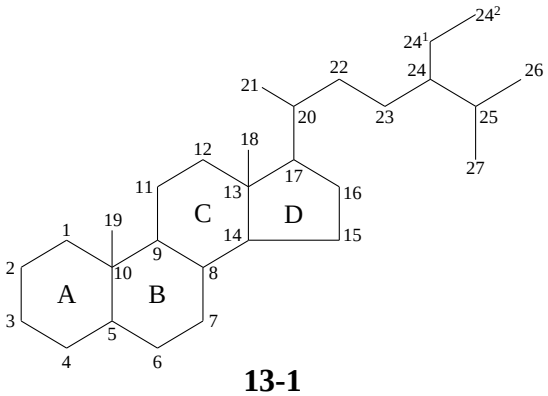

F
O
Cl
O

Chapter 13

Steroid Derivatives. Commands for Specific Use

13.1 Numbering and Ring Letters of Steroids

According to the IUPAC-IUB nomenclature of steroids [1, 3S-1.1], the carbon atoms of a steroid skeleton with a 17-side chain are numbered sequentially and the four rings are designated by alphabets A–D.



13-1

The old locant numbers 28 and 29 have been replaced by the new locant numbers 24^1 and 24^2 in the IUPAC-IUB nomenclature [1, 3S-1.1], because the numbers 28, 29, and 30 are assigned to the additional methyl groups at C-4 and C-14 in triterpenoids.

According to the IUPAC-IUB nomenclature [1, 3S-1.2], if one or more of the carbon atoms shown in **13-1** is not present and a steroid name is used, the numbering of the remainder is undisturbed. The locant numbers adopted for drawing steroid derivatives in the XymTEX system obey this principle, so that the locant numbers of the skeletal part are selected between 1–17, while those of the chain part are selected between 20–25 (except 21). The numbers 18, 19, and 21 are not selected as locant numbers, because they are respectively regarded as the substituents at the C-13, C-10, and C-20 in the XymTEX system. Moreover, the locant numbers 26 and 27 are regarded as the substituents at C-25, so that they are incapable of accommodating further substituents.

13.2 Basic Skeletons for Drawing Steroids

This section is devoted to introduce XymTEX commands for specific use of drawing basic skeletons of steroids.

13.2.1 Macros for Drawing Basic Skeletons

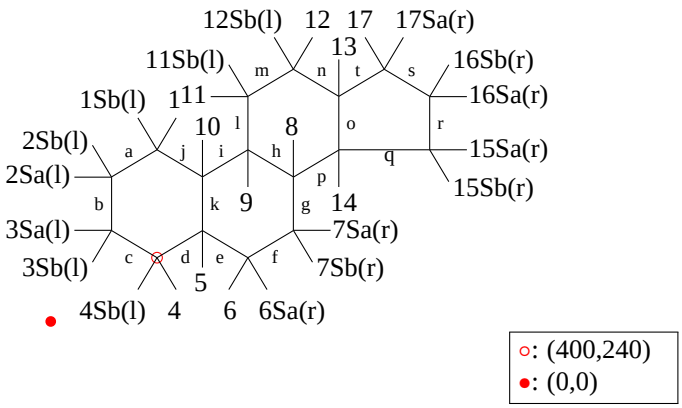
List of Names of Basic Commands

The following XƎMTEX commands for specific use are defined to draw basic skeletons of steroids, which are printed out in Table 13.1. Each of these macros is capable of accommodating substituents in a required argument (⟨subslist⟩) as well as bond descriptors (locant alphabets) in an optional argument (⟨bondlist⟩):

```
\steroid[⟨bondlist⟩]{⟨subslist⟩}
\steroidethylchain[⟨bondlist⟩]{⟨subslist⟩}
\steroidchain[⟨bondlist⟩]{⟨subslist⟩}
\steroidChain[⟨bondlist⟩]{⟨subslist⟩}
\steroidshortchain[⟨bondlist⟩]{⟨subslist⟩}
\steroidShortChain[⟨bondlist⟩]{⟨subslist⟩}
\steroidspiro[⟨bondlist⟩]{⟨subslist⟩} \steroidfuros[⟨bondlist⟩]{⟨subslist⟩}
```

Skeletal Ring Parts of Steroids

Locant numbers (1–17) for designating substitution positions and bond descriptors (locant alphabets a–t) are common to these commands. They are represented by the following diagram of `\steroid`:



The handedness for each oriented or double-sided position is shown with a character set in parentheses (r, l, and lr), where the designation of overcrowded positions is omitted.

The optional argument ⟨bondlist⟩ is based on the assignment of characters (a–t) to respective bonds as shown in the above diagram and Table 13.2.

A bond modifier in the argument ⟨subslist⟩ for n = 1–17 (except fused positions) is selected from the list of bond modifiers (Table 3.2). The substitution at the fused positions (n = 5, 8, 9, 10, 13 and 14) is similarly designated as for fused bicyclic or tricyclic compounds (Table 13.3).

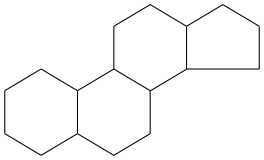
The following examples of `\steroid` illustrate the specification of ⟨bondlist⟩ and ⟨subslist⟩, where each locant number of two digits is surrounded by a pair of braces according to the methodology of TEX/LATEX.

Examples of `\steroid`:

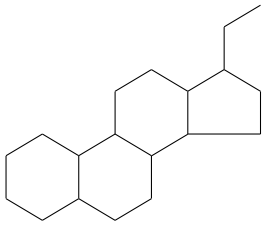
```
\steroid[ackhf]{{{13}B}==\lmoiety{H$_{3}$C};{{14}A}==H}\hskip1cm
\steroid[d]{3D==O;9A==Br;{{11}D}==O;%
{{17}B}==COCH$_3$;{{14}A}==H;%
{{13}B}==\lmoiety{H$_3$C};{{10}B}==\lmoiety{H$_3$C}}
```

According to the IUPAC-IUB nomenclature [1, 3S-1.4], α-bonds are shown as broken lines (⋯⋯), while β-bonds are shown as wedges (▬). The above codes produce:

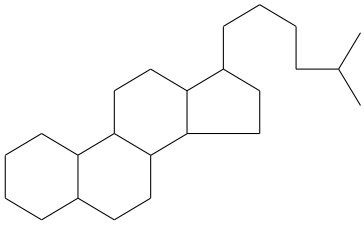
Table 13.1. Basic Skeletons for Drawing Steroids



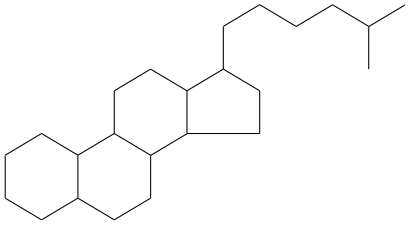
`\steroid{}`



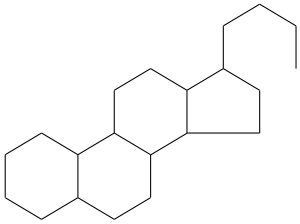
`\steroidethylchain{}`



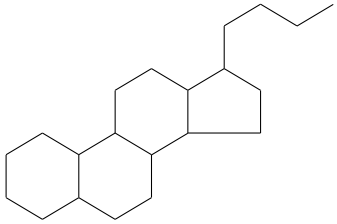
`\steroidchain{}`



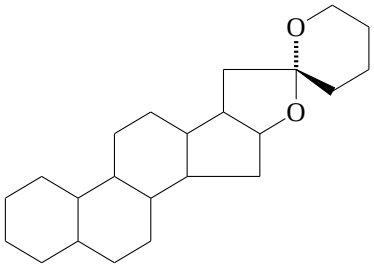
`\steroidChain{}`



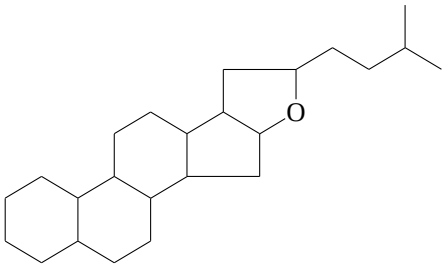
`\steroidshortchain{}`



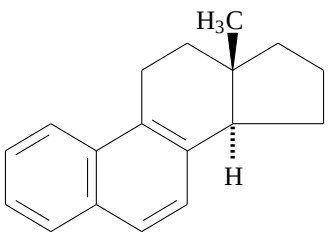
`\steroidShortChain{}`



`\steroidspiro{}`



`\steroidfuros{}`



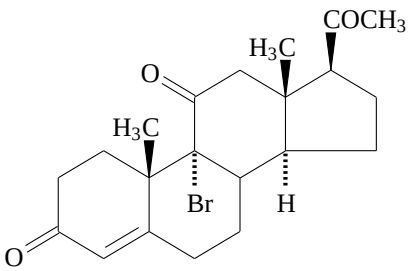


Table 13.2. Argument ⟨bondlist⟩ for Command `\steroid` and Related Commands

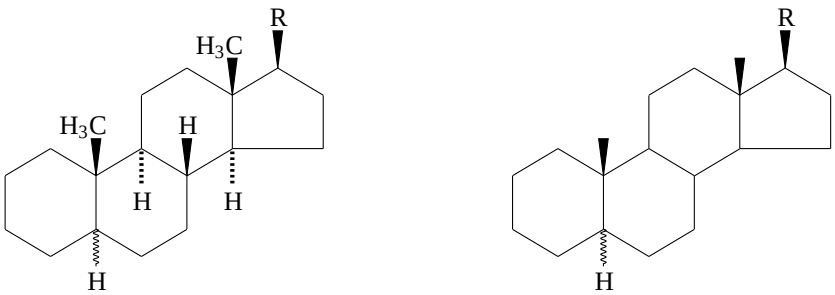
Character	Printed structure	Character	Printed structure
none	steroid skeleton		
a	1,2-double bond	b	2,3-double bond
c	3,4-double bond	d	4,5-double bond
e	6,5-double bond	f	6,7-double bond
g	7,8-double bond	h	9,8-double bond
i	9,10-double bond	j	1,10-double bond
k	5,10-double bond	l	9,11-double bond
m	12,11-double bond	n	12,13-double bond
o	14,13-double bond	p	8,14-double bond
q	14,15-double bond	r	15,16-double bond
s	17,16-double bond	t	17,13-double bond
A	aromatic A ring	B	aromatic B ring
C	aromatic C ring		

Table 13.3. The Argument ⟨subslist⟩ for Fused Positions in `\steroid` and Related Commands

Character	Printed structure
n or *n*S	exocyclic single bond at n-atom
*n*A	alpha single bond at n-atom (boldface)
*n*B	beta single bond at n-atom (dotted line)
*n*U	unspecified single bond at n-atom

According to the IUPAC-IUB nomenclature [1, 3S-1.4 Note 1], angular methyl groups, which are written out explicitly in the left formula, may be indicated by a bond without lettering as in the right formula, if there is no ambiguity. For this purpose, the declaration `\lmoiety{H$_{3}$C}` is replaced by `\null`. The hydrogen atoms at the bridgehead C-8, C-9, and C-14 may be omitted if they are oriented 8β, 9α, and 14α.

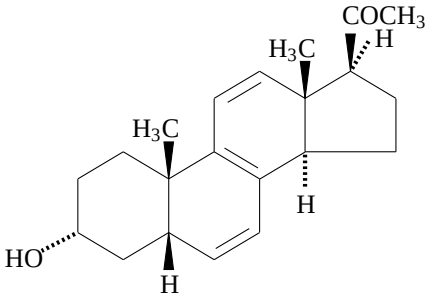
```
\steroid{5U==H;9A==H;{14}A==H;8B==H;%
{10}B==\lmoiety{H$_{3}$C};{13}B==\lmoiety{H$_{3}$C};%
{17}B==R}
\hskip1cm
\steroid{5U==H;{10}B==\null;{13}B==\null;{17}B==R}
```



In order to avoid the overcrowding of substitution, you can use TEX primitive commands such as `\raise` and `\kern`.

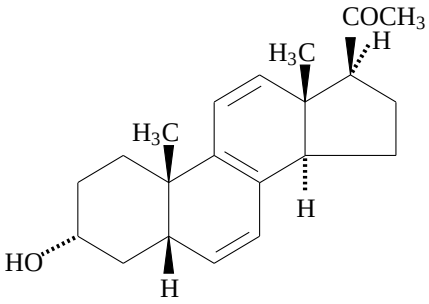
```
\steroid[fhm]{3A==HO;5B==H;{{10}B}==\lmoiety{H$_{3}$C};%
{{13}B}==\lmoiety{H$_{3}$C};%
{{14}A}==H;{{17}B}==\raise.5ex\hbox{COCH$_{3}$};%
{{17}SA}=={\kern.5em\lower1.5ex\hbox{H}}}
```

This command produces:



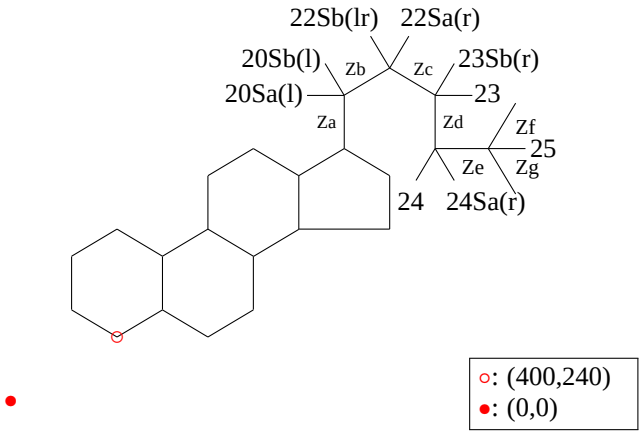
A similar adjustment is also available by using the command `\put` of the LaTeX picture environment. For example, the setting `\put(40,-60){H}` represents a shift of horizontal 4pt and vertical −6pt from the origin located at the terminal of the respective valence bond.

```
\steroid[fhm]{3A==HO;5B==H;{{10}B}==\lmoiety{H$_{3}$C};%
{{13}B}==\lmoiety{H$_{3}$C};%
{{14}A}==H;{{17}B}==\put(0,30){COCH$_{3}$};%
{{17}SA}==\put(40,-60){H}}
```



Chain Parts of Steroids

The macro `\steroidchain` (carom.sty) is to draw a steroid derivative with the side chain. Locant numbers for designating substitution positions and bond descriptors for the side chain are represented by the following diagram of `\steroidchain`:



The handedness for each oriented or double-sided position is shown with a character set in parentheses, where the designation of overcrowded positions is abbreviated.

The option argument ⟨bondlist⟩ is based on the assignment of characters (a–t) to respective bonds as shown in the above diagram and Table 13.2. The locant-numbering of chain carbons is also designated with the ⟨bondlist⟩ in the form of two-character indicators (Za–Zg) as collected in Table 13.4. A bond modifier in the argument ⟨subslist⟩ for n = 1–25 (except fused positions and terminal positions not to be specified, *e.g.*,

Table 13.4. Argument ⟨bondlist⟩ for Chain Carbons (`\steroidchain`)

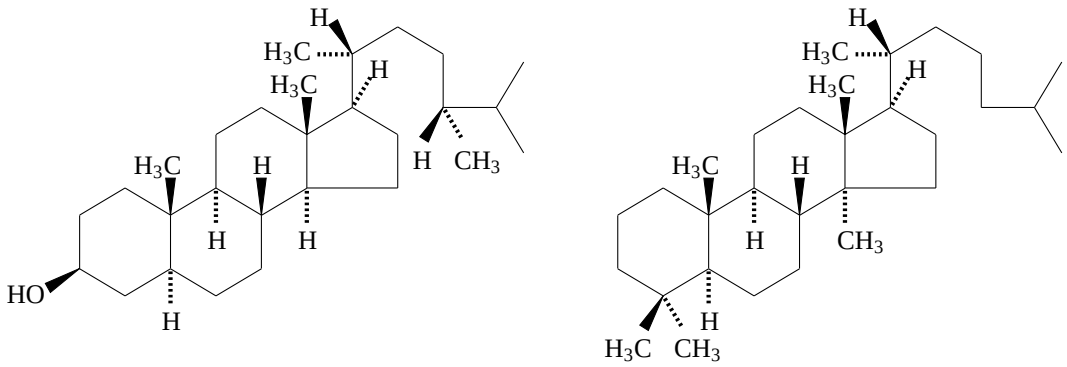
Character	Printed structure	Character	Printed structure
Z	no action		
Za	17,20-double bond	Zb	20,22-double bond
Zc	22,23-double bond	Zd	23,24-double bond
Ze	24,25-double bond	Zf	25,26-double bond
Zg	25,27-double bond		

18) can be one of bond modifiers shown in Table 3.2. On the other hand, a bond modifier in the argument ⟨subslist⟩ for n = 5, 8, 9, 10, 13, 14, or 25 (fused positions etc.) can be selected from bond modifiers shown in Table 13.3.

For example, the `\steroidchain` macro prints (24*R*)-24-methyl-5α-cholestan-3β-ol (campestanol) and 5α-lanostane only by replacing substituents in the argument ⟨subslist⟩. Thus, the statements

```
\steroidchain{3B==HO;5A==H;{{10}B}==\lmoiety{H$_3$C};9A==H;8B==H;%
{{17}SA}==\lower1ex\hbox{ H};{{13}B}==\lmoiety{H$_3$C};{{14}A}==H;%
{{20}SA}==H$_3$C;{{20}SB}==H;{{24}SA}==CH$_3$;{{24}SB}==H}
\steroidchain{4SB==\lmoiety{H$_3$C};4SA==CH$_3$;5A==H;%
{{17}SA}==\lower1ex\hbox{ H};%
{{10}B}==\lmoiety{H$_3$C};9A==H;8B==H;{{13}B}==\lmoiety{H$_3$C};%
{{14}A}==CH$_3$;{{20}SA}==\lmoiety{H$_3$C};{{20}SB}==H}
```

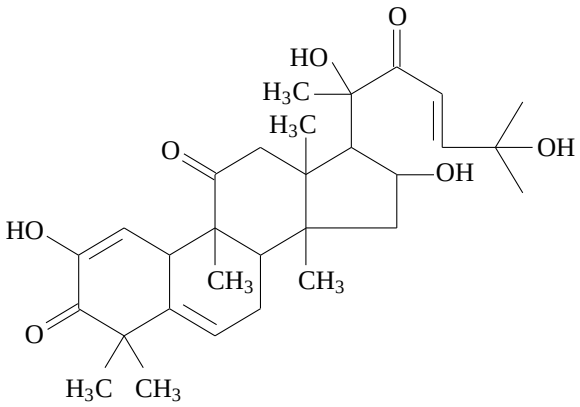
typeset the following structural diagrams:



The following example of drawing cucurbitacin I illustrates the designation of double bonds in the side chain. Thus, a single macro is capable of covering a wide variety of derivatives by altering the description in the arguments ⟨bondlist⟩ and ⟨subslist⟩.

```
\steroidchain[ae{Zd}]{2==HO;3D==O;4Sb==\lmoiety{H$_3$C};4Sa==CH$_3$;%
9Sa==CH$_{3}$;{{11}D}==O;{{13}}==\lmoiety{H$_3$C};%
{{14}}==CH$_3$;{{20}Sa}==\lmoiety{H$_3$C};{{20}Sb}==HO;%
{{16}Sa}==OH;{{22}D}==O;{{25}}==OH}
```

produces

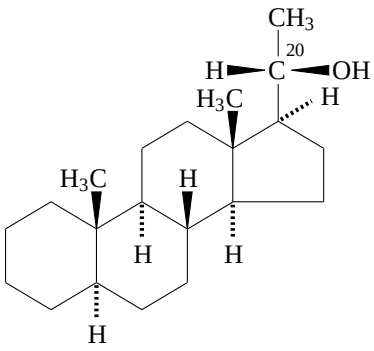


13.2.2 Modes of Basic Derivations

Substitutions

In the pregnane series, the stereochemistry at C-20 was formerly designated by the so-called 20α/20β convention, which is now discouraged in favor of the CIP (Cahn-Ingold-Prelog) priority system.

In the process of applying the 20α/20β convention, the side chain of a pregnane skeleton is placed in agreement with a Fischer projection. Such a Fischer projection can be depicted by an equivalent expression using wedged and bold dashed bonds. To exemplify a 20α substituent, the following formula is depicted by nesting the `\tetrahedral` command in the `\steroid` command, where a (yl) function of XyMTEX is used.

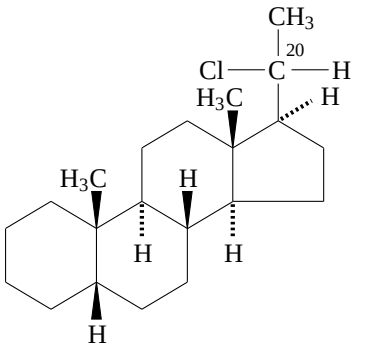


5α-pregnan-20α-ol (formerly)
(20*S*)-5α-pregnan-20-ol

```
\begin{XyMcompd}(1200,1250)(300,150){}{}
\steroid{5A==H;%
{10}B==\lmoiety{H$_{3}$C};8B==H;9A==H;{14}A==H;%
{13}B==\lmoiety{H$_{3}$C};
{17}==\tetrahedral{3==(yl);%
0==C\rlap{\raisebox{5pt}{$^{20}$}};%
2B==H;4B==OH;1==CH$_{3}$};%
{17}GA==H}
\end{XyMcompd}
```

In the above program, the `XyMcompd` environment of the chemist package is used in order to secure an adequate drawing area (the argument `(1200,1250)`) for accommodating the formula to be drawn. The second argument `(300,150)` indicates the *x*- and *y* shift values applied to the drawing area.

For the purpose of the strict adoption of a Fischer projection, the code `2B==H;4B==OH;` should be replaced by the code `2==H;4==OH;` in the main argument of the inner `\tetrahedral` command. To exemplify a 20β substituent in this way, the following formula is depicted:

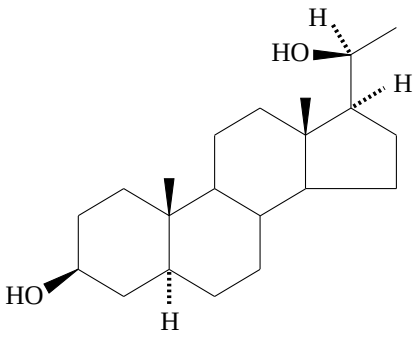


20β-chloro-5β-pregnane (formerly)
(20*R*)-20-chloro-5β-pregnane

```
\steroid{5B==H;%
{10}B==\lmoiety{H$_{3}$C};8B==H;9A==H;{14}A==H;%
{13}B==\lmoiety{H$_{3}$C};
{17}==\tetrahedral{3==(yl);%
0==C\rlap{\raisebox{5pt}{$^{20}$}};%
2==Cl;4==H;1==CH$_{3}$};%
{17}GA==H}
```

Even for the purpose of naming pregnane series, the CIP priority system is now preferred to designate the stereochemistry at C-20, where a Fischer projection is no longer necessary. Moreover, methyl substituents at C-10 and C-13 are frequently expressed by wedged bonds without the explicit specification of CH_3; and hydrogens at C-8, C-9, and C-14 along with their incident bonds are sometimes omitted. However, a hydrogen

at C-5 is always designated by a wedged bond (5β) or a bold dashed bond (5α) (with the specification of the atom H), because the configuration at C-5 is not contained in the name of the basic skeleton *pregnane*.

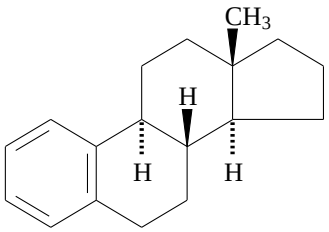


(20*S*)-5α-pregnan-3β,20-diol

```
\steroidethylchain{5A==H;3B==HO;%
{10}B==\null;{13}B==\null;%
{20}Su==HO;{20}Sd==H;{17}GA==H}
```

Unsaturation

To specify double bonds in a steroid skeleton, the optional argument (⟨bondlist⟩) of each command is used. For example, estra-1,3,5(10)-triene is depicted by using the `\steroid` command with the optional argument `[ack]`, where the locant alphabet '`a`' denotes the unsaturation between C-1 and C-2, the locant alphabet '`c`' denotes the unsaturation between C-3 and C-4, and the locant alphabet '`k`' denotes the unsaturation between C-5 and C-10.

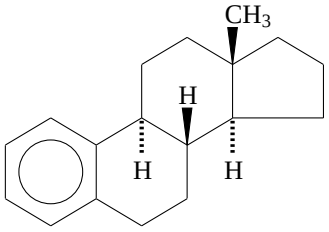


estra-1,3,5(10)-triene

```
\steroid[ack]{8B==H;9A==H;{13}B==CH$_{3}$;%
{14}A==H}
```

Strictly speaking, another set of double bonds can be selected, i.e., 1(10),2,4, to show the aromatization of ring A. According to the IUPAC-IUB nomenclature [1, 3S-2.5], we select 1,3,5(10) by considering that the sequence of locant numbers (containing implicit ones such as 1(2) and 3(4)) is not disturbed as far as possible.

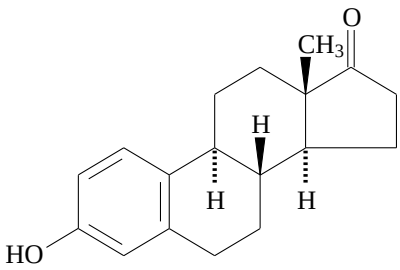
On the contrary to the IUPAC-IUB nomenclature, the ring A of estra-1,3,5(10)-triene exhibits aromatic nature. The explicit expression of aromaticity is available by declaring '`A`' in the ⟨bondlist⟩ as follows:



estra-1,3,5(10)-triene

```
\steroid[A]{8B==H;9A==H;{13}B==CH$_{3}$;%
{14}A==H}
```

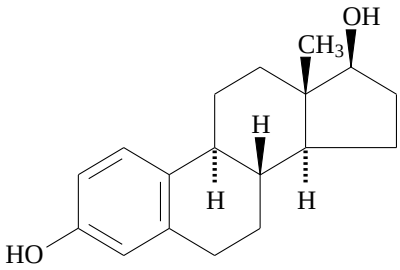
Estrone was isolated from the urine of pregnant women as the first isolated one of estrogens (female sex hormones). The structural formula of estrone is drawn by using the command `\steroid`.



3-hydroxyestra-1,3,5(10)-trien-17-one
estrone

```
\steroid[ack]{3==HO;{17}D==O;%
8B==H;9A==H;{13}B==CH$_{3}$;{14}A==H}
```

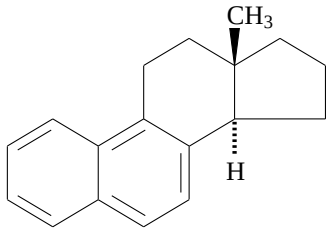
Estradiol, which is a much more potent estrogen than estrone, is drawn by using the command `\steroid` as follows:



estra-1,3,5(10)-triene-3,17β-diol
estradiol

```
\steroid[ack]{3==HO;{17}B==OH;%
8B==H;9A==H;{13}B==CH$_{3}$;{14}A==H}
```

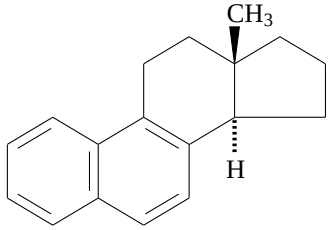
If there is a choice of locants, single ones (e.g., 5,7,9 for the aromatization of ring B) are preferred to compound locants (e.g., 5(10),6,8). For example, the following set of locants generated by the argument `[acegi]`:



estra-1,3,5,7,9-pentaene (preferred)

```
\steroid[acegi]{{13}B==CH$_{3}$;{14}A==H}
```

is preferred to an alternative set of locants for aromatization:

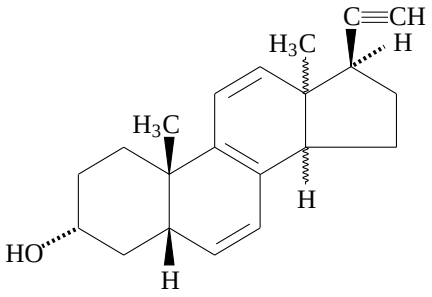


estra-1,3,5(10),6,8-pentaene (not preferred)

```
\steroid[acfHk]{{13}B==CH$_{3}$;{14}A==H}
```

which is generated by the argument `[acfHk]`. Note that the bond indicator `H` puts a double bond inside ring B, while the lowercase indicator `h` puts a double bond inside ring C. On a similar line, the selection of a further set of locants 1(10),2,4,6,8 in not preferred.

The following example illustrates a method for drawing double bonds, where the lowercase indicator `h` in place of the uppercase one puts a double bond inside ring C. It shows also a method for drawing substituents with an undetermined configuration (ξ-bond), where the alphabet `U` in the descriptor `{14}U==H` means an undetermined configuration:

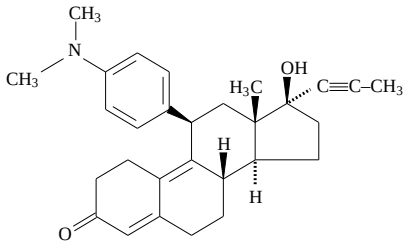


5β,13ξ,14ξ-pregna-6,8,11-trien-20-yn-3α-ol

```
\steroid[fhm]{3A==HO;5B==H;%
{10}B==\lmoiety{H$_{3}$C};%
{13}U==\lmoiety{H$_{3}$C};{14}U==H;%
{17}B=={C\triplebond CH};{17}GA==H}
```

Note that the command `\triplebond` has been defined in the chemist package. The command `\lmoiety` is used to draw a leftward substituent at a site having an implicit rightward substituent.

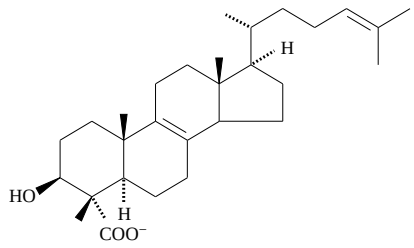
The formula of mifepristone (RU-486), which is a synthetic steroid used as an abortifacient in the first two month of pregnancy, is drawn by using the command `stereoid`.



11β-[4-(dimethylamino)phenyl]-17β-hydroxy-
17α-(1-propynyl)estra-4,9-dien-3-one
(RU-486, mifepristone)

```
\steroid[di]{3D==O;8B==H;%
{11}B==\bzdrv{3==(yl);%
6==\Dtrigonal{0==N;1==CH$_{3}$;%
3==CH$_{3}$;2==(yl)}};%
{13}B==\lmoiety{H$_{3}$C};{14}A==H;%
{17}GA=={C\triplebond C--CH$_{3}$};{17}B==OH}
```

Other commands for drawing steroid skeletons (Table 13.1) are also capable of putting double bonds by using their arguments ⟨bondlist⟩, which are prepared as optional arguments. The following compound is drawn by using `\steroidChain` with the descriptor `h{Ze}` in the optional argument (⟨bondlist⟩). A double bond in the 17-side chain is specified by an alphabet with the letter `Z` (e.g., `{Ze}`).



3β-hydroxy-4β-methyl-5α-cholesta-8,24-diene-4α-carboxylate
or 3β-hydroxy-30-norlanosta-8,24-dien-28-oate

```
\steroidChain[h{Ze}]
{3B==HO;4SB==\null;4SA==COO$^{-}$;
5A==H;{10}B==\null;{13}B==\null;%
{17}GA==H;{20}A==\null}
```

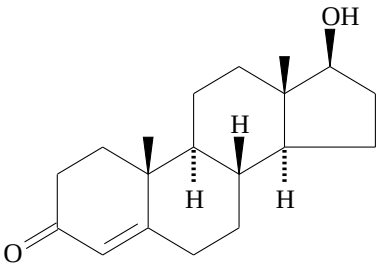
The resulting compound can be named as a derivative of cholestane or as a derivative of lanostane (one of triterpenes). The prefix 30-nor in the latter name means that the 30-methyl (at the C-14 position of the steroid numbering) is deleted from the parent name lanostane. The α- and β-methyl groups at the C-4 of the lanostane skeleton are numbered to be 28 and 29 respectively. The end -28-oate of the name stems from this convention of locant numbering.

13.2.3 Stereochemical Modifications

As for the systematic nomenclature for stereochemical modifications of steroids, see IUPAC-IUB (1989) 3S-5 [1].

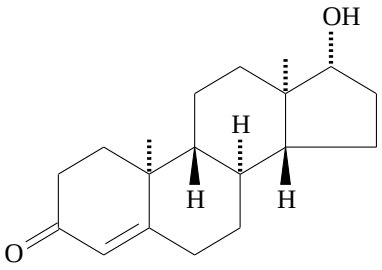
Enantiomers—Use of the Prefix *ent-*

When either steroid derivative of an enantiomeric pair is referred to by using a systematic name (or a trivial name), the other one (its enantiomer) is designated by using the prefix *ent-* (a contracted form of *enantio-*), which means the enantiomeric relationship between the two derivatives at issue. It should be noted that this prefix denotes inversion at all asymmetric centers whether these are cited explicitly or are implied in the name. For example, the descriptor 17β in the name of the latter derivative is in fact inverted into 17α, as found in the corresponding formula. See IUPAC-IUB (1989) 3S-5.1 [1].



17β-hydroxyandrost-4-en-3-one
(testosterone)

```
\steroid[d]{3D==O;8B==H;9A==H;%
{10}B==\null;%
{13}B==\null;{14}A==H;{17}B==OH}
```

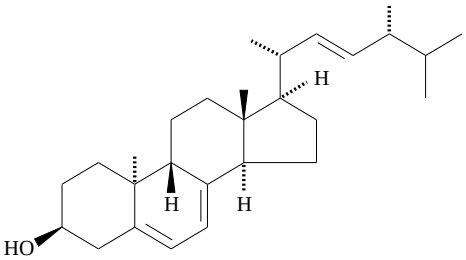


ent-17β-hydroxyandrost-4-en-3-one
(*ent*-testosterone)

```
\steroid[d]{3D==O;8A==H;9B==H;%
{10}A==\null;%
{13}A==\null;{14}B==H;{17}A==OH}
```

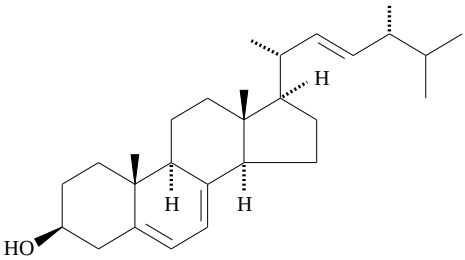
Use of α and β for Inverted Bridgeheads

Suppose that not more than half of the asymmetric centers whose configurations need not be specified in a name of the parent compound are inverted into opposite configurations. Then such inverted centers are specified by using α and β-descriptors. An example (lumisterol) is depicted as follows, which also exemplifies double bond specification at a side chain. Note that 9β and 10α are such inverted asymmetric centers to be specified. See IUPAC-IUB (1989) 3S-5.2 [1]. The trivial name ergosterol is used to refer to the 9α,10β-stereoisomer, which are not explicitly specified in the corresponding systematic name, because the parent name ergosterol implies the configurations of 9α,10β, which are not explicitly specified, as found in the second formula below.




```
\steroidChain[eg{Zc}]%
{3B==HO;9B==H;{10}A==\null;%
{13}B==\null;{14}A==H;{17}GA==H;%
{20}A==\null;{24}A==\null}
```

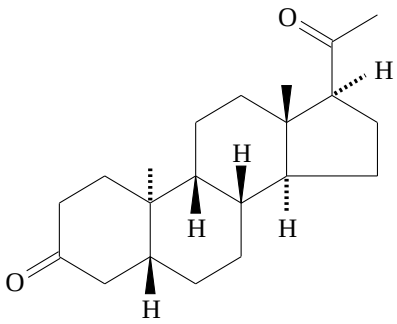
(22*E*)-9β,10α-ergosta-5,7,22-trien-3β-ol
(trivial name: lumisterol)




```
\steroidChain[eg{Zc}]%
{3B==HO;9A==H;{10}B==\null;%
{13}B==\null;{14}A==H;{17}GA==H;%
{20}A==\null;{24}A==\null}
```

(22*E*)-ergosta-5,7,22-trien-3β-ol
(trivial name: ergosterol)

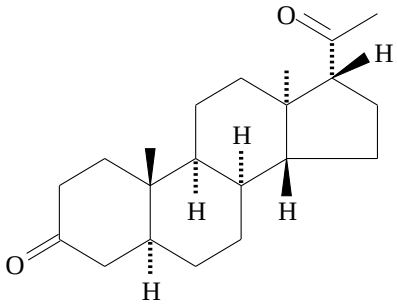
The name of the following derivative is based on 5β-pregnane-3,20-dione, whose bridgeheads (implied by 9α and 10β) are inverted into opposite configuration, as denoted by 9β and 10α. See also IUPAC-IUB (1989) 3S-5.2 [1].



5β,9β,10α-pregnane-3,20-dione

```
\steroidethylchain{3D==O;5B==H;8B==H;%
9B==H;{10}A==\null;{13}B==\null;{14}A==H;%
{17}GA==H;{20}D==O}
```

The enantiomer of the above derivative is named by using the prefix *ent*-. The name based on 5α-pregnane-3,20-dione (in a pair of parentheses) is not suitable because the number of inverted centers is more than half of its asymmetric centers.

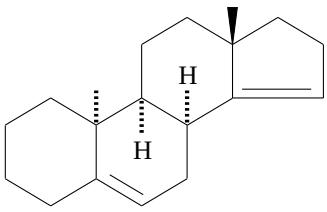


ent-5β,9β,10α-pregnane-3,20-dione
(not 5α,8α,13α,14β,17α-pregnane-3,20-dione)

```
\steroid{3D==O;5A==H;8A==H;%
9A==H;{10}B==\null;{13}A==\null;{14}B==H;%
{17}GB==H;%
{17}A==\trimethylenei[a]{1==O}{2==(yl)}}
```

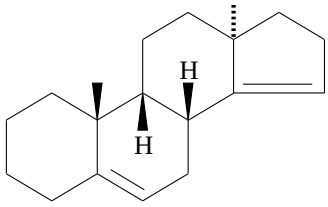
Selection of Starting Structures for Assigning α/β and *ent*-

Suppose that just the half of the asymmetric centers whose configurations need not be specified in a name of the parent compound are inverted into opposite configurations. The youngest sequence selected from the series 8, 9, 10, 13, 14, and 17 is adopted to decide whether the prefix *ent*- is used or not.



8α,10α-androsta-5,14-diene

```
\steroid[eq]{8A==H;9A==H;%
{10}A==\null;{13}B==\null}
```



ent-8α,10α-androsta-5,14-diene
(not 9β,13α-androsta-5,14-diene)

```
\steroid[eq]{8B==H;9B==H;%
{10}B==\null;{13}A==\null}
```

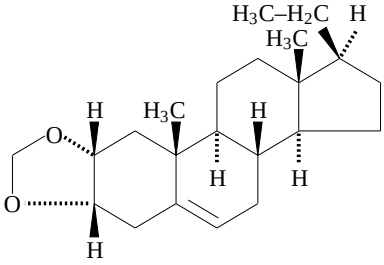
Note that 8α,10α has preference over 9β,13α for the α/β specification of inverted bridgeheads, because 8β, 9α, 10β, and 13β are the implicit configurations of the starting steroid, i.e., androsta-5,14-diene.

13.2.4 Steroids with Additional Rings

The commands listed in Table 13.1 serve as parent skeletons for the addition technique, where their ⟨bondlist⟩ accommodates fusing components.

Steroids with Fused Rings

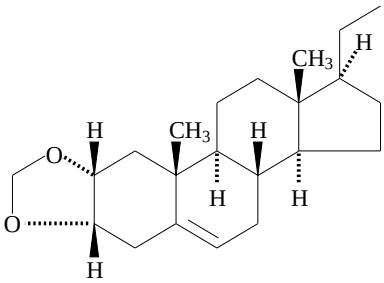
Steroid skeletons listed in Table 13.1 are capable of accommodating fused rings in their ⟨bondlist⟩. For example, 2α,3α-dihydroxyl groups of pregn-5-ene-2α,3α-diol can form a 1,3-dioxolane ring. The resulting 1,3-dioxolane ring can be drawn by using `\fivefusevi` in the ⟨bondlist⟩ of `\steroid`, as shown in the following structure:



2α,3α-(methylenedioxy)pregn-5-ene

```
\steroid[e%
{B{\fivefusevi({aA}{cA}){1==O;4==O}{}{b}}}]%
{2GB==H;3FB==H;%
{10}B==\lmoiety{H$_{3}$C};8B==H;9A==H;{14}A==H;%
{13}B==\lmoiety{H$_{3}$C};
{17}SB==H$_{3}$C--H$_{2}$C;{17}SA==H}
```

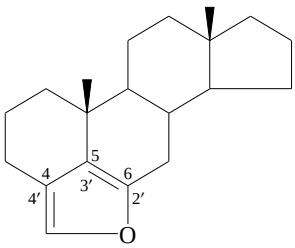
For the nomenclature, see IUPAC-IUB (1989) 3S-10.1 [1]. By using the `\pregnane` command, a simpler program is available as follows:



2α,3α-(methylenedioxy)pregn-5-ene

```
\pregnane[e%
{B{\fivefusevi({aA}{cA}){1==O;4==O}{}{b}}}]%
{2GB==H;3FB==H}
```

Fusion of a furan ring component to a steroid can be named by means of a modification of fusion nomenclature. For a modification of fusion nomenclature to be applied to steroids, see IUPAC-IUB (1989) 3S-10.2 [1]. The following example exemplifies such a fusion as described by the descriptor [4′,3′,2′:4,5,6], where the former three integers indicate the fusion positions of the furan ring, while the latter three indicate those of the steroid skeleton. The latter ascending sequence (i.e., 4,5,6) of the steroid is preferred so as to result in the descending order of the former sequence (i.e., 4′,3′,2′) of the furan ring. The furan ring component is drawn by means of the `\fivefusevi` command, which is incorporated in the optional argument (⟨bondlist⟩) of the `\steroid` command.

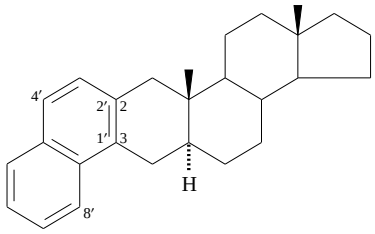


furo[4′,3′,2′:4,5,6]androstane

```
\steroid
[{c{\fivefusevi[ad]{3==O}{}{e}[a]}}]
{{10}B==\null;{13}B==\null}
```

Fusion of a naphthalene ring component to a steroid can be also named by means of a modification of fusion nomenclature. The following example exemplifies such a fusion as described by the descriptor [2′,1′:2,3], which shows that the locant numbers involved in fusion are ordered in accord with those (i.e., 2,3) of the steroid skeleton.

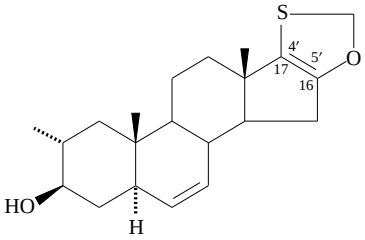
The naphthalene ring component is drawn by means of two `\sixfusev` commands, which are nested by using the optional arguments.



naphtho[2′,1′:2,3]-5α-androstane

```
\begin{XyMcompd}(1600,1100)(-250,-50){}{}
\steroid[{B{\sixfusev[bdf
{D{\sixfusev[ce]{}{}{a}}}]{}{}{b}}}]
{5A==H;{10}B==\null;{13}B==\null}
\end{XyMcompd}
```

The following example shows fusion of a heterocycle (a [1,3]oxathiolo unit) to a steroid skeleton at the bond between the C-16 and the C-17. The fusion of the [1,3]oxathiolo unit is depicted by means of the `\fivefusev` command.

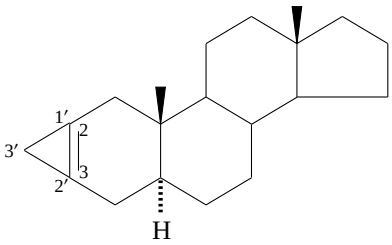


2α-methyl[1,3]oxathiolo[5′,4′:16,17]-5α-androst-6-en-3β-ol

```
\begin{XyMcompd}(1600,1100)(0,100){}{}
\steroid[%
f{s{\fivefusev[e]{2==O;4==S}{}{e}}}]
{2A==\null;3B==HO;5A==H;%
{10}B==\null;{13}B==\null}
\end{XyMcompd}
```

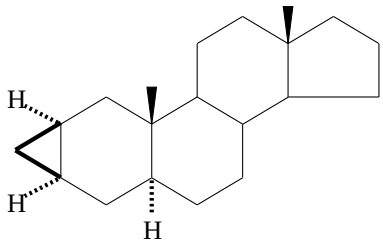
The numbering of the steroid moiety is retained and the atoms of the attached component are identified by primed locants. As found in the descriptor [5′,4′:16,17], the locant numbers involved in fusion are ordered in accord with those (i.e., 16,17) of the steroid skeleton.

The descriptor 3′*H* in the following IUPAC name is an indicated hydrogen to specify the unsaturation of a fused cyclopropene ring. The descriptor [2,3] for designating the fused position is an abbreviation of [1′,2′:2,3].



3′*H*-cyclopropa[2,3]-5α-androstane

```
\steroid[b{b\threefusehi{}{}{b}}]
{5A==H;{10}B==\null;{13}B==\null}
```

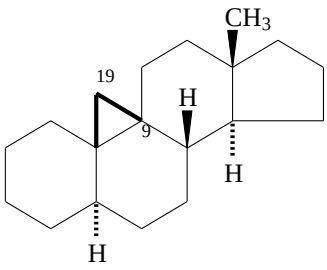


2α,3α-dihydro-3′*H*-cyclopropa[2,3]-5α-androstane

```
\steroid
[{b\threefusehi({aB}{cB}){}{}{b}}]
{5A==H;{10}B==\null;{13}B==\null;%
2A==H;3A==H}
```

Additional Rings Formed within the Steroid Skeleton

A cyclopropane ring fusion is exemplified by the following structure, where the `\threefuseh` command is used as an optional argument (⟨bondlist⟩). The bond identifier `I` (uppercase) is used in place of `i` (lowercase) to assure the correct ring fusion at a bond between 9 and 10. The designator, 9,19-cyclo, in the IUPAC nomenclature (cf. IUPAC-IUB (1989) 3S-2.10 [1]) means that the 19-methyl (at the C-10) is linked to the C-9, forming a cyclopropane ring.

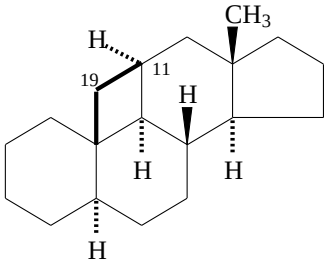


9,19-cyclo-5α,9β-androstane

```
\steroid[{I\threefuseh({bB}{cB}){}{}{a}}]
{5A==H;8B==H;{13}B==CH$_{3}$;{14}A==H}
```

Note that the optional arguments `({bB}{cB})` specify the boldfaced bonds of the fused cyclopropane ring. Because the 19-methyl is linked implicitly through a β-bond to the C-10 of 5α-androstane, the IUPAC name does not contain the designation of the C-10 position. On the other hand, the 5α-androstane implies a 9α-configuration so that 9β is explicitly declared in the resulting IUPAC name.

The linkage between the 19-methyl (at the C-10) and the C-11 results in the formation of a cyclobutane ring. The resulting ring is depicted by using two commands, `\threefuseh` and `\threefusehi`, as shown in the following example.

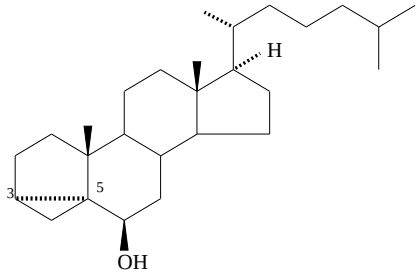


11β,19-cyclo-5α-androstane

```
\steroid[{I\threefuseh({bB}){}{}{a}[c]}%
{l\threefusehi({cB}){}{}{b}[a]}]
{5A==H;8B==H;9A==H;%
{13}B==CH$_{3}$;{14}A==H;{11}A==H}
```

The descriptor "11β,19" means that the configuration of C-19 (the methyl substituent at C-10) is specified implicitly by the parent name, 5α-androstane.

The linkage between the C-3 and the C-5 results in the formation of a cyclopropane ring as well as a cyclopentane ring. The linking bond is drawn by using `\PutDashedBond` for drawing a dashed bold line, which is declared in the ⟨bondlist⟩ of the outer `\steroidChain` command according to the replacement technique, as shown in the following example.



3α,5-cyclo-5α-cholestan-6β-ol

```
\steroidChain[{b\null}%dummy
{b{\PutDashedBond(6,0)(336,0){2pt}%
}}]
{6B==OH;{10}B==\null;{13}B==\null;%
{17}GA==H;{20}A==\null}
```

Note:

1. The command `\PutDashedBond(6,0)(336,0){2pt}` can be used in the PostScript-compatible mode and the PDF-compatible mode as well as the TEX/LATEX mode of the XƎMTEX system. The command is essentially equivalent to the command `\psline` of the PSTricks package, so that it can be replaced as follows if you work in the the PostScript-compatible mode.

```
\steroidChain[{b\null}%dummy
{b{\psline[unit=0.1pt,linewidth=2pt,%
linestyle=dashed,dash=1pt 1.5pt](6,0)(336,0)
}}]
{6B==OH;{10}B==\null;{13}B==\null;%
{17}GA==H;{20}A==\null}
```

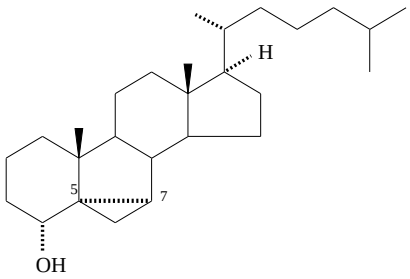
2. On the other hand, the command \PutDashedBond is essentially equivalent to the command \draw of the pgf package, so that it can be replaced as follows if you work in the the PDF-compatible mode.

```
\steroidChain[{b\null}%dummy
{b{\tikz{%
\pgfpathrectangle{\pgfpointorigin}{\pgfpointorigin}
\pgfusepath{use as bounding box}
\draw[dashed,line width=2pt,dash pattern=on 1pt off 1.2pt]%
(.6pt,0) --(33.6pt,0);}
}}]
{6B==OH;{10}B==\null;{13}B==\null;%
{17}GA==H;{20}A==\null}
```

3. Finally, the command \PutDashedBond is essentially equivalent to the command \dottedline of the epic package, so that it can be replaced as follows if you work in the the TEX/LATEX-compatible mode. This setting works well in the PostScript-compatible mode and the PDF-compatible mode.

```
\steroidChain[{b\null}%dummy
{b{\linethickness{2pt}\dottedline{30}(6,0)(336,0)%
}}]
{6B==OH;{10}B==\null;{13}B==\null;%
{17}GA==H;{20}A==\null}
```

The linkage between the C-5 and the C-7 results in the formation of a cyclopropane ring as well as a cyclopentane ring. The linking bond is also drawn by using \PutDashedBond, as shown in the following example.

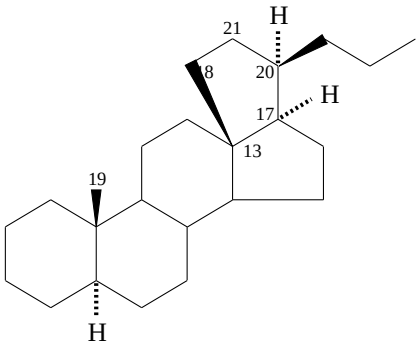


5,7α-cyclo-5α-cholestan-4α-ol

```
\steroidChain[{b\null}%dummy
{d{\PutDashedBond(6,0)(336,0){2pt}}}]%
{4A==OH;{10}B==\null;{13}B==\null;%
{17}GA==H;{20}A==\null}
```

The descriptor “3α,5” or “5,7α” means that the configuration at the C-5 is specified implicitly by the steroid name, so that the locant 5 needs not be attached by α or β. On the other hand, the basic name 5α-cholestan-4α-ol requires 5α.

The following structure is formed by means of a direct link between two carbon atoms of the steroid skeleton (C-18) and the attached side chain (C-21), as found in the descriptor “18,21-cyclo” of the IUPAC name. The bond between the C-13 and the C-18 is drawn by means of the \WedgeAsSubst command.



(20*R*)-18,21-cyclo-5α-cholane

```
\steroid[{T{\sixfusev
{4s==\WedgeAsSubst(0,0)(-1,2){158};
2s==\WedgeAsSubst(0,0)(5,3){171};
2s==\put(171,103){%
\trimethylenei{}{1==(yl)}}%
}{2FA==H}{c}[de]}}]
{5A==H;{10}B==\null;{17}GA==H}
```

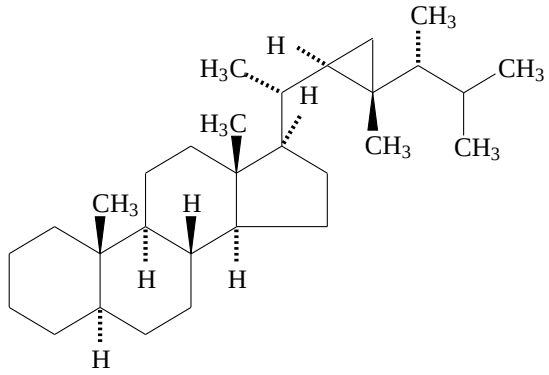
Additional Rings Formed within Side Chains

The formula of gorgostane is drawn by a rather dirty technique, which is based on nested ring fusions by `\sixfusev` and `\threefusehi`. Because the straight-forward function of ring fusion on a 17-side chain is not supported in XyMTEX, the side chain and the fused cyclopropane ring between C-22 and C-23 are drawn by using `\sixfusev` which is combined with `\threefusehi`. The construction of the side chain is represented by the nested scheme 6 (← 3) ← 6. After the following definition of the command `\gorgostane`,

```
\def\gorgostane{%
\begin{XyMcompd}(1950,1350)(260,140){}{}
\steroid[{s{\sixfusev[%
{a{\threefusehi{}{1Sd==H;2Su==CH$_{3}$}{a}}}%
{b{\sixfusev{3==CH$_{3}$}{1A==CH$_{3}$;2==CH$_{3}$}{E}[cd]}}%
]{}{6A==H$_{3}$C}{D}[bc]}}]{5A==H;8B==H;9A==H;{10}B==CH$_{3}$;%
{13}B==\lmoiety{H$_{3}$C};%
{14}A==H;{17}SA==~H}
\end{XyMcompd}}
```

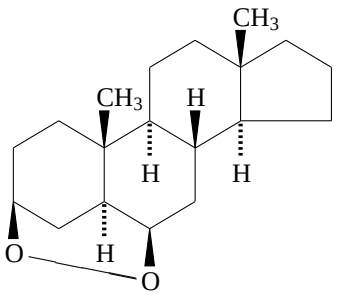
we use `\gorgostane` so that the following formula is obtained:

```
\gorgostane
```



Bridged Steroids

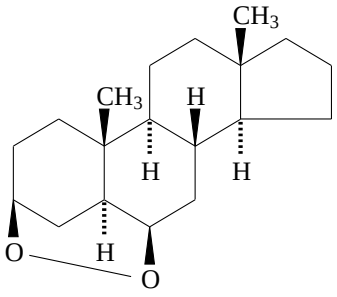
A peroxide bridge between non-adjacent positions of a steroid skeleton cannot be drawn by standard techniques supported by the XyMTEX system. But raw commands of the LaTeX 2ε picture environment can be used in the arguments of XyMTEX commands. The following program involves the command `\put(20,20){\line(5,-1){403}}`, which draws a straight line between two oxygen atoms. For the nomenclature, see IUPAC-IUB (1989) 3S-10.1 [1].



3β,6β-epidioxy-5α-androstane

```
\steroid{5A==H;8B==H;9A==H;{10}B==CH$_{3}$;%
{13}B==CH$_{3}$;{14}A==H;%
3FB==O\put(20,20){\line(5,-1){403}};6B==O}
```

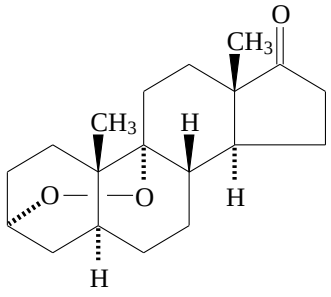
Such a peroxide bridge can be also drawn by means of `\PutBondLine`, which is supported in the three modes of the XyMTEX system, i.e., the PostScript-compatible mode, the PDF-compatible mode, and TEX/LATEX-compatible mode.



3β,6β-epidioxy-5α-androstane

```
\steroid{5A==H;8B==H;9A==H;{10}B==CH$_{3}$;%
{13}B==CH$_{3}$;{14}A==H;%
3FB==O\PutBondLine(20,20)(403,-60){0.4pt};%
6B==O}
```

Drawing a peroxide bridge between the C-3 and the C-9 requires a combined use of `\PutBondLine` and `\PutDashedBond`, where the latter specifies a dashed line for linking between the C-3 and the oxygen atom. Although these commands are used in the argument of `\put` in the following program, the `\put` can be omitted after appropriate adjustment of output positions.

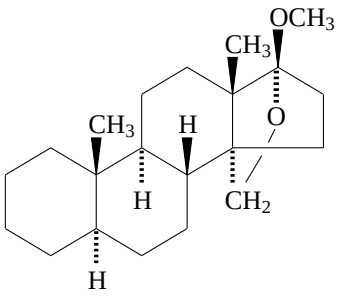


3α,9-epidioxy-5α-androstan-17-one

```
\steroid{5A==H;{10}B==CH$_{3}$;8B==H;%
{13}B==CH$_{3}$;{14}A==H;{17}D==O;%
9A==O\put(0,0){%
\PutBondLine(-80,40)(-178,40){0.4pt}}%
\put(-171,0){%
\PutBondLine(-80,40)(-171,40){0.4pt}}%
\put(-392,40){\makebox(0,0){O}}%
\put(-392,40){%
\PutDashedBond(-40,-30)(-155,-108){2pt}}}
```

As for the name of this derivative, the configuration at C-9 is implicitly determined to be 9α in terms of the name of 5α-androstane. As a result, the locant number 9 without α is contained in the above name.

A epoxymethano (O–CH_2) bridge linking C-17 and C-14 is recognized to form a tetrahydrofuran ring. The bridge is also drawn by a combined use of `\PutBondLine` and `\PutDashedBond`. For example, because the control position after the output of `{14}A==CH$_{2}$` is the end of the CH_2 group, the position `(-100,100)` of the subsequent `\PutBondLine` is located at the upper right position of the C of the CH_2 group, from which the straight line due to the `\PutBondLine` starts, aiming at the `(-40,200)` position.

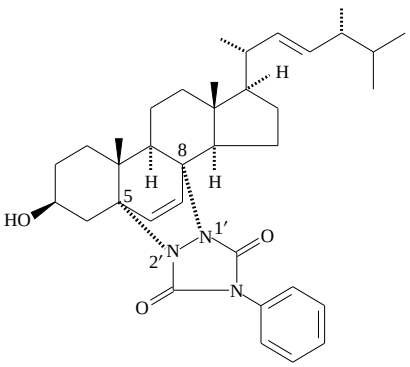


17β-methoxy-17α,14-(epoxymethano)-5α-androstane

```
\steroid{5A==H;{10}B==CH$_{3}$;8B==H;
9A==H;{13}B==CH$_{3}$;%
{14}A==CH$_{2}$%
\PutBondLine(-100,100)(-40,200){0.4pt}%
\PutBondLine(-15,250)(10,300){0.4pt}%
\put(15,350){\makebox(0,0){O}}%
\PutDashedBond(15,400)(15,520){2pt};%
{17}B==OCH$_{3}$}
```

The configuration at C-14 is implicitly determined to be 14α in terms of the name of 5α-androstane so that the resulting name contains the locant number 14 without α.

The following structure shows a Diels-Alder adduct, which can be derived by a cycloaddition between an N=N double bond (at the N-1 and N-2 of 4-phenyl-[1,2,4]triazoline-3,5-dione) and the 5,7-diene moiety (at the C-5 and C-8 terminals of the diene moiety of ergosterol). The descriptor "5,8-[1,2]" indicates the location of the Diels-Alder addition. To specify substitution positions in the Diels-Alder adduct, the locants of the steroid skeleton is denoted by an integer without a prime, while those of the triazolinedione is denoted by an integer with a prime.



(22E)-3β-hydroxy-4′-phenyl-5,8-[1,2]epi[1,2,4]triazolo-5α,8α-ergosta-6,22-diene-3′,5′-dione

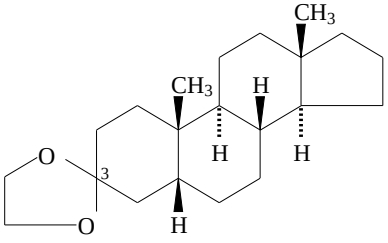
```
\steroidChain[f{Zc}%
{d{\PutDashedBond(0,0)(250,-250){2pt}%
\PutDashedBond(435,-140)(342,200){2pt}%
\put(250,-250){\fiveheterovi%
{1==N;3==N;5==N}%
{5==(yl);2D==O;4D==O;3==\bzdrv{6==(yl)}}}}}]%
{3B==HO;9A==H;%
{10}B==\null;{13}B==\null;{14}A==H;%
{17}GA==H;%
{20}A==\null;{24}A==\null}
```

The "5,8-[1,2]" moiety of the structure is drawn by using `\PutDashedBond` and `\put`, where the inner original point `(0,0)` is located at the C-5 (i.e., the terminal carbon of the double bond denoted by `d`). The width of the dashed lines between 5 and 2′ and between 8 and 1′ are specified by the last argument to be 2pt.

Steroids with Spiro Rings

The macros for drawing steroids in the present status do not support the atomlist functions so that spiro rings attached on the steroid skeleton cannot be directly drawn by using such atomlists. There are three alternative (non-standard) methods for drawing steroid with spiro rings.

The first method is a rather forcible one, where a spiro unit (`\fiveheterovi`) is described in the substlist (the main argument as a substituent list) as follows:



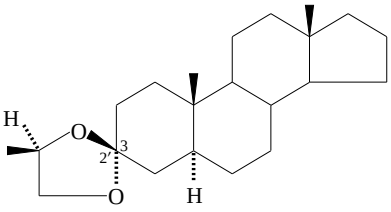
5β-androstane-3-one ethylene acetal

```
\steroid{5B==H;8B==H;9A==H;{10}B==CH$_{3}$;%
{13}B==CH$_{3}$;{14}A==H;%
3F==\raisebox{-80\unitlength}{%
\fiveheterovi{1==O;3==O}{3==(yl)}[ab]};%
3G==}
```

According to the traditional nomenclature, the above compound is named as an acetal (ketal) of 5β-androstane-3-one, which may be reacted with ethylene glycol so as to produce the ethylene acetal.

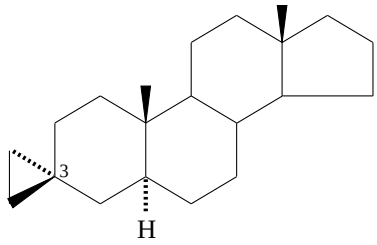
The second method for drawing spiro-steroids is a more plausible one, which uses the optional argument for treating unsaturation. For example, the descriptor `b` (or `B`) for designating a double bond between the

C-2 and C-3 utilizes the x, y-coordinates of the C-3 (or C-2) during the process of setting the double bond. Hence, we can put a spiro ring (due to the `\fiveheterovi` command or `\threeheterovi`) on the C-3 atom by virtue of the descriptor b, as exemplified by the following two structures.



(4′*R*)-4′-methyl-(3*S*)-spiro[5α-androstane-3,2′-[1,3]dioxolane]

```
\steroid[%
{b{\fiveheterovi({bA}){1==O;3==O}%
{2==(yl);5Su==\null;5Sd==H}[a]}}%
{b{\WedgeAsSubst(0,0)(-5,3){120}}}]
{5A==H;{10}B==\null;{13}B==\null}
```

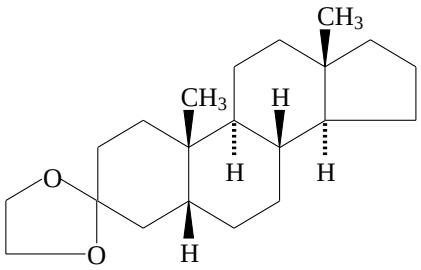


spiro[5α-androstane-3,1′-cyclopropane]
also 3,3-ethylene-5α-androstane

```
\steroid[%
{b{\threeheteroh({cA}){}{1==(yl)}[a]}}%
{b{\WedgeAsSubst(0,0)(-5,-3){168}}}]
{5A==H;{10}B==\null;{13}B==\null}
```

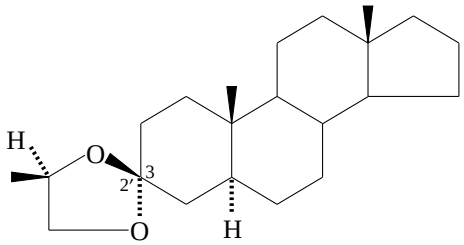
The names of the two compounds shown above are based on the nomenclature for spiro union. For example, the name "spiro[$\cdots$-3,2′-$\cdots$]" means that the position 3 of the first unit (5α-androstane for $\cdots$) is linked the the position 2′ of the second unit ([1,3]dioxolane for $\cdots$).

The third method for drawing spiro-steroids is a more systematic one, i.e., the replacement technique, where the ⟨atomlist⟩ of a spiro ring (e.g., `\fiveheterovi`) is used to put a steroid moiety as substituent, which is generated by by declaring a (yl)-function in the ⟨subslist⟩ of `\steroid`. Thus, the code `2s==\steroid{3==(yl);` in the steroid moiety specifies the joint position of the spiro union, which is represented by "spiro[$\cdots$-3,2′-$\cdots$]" in the IUPAC name.



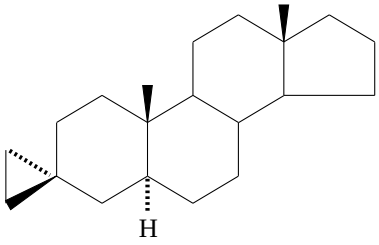
5β-androstane-3-one ethylene acetal

```
\begin{XyMcompd}(1450,1000)(250,300){}{}
\fiveheterovi{1==O;3==O;2s==\steroid%
{3==(yl);5B==H;8B==H;9A==H;{10}B==CH$_{3}$;%
{13}B==CH$_{3}$;{14}A==H}}{}
\end{XyMcompd}
```



(4′*R*)-4′-methyl-(3*S*)-spiro[5α-androstane-3,2′-[1,3]dioxolane]

```
\begin{XyMcompd}(1500,900)(-400,-200){}{}
\fiveheterovi({bA})
[{b{\WedgeAsSubst(0,0)(-5,3){120}}}]
{1==O;3==O;%
2s==\steroid{3==(yl);5A==H;%
{10}B==\null;{13}B==\null}}%
{2==(yl);5Su==\null;5Sd==H}[a]%
\end{XyMcompd}
```



spiro[5α-androstane-3,1′-cyclopropane]
also 3,3-ethylene-5α-androstane

```
\begin{XyMcompd}(1250,800)(300,150){}{}
\threeheteroh({cA})%
{1s==\steroid{3==(yl);5A==H;%
{10}B==\null;{13}B==\null};
1s==\WedgeAsSubst(0,0)(-5,-3){183}}{}[a]%
\end{XyMcompd}
```

13.2.5 Vitamin D_2

Irradiation of ergosterol (and lumisterol) described in Subsection 13.2.3 causes the opening of the B ring to produce previtamin D_2 having a conjugated triene, which is a precursor of vitamin D_2 (ergocalciferol), as shown in Fig. 13.1.

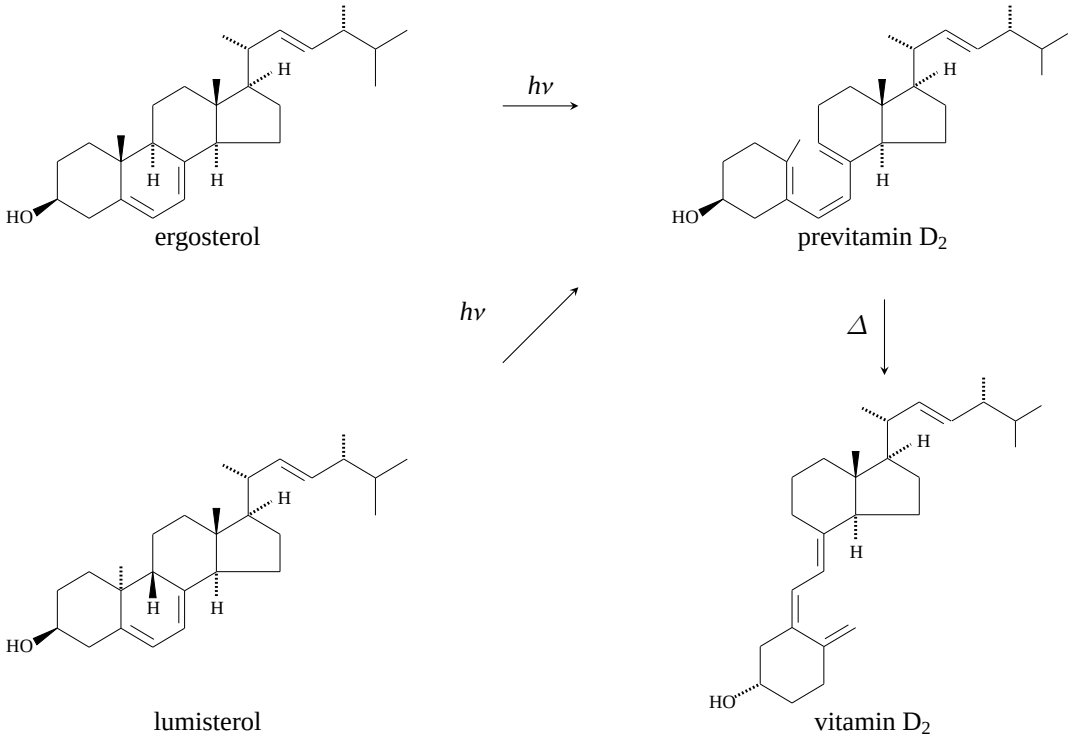


Figure 13.1. Photochemistry of ergosterol and lumisterol

These two photochemical conversions are conrotatory pericyclic processes, which are symmetry-allowed [2, Section 5.1] and proceed smoothly because of no steric hindrance between the 10β methyl and the 9α hydrogen in ergosterol and between the 10α methyl and the 9β hydrogen in lumisterol. On the other hand, the 9β,10β-isomer ((22E)-9β,10β-ergosta-5,7,22-trien-3β-ol) and the 9α,10α-isomer ((22E)-9α,10α-ergosta-5,7,22-trien-3β-ol) do not undergo such ring openings because of steric hindrance, although these conrotatory pericyclic processes are symmetry-allowed. Instead, the 9β,10β-isomer and the 9α,10α-isomer undergo other symmetry-allowed photochemical processes so as to give cyclobutene rings.

To draw the scheme shown in Fig. 13.1, the programs for drawing lumisterol and ergosterol shown in Subsection 13.2.3 are used to define `\lumisterol` and `\ergosterol` as follows:

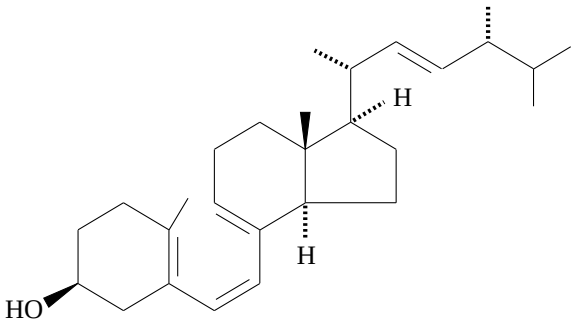
```
\def\lumisterol{%
\begin{XyMcompd}(2050,1150)(0,250){}{}
\steroidChain[eg{Zc}]%
{3B==HO;9B==H;{10}A==\null;%
{13}B==\null;{14}A==H;{17}GA==H;%
{20}A==\null;{24}A==\null}
\end{XyMcompd}
}

\def\ergosterol{%
\begin{XyMcompd}(2050,1150)(0,250){}{}
\steroidChain[eg{Zc}]%
{3B==HO;9A==H;{10}B==\null;%
{13}B==\null;{14}A==H;{17}GA==H;%
{20}A==\null;{24}A==\null}
\end{XyMcompd}
```

```
}
```

The command \previtaminD is defined to draw the intermediate, previtamin D_2. The command consists of a multiple nested fusion, which is schematically represented by $6 \leftarrow 6 \leftarrow 6 \leftarrow 5 \leftarrow 6 \leftarrow 3$. The last step ($\leftarrow 3$) is an application of the replacement technique for drawing a spiro compound.

```
\def\previtaminD{%
\begin{XyMcompd}(2050,1150)(0,250){}{}
\sixheterov[{b{\sixfusev[ace%
{a{\sixfusev[{b{\fivefusevi[{a{\sixfusev[a]{%
2s==\trimethylene{}{1==(yl);2A==\null;3==\null;3W==\null}
}{6A==\null}{D}[bc]}}]{}{1GA==H}{D}}}%
]{}{2FB==\null;3GA==H}{D}}}]{}{}{E}[f]}}]%
{}{2Sb==\null;5B==HO}
\end{XyMcompd}
}
```

Output of \previtaminD without size reduction:

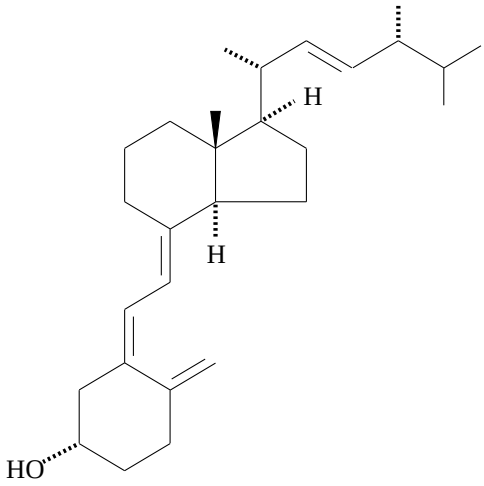


(6*Z*, 22*E*)-(3*S*)-9,10-secoergosta-5(10),6,8,22-tetraen-3-ol
(previtamin D_2)

To draw vitamin D_2 (ergocalciferol), the command \vitaminDii is defined as follows. The command consists of a multiple nested fusion, which is schematically represented by $6 \leftarrow 6 \leftarrow 6 \leftarrow 6 \leftarrow 5 \leftarrow 6 \leftarrow 3$. The last three steps ($6 \leftarrow 5 \leftarrow 6 \leftarrow 3$) are common to the command \previtaminD.

```
\def\vitaminDii{%
\begin{XyMcompd}(1650,1750)(0,250){}{}
\sixheterov[{a{\sixfusev[ce%
{f{\sixfusev[b%
{a{\sixfusev[
{b{\fivefusevi[
{a{\sixfusev[a]{%
2s==\trimethylene{}{1==(yl);2A==\null;3==\null;3W==\null}
}{6A==\null}{D}[bc]}}
]{}{1GA==H}{D}}}
]{}{2FB==\null;3GA==H}{D}
}}
]{}{}{C}[def]}}]{}{}{D}[ab]}}]{}{5A==HO}
\end{XyMcompd}
}
```

Output of \vitaminDii without size reduction:



(5*Z*, 7*E*, 22*E*)-(3*S*)-9,10-secoergosta-5,7,10(19),22-tetraen-3-ol
(vitamin D_2 or ergocalciferol)

Finally, the newly-defined commands are arranged by using the LaTeX 2$_\varepsilon$ `tabular` environment, where the size of each formula is reduced by means of `\scalebox` supported by the graphicx package. The commands `\reactrarrow`, `\reactnearrow`, and `\reactdarrow`, which are defined in the chemist package, are used to draw arrows representing chemical reactions.

```
\begin{tabular}{ccc}
\scalebox{0.7}{\ergosterol} &
\reactrarrow{0pt}{1cm}{$h\nu$}{\strut} & \scalebox{0.7}{\previtaminD} \\
ergosterol & & previtamin D$_{2}$ \\[10pt]
& \reactnearrow{0pt}{1cm}{\raisebox{10pt}{\rlap{$h\nu$}}}{\strut} &
\reactdarrow{0pt}{1cm}{$\Delta$}{\strut}  \\
\scalebox{0.7}{\lumisterol} && \scalebox{0.7}{\vitaminDii} \\
lumisterol & & vitamin D$_{2}$
\end{tabular}
```

The output of this tabulated scheme is shown in Fig. 13.1.

13.3 Parent Structures for Steroids

13.3.1 Fundamental Parent Structures without a 17-Side Chain

A fundamental parent structure for a series of steroids is selected to be nearly full saturated and to contain acyclic hydrocarbon groups that occur in most of the series. Table 13.5 lists the commands for drawing gonanes, estranes, and androstanes, which are most fundamental parent structures without a 17-side chain. They are differentiated according to the presence or absence of methyl groups at C-10 and C-13.

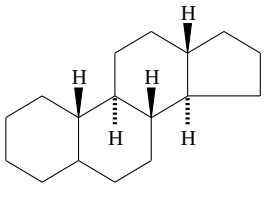
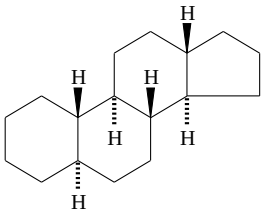
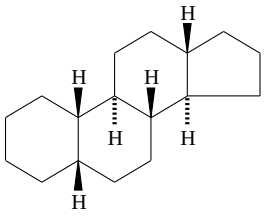
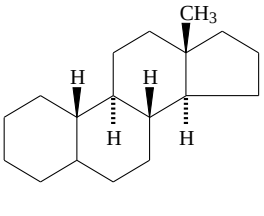
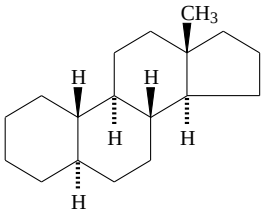
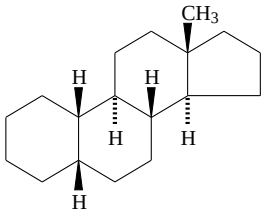
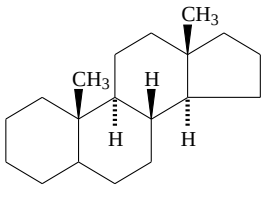
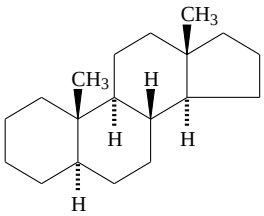
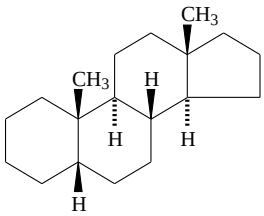
The commands listed in Table 13.5 are XeLaTeX commands of specific use, which have the following formats:

```
\gonane...[⟨bondlist⟩]{⟨subslist⟩}
\estrane...[⟨bondlist⟩]{⟨subslist⟩}
\androstane...[⟨bondlist⟩]{⟨subslist⟩}
```

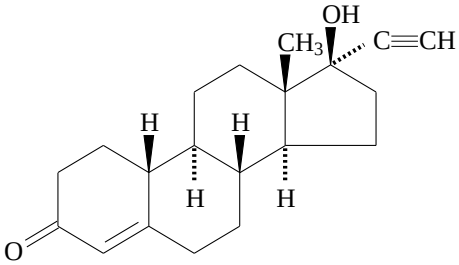
where the symbol `...` of each command name represents no suffix or the suffix `alpha` or `beta`.

Locant numbers (1–17) for designating substitution positions and bond descriptors (locant alphabets a–t) are common to the command `\steroid`. The optional argument ⟨bondlist⟩ is based on the assignment of characters (a–t) to respective bonds as shown in Table 13.2. A bond modifier in the argument ⟨subslist⟩ for n = 1–17 (except fused positions) is selected from the list of bond modifiers (Table 3.2).

Table 13.5. Gonanes, Estranes and Androstanes

5-unspecified	5α series	5β series
		
`\gonane{}`	`\gonanealpha{}` 5α-gonane	`\gonanebeta{}` 5β-gonane
		
`\estrane{}`	`\estranealpha{}` 5α-estrane	`\estranebeta{}` 5β-estrane
		
`\androstane{}`	`\androstanealpha{}` 5α-androstane	`\androstanebeta{}` 5β-androstane

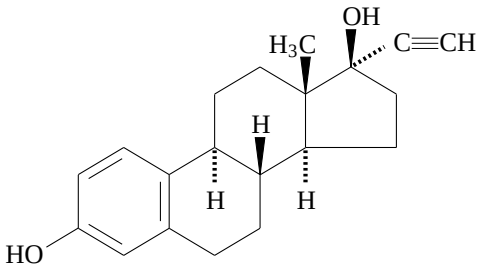
The formula of norethindrone (or norethinsterone), which is used as a component of some combined oral contraceptive pills, is drawn by means of the command `\estrane`.



17α-ethynyl-17β-hydroxyestr-4-en-3-one
norethindrone (or norethinsterone)

```
\begin{XyMcompd}(1700,1100)(0,150){}{}
\estrane[d]{3D==O;{17}B==OH;%
{17}GA=={C\triplebond CH}}
\end{XyMcompd}
```

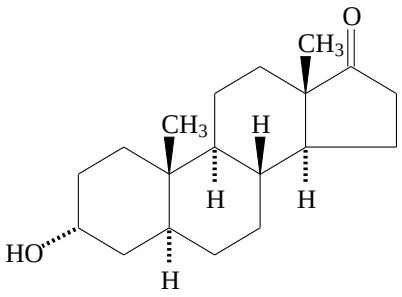
The formula of ethynylestradiol, which is also used as a component of some combined oral contraceptive pills, is drawn by means of the command `\steroid` in place of the command `\estrane`, because the latter command draws the 10β-hydrogen automatically.



17α-ethynylestra-1,3,5(10)-triene-3,17β-diol
ethynylestradiol

```
\begin{XyMcompd}(1700,1100)(0,150){}{}
\steroid[ack]{3==HO;8B==H;9A==H;%
{13}B==\lmoiety{H$_{3}$C};{17}B==OH;%
{14}A==H;{17}GA=={C\triplebond CH}}
\end{XyMcompd}
```

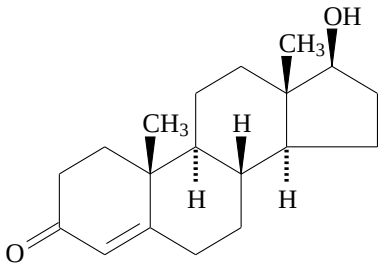
Androsterone is the first isolated androgen (male sex hormone). The structural formula is drawn by the command `\androstanealpha`.



3α-hydroxy-5α-androstan-17-one
androsterone

```
\androstanealpha{3A==HO;{17}D==O}
```

However, testosterone isolated later was found to be a true male sex hormone (androgen), which promotes the development of secondary male characteristics such as the growth of facial and body hair and muscular development. Androsterone is a metabolized form of testosterone so as to be excreted in the urine. The structural formula of testosterone is drawn by using the `\androstane` command as follows:

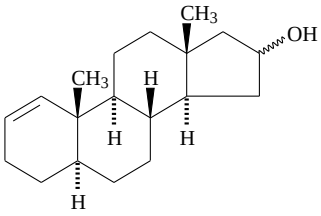


17β-hydroxyandrost-4-en-3-one
testosterone

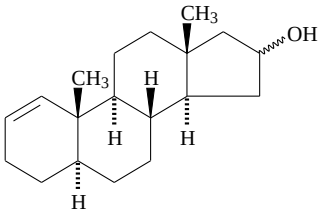
```
\androstane[d]{3D==O;{17}B==OH}
```

An alternative program for drawing testosterone has been described in the preceding chapter (Use of the prefix *ent*-).

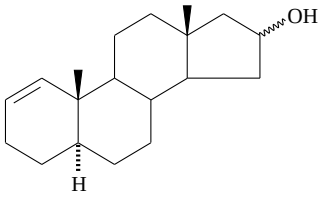
The formula of 5α-androst-1-en-16ξ-ol is drawn in two ways by using `\androstane` (for an unspecified 5-configuration) and `\androstanealpha` (for a 5α-configuration):




```
\androstane[a]{5A==H;
{16}U==OH}
```




```
\androstanealpha[a]
{{16}U==OH}
```

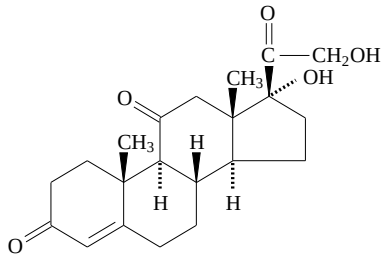



```
\steroid[a]{5A==H;
{10}B==\null;
{13}B==\null;{16}U==OH}
```

5α-androst-1-en-16ξ-ol

The implicit configurations of hydrogens at C-8, C-9, and C-14 are permitted to be omitted. To draw such a simplified formula, we start from the basic command `\steroid` without no modifiers, as exemplified in the last structure.

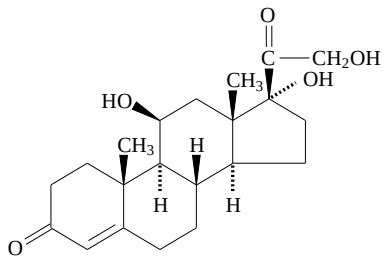
Adrenocortical hormones secreted from the adrenal cortex include steroid derivatives. The adrenocortical steroids are involved in the regulation of biological activities such as the metabolism of carbohydrate, protein, and lipid. The formula of cortisone, which is an adrenocortical hormone, is drawn by using the command `\androstane`.



17α,21-dihydroxypregn-4-ene-3,11,20-trione
cortisone

```
\begin{XyMcompd}(1700,1300)(0,150){}{}
\androstane[d]{3D==O;{11}D==O;%
{17}GA==OH;%
{17}B==\tetrahedral{3==(yl);%
0==C;1D==O;4==CH$_{2}$OH}}
\end{XyMcompd}
```

The formula of cortisol (hydrocortisone), which is an active form of cortisone, is drawn also by using the command `\androstane`.



11β,17α,21-trihydroxypregn-4-ene-3,20-dione
cortisol (hydrocortisone)

```
\begin{XyMcompd}(1700,1300)(0,150){}{}
\androstane[d]{3D==O;{11}B==HO;%
{17}GA==OH;%
{17}B==\tetrahedral{3==(yl);%
0==C;1D==O;4==CH$_{2}$OH}}
\end{XyMcompd}
```

13.3.2 Fundamental Parent Structures with a Short 17-Side Chain

Table 13.6 lists the commands for drawing pregnanes and cholanes, which are fundamental parent structures having a short side chain at the C-17 of the steroid skeleton.

The commands listed in Table 13.6 are XyMTEX commands of specific use, which have the following formats:

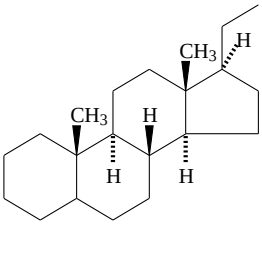
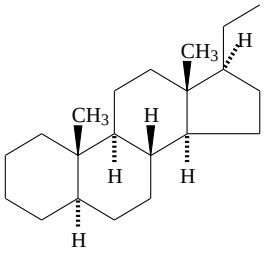
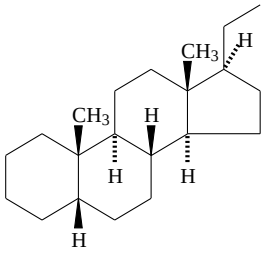
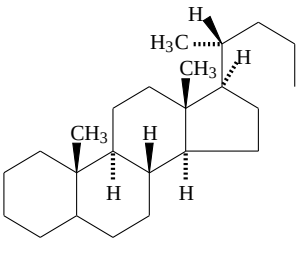
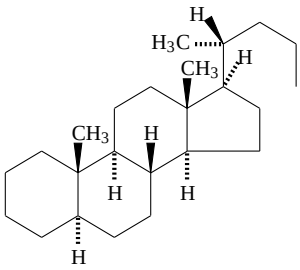
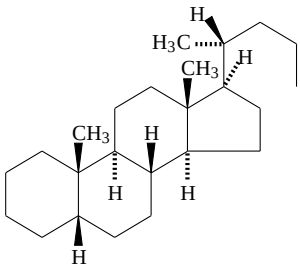
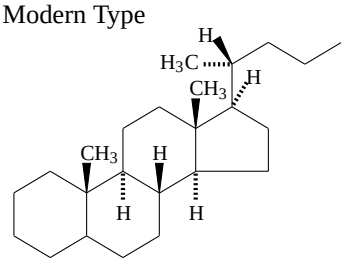
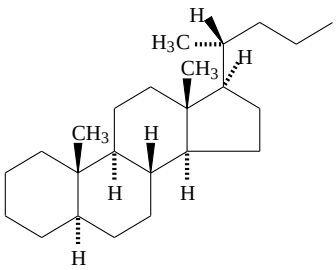
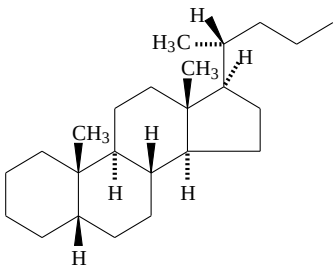
```
\pregnane...[⟨bondlist⟩]{⟨subslist⟩}
\cholanE[⟨bondlist⟩]{⟨subslist⟩}
\cholane...[⟨bondlist⟩]{⟨subslist⟩}
```

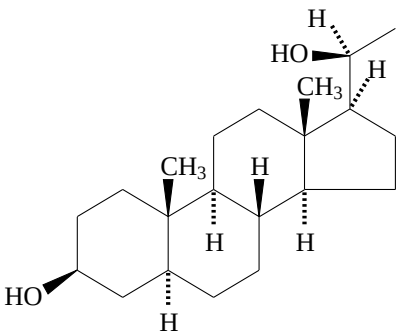
where the symbol `...` of each command name represents no suffix or the suffix `alpha`, `beta`, `Alpha`, or `Beta`.

Locant numbers (1–17) for designating substitution positions and bond descriptors (locant alphabets a–t) are common to the command `\steroid`. The optional argument ⟨bondlist⟩ is based on the assignment of characters (a–t) to respective bonds as shown in Table 13.2. A bond modifier in the argument ⟨subslist⟩ for n = 1–17 (except fused positions) is selected from the list of bond modifiers (Table 3.2).

The following structure can be drawn by using the command `\pregnanealpha` with a filled substlist, where the implicit substituents at 10β, 13β, etc. are printed automatically even if unspecified.

Table 13.6. Pregnanes and Cholanes

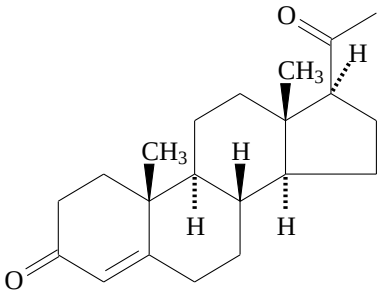
5-unspecified	5α series	5β series
		
`\pregnane{}`	`\pregnanealpha{}` 5α-pregnane	`\pregnanebeta{}` 5β-pregnane
		
`\cholanE{}`	`\cholanealpha{}` 5α-cholane	`\cholanebeta{}` 5β-cholane
Modern Type		
		
`\cholane{}`	`\cholaneAlpha{}` 5α-cholane	`\cholaneBeta{}` 5β-cholane



(20*S*)-5α-pregnan-3β,20-diol

```
\begin{XyMcompd}(1400,1200)(0,150){}{}
\pregnanealpha{3B==HO;{20}Su==HO;{20}Sd==H}
\end{XyMcompd}
```

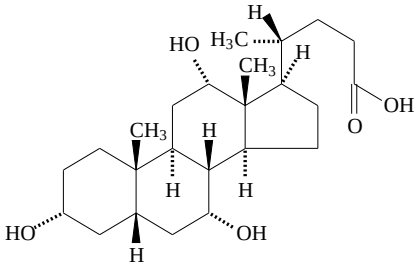
Progesterone, which is an important progestin (pregnancy hormone), is secreted after ovulation occurs to prepare the lining of the uterus for implantation of the fertilized ovum and to complete pregnancy. The formula of progesterone is drawn by using the command `\pregnane`.

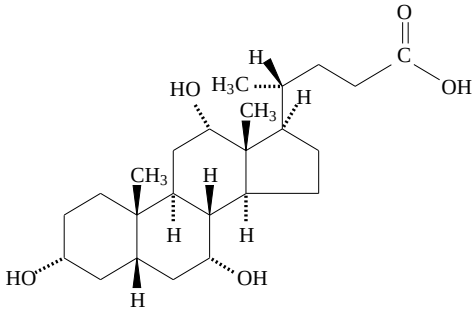


pregn-4-ene-3,20-dione
progesterone

```
\pregnane[d]{3D==O;{20}D==O}
```

The formula of cholic acid, which is a bile acid, is drawn by using the command `\pregnanealpha` or `\pregnaneAlpha`. The latter command should be combined with a dirty technique during placing a COOH group at the terminal position of the side chain.





```
\cholanebeta
{3A==HO;7A==OH;%
{12}Sd==\lmoiety{HO};%
{24}D==O;{24}F==OH}
```

```
\cholaneBeta[{s\null}%
{s{\put(513,303){%
\Dtrigonal{3==(yl);0==C;%
1D==O;2==OH}}}}]
{3A==HO;7A==OH;%
{12}Sd==\lmoiety{HO}}
```

3α,7α,12α-trihydroxy-5β-cholan-24-oic acid
cholic acid

13.3.3 Fundamental Parent Structures with a 17-Side Chain

Chain Folding of Classical Type

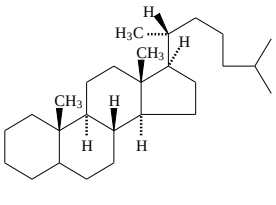
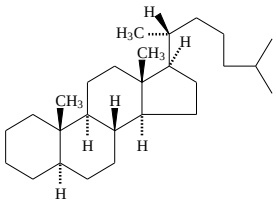
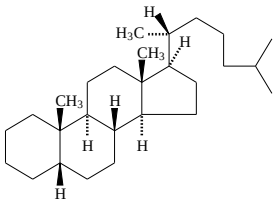
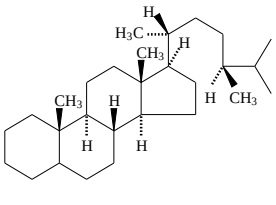
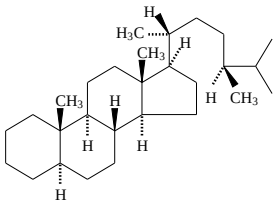
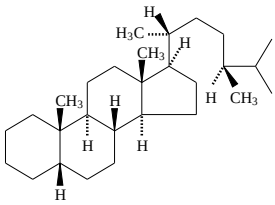
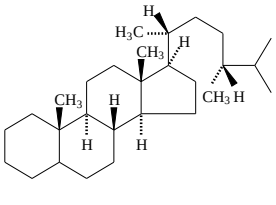
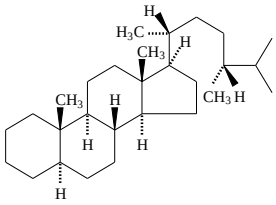
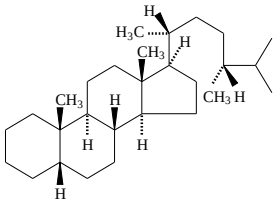
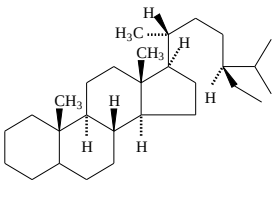
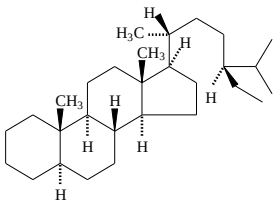
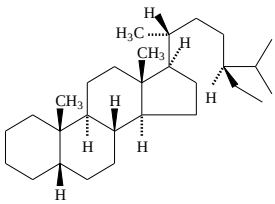
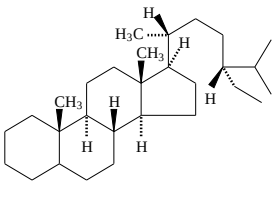
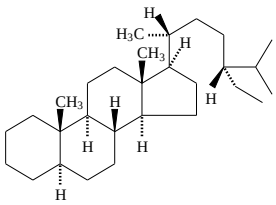
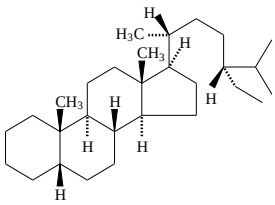
Table 13.7 lists the commands for drawing cholestanes, ergostanes, and campestanes, which are fundamental parent structures having a side chain of classical-type folding at the C-17 of the steroid skeleton. The bond between C-22 and C-23 is suitable for drawing a cisoid double bond.

The commands listed in Table 13.7 are X$_{\!}$MT$_{\!}$EX commands of specific use, which have the following formats:

```
\cholestanE[⟨bondlist⟩]{⟨subslist⟩}
\cholestane...[⟨bondlist⟩]{⟨subslist⟩}
\ergostanE[⟨bondlist⟩]{⟨subslist⟩}
\ergostane...[⟨bondlist⟩]{⟨subslist⟩}
\campestanE[⟨bondlist⟩]{⟨subslist⟩}
\campestane...[⟨bondlist⟩]{⟨subslist⟩}
\poriferastanE[⟨bondlist⟩]{⟨subslist⟩}
\poriferastane...[⟨bondlist⟩]{⟨subslist⟩}
\stigmastanE[⟨bondlist⟩]{⟨subslist⟩}
\stigmastane...[⟨bondlist⟩]{⟨subslist⟩}
```

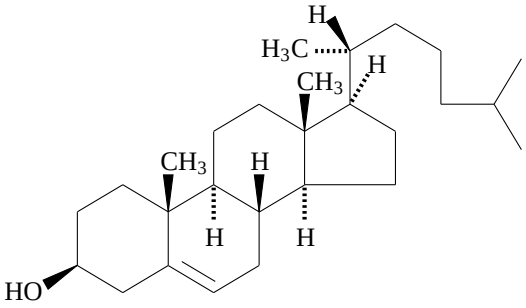
where the symbol `...` of each command name represents the suffix `alpha` or `beta`.

Table 13.7. Cholestanes, Ergostanes, Campestanes, etc. with Chain Folding of Classical Type

5 unspecified	5α series	5β series
		
`\cholestanE{}`	`\cholestanealpha{}` 5α-cholestane	`\cholestanebeta{}` 5β-cholestane
		
`\ergostanE{}`	`\ergostanealpha{}` 5α-ergostane	`\ergostanebeta{}` 5β-ergostane
		
`\campestanE{}`	`\campestanealpha{}` 5α-campestane	`\campestanebeta{}` 5β-campestane
		
`\poriferastanE{}`	`\poriferastanealpha{}` 5α-poriferastane	`\poriferastanebeta{}` 5β-poriferastane
		
`\stigmastanE{}`	`\stigmastanealpha{}` 5α-stigmastane	`\stigmastanebeta{}` 5β-stigmastane

Locant numbers (1–17) for designating substitution positions and bond descriptors (locant alphabets a–t) are common to the command `\steroid`. The optional argument ⟨bondlist⟩ is based on the assignment of characters (a–t) to respective bonds as shown in Table 13.2. A bond modifier in the argument ⟨subslist⟩ for n = 1–17 (except fused positions) is selected from the list of bond modifiers (Table 3.2).

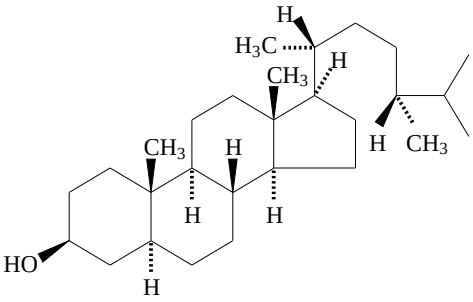
Although cholesterol occurs widely in the body, the full information on its biological functions is not yet obtained. The formula of cholesterol is drawn by using the command `\cholestanE`, which gives a 17-side chain of classical-type folding.



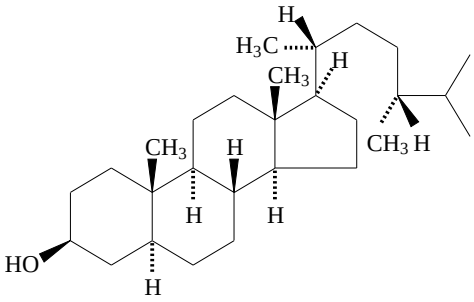
cholest-5-en-3β-ol
(cholesterol)

```
\cholestanE[e]{3B==HO}
```

The formula of campestanol is drawn by `\cholestanealpha` or `\campestanealpha`.



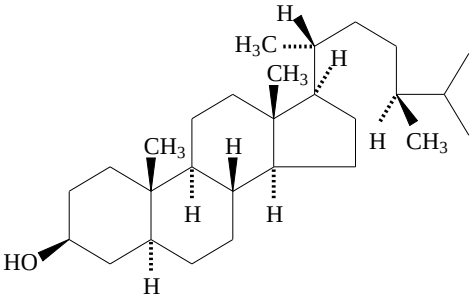
```
\cholestanealpha{3B==HO;%
{24}SA==CH$_{3}$;{24}SB==H}
```



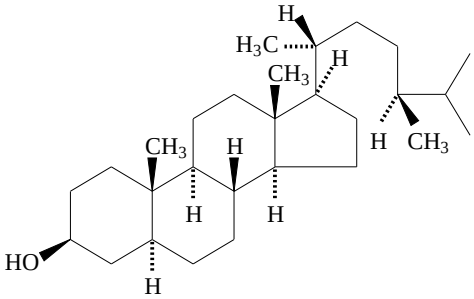
```
\campestanealpha{3B==HO}
```

(24*R*)-24-methyl-5α-cholestan-3β-ol (trivial name: campestanol)

Similarly, two ways for drawing ergostanol are shown as follows:



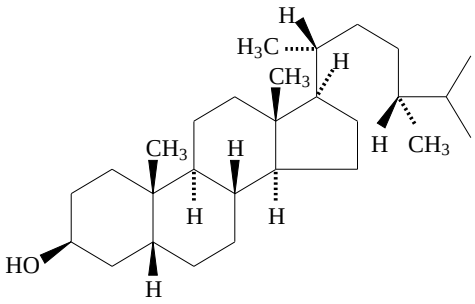
```
\cholestanealpha{3B==HO;%
{24}Su==CH$_{3}$;{24}Sd==H}
```



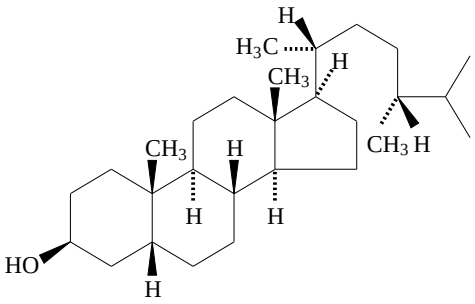
```
\ergostanealpha{3B==HO}
```

(24*S*)-24-methyl-5α-cholestan-3β-ol (trivial name: ergostanol)

The formula of a 5β isomer is drawn by `\cholestanebeta` or `\campestanebeta`.



```
\cholestanebeta{3B==HO;%
{24}SA==CH$_{3}$;{24}SB==H}
```



```
\campestanebeta{3B==HO}
```

(24*R*)-24-methyl-5β-cholestan-3β-ol

Chain Folding of Modern Type

Table 13.8 lists the commands for drawing cholestanes, ergostanes, and campestanes, which are fundamental parent structures having a side chain of modern-type folding at the C-17 of the steroid skeleton.

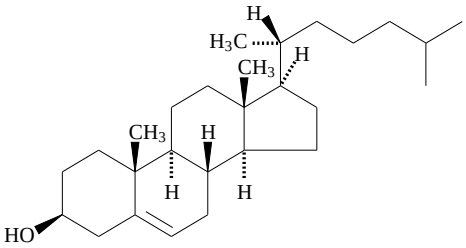
The commands listed in Table 13.8 are X$\mathfrak{y}$MTEX commands of specific use, which have the following formats:

```
\cholestane...[⟨bondlist⟩]{⟨subslist⟩}
\ergostane...[⟨bondlist⟩]{⟨subslist⟩}
\campestane...[⟨bondlist⟩]{⟨subslist⟩}
\poriferastane...[⟨bondlist⟩]{⟨subslist⟩}
\stigmastane...[⟨bondlist⟩]{⟨subslist⟩}
```

where the symbol `...` of each command name represents no suffix or the suffix `Alpha` or `Beta`.

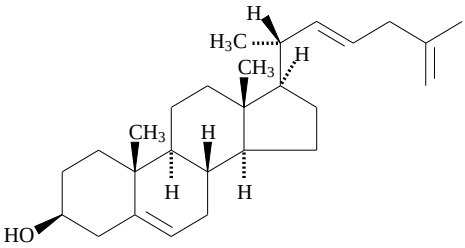
Locant numbers (1–17) for designating substitution positions and bond descriptors (locant alphabets a–t) are common to the command `\steroid`. The optional argument ⟨bondlist⟩ is based on the assignment of characters (a–t) to respective bonds as shown in Table 13.2. A bond modifier in the argument ⟨subslist⟩ for n = 1–17 (except fused positions) is selected from the list of bond modifiers (Table 3.2).

The bond between C-22 and C-23 is suitable for drawing a transoid (22*E*) double bond, as found in the second formula below.



```
\cholestane[e]{3B==HO}
```

cholest-5-en-3β-ol
(cholesterol)

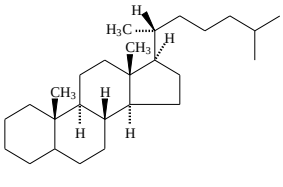
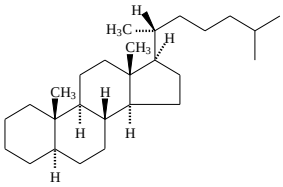
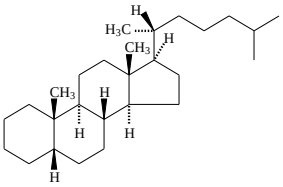
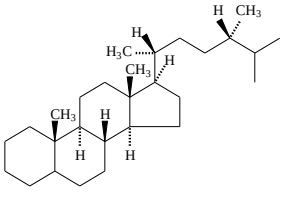
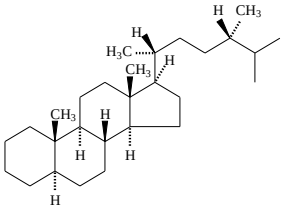
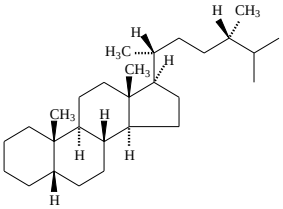
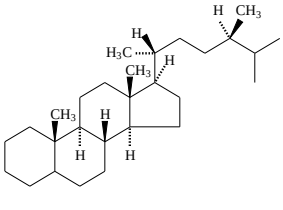
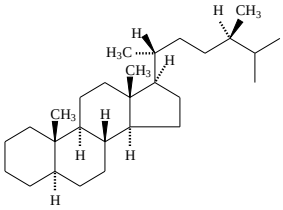
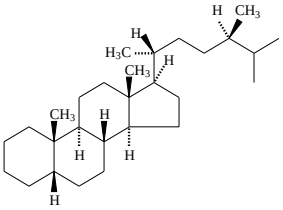
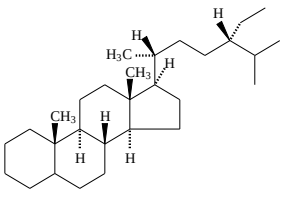
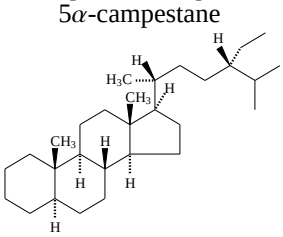
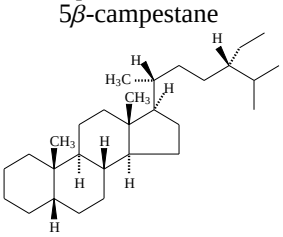
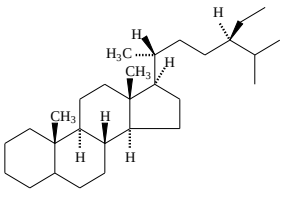
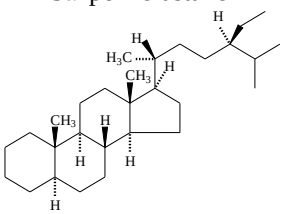
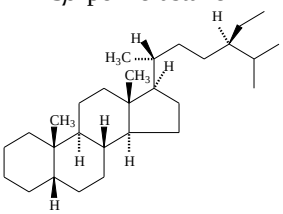


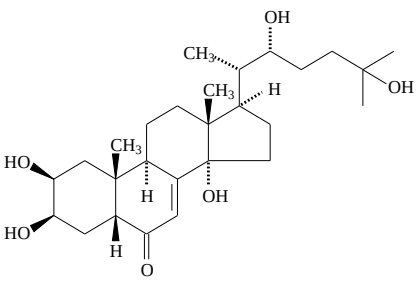
```
\cholestane[e{Zc}{Zg}]{3B==HO}
```

(22*E*)-cholesta-5,22,25-trien-3β-ol

Even if a compound has a systematic name based on cholestane, the command `\steroidChain` is sometimes necessary to complete a correct structure. For example, the following structure of ecdysone shows that the 7-ene is inconsistent with the 8β-hydrogen of the command `\cholestane`, which hence cannot be used for this purpose.

Table 13.8. Cholestanes, Ergostanes, Campestanes, etc. with Chain Folding of Modern Type

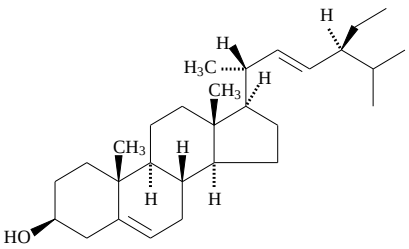
5 unspecified	5α series	5β series
		
`\cholestane{}`	`\cholestaneAlpha{}` 5α-cholestane	`\cholestaneBeta{}` 5β-cholestane
		
`\ergostane{}`	`\ergostaneAlpha{}` 5α-ergostane	`\ergostaneBeta{}` 5β-ergostane
		
`\campestane{}`	`\campestaneAlpha{}` 5α-campestane	`\campestaneBeta{}` 5β-campestane
		
`\poriferastane{}`	`\poriferastaneAlpha{}` 5α-poriferastane	`\poriferastaneBeta{}` 5β-poriferastane
		
`\stigmastane{}`	`\stigmastaneAlpha{}` 5α-stigmastane	`\stigmastaneBeta{}` 5β-stigmastane



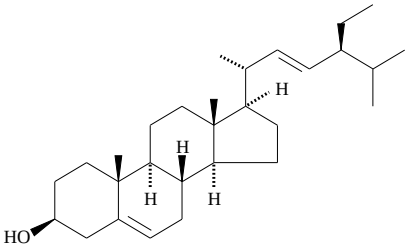
(22*R*)-2β,3β,14,22,25-pentahydroxy-5β-cholest-7-en-6-one ecdysone

```
\steroidChain[g]{%
2B==HO;3B==HO;5B==H;6D==O;
9A==H;{10}B==CH$_{3}$;
{13}B==CH$_{3}$;{14}A==OH;
{17}GA==H;{20}A==CH$_{3}$;
{22}A==OH;{{25}}==OH}
```

Stigmasterol is a plant steroid, which is obtained commercially from soybean oil. The 22*E*-olefinic function requires the command for drawing a 17-side chain of modern-type folding. Its formula is drawn by using the command `\stigmastane` or `\steroidChain`.



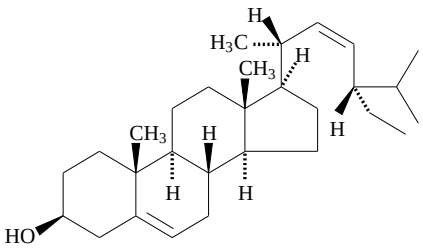
```
\stigmastane[e{Zc}]{3B==HO}
```



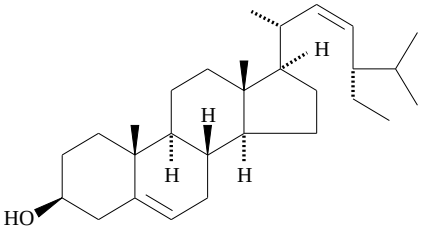
```
\steroidChain[e{Zc}]{3B==HO;8B==H;%
9A==H;{10}B==\null;{13}B==\null;%
{14}A==H;{20}A==\null;%
{17}GA==H;{24}B==%
\dimethylene{}{1==(yl)}}} \\
```

(22*E*)-stigmasta-5,22-dien-3β-ol (stigmasterol)

The 22*Z*-olefinic function requires the command for drawing a 17-side chain of classical-type folding. Two different expressions with and without designating methyl substituents explicitly are depicted as follows. Its formula is drawn by using the command `\stigmastanE` or `\steroidchain`.



```
\stigmastanE[e{Zc}]{3B==HO}
```



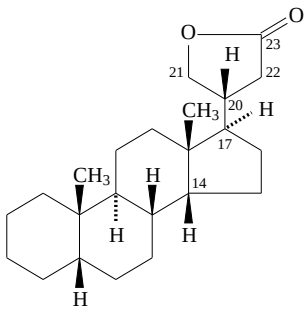
```
\steroidchain[e{Zc}]{3B==HO;%
8B==H;9A==H;%
{10}B==\null;{13}B==\null;%
{14}A==H;{20}A==\null;%
{17}GA==H;{24}A==%
\dimethylenei{}{1==(yl)}}
```

(22*Z*)-stigmasta-5,22-dien-3β-ol

13.4 Steroids with Heterocyclic Substituents

13.4.1 Cardanolides

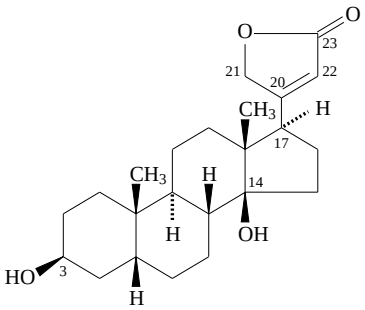
The formula of 5β-cardanolide is drawn by using `\steroid`, where the 14β-configuration and the 20*R*-configuration are implicitly determined in the name. Note that the configuration of C-20 is the same as that of the C-20 of cholesterol, as the locants indicate. The formation of the lactone ring does not suffer the specification of *RS*-stereodescriptors at the C-20. The priority sequence 21(OHH) > 17(CCH) > 22 (CHH) > H for 5β-cardanolide provides an *R*-stereodescriptor just as the counterpart 17(CCH) > 22(CHH) > 21 (HHH) > H for cholesterol provides an *R*-stereodescriptor.



5β-cardanolide

```
\begin{XyMcompd}(1300,1400)(250,150){}{}
\steroid{5B==H;8B==H;9A==H;%
{10}B==CH$_{3}$;{13}B==CH$_{3}$;%
{14}B==H;{17}GA==H;%
{{17}}==\fiveheterov{4==O;%
1s==\WedgeAsSubst(0,0)(0,1){140};%
1s==\put(0,180){H}}{1==(yl);3D==O}}
\end{XyMcompd}
```

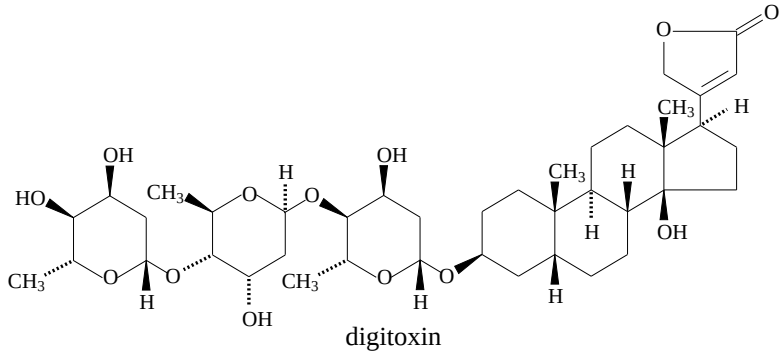
The formula of digitoxigenin, which is a cardiac aglycon isolated by hydrolysis of digitalis, is drawn by using `\steroid`.



3β,14-dihydroxy-5β-card-20(22)-enolide
digitoxigenin

```
\begin{XyMcompd}(1500,1400)(50,150){}{}
\steroid{3B==HO;5B==H;8B==H;9A==H;%
{10}B==CH$_{3}$;{13}B==CH$_{3}$;%
{14}B==OH;{17}GA==H;%
{{17}}==\fiveheterov[a]{4==O}%
{1==(yl);3D==O}}
\end{XyMcompd}
```

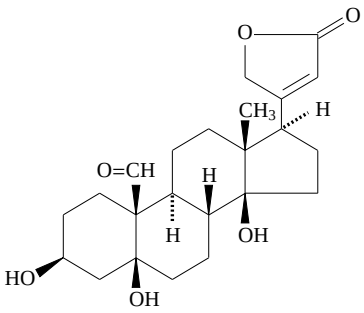
Digitalis contains digitoxigenin in the form of a cardiac glycoside, which is known as digitoxin. The sugar molecules joined in acetal linkages to the 3-OH of digitoxigenin can be drawn by the substitution technique, where three nested `\lyl` commands are accompanied with (yl)-functions, so as to complete the formula of digitoxin as follows:



digitoxin

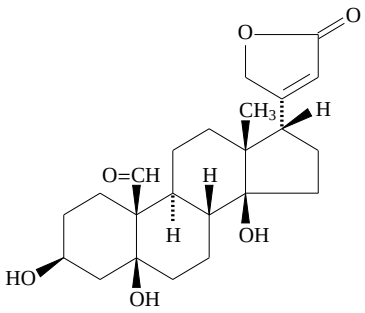
```
\begin{XyMcompd}(3600,1500)(-2000,50){}{}
\steroid{%
3B==\lyl(3==O){3==\sixheterovi{1==O}{2==(yl);2GB==H;4B==OH;6A==CH$_{3}$;%
5B==\lyl(5==O){5==\sixheterov{1==O}{2==(yl);2FA==H;4A==OH;6B==CH$_{3}$;%
5A==\lyl(3==O){3==\sixheterovi{1==O}{2==(yl);2GB==H;%
4B==OH;6A==CH$_{3}$;5B==HO}}%
}}}};%
5B==H;8B==H;9A==H;%
{10}B==CH$_{3}$;{13}B==CH$_{3}$;%
{14}B==OH;{17}GA==H;%
{{17}}==\fiveheterov[a]{4==O}%
{1==(yl);3D==O}}
\end{XyMcompd}
```

The structural formulas of strophanthidin and 17α-strophanthidin are drawn by using `steroid`, where `\put(50,20){\lmoiety{O=CH}}` (in the left formula) or `\lmoiety{O=C\rlap{H}}` is used to adjust the position of the C-10 substituent.




```
\steroid{%
3B==HO;5B==OH;8B==H;9A==H;%
{10}B==\put(50,20){\lmoiety{O=CH}};%
{13}B==CH$_{3}$;%
{14}B==OH;{17}GA==H;%
{{17}}==\fiveheterov[a]{4==O}%
{1==(yl);3D==O}}
```

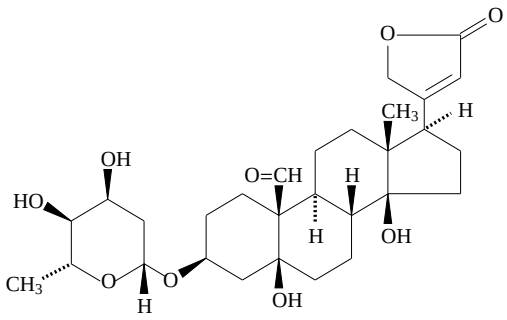
strophanthidin
3β,5,14-trihydroxy-19-oxo-5β-card-20(22)-enolide




```
\steroid{%
3B==HO;5B==OH;8B==H;9A==H;%
{10}B==\lmoiety{O=C\rlap{H}};%
{13}B==CH$_{3}$;%
{14}B==OH;{17}GB==H;%
{17}A==\fiveheterov[a]{4==O}%
{1==(yl);3D==O}}
```

17α-strophanthidin
3β,5,14-trihydroxy-19-oxo-5β,17α-card-20(22)-enolide

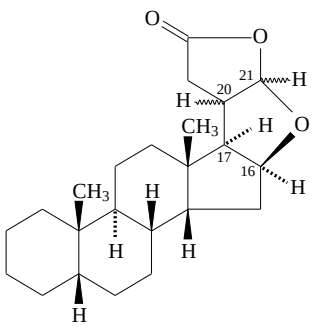
Strophanthidin is the aglycon of corchoroside A, whose formula is drawn by using `steroid`. The sugar molecule joined to the 3-OH of strophanthidin can be drawn by using a nested `\lyl` command so as to complete the formula of corchoroside A as follows:



corchoroside A

```
\begin{XyMcompd}(2200,1400)(-650,150){}{}
\steroid{%
3B==\lyl(3==O){3==\sixheterovi{1==O}{%
2==(yl);
2GB==H;4B==OH;6A==CH$_{3}$;5B==HO}};%
5B==OH;8B==H;9A==H;%
{10}B==\lmoiety{O=C\rlap{H}};%
{13}B==CH$_{3}$;%
{14}B==OH;{17}GA==H;%
{{17}}==\fiveheterov[a]{4==O}%
{1==(yl);3D==O}}
\end{XyMcompd}
```

The oxygen-linkage between C-16 and C-21 of 5β-cardanolide generates another five-membered ring. Although a straight-forward method for drawing such an additional ring is unavailable, the formula can be drawn by means of a dirty technique as follows:



16β,21ξ-epoxy-5β,20ξ-cardanolide

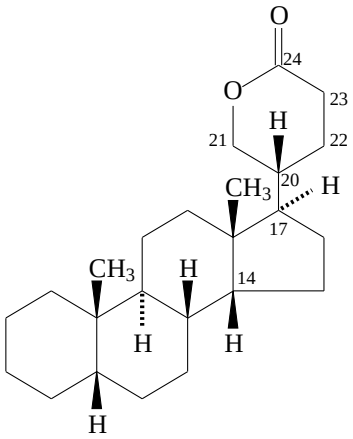
```
\steroid[%
{r{\sixfusev[%
{f{\fivefusev{3==O}{4D==O;2SU==H}{a}}}]
{1s==\PutBondLine(0,0)(150,-150){0.4pt};%
4s==\WedgeAsSubst(0,0)(1,1){150};%
1s==\put(160,-240){O}
}{6SU==H}{d}[abc]}}]
{5B==H;8B==H;9A==H;%
{10}B==CH$_{3}$;{13}B==CH$_{3}$;%
{14}B==H;{17}GA==H;{16}GA==H}
```

Note that the skeletal bonds C-16—C-17—C20—C21 of the furan ring stem from the six-membered ring generated by the command `\sixfusev`, in which the bonds '`a`', '`b`', and '`c`' are deleted by setting the ⟨delbdlist⟩ (`[abc]`). As a result, the bonds '`d`', '`e`', and '`f`' remain to give the skeleton C-16—C-17—C20—

C21 of the furan ring. The other skeletal bonds of the furan ring are drawn by using `\PutBondLine` for a straight-lined bond and `\WedgeAsSubst` for a wedged bond, while the oxygen atom is placed by using `\put`.

13.4.2 Bufanolides

Bufanolides belong to the squill-toad poison group of lactones, where the configurations of 14β and 20R are implied in the name. The lactone moiety can be drawn by the substitution technique, where the command `\sixheterov` with using a (yl)-function is declared in the ⟨subslist⟩ of the command `\steroid`.



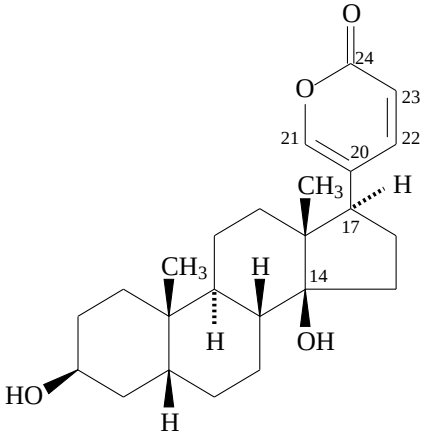
5β-bufanolide

```
\begin{XyMcompd}(1200,1600)(250,150){}{}
\steroid{5B==H;8B==H;9A==H;%
{10}B==CH$_{3}$;{13}B==CH$_{3}$;%
{14}B==H;{17}GA==H;%
{{17}}==\sixheterovi{5==O;%
1s==\WedgeAsSubst(0,0)(0,1){140};%
1s==\put(0,200){\makebox(0,0){H}}%
{1==(yl);4D==O}}
\end{XyMcompd}
```

Note that the β-hydrogen located at the C-20 is drawn by combining the command `\WedgeAsSubst` for drawing the wedged bond with the commands `\put` and `\makebox` for placing the letter H. The latter two commands are supported by the picture environment of the LaTeX system.

Unsaturated derivatives with two double bonds are named by replacing the suffix -adienolide. In the IUPAC name of the following compound (trivial name: bufalin), the configurations of the two hydroxyl groups are differently specified, i.e., 3β-hydroxy (an explicit specification) and 14-hydroxy (an implicit specification in the name “bufadienolide”).

The structure of bufalin (3β,14-dihydroxy-5β-bufa-20,22-dienolide) is drawn by the substitution technique, where the lactone moiety is generated by declaring a (yl)-function in `\sixheterovi`.

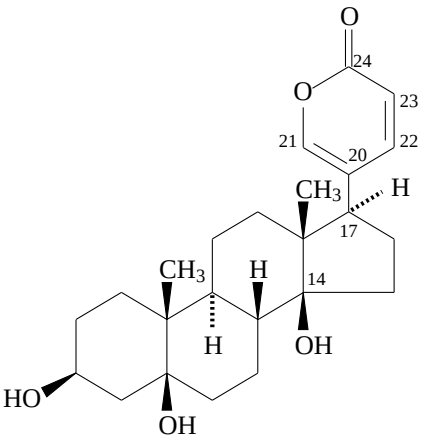


3β,14-dihydroxy-5β-bufa-20,22-dienolide
bufalin

```
\begin{XyMcompd}(1400,1600)(50,150){}{}
\steroid{%
3B==HO;5B==H;8B==H;9A==H;%
{10}B==CH$_{3}$;{13}B==CH$_{3}$;%
{14}B==OH;{17}GA==H;%
{{17}}==\sixheterovi[bf]{5==O}
{1==(yl);4D==O}}
\end{XyMcompd}
```

In the IUPAC name of the following compound (trivial name: telecinobufagin), the configurations of the three hydroxyl groups are differently specified, i.e., 3β-hydroxy (an explicit specification), 5-hydroxy (an indirect specification as shown in 5β-bufadienolide), and 14-hydroxy (an implicit specification in the name “bufadienolide”).

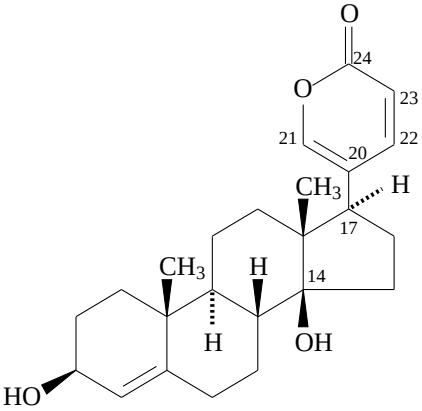
The structure of telecinobufagin (3β,5,14-trihydroxy-5β-bufa-20,22-dienolide) is also drawn by the substitution technique, where the lactone moiety is generated by declaring a (yl)-function in `\sixheterovi`.



3β,5,14-trihydroxy-5β-bufa-20,22-dienolide
telecinobufagin

```
\begin{XyMcompd}(1400,1600)(50,150){}{}
\steroid{%
3B==HO;5B==OH;8B==H;9A==H;%
{10}B==CH$_{3}$;{13}B==CH$_{3}$;%
{14}B==OH;{17}GA==H;%
{{17}}==\sixheterovi[bf]{5==O}
{1==(yl);4D==O}}
\end{XyMcompd}
```

Unsaturated derivatives with three double bonds are named by replacing the suffix -atrienolide. The structure of scillarenin (3β,14-dihydroxybufa-4,20,22-trienolide) is also drawn by the substitution technique, where the lactone moiety generated by declaring a (yl)-function in `\sixheterovi` is placed in the ⟨subslist⟩ of the outer command `\steroid`.



3β,14-dihydroxybufa-4,20,22-trienolide
scillarenin

```
\begin{XyMcompd}(1400,1600)(50,150){}{}
\steroid[d]{%
3B==HO;8B==H;9A==H;%
{10}B==CH$_{3}$;{13}B==CH$_{3}$;%
{14}B==OH;{17}GA==H;%
{{17}}==\sixheterovi[bf]{5==O}
{1==(yl);4D==O}}
\end{XyMcompd}
```

13.5 Steroids with Spiro and Fused Heterocycles

13.5.1 Spirostans

Flat Spiro Rings

In one stereochemical convention, spiro junction in spirostans is expressed by a flat formula (a projection on to the plane of the paper) using a wedged bond and a dashed-line bond. Such flat formulas are supported by the commands listed in Table 13.9.

The commands listed in Table 13.9 are XyMTEX commands of specific use, which have the following formats:

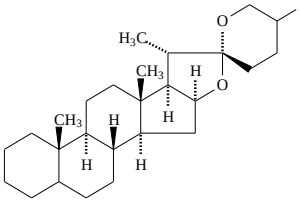
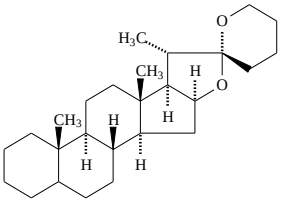
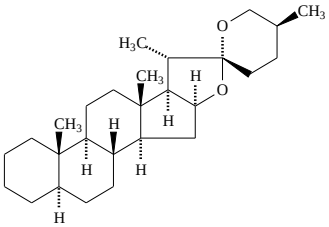
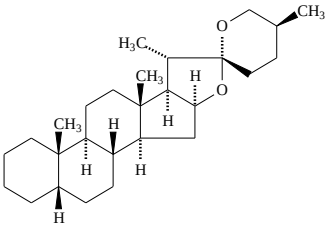
```
\spirostan...[⟨bondlist⟩]{⟨subslist⟩}
```

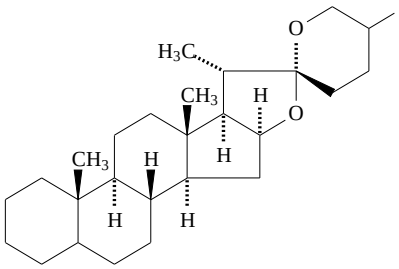
where the symbol `...` of each command name represents no suffix or the suffix `nor`, `alpha`, or `beta`.

Locant numbers (1–17) for designating substitution positions and bond descriptors (locant alphabets a–t) are common to the command `\steroid`. The optional argument ⟨bondlist⟩ is based on the assignment of characters (a–t) to respective bonds as shown in Table 13.2. A bond modifier in the argument ⟨subslist⟩ for n = 1–17 (except fused positions) is selected from the list of bond modifiers (Table 3.2).

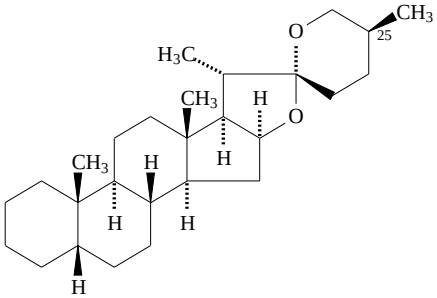
The command `spirostan` is used to draw a spirostan with an unspecified configuration of the 25-methyl group. To draw a 25S-derivative, we overwrite a wedged bond at the C-25 by using the ⟨subslist⟩ of the `\spirostan`.

Table 13.9. Spirostans

5 unspecified	nor
	
`\spirostan{}` a spirostan	`\spirostannor{}` norspirostan
5α series	**5β series**
	
`\spirostanalpha{}` 5α-spirostan	`\spirostanbeta{}` 5β-spirostan

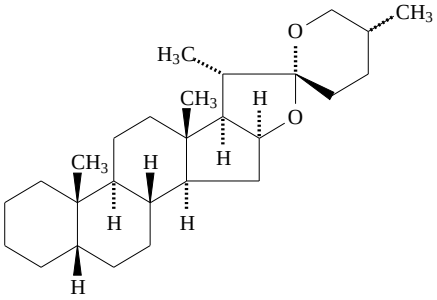


`\spirostan{}`
a spirostan

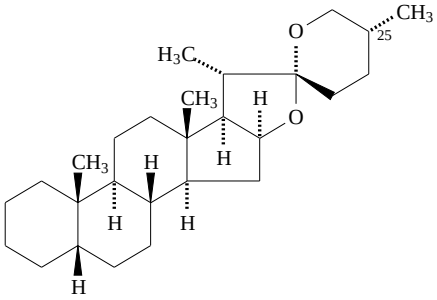


`\spirostan{5B==H;{25}B==CH$_{3}$}`
(25*S*)-5β-spirostan

For the purpose of drawing a 25*R*-derivative, the overwriting method using `\spirostan` gives an insufficient result, as shown in the first formula below. Instead, we use the command `\spirostannor` to obtain a more acceptable formula, as shown in the second formula below.

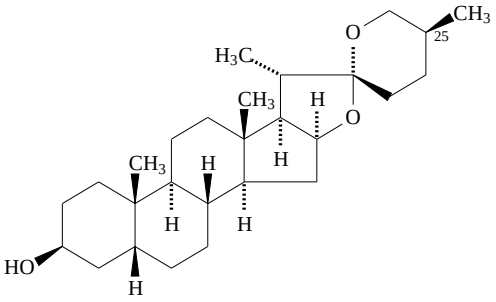


`\spirostan{5B==H;{25}A==CH$_{3}$}`
(25*R*)-5β-spirostan (insufficient)



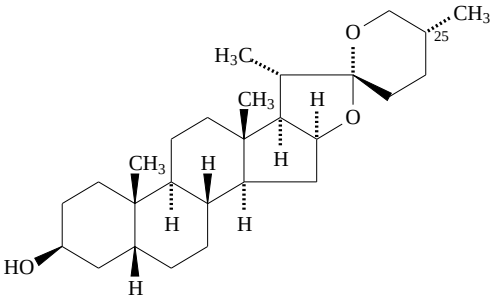
`\spirostannor{5B==H;{25}A==CH$_{3}$}`
(25*R*)-5β-spirostan

Epimerization at the C-25 results in the formation of 25*S* and 25*R* stereoisomers of 5β-spirostan-3β-ol. They are differentiated by the prefixes 25*S* and 25*R*, as follows:




```
\spirostannor{3B==HO;5B==H;
{25}B==CH$_{3}$}
```

(25*S*)-5β-spirostan-3β-ol
sarsasapogenin

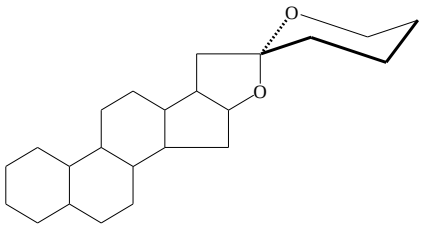



```
\spirostannor{3B==HO;5B==H;
{25}A==CH$_{3}$}
```

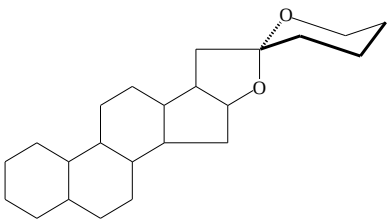
(25*R*)-5β-spirostan-3β-ol

Chair-Form Spiro Rings

In another stereochemical convention, the spiro pyran ring is expressed as a chair form, which is perpendicular to the plane paper. To draw such an expression, we apply the replacement technique to the command `\pyranoseChairi` after declaring a (yl)-function as follows.



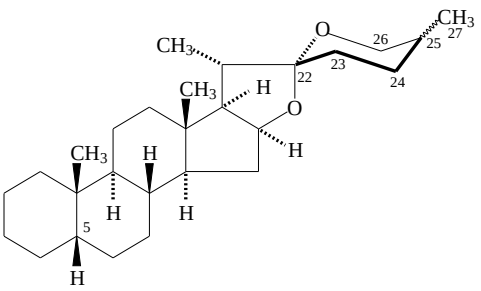

```
\steroid[%
{s{\fivefusev{2==O;%
3s==\pyranoseChairi{1==(yl)}}{}{e}%
}}]{}
```




```
\steroid[%
{s{\fivefusev{2==O;%
3s==\mbox{\changeunitlength{0.08pt}%
\pyranoseChairi{1==(yl)}}}{}{e}%
}}]{}
```

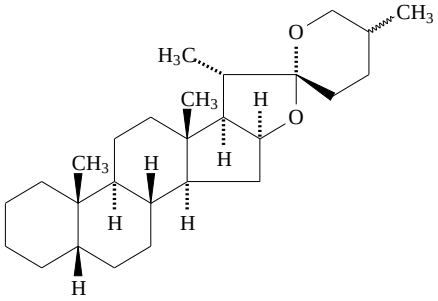
The size of the pyran ring can be reduced by using `\changeunitlength`, as exemplified by the second formula depicted above. It is safe to use the command `\mbox`, so that the change of a unit length by `\changeunitlength` is limited to the argument of `\mbox`.

Because the name spirostan specifies the configurations shown for all the asymmetric centers except positions 5 and 25, the prefix 5α- and 5β is added to specify the configuration of the C-5 according to steroid convention, while 25*R* or 25*S* is added to specify the configuration of C-25 according to the sequence-rule procedure. The following formulas illustrate two different expressions of (25ξ)-5β-spirostan, where the configuration of C-25 is not determined, as shown by a wavy line in each expression and by the prefix 25ξ in the name.



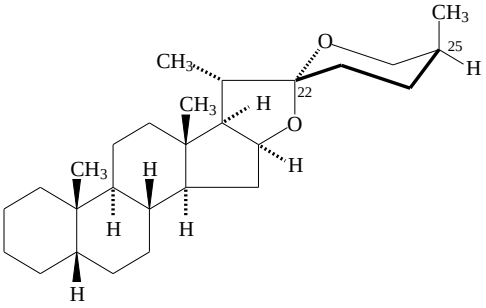
```
\steroid[%
{s{\fivefusev{2==O;%
3s==\mbox{\changeunitlength{0.07pt}%
\pyranoseChairi{1==(yl);%
4U=={\normalsize CH$_{3}$}}}}
{4A==CH$_{3}$}{e}%
}}]{5B==H;{10}B==CH$_{3}$;
8B==H;9A==H;{13}B==CH$_{3}$;
{14}A==H;{17}GA==H;{16}GA==H}
```

(25ξ)-5β-spirostan



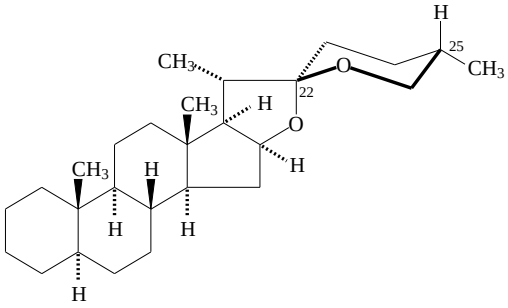
```
\spirostannor{5B==H;{25}U==CH$_{3}$}
```

A fixed configuration at the C-25 atom of the spirostan skeleton is depicted as follows by using the ⟨subslist⟩ of the command `\pyranoseChairi` or `\pyranoseChairii`, which is defined in a similar way to the command `chairi` for drawing chair-form derivatives of cyclohexane.



```
\steroid[%
{s{\fivefusev{2==O;%
3s==\mbox{\changeunitlength{0.08pt}%
\pyranoseChairi{1==(yl);%
4Sa=={\normalsize CH$_{3}$};%
4Se=={\normalsize H}}}}%
{4A==CH$_{3}$}{e}%
}}]{5B==H;{10}B==CH$_{3}$;
8B==H;9A==H;{13}B==CH$_{3}$;
{14}A==H;{17}GA==H;{16}GA==H}
```

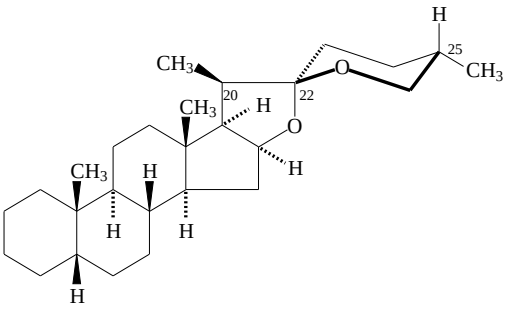
(25S)-5β-spirostan



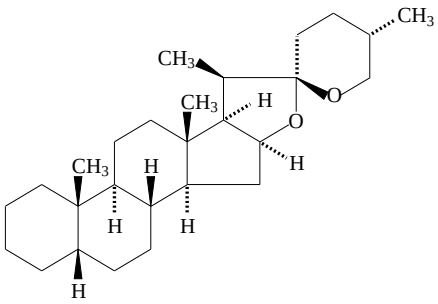
```
\steroid[%
{s{\fivefusev{2==O;%
3s==\mbox{\changeunitlength{0.08pt}%
\pyranoseChairii{1==(yl);%
4Se=={\normalsize CH$_{3}$};%
4Sa=={\normalsize H}}}}%
{4A==CH$_{3}$}{e}%
}}]{5A==H;{10}B==CH$_{3}$;
8B==H;9A==H;{13}B==CH$_{3}$;
{14}A==H;{17}GA==H;{16}GA==H}
```

(22R, 25S)-5α-spirostan

The following formulas of cyclopseudoneogenin (flat and chair-form types) show a stereoisomer of (22R, 25S)-5α-spirostan depicted above, where the configurations of C-5 and C-20 are inverted. The prefix (20R, 22S, 25S) of the systematic name contains the specification of the configuration at the C-20, which is different from the implicit configuration of the name spirostan.



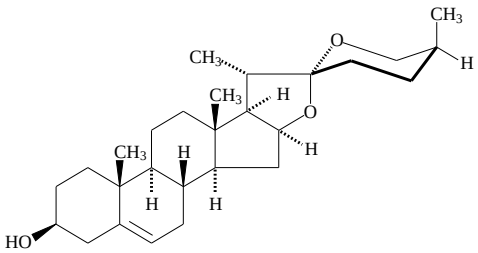
```
\steroid[%
{s{\fivefusev{2==O;%
3s==\mbox{\changeunitlength{0.08pt}%
\pyranoseChairii{1==(yl);%
4Se=={\normalsize CH$_{3}$};%
4Sa=={\normalsize H}}}}%
{4B==CH$_{3}$}{e}%
}}]{5B==H;{10}B==CH$_{3}$;
8B==H;9A==H;{13}B==CH$_{3}$;
{14}A==H;{17}GA==H;{16}GA==H}
```



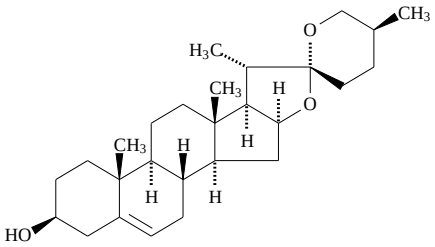
```
\steroid[%
{s{\fivefusev{2==O;%
3s==\sixheterovi({eA}){%
1==O;
6s==\WedgeAsSubst(0,0)(5,-3){140}%
}{6==(yl);3A==CH$_{3}$}
}{4B==CH$_{3}$}{e}}}]
{5B==H;8B==H;9A==H;%
{10}B==CH$_{3}$;%
{13}B==CH$_{3}$;{14}A==H;
{17}GA==H;{16}GA==H}
```

(20*R*, 22*S*, 25*S*)-5β-spirostan (trivial name: cyclopseudoneogenin)

Yamogenin ((25*S*)-spirost-5-en-3β-ol), an aglycon of a saponin extracted from yams (Yamanoimo), is shown below, where structural formulas of two types for yamogenin are drawn.



```
\steroid[e%
{s{\fivefusev{2==O;%
3s==\mbox{\changeunitlength{0.08pt}%
\pyranoseChairi{1==(yl);%
4Sa=={\normalsize CH$_{3}$};%
4Se=={\normalsize H}}}}%
{4A==CH$_{3}$}{e}%
}}]{3B==HO;{10}B==CH$_{3}$;
8B==H;9A==H;{13}B==CH$_{3}$;
{14}A==H;{17}GA==H;{16}GA==H}
```

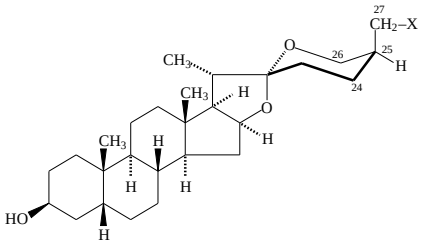


```
\spirostannor[e]{3B==HO;%
{25}B==CH$_{3}$}
```

(25*S*)-spirost-5-en-3β-ol (trivial name: yamogenin)

Formulas of two types for diosgenin ((25*R*)-spirost-5-en-3β-ol), which is the C-25 epimer of yamogenin, can be drawn similarly by exchanging `4Sa` and `4Sb` in the first program and by placing `{25}A==CH$_{3}$` in place of `{25}B==CH$_{3}$` of the second program.

RS-Stereodescriptors for configurations at the C-25 of spirostans are influenced by substituents around the C-25 atoms, even if the carbon skeletons around the C-25 are unchanged to give fixed configurations. The following three compounds are typical examples, where their *RS*-stereodescriptors varies in accord with the priority sequences, although their configurations at the C-25 are chemically unchanged.



X = H: 25*S*
26(OHH) > 24(CHH) > 27(HHH) > H
(25*S*)-5β-spirostan-3β-ol (sarsasapogenin)

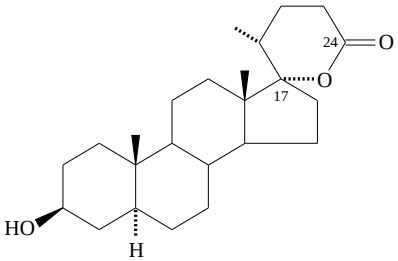
X = OH: 25*R*
26(O(C)HH) > 27(O(H)HH) > 24(CHH) > H
(25*R*)-5β-spirostan-3β,27-diol

X = Br: 25*S*
27(BrHH) > 26(OHH) > 24(CHH) > H
(25*S*)-27-bromo-5β-spirostan-3β-ol

```
\steroid[%
{s{\fivefusev{2==O;%
3s==\mbox{\changeunitlength{0.08pt}\pyranoseChairi{1==(yl);%
4Sa=={\normalsize CH$_{2}$--X};%
4Se=={\normalsize H}}}}{4A==CH$_{3}$}{e}%
}}]{3B==HO;5B==H;{10}B==CH$_{3}$;8B==H;9A==H;{13}B==CH$_{3}$;
{14}A==H;{17}GA==H;{16}GA==H}
```

13.5.2 Spiro Lactone Rings Other Than Spirostans

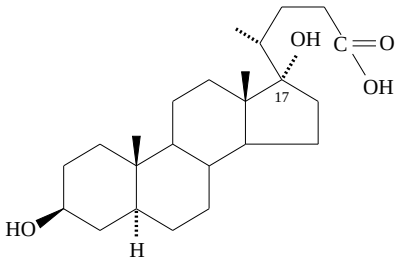
Steroids with a spiro lactone function, other than spirostans, can be drawn by putting a command for a spiro ring in the optional ⟨bondlist⟩ of such a command as `\steroid` according to the replacement technique where the fused component is generated by declaring a (yl) function in `\sixheteroh`.



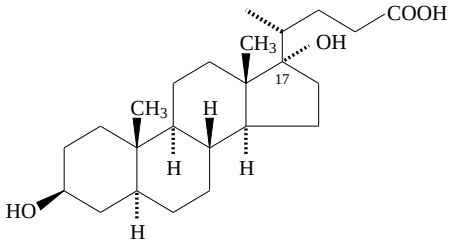
3β-hydroxy-5α-cholano-24,17-lactone

```
\steroid[%
{s{\sixheteroh({eA}){5==O}
{6==(yl);4D==O;1Sd==\null}}}]
{5A==H;3B==HO;{10}B==\null;%
{13}B==\null}
```

The name 3β-hydroxy-5α-cholano-24,17-lactone is based on the corresponding hydroxy-carboxylic acid, which can, for example, be drawn in the following two ways. Thus the name of the lactone contains the locant 24 of the acid group and the locant of the 17-hydroxyl group, where the lactonized hydroxyl group is not explicitly stated.




```
\steroid[{s{\sixheteroh
{4==C}{6==(yl);4D==O;4G==OH;%
1Sd==\null}[de]}}]
{5A==H;3B==HO;{10}B==\null;%
{13}B==\null;{17}SA==OH}
```



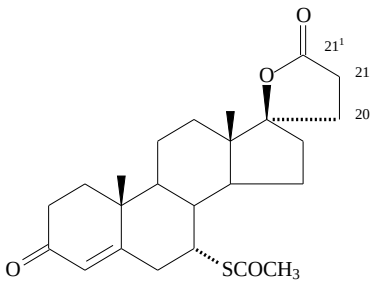

```
\androstanealpha
{3B==HO;{17}GA==OH;%
{{17}}==\trimethylene{1s==%
\PutDashedBond(0,0)(-171,103){2pt}%
}{1==(yl);3W==COOH}}
```

3β,17α-dihydroxy-5β-cholan-24-oic acid

Note that the ring D due to `\steroid` and the six-membered ring due to `\sixheteroh` are fused at C-17 in the left structure so as to form a hypothetical spiro ring system (an irregular application of the addition technique), where the bonds '`d`' and '`e`' of the latter ring are deleted by setting the ⟨delbdlist⟩ (`[de]`). As a result, the bonds '`a`', '`b`', '`c`', and '`f`' remain to give the side chain C-17–'`f`'–C–'`a`'–C–'`b`'–C–'`c`'–C(=O) in the form of a folded line. On the other hand, the right structure depicted above is based on the substitution technique, where the command `\trimethylene` is placed in the ⟨subslist⟩ of `\androstanealpha` after

declaring a (yl)-function. The double usage of pairs of braces ({{17}}==) or an addition of a harmless letter such as 'S' ({17}S==) is necessary because of the inner treatment of arguments in the XƎMTEX system.

Because a steroid skeleton with a short side chain up to C-21 is named pregnane, a derivative having a carboxylic acid group at the C-21 is called a pregnane-21-carboxylic acid. The following lactone is named as a lactone of such a pregnane-21-carboxylic acid, where the linkage between the C-21 and the C-17 is brought about by the unit -COO- in the lactone ring.



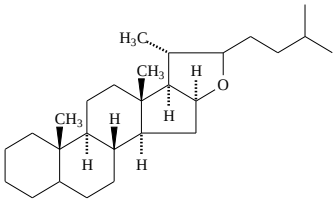
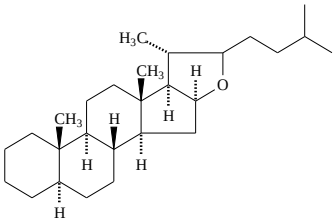
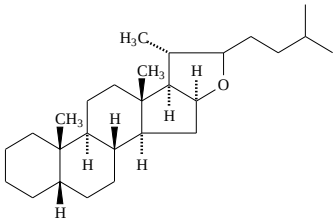
7α-acetylthio-3-oxo-17α-pregn-4-ene-21,17-carbolactone
(internationally non-proprietary name: spironolactone)

```
\begin{XyMcompd}(1550,1250)(50,200){}{}
\steroid[d%
{s{\fiveheterovi({cA})[%
{d{\WedgeAsSubst(0,0)(0,1){160}}}]
{5==O}
{4==(yl);1D==O}[d]}}]
{3D==O;{10}B==\null;%
{13}B==\null;7A==SCOCH$_{3}$}
\end{XyMcompd}
```

13.5.3 Furostans

Furostans are steroids with a fused furan ring. Commands for drawing furostans are listed in Table 13.10. The configurations of the C-5 (α or β) and the C-22 (R, S, or ξ) as well as the C-25 (R, S, or ξ if necessary) should be specified afterwards in the prefix of a systematic name, while all of the remaining asymmetric centers are implicitly involved in the name furostan. In particular, note that the configuration of 20S is implied by the name furostan.

Table 13.10. Furostans

5 unspecified	5α series	5β series
		
`\furostan{}`	`\furostanalpha{}`	`\furostanbeta{}`
	5α-furostan	5β-furostan

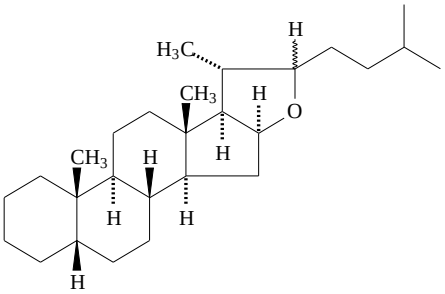
The commands listed in Table 13.10 are XƎMTEX commands of specific use, which have the following formats:

```
\furostan...[⟨bondlist⟩]{⟨subslist⟩}
```

where the symbol `...` of each command name represents no suffix or the suffix `nor`, `alpha`, or `beta`.

Locant numbers (1–17) for designating substitution positions and bond descriptors (locant alphabets a–t) are common to the command `\steroid`. The optional argument ⟨bondlist⟩ is based on the assignment of characters (a–t) to respective bonds as shown in Table 13.2. A bond modifier in the argument ⟨subslist⟩ for n = 1–17 (except fused positions) is selected from the list of bond modifiers (Table 3.2).

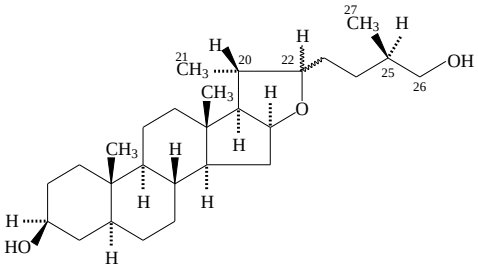
The structural formula of (22ξ)-5β-furostan is easily drawn by using `\furostanbeta`, where the descriptor `{22}U==H` outputs a wavy bond of a 22ξ-hydrogen, whose configuration is unspecified.



(22ξ)-5β-furostan

```
\furostanbeta{{22}U==H}
```

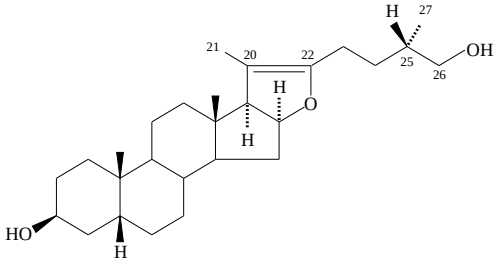
It should be noted that the side chain drawn by `\furostanbeta` is linked to C-22 through a straight-lined bond while the the hydrogen at the C-22 is linked through a wavy bond. If both of the bonds are desired to be drawn as wavy bonds, the command `\tetramethylene` is used with `3U` (a designator for a wavy bond) in the ⟨subslist⟩ of the command `\fivefusev`, as shown in the following example:



(22ξ, 25R)-5α-furostan-3β,26-diol
dihydropseudotigogenin

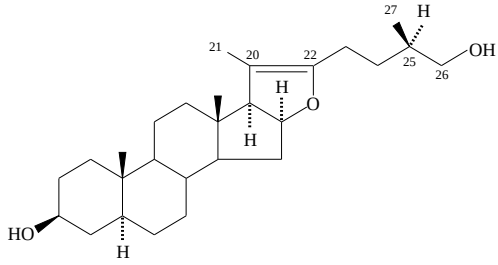
```
\steroid[{s{\fivefusev{2==O}
{4SA==CH$_{3}$;4SB==H;5FA==H;3FU==H;%
3U==\tetramethylenei{}{1==(yl);%
3SB==CH$_{3}$;3SA==H;4W==OH}}{e}}}]
{3SB==HO;3SA==H;5A==H;%
8B==H;9A==H;{14}A==H;%
{10}B==CH$_{3}$;%
{13}B==CH$_{3}$;%
{20}S==CH$_{3}$;{16}FA==H}
```

The first formula below requires a more complicated combination of commands such as `\steroid`, `fivefusev`, and `\pentamethylene`. The trivial name pseudosarsasopgenin indicates the relationship to sarsasapogenin, which is a synonym of (25S)-5β-spirostan-3β−ol. The second formula below, which is a diastereomer of the first one, can be drawn in a similar way. The trivial name pseudotigogenin indicates the relationship to tigogenin, which is a synonym of (25R)-5α-spirostan-3β−ol.



```
\steroid[{s{\fivefusev[c]{2==O;%
3s==\pentamethylene{}{1==(yl);%
4SA==\null;4SB==H;5W==OH}
}{4==\null;5FA==H}{e}}}]
{3B==HO;5B==H;%
{10}B==\null;%
{13}B==\null;%
{20}S==\null;{16}FA==H}
```

(25S)-5β-furost-20(22)-en-3β,26-diol
pseudosarsasapogenin

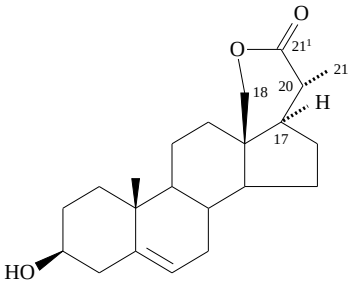


```
\steroid[{s{\fivefusev[c]{2==O;%
3s==\pentamethylene{}{1==(yl);%
4SB==\null;4SA==H;5W==OH}
}{4==\null;5FA==H}{e}}}]
{3B==HO;5A==H;%
{10}B==\null;%
{13}B==\null;%
{20}S==\null;{16}FA==H}
```

(25R)-5α-furost-20(22)-en-3β,26-diol
pseudotigogenin

13.5.4 Fused Lactone Rings Other Than Furostans

A derivative having a carboxylic acid group at the C-21 is regarded a pregnane-21-carboxylic acid. The following lactone is named as a lactone of such a pregnane-21-carboxylic acid, where the linkage between the C-21 and the C-18 is brought about by the unit -COO- in the lactone ring.



(20*R*)-3β-hydroxypregn-5-ene-20,18-carbolactone

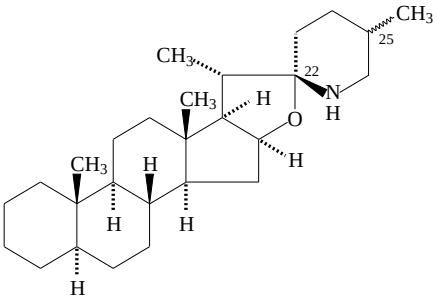
```
\steroid[e%
{s{\sixheteroh{2==O}%
{5==(yl);3D==O;4Sd==\null}[aef]}}%
{o{\WedgeAsSubst(0,0)(0,1){240}}}%
{o\PutBondLine(0,240)(-30,400){0.4pt}}]%
{3B==HO;{10}B==\null;{17}GA==H}
```

Note that the skeletal bonds C-17—C-20—C21[1]—O of the lactone ring stem from the six-membered ring generated by the command `\sixheteroh`, in which the bonds ‘a’, ‘e’, and ‘f’ are deleted by setting the ⟨delbdlist⟩ (`[aef]`). As a result, the bonds ‘b’, ‘c’, and ‘d’ remain to give the skeleton C-17—C-20—C21[1]—O of the lactone ring. The other skeletal bonds of the lactone ring are drawn by using `\PutBondLine` for a straight-lined bond and `\WedgeAsSubst` for a wedged bond.

13.5.5 Steroid Alkaloids

Spirosolanes

The structural formula of spirosolane is drawn in a similar way to spirostan. Because the bond between N and H is not drawn usually, the command `\downnobond` is used to place N and H up and down without a bond. The name spirosolane does not imply the configurations at the C-22 and C-25 (in addition to C-5) so that these are explicitly specified by the prefixes. The other asymmetric centers are implied in the name spirosolane.

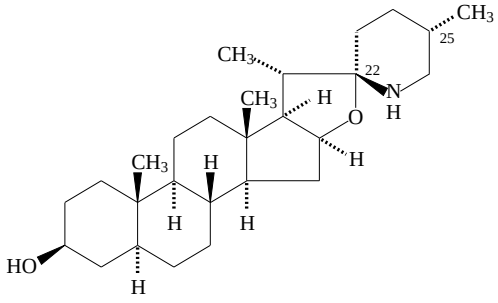


(22*S*, 25ξ)-5α-spirosolane

```
\steroid[{s{\fivefusev{2==O;%
3s==\sixheterovi({eA}){%
1==\downnobond{N}{H};%
6s==\WedgeAsSubst(0,0)(5,-3){140}%
}{6==(yl);3U==CH$_{3}$}
}{4A==CH$_{3}$}{e}}}]
{5A==H;8B==H;9A==H;{10}B==CH$_{3}$;%
{13}B==CH$_{3}$;{14}A==H;
{17}GA==H;{16}GA==H}
```

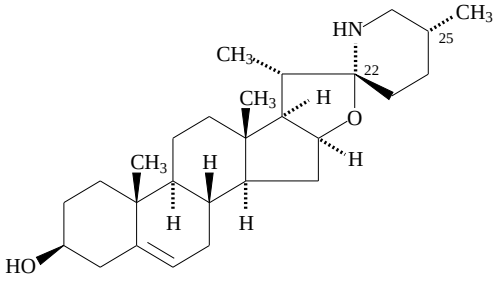
The name tomatanine has been used in place of spirostan. According to this convention, the above compound is named (22*S*, 25ξ)-5α-tomatanine.

Tomatidine and solasodine are systematically named as spirosolane derivatives, where the configurations of C-22, C-25 and C-5 are explicitly specified in addition to the configuration of a newly introduced C-3 substituent. The drawing of their structural formulas is straightforward after the above code for the spirosolane skeleton is available. What we have to do is the specification of double bonds and substituents as follows:



(22*S*, 25*S*)-5α-spirosolan-3β-ol

```
\steroid[%
{s{\fivefusev{2==O;%
3s==\sixheterovi({eA}){%
1==\downnobond{N}{H};
6s==\WedgeAsSubst(0,0)(5,-3){140}%
}{6==(yl);3A==CH$_{3}$}
}{4A==CH$_{3}$}{e}}}]
{3B==HO;5A==H;8B==H;9A==H;%
{10}B==CH$_{3}$;%
{13}B==CH$_{3}$;{14}A==H;
{17}GA==H;{16}GA==H}
```

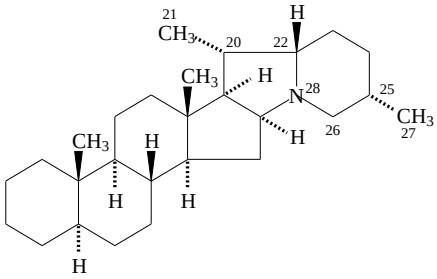


(22*R*, 25*R*)-spirosol-5-en-3β-ol

```
\steroid[e%
{s{\fivefusev{2==O;3s==%
\sixheterovi({eA}){5==\lmoiety{HN};%
6s==\WedgeAsSubst(0,0)(5,-3){171}%
}{6==(yl);3A==CH$_{3}$}[f]%
}{4A==CH$_{3}$}{e}}}]
{3B==HO;8B==H;9A==H;{10}B==CH$_{3}$;%
{13}B==CH$_{3}$;{14}A==H;
{17}GA==H;{16}GA==H}
```

Solanidanines

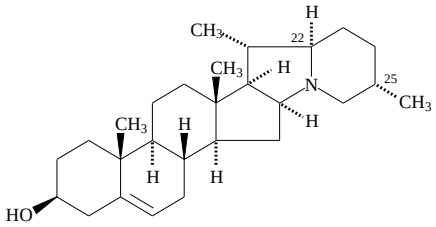
The parent skeleton named solanidanine (CAS name: solanidane) is drawn by `\steroid` in combination with nested commands `\fivefusev` and `\sixfusev`. The stereodescriptors 22*S* and 25*S* for the following compound should be described in the prefix of the systematic name. Note that 16αH, 17αH, and 20*S* (in addition to usual implicit locants of a steroid skeleton) is implied by the name solanidanine or solanidenine.



(22*S*, 25*S*)-5α-solanidanine

```
\steroid[%
{s{\fivefusev[%
{b{\sixfusev{5==N}{3A==CH$_{3}$;%
6GB==H}{e}}}]
{2==\null}{4A==CH$_{3}$}{e}}}]
{5A==H;8B==H;9A==H;{10}B==CH$_{3}$;%
{13}B==CH$_{3}$;{14}A==H;
{17}GA==H;{16}GA==H}
```

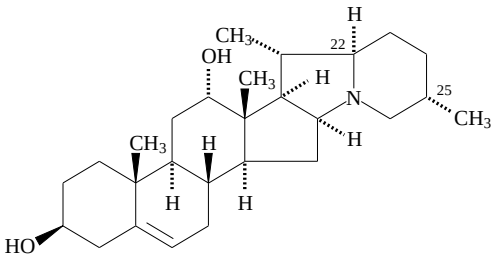
For the purpose of obtaining a systematic name for a solanidanine derivative having a double bond, the end -anine is replaced by -enine to give solanidenine as the name of the skeleton. An additional set of substituents is represented usually as exemplified in the following compound.



(22*R*, 25*S*)-solanid-5-enin-3β-ol
solanidine

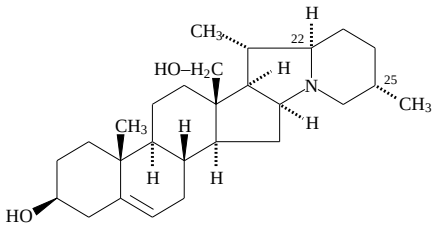
```
\steroid[e%
{s{\fivefusev[
{b{\sixfusev{5==N}{3A==CH$_{3}$;%
6GA==H}{e}}}
]{2==\null}{4A==CH$_{3}$}{e}}}]
{3B==HO;8B==H;9A==H;{10}B==CH$_{3}$;%
{13}B==CH$_{3}$;{14}A==H;
{17}GA==H;{16}GA==H}
```

The structural formulas of rubijervine and isorubijervine can be drawn in a similar way, where the respective substitution lists (⟨subslist⟩) of `\steroid` are slightly modified.



```
\steroid[e%
{s{\fivefusev[
{b{\sixfusev{5==N}{3A==CH$_{3}$;%
6GA==H}{e}}}
]{2==\null}{4A==CH$_{3}$}{e}}}]
{3B==HO;8B==H;9A==H;%
{10}B==CH$_{3}$;{12}A==OH;%
{13}B==CH$_{3}$;{14}A==H;%
{17}GA==H;{16}GA==H}
```

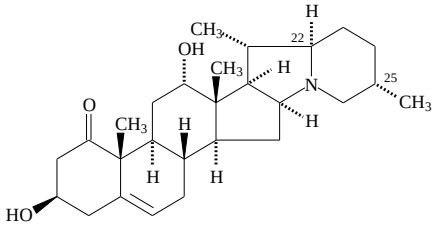
(22*R*, 25*S*)-solanid-5-enine-3β,12α-diol
rubijervine



```
\steroid[e%
{s{\fivefusev[
{b{\sixfusev{5==N}{3A==CH$_{3}$;%
6GA==H}{e}}}
]{2==\null}{4A==CH$_{3}$}{e}}}]
{3B==HO;8B==H;9A==H;%
{10}B==CH$_{3}$;{13}B==%
\lmoiety{HO--H$_{2}$C};{14}A==H;
{17}GA==H;{16}GA==H}
```

(22*R*, 25*S*)-solanid-5-enine-3β,18-diol
isorubijervine

The following compound can be regarded as the 1-oxo derivative of rubijervine, so that only the code `1D==O` is added to the ⟨subslist⟩ of `\steroid` in the abovementioned program for drawing rubijervine.

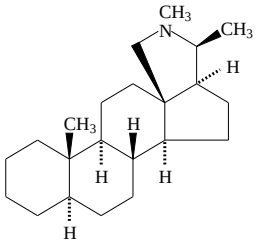


(22*R*, 25*S*)-3β,12α-dihydroxysolanid-
5-enin-1-one

```
\steroid[e%
{s{\fivefusev[
{b{\sixfusev{5==N}{3A==CH$_{3}$;%
6GA==H}{e}}}
]{2==\null}{4A==CH$_{3}$}{e}}}]
{1D==O;3B==HO;8B==H;9A==H;%
{10}B==CH$_{3}$;%
{12}A==OH;{13}B==CH$_{3}$;{14}A==H;
{17}GA==H;{16}GA==H}
```

Conanines

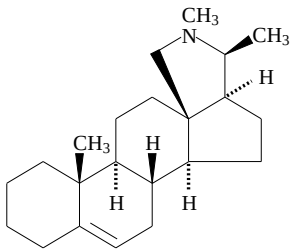
The name conanine implies 17αH and 2*OS* in addition to the other asymmetric centers of the steroid skeleton. The formula of 5α-conanine is drawn as follows:



5α-conanine

```
\steroid[{T{\sixfusev
{4s==\WedgeAsSubst(0,0)(-1,2){158};%
1==\upnobond{N}{CH$_{3}$}
}{2B==CH$_{3}$}{c}[de]}}]
{5A==H;8B==H;9A==H;{14}A==H;%
{10}B==CH$_{3}$;{17}GA==H}
```

The introduction of a double bond between C-5 and C-6 gives con-5-enine, whose structure is drawn as follows:



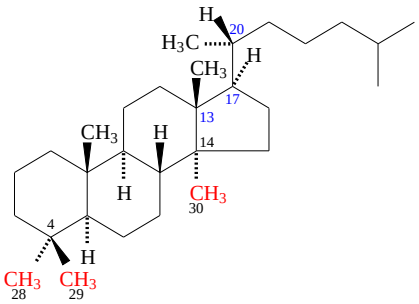
con-5-enine

```
\steroid[e{T{\sixfusev
{4s==\WedgeAsSubst(0,0)(-1,2){158};%
1==\upnobond{N}{CH$_{3}$}
}{2B==CH$_{3}$}{c}[de]}}]
{8B==H;9A==H;{14}A==H;%
{10}B==CH$_{3}$;{17}GA==H}
```

13.6 Tetracyclic Triterpenoids Related to Steroids

13.6.1 Lanostanes

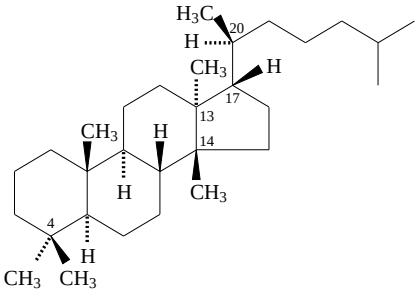
Tetracyclic triterpenoids can be regarded as 4,4,14-trimethyl-substituted steroids, where the methyl groups at 4α and 4β are numbered as C-28 and C-29 respectively, while the methyl group at the 14-position is specified by the locant 30. For example, 5α-lanostane represents a compound which is designated by a systematic name 4,4,14α-trimethyl-5α-cholestane. The configurations of 14α- and 20*R* (in addition of the other configurations specified by the steroid convention, e.g., 13β and 17β) are implied by the name 5α-lanostane, when this is used as a parent molecule in the process of naming further derivatives. The formula of 5α-lanostane is drawn by using the command `\steroidChain`.



5α-lanostane
4,4,14α-trimethyl-5α-cholestane

```
\steroidChain{4Su==CH$_{3}$;%
4Sd==CH$_{3}$;5A==H;%
8B==H;9A==H;{10}B==CH$_{3}$;%
{13}B==CH$_{3}$;{14}A==CH$_{3}$;%
{17}SA==\raisebox{-4pt}{~H};%
{20}SA==H$_{3}$C;{20}SB==H}
```

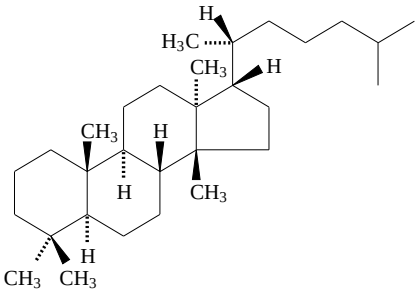
The trivial name 5α-tirucallane is used widely. Because the configurations at the C-20, C-13, C-14, and C-17 are inverted in comparison with the implied 20*R* etc. of the parent lanostane, the prefix of the following systematic name contains the descriptors 20*S* etc.



5α-tirucallane
(20*S*)-5α,13α,14β,17α-lanostane

```
\steroidChain
{4Su==CH$_{3}$;4Sd==CH$_{3}$;5A==H;%
8B==H;9A==H;{10}B==CH$_{3}$;%
{13}A==CH$_{3}$;{14}B==CH$_{3}$;%
{17}GB==H;{20}SB==H$_{3}$C;{20}SA==H}
```

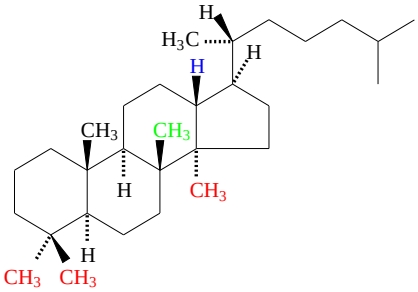
The trivial name 5α-euphane is widely used. The name lanostane for the systematic name implies 20*R*, which needs not be specified in the prefix of the following name.



5α-euphane
5α,13α,14β,17α-lanostane

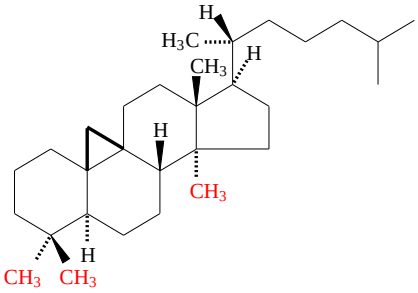
```
\steroidChain
{4Su==CH$_{3}$;4Sd==CH$_{3}$;5A==H;%
8B==H;9A==H;{10}B==CH$_{3}$;%
{13}A==CH$_{3}$;{14}B==CH$_{3}$;%
{17}GB==H;{20}SA==H$_{3}$C;{20}SB==H}
```

The structural formulas of dammarane, cycloartane, and protostane can be drawn in a similar way by using `steroidChain`.



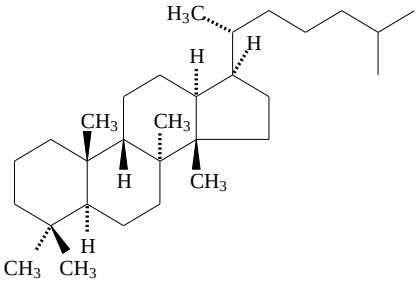
dammarane
8-methyl-18-nor-5α-lanostane
4,4,8,14-tetramethyl-18-nor-5α-cholestane

```
\steroidChain{4Su==CH$_{3}$;%
4Sd==CH$_{3}$;5A==H;%
8B==CH$_{3}$;9A==H;%
{10}B==CH$_{3}$;{13}B==H;%
{14}A==CH$_{3}$;%
{17}SA==\raisebox{-4pt}{~H};%
{20}SA==H$_{3}$C;{20}SB==H}
```



cycloartane
9,19-cyclo-9β-lanostane
4,4,14-trimethyl-9,19-cyclo-5α,9β-cholestane

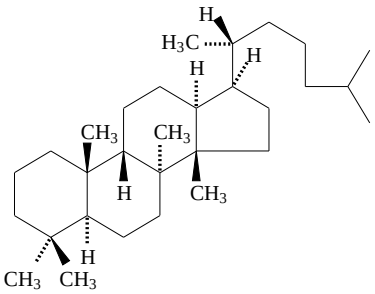
```
\steroidChain[{%
I\threefuseh({bB}{cB}){}{}{a}}]
{4Su==CH$_{3}$;4Sd==CH$_{3}$;%
5A==H;8B==H;{13}B==CH$_{3}$;%
{14}A==CH$_{3}$;%
{17}SA==\raisebox{-4pt}{~H};%
{20}SA==H$_{3}$C;{20}SB==H}
```



protostane
4,4,8,14-tetramethyl-18-nor-5α,8α,9β,13α,14β-cholestane

```
\steroidChain{4Su==CH$_{3}$;%
4Sd==CH$_{3}$;5A==H;%
8A==CH$_{3}$;9B==H;%
{10}B==CH$_{3}$;{13}A==H;%
{14}B==CH$_{3}$;%
{17}SA==\raisebox{-4pt}{~H};%
{20}A==H$_{3}$C}
```

The same compound (protostane) with an alternative folding of the side chain can be drawn by using `\steroidchain` in place of `\steroidChain`, where any modification of the ⟨subslist⟩ is not necessary. The result is shown below:



protostane
4,4,8,14-tetramethyl-18-nor-5α,8α,9β,13α,14β-cholestane

```
\steroidchain{4Su==CH$_{3}$;%
4Sd==CH$_{3}$;5A==H;%
8A==CH$_{3}$;9B==H;%
{10}B==CH$_{3}$;{13}A==H;%
{14}B==CH$_{3}$;%
{17}SA==\raisebox{-4pt}{~H};%
{20}SA==H$_{3}$C;{20}SB==H}
```

13.6.2 Biosynthesis of Steroids

Lanosterol, a tetracyclic triterpenoid, is an intermediate for the biosynthesis of cholesterol from squalene, as summarized in Fig. 13.2.

To draw the scheme shown in Fig. 13.2, commands for drawing respective compounds are defined by using the commands supported by the XyMTEX system. First, the command `\squalene` for drawing the

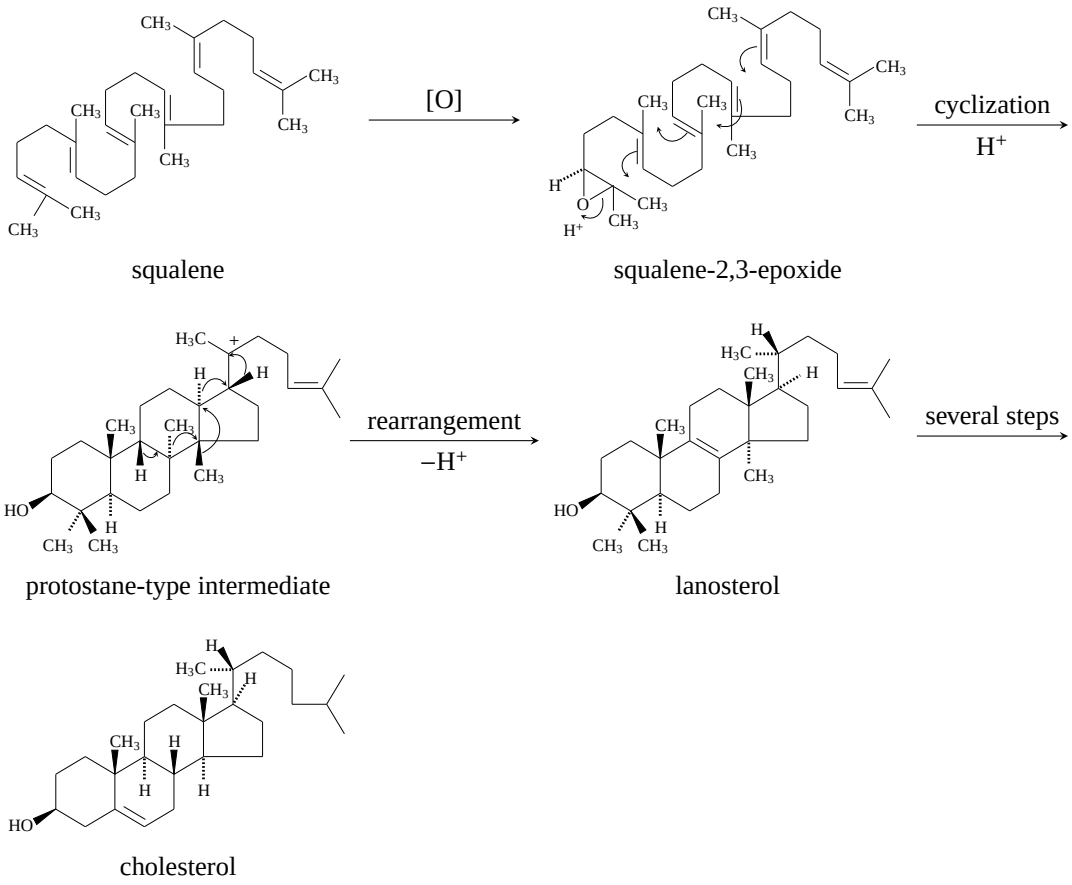
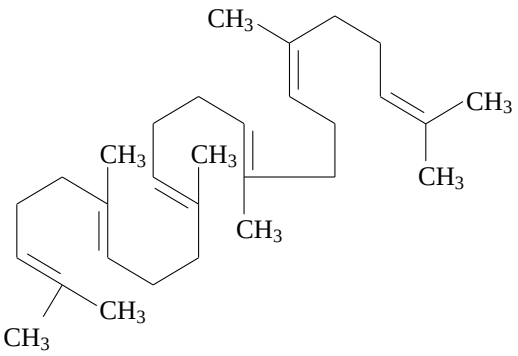


Figure 13.2. Biosynthesis of cholesterol from squalene

starting compound squalene is defined by the multiple nesting (6 ← 6 ← 6 ← 5 ← 6) of `sixfusev` and `\fivefusevi` in the ⟨bondlist⟩ of `\sixheterov`.

```
\def\squalene
{%
\begin{XyMcompd}(1800,1300)(250,0){}{}
\sixheterov[bd{B{\sixfusev[a{A{\sixfusev[{B{\fivefusevi[d%
{A{\sixfusev[e{c{\dimethylenei[a]{}{1==(yl);2==CH$_{3}$;2W==CH$_{3}$}}}]
{}{6==CH$_{3}$}{d}[c]}}]{}{}{d}[e]}}]{}{3G==CH$_{3}$}{d}[c]}}]
{}{2F==CH$_{3}$}{e}[f]}}]{}{4Sb==CH$_{3}$;4F==CH$_{3}$;2F==CH$_{3}$}[c]
\end{XyMcompd}
}
```

Output of `\squalene` without size reduction:

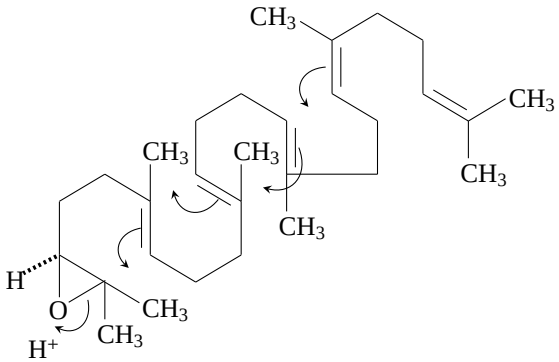


Second, the command `\squaleneepoxide` is defined for drawing squalene-2,3-epoxide, which contains arrows for representing electron shifts during cyclization. Each of these arrows is drawn by

using \electronlshiftarrow or \electronlshiftarrow[1], which is placed in the ⟨atomlist⟩ of \threefuseh, \sixfusev, or \fivefusevi. Each arrow is drawn from the midpoint of a starting double bond to the midpoint of a single bond to be formed according to a convention of organic chemistry. The epoxide ring is drawn by using \threefuseh, so that total multiple nesting is represented by the scheme, 6 (← 3) ← 6 ← 6 ← 5 ← 6.

```
\def\squaleneepoxide
{%
\begin{XyMcompd}(2000,1300)(50,-50){}{}
\sixheterov[b{D{\threefuseh{2==O;%
2==\put(-150,-150){H$^{+}$};%
2==\electronlshiftarrow[1](-50,-30)(75,70);%
}{}{c}}}%
{B{\sixfusev[a{A{\sixfusev[{B{\fivefusevi[d{A{\sixfusev[e{c{\dimethylenei%
[a]{}{1==(yl);2==CH$_{3}$;2W==CH$_{3}$}}}]{%
5s==\electronlshiftarrow(-85,-50)(-20,100);%
}{6==CH$_{3}$}{d}[c]}}%
]{4s==\electronlshiftarrow[1](-85,-50)(50,100);%
}{}{d}[e]}}%
]{}{3G==CH$_{3}$}{d}[c]}}%
]{1s==\electronlshiftarrow[1](-85,-60)(85,-95);%
}{2F==CH$_{3}$}{e}[f]}}]%1
{3s==\electronlshiftarrow(-85,-50)(-40,100);%
}{5A==H;4==CH$_{3}$;4F==CH$_{3}$;2F==CH$_{3}$}[c]%3
\end{XyMcompd}
}
```

Output of \squaleneepoxide without size reduction:

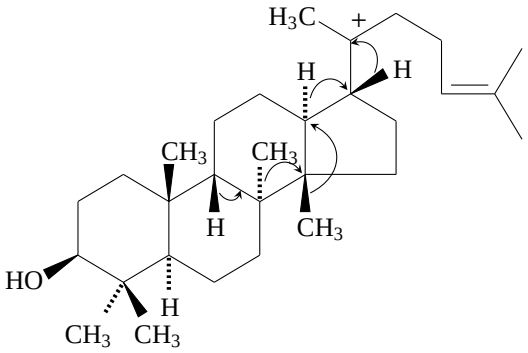


The intermediate of protostane-type is drawn by using \protostaneintermediate, which is defined on the basis of steroidchain. This formula contains arrows for representing electron shifts during cyclization. Each of these arrows is drawn by using the command \electronrshiftarrow or \electronrshiftarrow[1], which is placed before a substituent (H or CH_3) in the ⟨subslist⟩ of \steroidchain. This technique is based on the specification of \electronrshiftarrow or \electronrshiftarrow[1], which outputs a curved line having no size. According to a convention of organic chemistry, the starting point of each arrow is the midpoint of a cleaved bond, while its end point is the site (atom) at which a new bond is formed or the midpoint of a double bond to be formed.

```
\def\protostaneintermediate
{%
\begin{XyMcompd}(1800,1300)(50,0){}{}
\steroidchain[{Ze}{s{\put(0,250){+}}}]{3B==HO;4Su==CH$_{3}$;%
4Sd==CH$_{3}$;5A==H;%
8A==\electronrshiftarrow(50,-80)(190,-50)CH$_{3}$;%
9B==\electronrshiftarrow[1](50,160)(130,170)H;%
{10}B==CH$_{3}$;%
{13}A==\electronrshiftarrow(50,-70)(190,-40)H;%
```

```
{14}B==\electronrshiftarrow(50,160)(50,420)CH$_{3}$;%
{17}GB==\electronlshiftarrow(-160,130)(-70,20)H;%
{20}S==H$_{3}$C}
\end{XyMcompd}
}
```

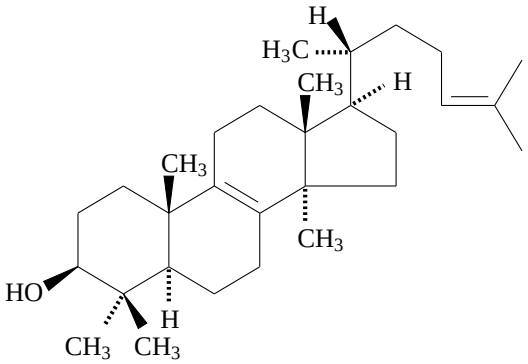
Output of `\protostaneintermediate` without size reduction:



The command `\lanosterol` is defined on the basis of `\steroidchain`.

```
\def\lanosterol
{%
\begin{XyMcompd}(1800,1300)(50,0){}{}
\steroidchain[h{Ze}]{3B==HO;4Su==CH$_{3}$;%
4Sd==CH$_{3}$;5A==H;{10}B==CH$_{3}$;{13}B==CH$_{3}$;%
{14}A==CH$_{3}$;{17}GA==H;{20}SA==H$_{3}$C;{20}SB==H}
\end{XyMcompd}
}
```

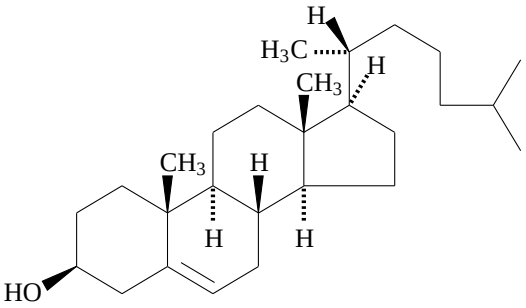
Output of `\lanosterol` without size reduction:



The command `\cholesterol` is defined by a rather straight-forward use of `\cholestanE`, which is supported by the preset version of the XyMTEX system.

```
\def\cholesterol
{%
\begin{XyMcompd}(1750,1100)(50,200){}{}
\cholestanE[e]{3B==HO}
\end{XyMcompd}
}
```

Output of `\cholesterol` without size reduction:



Finally, these commands are arranged by using the LaTeX 2ε `tabular` environment, where the size of each formula is reduced by means of `\scalebox` supported by the graphicx package. The command `\reactrarrow`, which is defined in the chemist package (or chmst-ps or chmst-pdf) automatically loaded by means of `\usepackage{xymtex}` (or `\usepackage{xymtex-ps}` or `\usepackage{xymtex-pdf}`), is used to draw an arrow representing a chemical reaction.

```
\begin{figure}[h]
\begin{center}
\begin{tabular}{cccc}
\scalebox{0.7}{\squalene} &
\reactrarrow{0pt}{2cm}{[O]}{\strut} &
\scalebox{0.7}{\squaleneepoxide} &
\reactrarrow{0pt}{2cm}{cyclization}{H$^{+}$} \\
\noalign{\vskip5pt}
squalene & & squalene-2,3-epoxide & \\
\noalign{\vskip15pt}
\scalebox{0.7}{\protostaneintermediate} &
\reactrarrow{0pt}{2cm}{rearrangement}{$-$H$^{+}$} &
\scalebox{0.7}{\lanosterol} &
\reactrarrow{0pt}{2cm}{several steps}{\strut} \\
\noalign{\vskip5pt}
protostane-type intermediate & & lanosterol & \\
\noalign{\vskip15pt}
\scalebox{0.7}{\cholesterol} &&& \\
\noalign{\vskip5pt}
cholesterol &&&\\
\end{tabular}
\end{center}
\caption{Biosynthesis of cholesterol from squalene}
\label{ff:Steroid-Biosyntheis}
\end{figure}
```

The tabulated scheme is incorporated in the `figure` environment of the LaTeX 2ε system. The output of the scheme is shown in Fig. 13.2.

References

[1] P. Moss and IUPAC and International Union of Biochemistry Joint Commission on Biochemical Nomenclature, *Pure Appl. Chem.*, **61**, 1783–1822 (1989).

[2] R. B. Woodward and R. Hoffman, “The Conservation of Orbital Symmetry,” Verlag Chemie, Weinheim (1970).

Part III

Heterocyclic Compounds

Six-Membered Heterocycles. Commands for Specific Use

XƎMTEX commands for specific use `ComSpec` are short-cut commands of those for general use `ComGen`, where appropriate arguments are selected from the required and optional arguments of the latter (cf. Section 3.1 for the syntax). This chapter is devoted to introduce commands for drawing pyridine derivatives and related compounds. These commands are short-cut commands of `\sixheterov` etc. for general use.

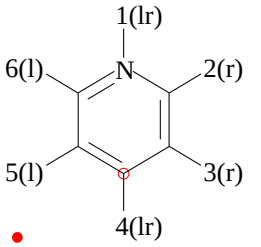
14.1 Drawing Vertical Forms of Six-Membered Heterocycles

14.1.1 Using Commands for Specified Use

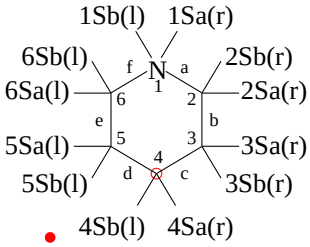
The XƎMTEX command `\pyridinev` and related macros are used to draw six-membered heterocyclic compounds of vertical type (hetarom.sty). Each of these commands typesets heterocycles with the specific arrangement of heteroatoms on its skeleton. The formats of these commands are as follows:

```
\pyridinev[⟨bondlist⟩]{⟨subslist⟩}
\pyrazinev[⟨bondlist⟩]{⟨subslist⟩}
\pyrimidinev[⟨bondlist⟩]{⟨subslist⟩}
\pyridazinev[⟨bondlist⟩]{⟨subslist⟩}
\triazinev[⟨bondlist⟩]{⟨subslist⟩}
```

By using the command `\pyridinev` as an example, the mode of locant numbering for designating substitution positions is shown as follows along with the bond descriptors (locant alphabets) for assigning inner double bonds:



○: (400,240)
●: (0,0)



○: (400,240)
●: (0,0)

The optional argument ⟨bondlist⟩ specifies bonds to be doubled as shown in Table 14.1. Since a specific character is assigned to a specific bond of each heterocycle, the concrete meaning of the character is different from one heterocycle to another. However, the methodology is common in drawing all heterocycles so that the commands of XƎMTEX are easy to use.

Table 14.1. Argument ⟨bondlist⟩ for Commands \pyridinev, *etc.*

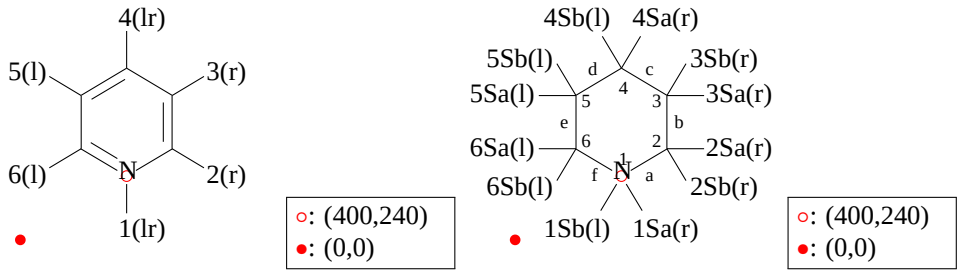
Character	Printed structure
none or r	pyridine (right-handed)
l	pyridine (left-handed)
H or [ ]	fully saturated ring
a	1,2-double bond
b	2,3-double bond
c	4,3-double bond
d	4,5-double bond
e	5,6-double bond
f	6,1-double bond
A	aromatic circle
{*n*+}	plus at the *n*-nitrogen atom (*n* = 1 to 6)

The argument ⟨subslist⟩ shows each substituent with a locant number and a bond modifier shown in Table 3.2, in which *n* is an Arabic numeral between 1 and 6.

The XeLaTeX command \pyridinevi and related macros are used to draw six-membered heterocyclic compounds of inverse horizontal type (hetarom.sty). The formats of these commands are as follows:

```
\pyridinevi[⟨bondlist⟩]{⟨subslist⟩}
\pyrazinevi[⟨bondlist⟩]{⟨subslist⟩}
\pyrimidinevi[⟨bondlist⟩]{⟨subslist⟩}
\pyridazinevi[⟨bondlist⟩]{⟨subslist⟩}
\triazinevi[⟨bondlist⟩]{⟨subslist⟩}
```

By using the command \pyridinevi as an example, the mode of locant numbering for designating substitution positions is shown as follows along with the bond descriptors (locant alphabets) for assigning inner double bonds:



The optional argument ⟨bondlist⟩ specifies bonds to be doubled as shown in Table 14.1. The argument ⟨subslist⟩ shows each substituent with a locant number and a bond modifier shown in Table 3.2, in which *n* is an Arabic numeral between 1 and 6.

The locant numbers and alphabets of the XeLaTeX commands with the suffix 'v' are compared with those of their inverse macros with the suffix 'vi' (Fig. 14.1).

For example, the statements,

```
\pyridinev{2==Cl;6==Cl;4==F}
\pyrazinev{2==Cl;6==Cl}
\pyrimidinev{2==Cl;6==Cl;4==F}
\pyridazinev{6==Cl;4==F}
\triazinev{2==Cl;6==Cl;4==F}
```

produce the following structures:

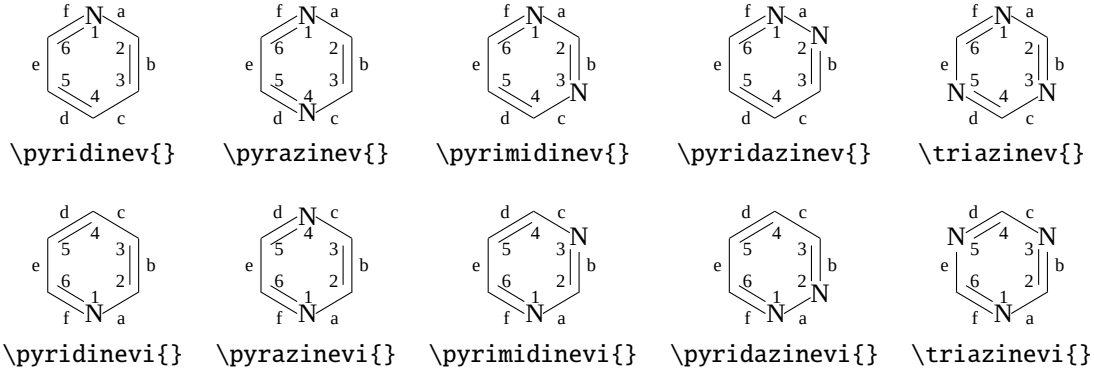
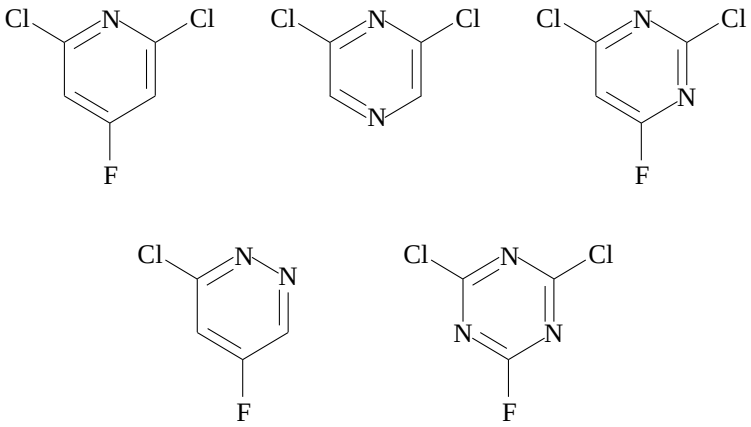


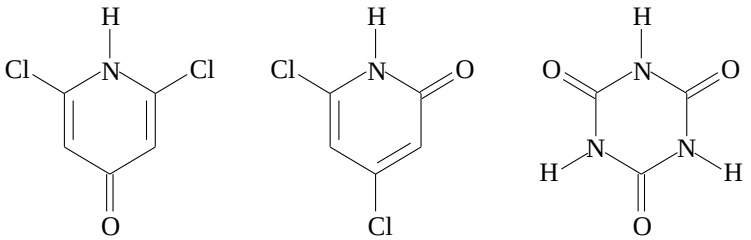
Figure 14.1. Locant numbers and alphabets of XƎMTEX commands of vertical type for specific use of drawing six-membered heterocycles. The first row collects XƎMTEX commands with suffix 'v' and the second row collects the corresponding ones with suffix 'vi'.



It should be noted that the default setting of the ⟨bondlist⟩ is to depict a fully unsaturated ring (so-called a mancude-ring system, usually an aromatic ring). By setting an appropriate character string, a single macro is used to typeset both partially saturated and unsaturated derivatives. Moreover, a fully saturated ring can be obtained by setting a null argument or H in ⟨bondlist⟩. This specification can be illustrated with the following examples.

```
\pyridinev[be]{1==H;2==Cl;6==Cl;4D==O}\qquad
\pyridinev[ce]{1==H;4==Cl;6==Cl;2D==O}\qquad
\triazinev[H]{2D==O;4D==O;6D==O;1==H;3==H;5==H}
```

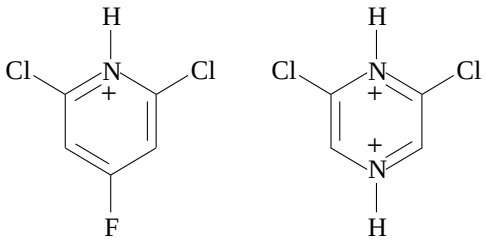
produce the following structures:



In order to depict a charge on a nitrogen, you write the statements, for example:

```
\pyridinev[r{1+}]{1==H;2==Cl;6==Cl;4==F}\qquad
\pyrazinev[l{1+}{4+}]{1==H;4==H;2==Cl;6==Cl}
```

Then you obtain the following structures:



In these cases, a character ‘r’ or ‘l’ should be added to the argument ⟨bondlist⟩, because the defaults are hidden by writing other characters in the ⟨bondlist⟩.

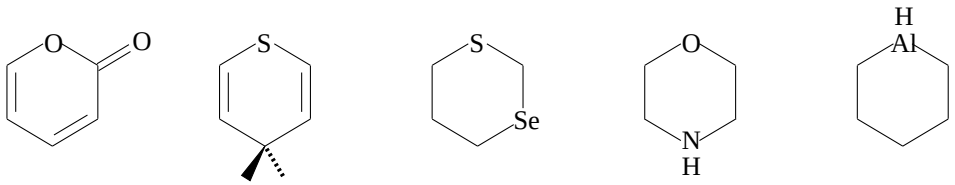
14.1.2 Using Commands for General Use

As already described in Subsection 3.4.4, the XMTEX commands \sixheterov and \sixheterovi for general use are general macros for drawing six-membered heterocyclic derivatives of vertical type (het-arom.sty). It is especially useful to draw heterocyclic compounds having other skeletal atoms than nitrogen atoms.

Examples of \sixheterov:

```
\sixheterov[ce]{1==O}{2D==O}
\sixheterov[be]{1==S}{4SA==;4SB==}
\sixheterov{1==S;3==Se}{}
\sixheterov{1==O;4==\downnobond{N}{H}}{}
\sixheterov{1==\upnobond{Al}{H}}{}
```

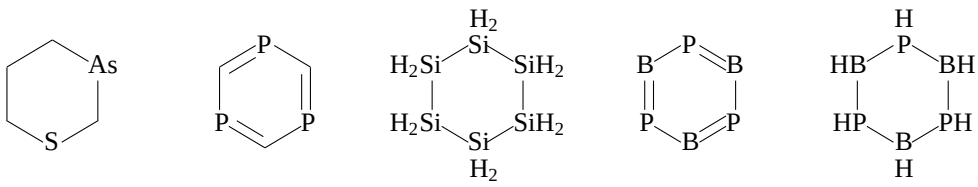
produce



Examples of \sixheterovi:

```
\sixheterovi{1==S;3==As}{}
\sixheterovi[bdf]{2==P;4==P;6==P}{}
\sixheterovi{1==\downnobond{Si}{H$_{2}$};%
2==SiH$_{2}$;3==SiH$_{2}$;%
4==\upnobond{Si}{H$_{2}$};5==H$_{2}$Si;6==H$_{2}$Si}{}
\sixheterovi[ace]{1==B;2==P;3==B;4==P;5==B;6==P}{}
\sixheterovi{1==\downnobond{B}{H};2==PH;3==BH;%
4==\upnobond{P}{H};5==HB;6==HP}{}
```

produce

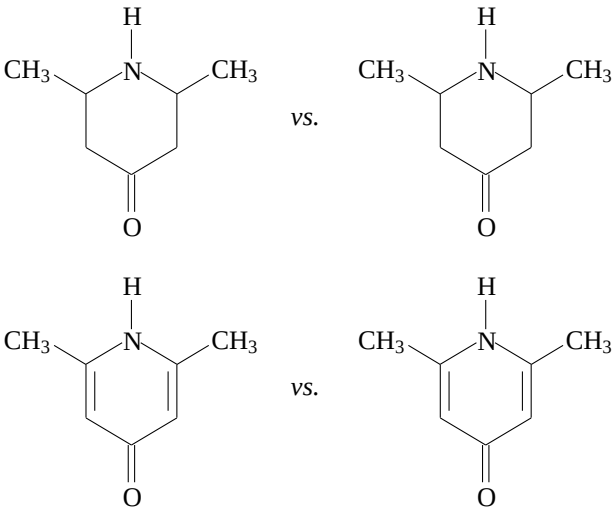


It should be noted that the same compound can be drawn in different ways. This fact is obvious because all the commands, \pyridinev, \pyrazinev, \pyrimidinev, \pyridazinev, and \triazinev, are based on the macro \sixheterov.

Examples for \pyridinev vs. \sixheterov:

```
\pyridinev[H]{1==H;4D==O;2==CH$_{3}$;6==CH$_{3}$}\qquad
\raisebox{1.5cm}{\em vs.} \qquad
\sixheterov{1==N}{1==H;4D==O;2==CH$_{3}$;6==CH$_{3}$} \par
\bigskip
\pyridinev[be]{1==H;4D==O;2==CH$_{3}$;6==CH$_{3}$}\qquad
\raisebox{1.5cm}{\em vs.} \qquad
\sixheterov[be]{1==N}{1==H;4D==O;2==CH$_{3}$;6==CH$_{3}$}
```

produce



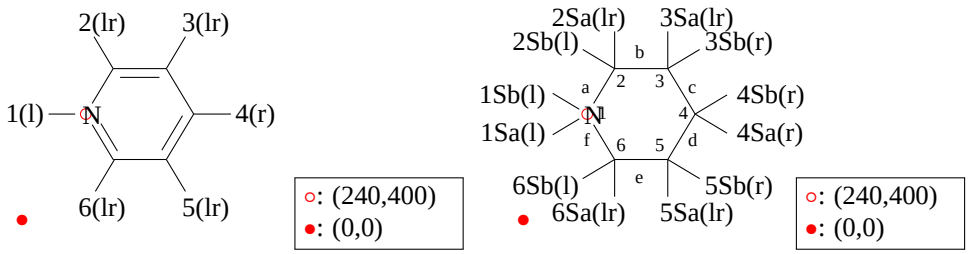
14.2 Drawing Horizontal Forms of Six-Membered Heterocycles

14.2.1 Using Commands for Specified Use

The macro \pyridineh and related macros are used to draw six-membered heterocyclic compounds of horizontal type (hetaromh.sty). The formats of these commands are as follows:

```
\pyridineh[⟨bondlist⟩]{⟨subslist⟩}
\pyrazineh[⟨bondlist⟩]{⟨subslist⟩}
\pyrimidineh[⟨bondlist⟩]{⟨subslist⟩}
\pyridazineh[⟨bondlist⟩]{⟨subslist⟩}
\triazineh[⟨bondlist⟩]{⟨subslist⟩}
```

The following diagrams show the numbering for designating substitution positions as well as the bond specification for placing double bonds:

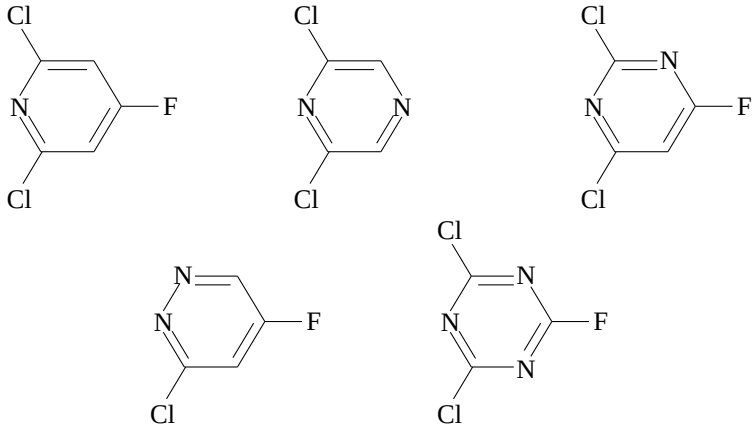


Each macro can be used to typeset both saturated and unsaturated derivatives. For example, the statements,

```
\pyridineh{2==Cl;6==Cl;4==F}
```

```
\pyrazineh{2==Cl;6==Cl}
\pyrimidineh{2==Cl;6==Cl;4==F}
\pyridazineh{6==Cl;4==F}
\triazineh{2==Cl;6==Cl;4==F}
```

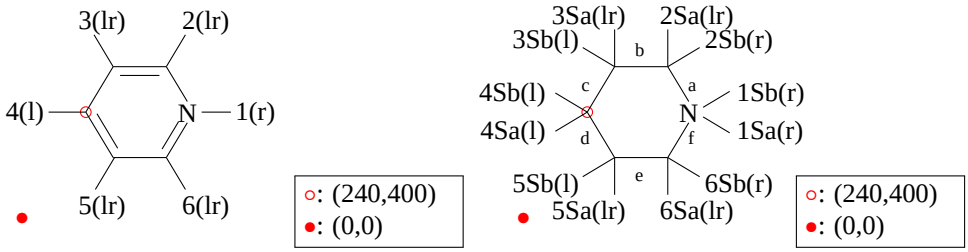
produce the following structures:



The X$\mathfrak{Z}$MTEX command `\pyridinehi` and related macros are used to draw six-membered heterocyclic compounds of inverse horizontal type (hetarom.sty). The formats of these commands are as follows:

```
\pyridinehi[⟨bondlist⟩]{⟨subslist⟩}
\pyrazinehi[⟨bondlist⟩]{⟨subslist⟩}
\pyrimidinehi[⟨bondlist⟩]{⟨subslist⟩}
\pyridazinehi[⟨bondlist⟩]{⟨subslist⟩}
\triazinehi[⟨bondlist⟩]{⟨subslist⟩}
```

The numbering for designating substitution positions and the bond specification are shown in the following diagrams:



The locant numbers and alphabets of the X$\mathfrak{Z}$MTEX commands with the suffix '`h`' are compared with those of their inverse macros with the suffix '`hi`' (Fig. 14.2).

Each macro can typeset both saturated and unsaturated derivatives, where the default produces a fully unsaturated (aromatic) one. For example, the statements,

```
\pyridinehi{2==Cl;6==Cl;4==F}
\pyrimidinehi{2==Cl;6==Cl;4==F}
\pyridazinehi{6==Cl;4==F}
\triazinehi{2==Cl;6==Cl;4==F}
```

produce the following structures:

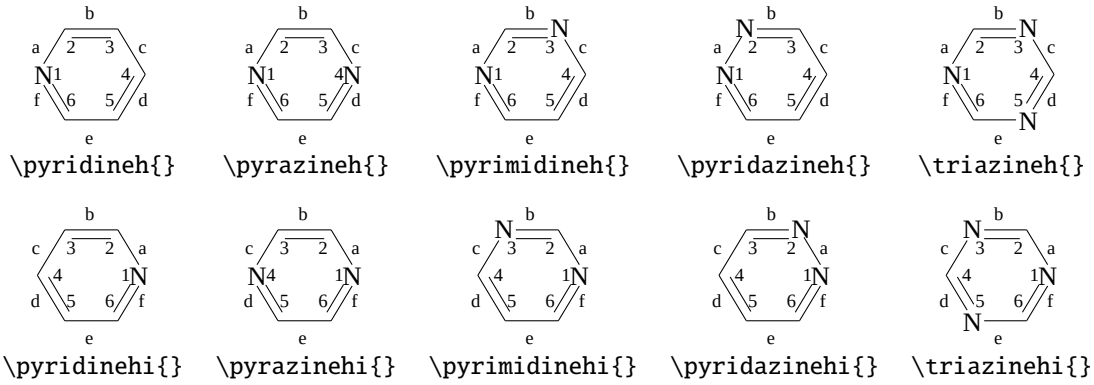
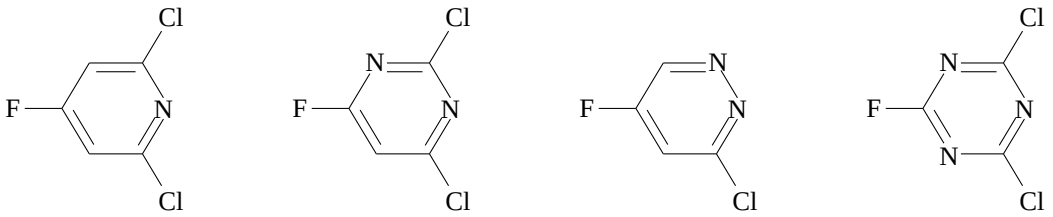


Figure 14.2. Locant numbers and alphabets of XeLaTeX commands of horizontal type for specific use of drawing six-membered heterocycles. The first row collects XeLaTeX commands with suffix '`h`' and the second row collects the corresponding ones with suffix '`hi`'.



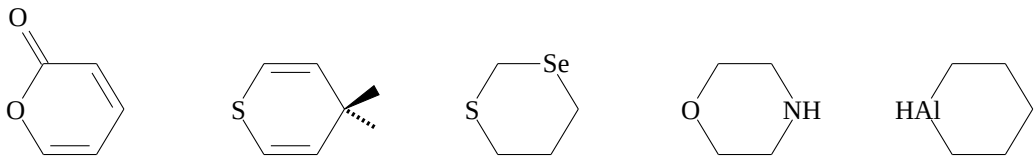
14.2.2 Using Commands for General Use

As already described in Section 3.4.4, the XeLaTeX commands `\sixheteroh` and `\sixheterohi` for general use are general macros for drawing six-membered heterocyclic derivatives of horizontal type (hetarom.sty). It is especially useful to draw heterocyclic compounds having other skeletal atoms than nitrogen atoms.

Examples of `\sixheteroh`:

```
\sixheteroh[ce]{1==O~}{2D==O}
\sixheteroh[be]{1==S~}{4SA==;4SB==}
\sixheteroh{1==S~;3==Se}{}
\sixheteroh{1==O~;4==NH}{}
\sixheteroh{1==HAl}{}
```

produce

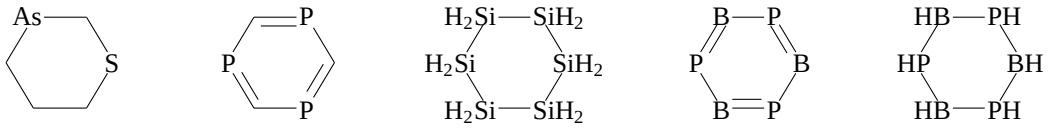


Note that such an input as `1==O~` (in place of `1==O`) is necessary to assure an appropriate position of output.

Examples of `\sixheterohi`:

```
\sixheterohi{1==S;3==As}{}
\sixheterohi[bdf]{2==P;4==P;6==P}{}
\sixheterohi{1==SiH$_{2}$;%
2==SiH$_{2}$;3==H$_{2}$Si;%
4==H$_{2}$Si;5==H$_{2}$Si;6==SiH$_{2}$}{}
\sixheterohi[ace]{1==B;2==P;3==B;4==P;5==B;6==P}{}
\sixheterohi{1==BH;2==PH;3==HB;%
4==HP;5==HB;6==PH}{}
```

produce



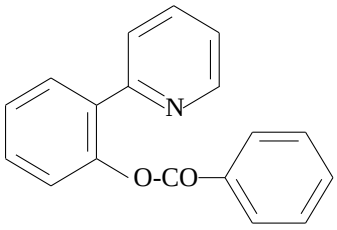
Note that such an input as `1==~S` (in place of `1==S`) or `4==P~` (in place of `4==P`) is necessary to assure an appropriate position of output.

14.3 Illustrative Examples of Drawing Six-Membered Heterocycles

14.3.1 Generation of Substituents by (yl)-Functions

Example 14.1. The structure **14-1** of a 2-phenylpyridine derivative [1] is drawn by dual application of the substitution technique. One substituent is drawn by declaring a (yl)-function in the ⟨subslist⟩ of the command `\pyridinevi`. The other substituent, which is generated by declaring a (yl)-function in the ⟨subslist⟩ of `\benzeneh`, is further included in the `\ryl` command to add a linking divalent unit (O-CO). The two substituents are declared in the ⟨subslist⟩ of the outer command `\benzenev`.

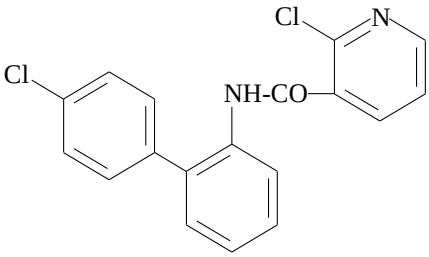
```
\benzenev{2==\pyridinevi{6==(yl)};%
3==\ryl(4==O-CO){4==\benzeneh{1==(yl)}}}
```



14-1 □

Example 14.2. The structure **14-2** of boscalid developed by BASF as a fungicide for speciality crops is drawn in a similar way to the above-mentioned dual application of the substitution technique. One substituent is drawn by declaring a (yl)-function in the ⟨subslist⟩ of the inner command `\benzenev`. The other substituent, which is generated by declaring a (yl)-function in the ⟨subslist⟩ of `\pyridinev`, is further included in the `\ryl` command to add a linking divalent unit (NH-CO). The two substituents are declared in the ⟨subslist⟩ of the outer command `\benzenev`.

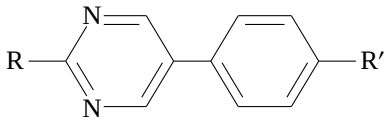
```
\benzenev{%
1==\ryl(8==NH-CO){4==\pyridinev{5==(yl);6==Cl}};
6==\benzenev{3==(yl);6==Cl}}
```



14-2 □

Example 14.3. The structure **14-3** of a pyrimidine derivative is drawn by the substitution technique. Because the commands `\pyrimidineh` and `\pyrimidinehi` (Fig. 14.2) print out pyrimidine structures having two skeletal nitrogen atoms at undesired positions, the macro `\sixheteroh` as a XeLaTeXcommand for general use is used to draw the desired pyrimidine structure **14-3**.

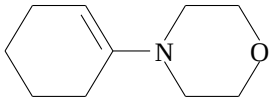
```
\benzeneh{1==\sixheteroh[bdf]{2==N;6==N}{4==(yl);1==R};4==R$^{\prime}$}
```



14-3 □

Example 14.4. The structure **14-4** of an enamine derived from cyclohexanone and morpholine is drawn by the substitution technique, where a morpholine substituent is generated by declaring a (yl)-function in the command `\sixheteroh` as a X$\mathrm{\mathfrak{Y}}$MTEX command for general use.

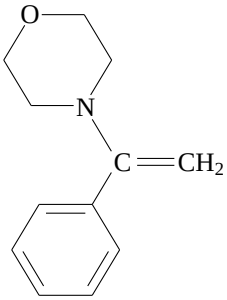
```
\cyclohexaneh[c]{4==\sixheteroh{1==N;4==O}{1==(yl)}}
```



14-4 □

Example 14.5. The structure **14-5** of α-morpholinostyrene [2] is drawn by the substitution technique. where two substituents are generated by declaring (yl)-functions, i.e., a morpholine substituent generated from `\sixheteroh` and a phenyl substituents generated from `\benzeneh`.

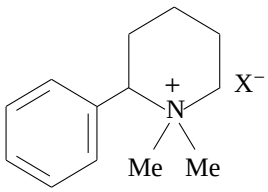
```
\Ltrigonal{0==C;1D==CH$_{2}$;%
2==\sixheteroh{2==O;5==N}{5==(yl)};%
3==\benzeneh{3==(yl)}}
```



14-5 □

Example 14.6. The structure **14-6** of a dimethylammonium salt [3, page 678] is drawn by the substitution technique, where the command `\benzenev` is used to draw a parent structure and the command `\pyridinevi` is used to draw a substituent by declaring a (yl)-function. A pair of charges (+ X$^-$) is printed out by means of a rather dirty setting based on the replacement technique (cf. `{n+}` of Table 14.1).

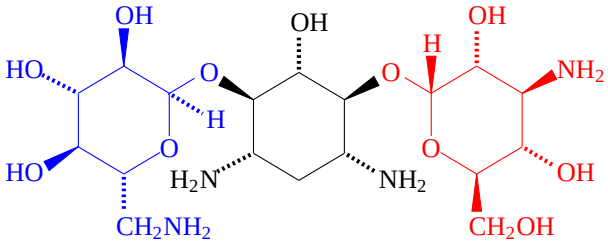
```
\benzenev{%
2==\pyridinevi[H{1{+\kern20pt X$^{-}$}}]%
{6==(yl);1Sa==Me;1Sb==Me}}
```



14-6 □

Example 14.7. The structure **14-7** of kanamicin as an antibiotic is drawn by the substitution technique, where one red-colored substituent is generated by using the command `\ryl` and a (yl)-function (the red colored code), while the other blue-colored substituent is generated by using the command `\lyl` and a (yl)-function (the blue-colored code),

```
\cyclohexanev{1A==OH;3A==NH$_{2}$;5A==H$_{2}$N;%
2B==\ryl(5==O~){5==\sixheterov{5==O}{6==(yl);1A==OH;2B==NH$_{2}$;%
3A==OH;4B==CH$_{2}$OH;6GB==H}};%
6B==\lyl(5==~O){5==\sixheterov{3==O}{2==(yl);1B==OH;%
4A==CH$_{2}$NH$_{2}$;5B==HO;6A==HO;2GA==H}}}
```

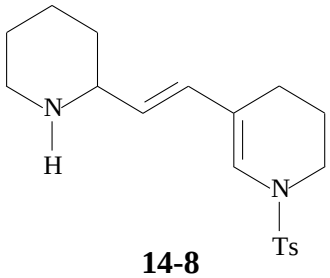


14-7

□

Example 14.8. The structure **14-8** of an intermediate for synthesizing (+)-aloperine [3, page 967] is drawn by the replacement technique, where the command `\tetramethylenei` is used to draw a tetramethylene unit as a parent structure and the command `\pyridinevi` is used to draw two piperidyl moieties by declaring (yl)-functions.

```
\tetramethylenei[b]{%
1s==\pyridinevi[H]{2==(yl);1==H};%
4s==\pyridinevi[e]{5==(yl);1==Ts}}{}
```



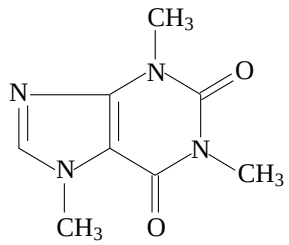
14-8

□

14.3.2 As Parent Structures for Ring Fusion

Example 14.9. The structure **14-9** of caffeine is drawn by the addition technique, where the command `\pyrimidinev` is used to draw a six-membered parent structure, which is attached by a fusing unit generated by `\fivefusev`.

```
\pyrimidinev[e%
{e\fivefusev[d]{1==N;4==N}{1==CH$_{3}$}{b}}%
]{1==CH$_{3}$;3==CH$_{3}$;2D==O;4D==O}
```

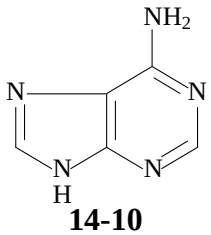


14-9

Compare this drawing with that of **2-35**. □

Example 14.10. In a similar way, the structure **14-10** of adenine is drawn by the addition technique, where the command `\pyrimidinevi` is used to draw a six-membered parent structure, which is attached by a fusing unit generated by `\fivefusev`.

```
\begin{XyMcompd}(650,750)(-100,150){}{}
\pyrimidinevi[ace%
{e\fivefusev[d]{1==\downnobond{N}{H};4==N}{}{B}}%
]{4==NH$_{2}$}
\end{XyMcompd}
```

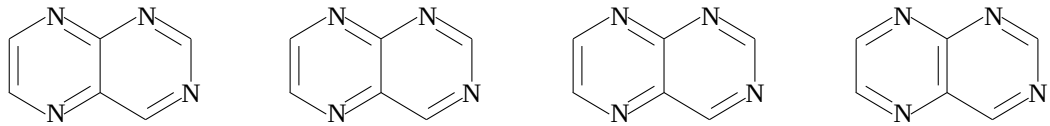


14-10

□

Example 14.11. Four ways of drawing pteridine [4, Table 2.8] are shown below. First, the right pyrimidine ring is regarded as a parent structure, which is drawn by using `\pyrimidinev`. An attached ring for the addition technique is generated by using `\sixfusev`. Thereby, we obtain the structural formula **14-11**. Second, the left pyrazine ring is regarded as a parent structure, which is drawn by using `\pyrazinev`. An attached ring for the addition technique is generated by using `\sixfusev`. Thereby, we obtain the structural formula **14-12**. Third, we are able to use the XyMTEX command `\decaheterov` for general use so as to generate the structural formula **14-13**. Finally, a single command `\pteridinev` is already prepared for drawing the structure of pteridine **14-14**.

```
\pyrimidinev[ac{e\sixfusev[ace]{1==N;4==N}{}{B}}]{}
\pyrazinev[ace{b\sixfusev[ac]{1==N;3==N}{}{E}}]{}
\decaheterov[acegi]{1==N;3==N;5==N;8==N}{}
\pteridinev{}
```

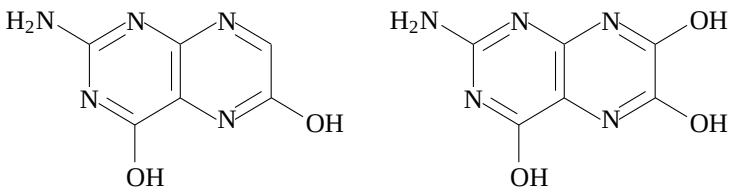


14-11 **14-12** **14-13** **14-14**

□

Example 14.12. The structure **14-15** of xanthopterin and the structure **14-16** of leucopterin contain a common azanaphthalene skeleton. They are drawn by the addition technique, where the azanaphthalene skeleton is generated by using `\pyrazinev` and an attached ring is generated by using `\sixfusev`.

```
\begin{XyMcompd}(1100,700)(-350,0){cpd:xanthopterin}{}
\pyrazinev[ac%
{e\sixfusev[bdf]{1==N;5==N}{4==OH;6==H$_{2}$N}{B}}%
]{3==OH}
\end{XyMcompd}
\qquad
\begin{XyMcompd}(1100,700)(-350,0){cpd:leucopterin}{}
\pyrazinev[ac%
{e\sixfusev[bdf]{1==N;5==N}{4==OH;6==H$_{2}$N}{B}}%
]{2==OH;3==OH}
\end{XyMcompd}
```



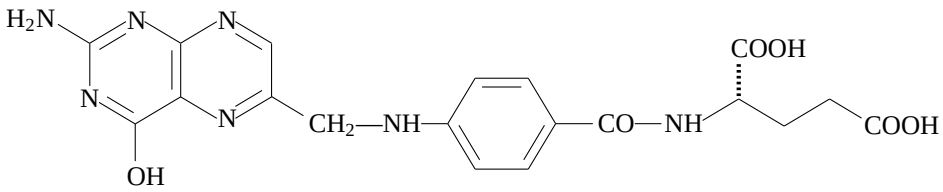
14-15 **14-16**

□

Example 14.13. In a similar way, the azanaphthalene skeleton in the structure **14-17** of folic acid is drawn by the addition technique. The side chain is depicted by a nested use of two `\ryl` commands, which provide substituents according to the substitution technique based on a (yl)-function.

```
\begin{XyMcompd}(3400,700)(-350,0){cpd:folicacid}{}
\pyrazinev[ac%
```

```
{e\sixfusev[bdf]{1==N;5==N}{4==OH;6==H$_{2}$N}{B}}%
]{3==\ryl(3==CH$_{2}$---NH){4==\benzeneh{1==(yl);%
4==\ryl(4==CO){4==%
\put(120,-10){\tetramethylene{1==NH}{1==(yl);2A==COOH;4W==COOH}}%
}}}}
\end{XyMcompd}
```



14-17

□

References

[1] L. Li, P. Yu, J. Cheng, F. Chen, and C. Pan, *Chem. Lett*, **41**, 600 (2012).

[2] R. Noyori, K. Yokoyama, and Y. Hayakawa, in “Organic Syntheses,” , Organic Syntheses Inc. (1978) Vol. 58 p 56.

[3] M. B. Smith, “Organic Synthesis,” 2nd ed., McGraw-Hill, New York (2002).

[4] IUPAC Chemical Nomenclature and Structure Representation Division, *Provisional Recommendations. Nomenclature of Organic Chemistry* (2004). http://www.iupac.org/reports/provisional/abstract04/favre_310305.html.

Chapter 15

Five- or Lower-Membered Heterocycles. Commands for Specific Use

This chapter is devoted to introduce commands for drawing 5- to 3-membered rings with skeletal hetero atoms. These commands are short-cut commands of `\fiveheterov` etc. for general use.

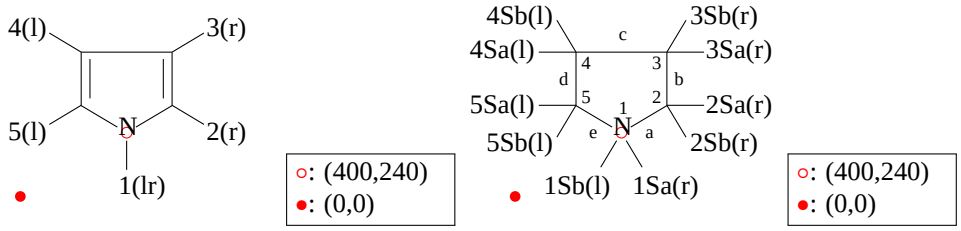
15.1 Drawing Vertical Forms of Five-Membered Heterocycles

15.1.1 Using Commands for Specific Use

The XƎMTEX command `\pyrrolev` and related macros typeset five-membered heterocyclic compounds of vertical type (hetarom.sty). The formats of these commands are as follows:

```
\pyrrolev[⟨bondlist⟩]{⟨subslist⟩}
\pyrazolev[⟨bondlist⟩]{⟨subslist⟩}
\imidazolev[⟨bondlist⟩]{⟨subslist⟩}
\isoxazolev[⟨bondlist⟩]{⟨subslist⟩}
\oxazolev[⟨bondlist⟩]{⟨subslist⟩}
\furanv[⟨bondlist⟩]{⟨subslist⟩}
\theophenev[⟨bondlist⟩]{⟨subslist⟩}
```

The following diagrams based on the command `pyrrolev` show the numbering for designating substitution positions as well as the bond specification for writing double bonds:



Each of the macros is capable of typesetting both saturated and unsaturated derivatives. The optional argument ⟨bondlist⟩ specifies bonds to be doubled as shown in Table 15.1. The default setting is to produce a fully unsaturated ring (a mancude-ring system); on the other hand, a null argument or H in ⟨bondlist⟩ produces a fully saturated ring.

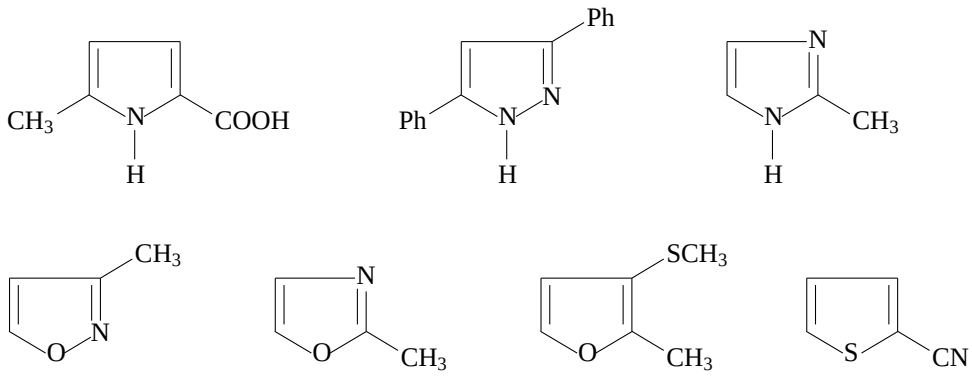
The argument ⟨subslist⟩ is used to specify each substituent with a locant number and a bond modifier shown in Table 3.2, in which *n* is an Arabic numeral between 1 and 5. For example, the statements,

Table 15.1. Argument ⟨bondlist⟩ for Commands `\pyrrolev`, *etc.*

Character	Printed structure
none	mother nucleus (a mancude-ring system)
H or [ ]	fully saturated form
a	1,2-double bond
b	2,3-double bond
c	4,3-double bond
d	4,5-double bond
e	5,1-double bond
A	aromatic circle
{*n*+}	plus at the *n*-nitrogen atom (*n* = 1 to 5)

```
\pyrrolev{1==H;2==COOH;5==CH$_{3}$}\qquad\qquad\qquad
\pyrazolev{1==H;3==Ph;5==Ph}\qquad
\imidazolev{1==H;2==CH$_{3}$} \par
\isoxazolev{3==CH$_{3}$}\qquad
\oxazolev{2==CH$_{3}$} \qquad
\furanv{2==CH$_{3}$;3==SCH$_{3}$} \qquad
\thiophenev{2==CN}
```

produce the following structures:

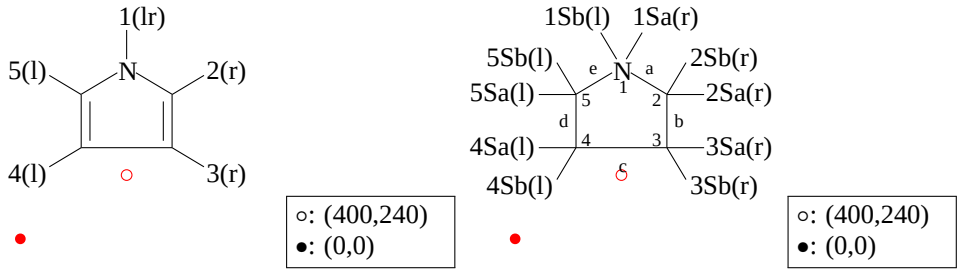


Note that these structures exhibit fully unsaturated rings (mancude-ring systems), because each ⟨bondlist⟩ is omitted.

The XeLaTeX command `\pyrrolevi` and related macros are used to draw five-membered heterocyclic compounds of inverse vertical type (hetarom.sty). The formats of these commands are as follows:

```
\pyrrolevi[⟨bondlist⟩]{⟨subslist⟩}
\pyrazolevi[⟨bondlist⟩]{⟨subslist⟩}
\imidazolevi[⟨bondlist⟩]{⟨subslist⟩}
\isoxazolevi[⟨bondlist⟩]{⟨subslist⟩}
\oxazolevi[⟨bondlist⟩]{⟨subslist⟩}
\furanvi[⟨bondlist⟩]{⟨subslist⟩}
\theophenevi[⟨bondlist⟩]{⟨subslist⟩}
```

The locant numbering and the bond specification are shown in the following diagrams based on `\pyrrolevi`.

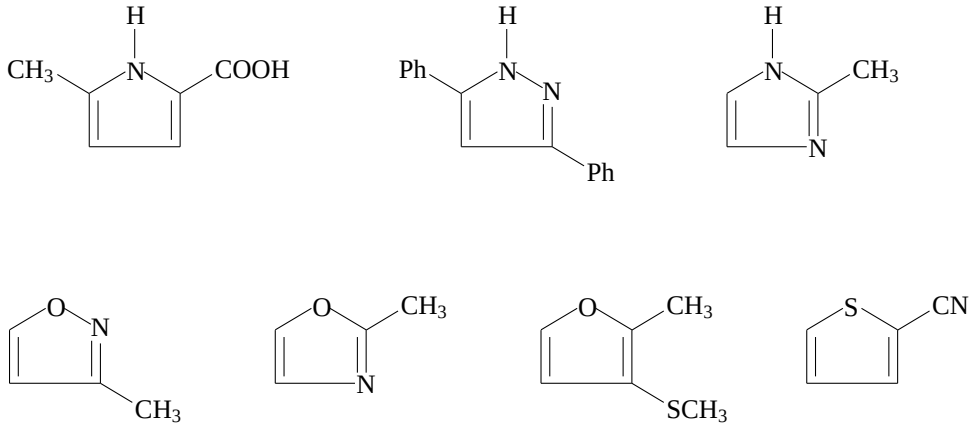


The arguments ⟨bondlist⟩ and ⟨subslist⟩ have the same formats as above (Tables 15.1 and 3.2). The following examples show the effect of changing the suffix ‘v’ into ‘vi’ by using the corresponding inverse commands.

Examples for `\pyrrolevi` etc.:

```
\pyrrolevi{1==H;2==COOH;5==CH$_{3}$}\qquad\qquad\qquad
\pyrazolevi{1==H;3==Ph;5==Ph}\qquad
\imidazolevi{1==H;2==CH$_{3}$}\par
\isoxazolevi{3==CH$_{3}$}\qquad
\oxazolevi{2==CH$_{3}$} \qquad
\furanvi{2==CH$_{3}$;3==SCH$_{3}$} \qquad
\thiophenevi{2==CN}
```

produce the following structures:



The locant numbers and alphabets of the X$\mathfrak{H}$MTEX commands with the suffix ‘v’ are compared with those of their inverse macros with the suffix ‘vi’ (Fig. 15.1). The first and second rows of Fig. 15.1 collect X$\mathfrak{H}$MTEX commands with suffix ‘v’, while the third and fourth rows collect the inverse commands with suffix ‘vi’.

The numbering in X$\mathfrak{H}$MTEX commands with suffix ‘v’ collected in Fig. 15.1 is selected to be anti-clockwise, while the numbering in X$\mathfrak{H}$MTEX commands with suffix ‘vi’ is selected to be clockwise.

15.1.2 Using Commands for General Use

As already described in Subsection 3.4.3, the X$\mathfrak{H}$MTEX commands `\fiveheterov` and `\fiveheterovi` for general use serve as general macros for drawing five-membered heterocyclic derivatives of vertical type (hetarom.sty). It is especially useful to draw heterocyclic compounds having combinations of skeletal atoms other than nitrogen atoms.

The following structures are cited from Chapter 2 (P-22) of IUPAC nomenclature [1] in order to demonstrate a variety of heterocyclic compounds accessible by using the X$\mathfrak{H}$MTEX command `\fivehetrov` for general use.

Examples for `\fiveheterov`:

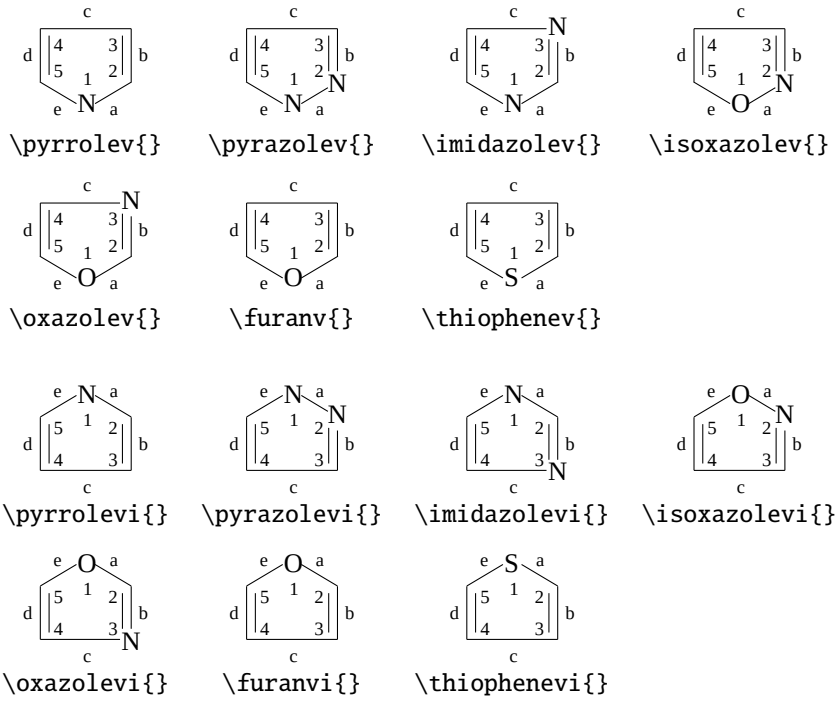
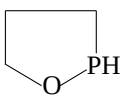
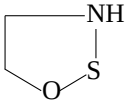


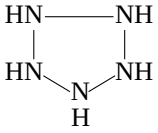
Figure 15.1. Locant numbers and alphabets of XƎMTEX commands of vertical type for specific use of drawing five-membered heterocycles. The first and second rows collect XƎMTEX commands with suffix ‘`v`’ and the third and fourth rows collect the inverse commands with suffix ‘`vi`’.



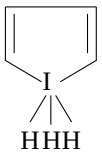
```
\fiveheterov
{1==O;2==PH}{}
```
1,2-oxaphospholane



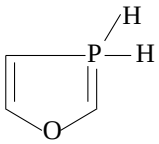
```
\fiveheterov
{1==O;2==S;3==NH}{}
```
1,2,3-oxathiazolidine



```
\fiveheterov
{1==\downnobond{N}{H};%
2==NH;3==NH;%
4==HN;5==HN}{}
```
pentaazolidine



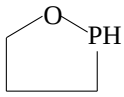
```
\fiveheterov[bd]
{1==I}{1==H;1Sa==H;1Sb==H}
```
1*H*-1λ^5-iodole



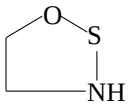
```
\fiveheterov
[bd]{1==O;3==P}
{3Sa==H;3Sb==H}
```
1,3λ^5-oxaphosphole

The following examples show the effect of changing the suffix ‘`v`’ into ‘`vi`’ by using the corresponding inverse command `\fiveheterovi`.

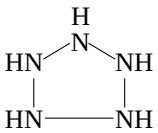
Examples for `\fiveheterovi`:



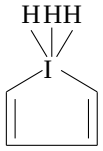
```
\fiveheterovi
{1==O;2==PH}{}
```
1,2-oxaphospholane



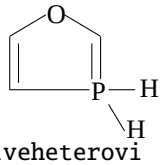
```
\fiveheterovi
{1==O;2==S;3==NH}{}
```
1,2,3-oxathiazolidine



```
\fiveheterovi
{1==\upnobond{N}{H};%
2==NH;3==NH;%
4==HN;5==HN}{}
```
pentaazolidine



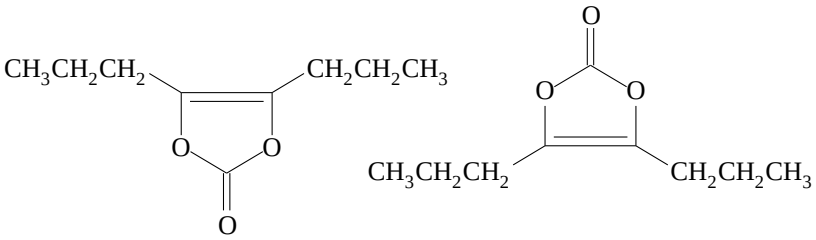
```
\fiveheterovi[bd]
{1==I}{1==H;1Sa==H;1Sb==H}
```
1*H*-1λ^5-iodole



```
\fiveheterovi
[bd]{1==O;3==P}
{3Sa==H;3Sb==H}
```
1,3λ^5-oxaphosphole

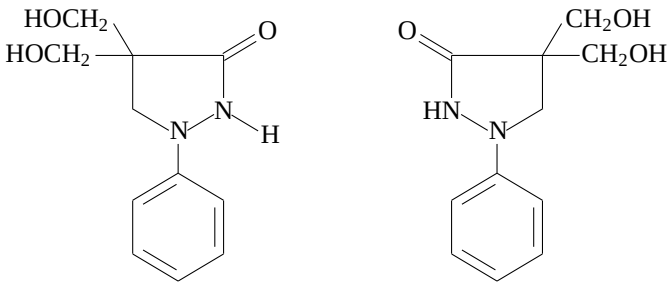
The following structures of dipropylvinylene carbonate (4,5-dipropyl-1,3-dioxolen-2-one) [2] require full entries of ⟨bondlist⟩, ⟨atomlist⟩, and ⟨subslist⟩ in the usage of `\fiveheterov` or `\fiveheterovi`.

```
\fiveheterov[c]{2==O;5==O}{1D==O;%
3==\ChemForm{CH_2CH_2CH_3};4==\ChemForm{CH_3CH_2CH_2}} \hskip2cm
\fiveheterovi[c]{2==O;5==O}{1D==O;%
3==\ChemForm{CH_2CH_2CH_3};4==\ChemForm{CH_3CH_2CH_2}}
```



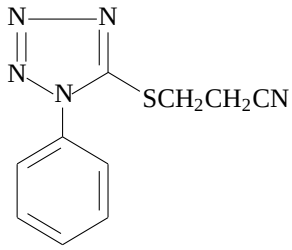
The structure of 4,4-di(hydroxymethyl)-1-phenyl-3-pyrazolidone as a developer in instant color photographic films [3,4] is drawn in two ways. One is based on `\pyrazolev` with preselected positions of two skeletal nitrogens. The other is based on `\fiveheterov` which is able to select the positions of two skeletal nitrogens.

```
\pyrazolev[H]{1==\benzenev{1==(yl)};2==H;3D==O;%
4Sa==HOCH$_{2}$;4Sb==HOCH$_{2}$} \qquad\qquad
\fiveheterov{1==N;5==HN}%
{1==\benzenev{1==(yl)};4D==O;%
3Sa==CH$_{2}$OH;3Sb==CH$_{2}$OH}
```



The structure of 5-(2-cyanoethylthio)-1-phenyltetrazole as a development inhibitor in instant color photographic films [3,4] is drawn by using `\fiveheterov`.

```
\fiveheterov[bd]{1==N;3==N;4==N;5==N}%
{1==\benzenev{1==(yl)};2==SCH$_{2}$CH$_{2}$CN}
```



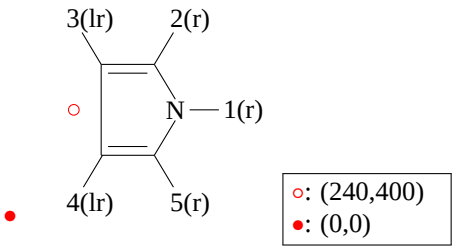
15.2 Drawing Horizontal Forms of Five-Membered Heterocycles

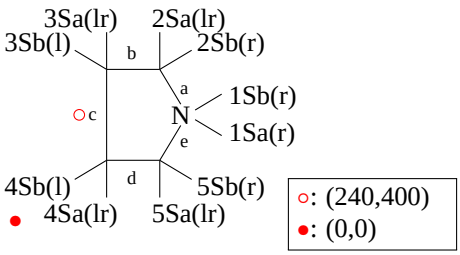
15.2.1 Using Commands for Specified Use

The XeLaTeX command `\pyrroleh` and related macros are used to draw five-membered heterocyclic compounds of horizontal type (hetaromh.sty). The formats of these commands are as follows:

```
\pyrroleh[⟨bondlist⟩]{⟨subslist⟩}
\pyrazoleh[⟨bondlist⟩]{⟨subslist⟩}
\imidazoleh[⟨bondlist⟩]{⟨subslist⟩}
\isoxazoleh[⟨bondlist⟩]{⟨subslist⟩}
\oxazoleh[⟨bondlist⟩]{⟨subslist⟩}
\furanh[⟨bondlist⟩]{⟨subslist⟩}
\theopheneh[⟨bondlist⟩]{⟨subslist⟩}
```

The following diagrams show the numbering for designating substitution positions:

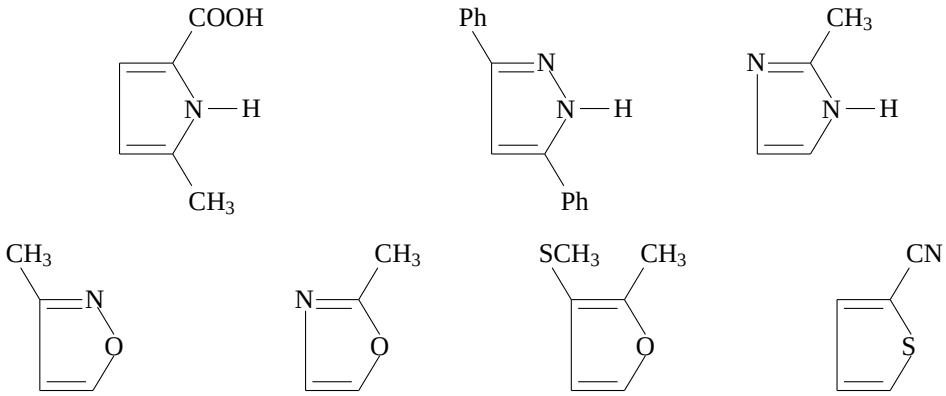




For ⟨bondlist⟩, see Table 15.1. The argument ⟨subslist⟩ has the same format as shown in Table 3.2. For example, the statements,

```
\pyrroleh{1==H;2==COOH;5==CH$_{3}$}\qquad\qquad\qquad
\pyrazoleh{1==H;3==Ph;5==Ph}\qquad
\imidazoleh{1==H;2==CH$_{3}$} \par
\isoxazoleh{3==CH$_{3}$}\qquad
\oxazoleh{2==CH$_{3}$} \qquad
\furanh{2==CH$_{3}$;3==SCH$_{3}$} \qquad
\thiopheneh{2==CN}
```

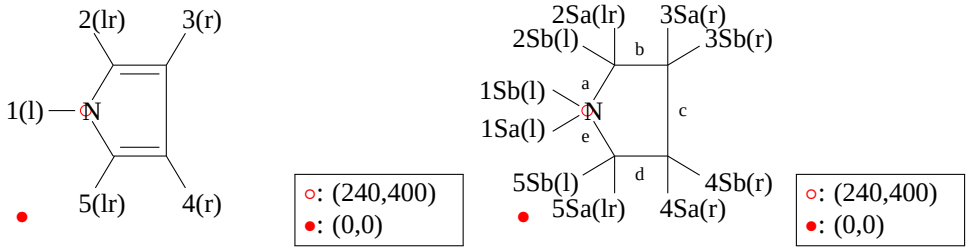
produce the following structures:



The XeLaTeX command `\pyrrolehi` and related macros are used to draw five-membered heterocyclic compounds of inverse horizontal type (hetaromh.sty). The formats of these commands are as follows:

```
\pyrrolehi[⟨bondlist⟩]{⟨subslist⟩}
\pyrazolehi[⟨bondlist⟩]{⟨subslist⟩}
\imidazolehi[⟨bondlist⟩]{⟨subslist⟩}
\isoxazolehi[⟨bondlist⟩]{⟨subslist⟩}
\oxazolehi[⟨bondlist⟩]{⟨subslist⟩}
\furanhi[⟨bondlist⟩]{⟨subslist⟩}
\theophenehi[⟨bondlist⟩]{⟨subslist⟩}
```

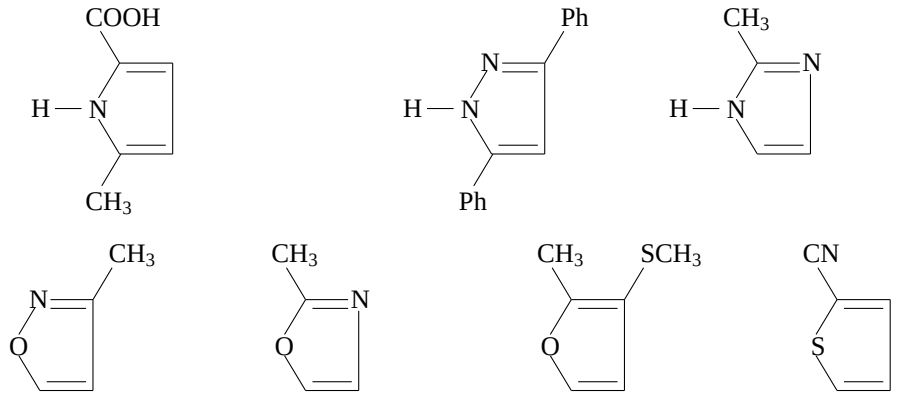
The locant numbering for designating substitution positions and the bond specification for setting double bonds are shown in the following diagrams:



The arguments ⟨bondlist⟩ and ⟨subslist⟩ have the same formats as above (Tables 15.1 and 3.2). For example, the statements,

```
\pyrrolehi{1==H;2==COOH;5==CH$_{3}$}\qquad\qquad\qquad
\pyrazolehi{1==H;3==Ph;5==Ph}\qquad
\imidazolehi{1==H;2==CH$_{3}$}\par
\isoxazolehi{3==CH$_{3}$}\qquad
\oxazolehi{2==CH$_{3}$} \qquad
\furanhi{2==CH$_{3}$;3==SCH$_{3}$} \qquad
\thiophenehi{2==CN}
```

produce the following structures:



The locant numbers and alphabets of the XeLaTeX commands with the suffix ‘h’ are compared with those of their inverse macros with the suffix ‘hi’ (Fig. 15.2). The first and second rows of Fig. 15.2 collect XeLaTeX commands with suffix ‘h’, while the third and fourth rows collect the inverse commands with suffix ‘hi’. The numbering in XeLaTeX commands with suffix ‘h’ is selected to be anti-clockwise, while the numbering in XeLaTeX commands with suffix ‘hi’ is selected to be clockwise. Compare Fig. 15.2 with Fig. 15.1.

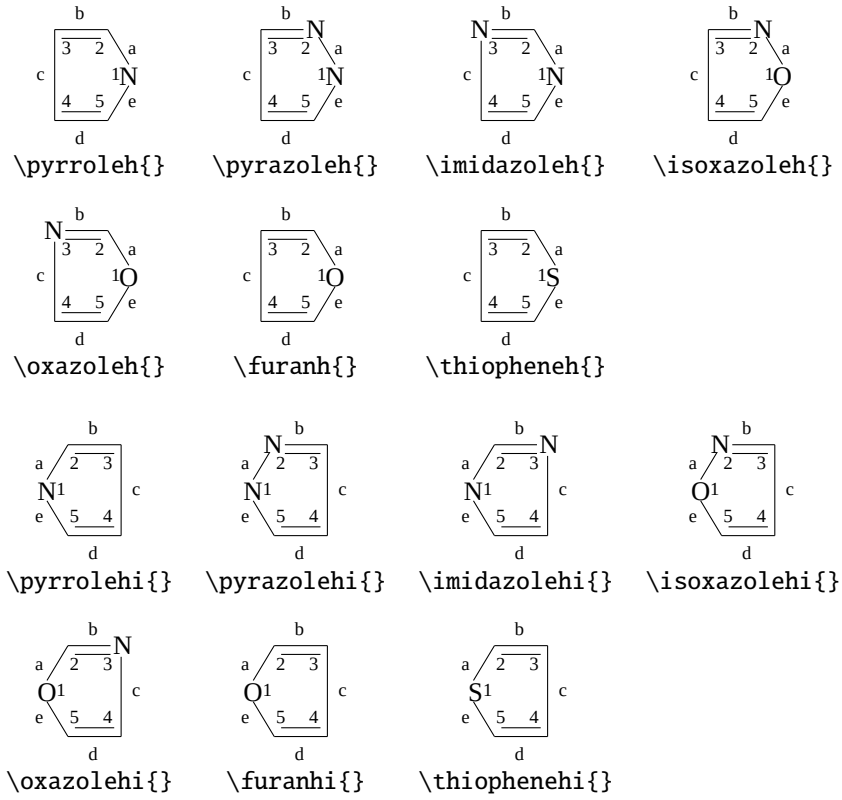


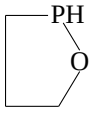
Figure 15.2. Locant numbers and alphabets of XeLaTeX commands of horizontal type for specific use of drawing five-membered heterocycles. The first and second rows collect XeLaTeX commands with suffix ‘h’ and the third and fourth rows collect the inverse commands with suffix ‘hi’.

15.2.2 Using Commands for General Use

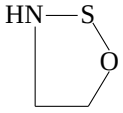
As already described in Subsection 3.4.3, the XeLaTeX commands `\fiveheteroh` and `\fiveheterohi` for general use serve as general macros for drawing five-membered heterocyclic derivatives of horizontal type

(hetarom.sty). It is especially useful to draw heterocyclic compounds having combinations of skeletal atoms other than nitrogen atoms.

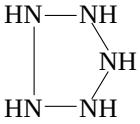
Examples for `\fiveheteroh`:



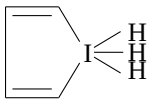
`\fiveheteroh`
`{1==O;2==PH}{}`
1,2-oxaphospholane



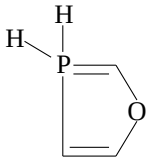
`\fiveheteroh`
`{1==O;2==S;3==HN}{}`
1,2,3-oxathiazolidine



`\fiveheteroh`
`{1==NH;%`
`2==NH;3==HN;%`
`4==HN;5==NH}{}`
pentaazolidine



`\fiveheteroh[bd]`
`{1==˜˜I}{1==H;1Sa==H;1Sb==H}`
1*H*-1λ^5-iodole

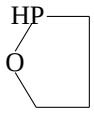


`\fiveheteroh`
`[bd]{1==O;3==P}`
`{3Sa==H;3Sb==H}`
1,3λ^5-oxaphosphole

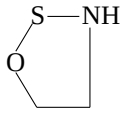
Note that the setting `1==˜˜I` is adopted in place of `1==I` to adjust the position of I in the printed-out structure of 1*H*-1λ^5-iodole. This is because the width of the letter I is narrower than the default setting of the X$\mathfrak{H}$MTEX system, which is suitable for accommodating usual letters such as N, O, and S. In addition, the handedness of each position should be taken into consideration. We should manually differentiate between `NH` and `HN` in `\fiveheteroh` as well as between `\upnobond{N}{H}` and `\downnobond{N}{H}` in `\fiveheterov`.

These results of the X$\mathfrak{H}$MTEX command `\fiveheteroh` for general use should be compared with the inverse counterpart `\fiveheterohi` listed below.

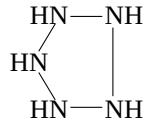
Examples for `\fiveheterohi`:



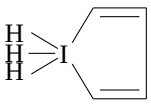
`\fiveheterohi`
`{1==O;2==HP}{}`
1,2-oxaphospholane



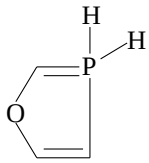
`\fiveheterohi`
`{1==O;2==S;3==NH}{}`
1,2,3-oxathiazolidine



`\fiveheterohi`
`{1==HN;%`
`2==HN;3==NH;%`
`4==NH;5==HN}{}`
pentaazolidine



`\fiveheterohi[bd]`
`{1==I˜˜}{1==H;1Sa==H;1Sb==H}`
1*H*-1λ^5-iodole



`\fiveheterohi`
`[bd]{1==O;3==P}`
`{3Sa==H;3Sb==H}`
1,3λ^5-oxaphosphole

Note again that the setting `1==I˜˜` in place of `1==I` is to adjust the position of I to be printed out in the structure of 1*H*-1λ^5-iodole.

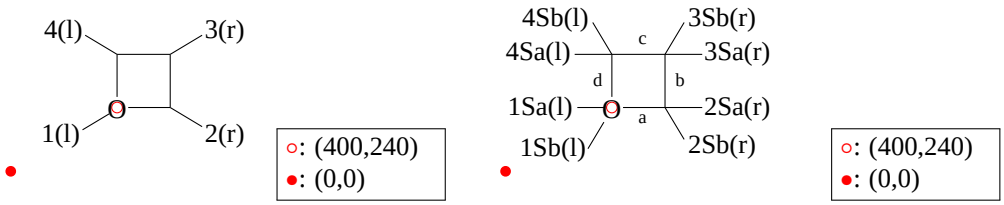
15.3 Drawing Four-Membered Heterocycles

15.3.1 Using Commands for Specific Use

The XeLaTeX command `\oxetane` and related macros are used to draw four-membered heterocyclic compounds (hetarom.sty). The formats of these commands are as follows:

```
\oxetane[⟨bondlist⟩]{⟨subslist⟩}
\azetidine[⟨bondlist⟩]{⟨subslist⟩}
\thietane[⟨bondlist⟩]{⟨subslist⟩}
```

The locant numbering is common in these commands as shown in the following diagram of `\oxetane`:



The handedness for each oriented or double-sided position is shown with a character set in parentheses. The optional argument ⟨bondlist⟩ is used for the bond specification shown in Table 15.2, which is essentially equivalent to Table 3.4 for the XeLaTeX command `\fourhetero` for general use. The default setting is to produce a fully saturated ring. The argument ⟨subslist⟩ is used to specify each substituent with a locant number and a bond modifier shown in Table 3.2, in which *n* is an Arabic numeral between 1 and 4.

Table 15.2. Argument ⟨bondlist⟩ for Commands `\oxetane` and others

Character	Printed structure	Character	Printed structure
none	mother compound (fully saturated)		
a	1,2-double bond	b	2,3-double bond
c	3,4-double bond	d	4,1-double bond
{*n*+}	plus at the *n*-nitrogen atom (*n* = 1 to 4)		

The XeLaTeX version 5.01 provides three commands of specific use for drawing four-membered heterocyclic compounds, as collected in Fig. 15.3.

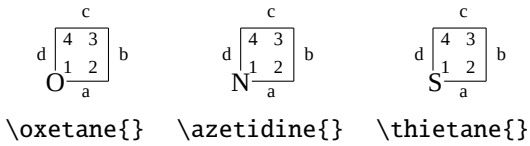
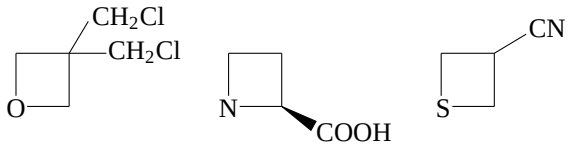


Figure 15.3. Locant numbers and alphabets of XeLaTeX commands for specific use of drawing four-membered heterocycles.

Examples for `\oxetane` etc.:

```
\oxetane{3Sa==CH$_{2}$Cl;3Sb==CH$_{2}$Cl}
\azetidine{2B==COOH}
\thietane{3==CN}
```

produce the following structures:



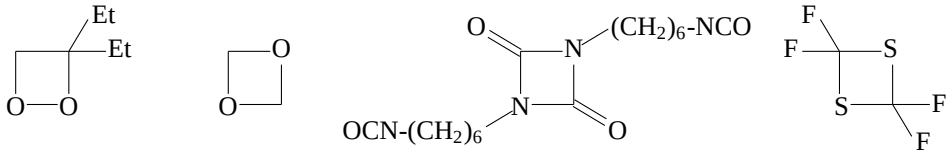
15.3.2 Using Commands for General Use

As already described in Subsection 3.4.2, the XƎMTEX command `\fourhetero` for general use serves as a general macro for drawing four-membered heterocyclic derivatives (hetarom.sty). It is especially useful to draw heterocyclic compounds having two or more skeletal atoms at given skeletal positions, e.g., 1,2-dioxetane, 1,3-dioxetane, 1,3-diazetidine, and 1,3-dithietane.

Examples for `\fourhetero`:

```
\fourhetero{1==O;2==O}{3Sa==Et;3Sb==Et}
\fourhetero{1==O;3==O}{} \quad\qquad
\fourhetero{1==N;3==N}{1==OCN-(CH$_{2}$)$_{6}$;3==(CH$_{2}$)$_{6}$-NCO;%
2D==O;4D==O} \qquad\qquad
\fourhetero{1==S;3==S}{2Sa==F;2Sb==F;4Sa==F;4Sb==F}
```

produce the following structures:



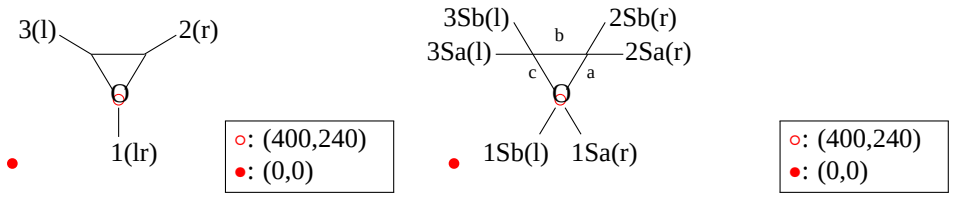
15.4 Drawing Vertical Forms of Three-Membered Heterocycles

15.4.1 Using Commands for Specific Use

The XƎMTEX command `\oxiranev` and related macros typeset three-membered heterocyclic compounds of vertical type (hetarom.sty). The formats of these commands are as follows:

```
\oxiranev[⟨bondlist⟩]{⟨subslist⟩}
\aziridinev[⟨bondlist⟩]{⟨subslist⟩}
\thiiranev[⟨bondlist⟩]{⟨subslist⟩}
```

The locant numbering is common as shown in the following diagram of `\oxiranev`:



The handedness for each oriented or double-sided position is shown with a character set in parentheses. The optional argument ⟨bondlist⟩ specifies double bonds as shown in Table 15.3, which is essentially equiv-

alent to Table 3.3 for `\threeheterov` etc. described in Subsection 3.4.1. The default setting is to produce a fully saturated ring.

Table 15.3. Argument ⟨bondlist⟩ for Command `\oxiranev` and Related Ones

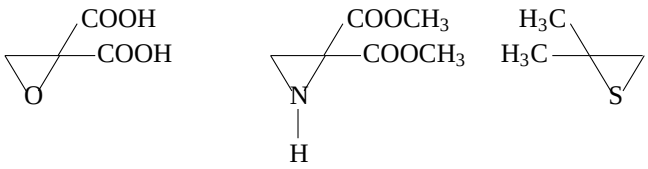
Character	Printed structure
none	saturated
a	1,2-double bond
b	2,3-double bond
c	3,1-double bond
A	aromatic circle
{*n*+}	plus at the n-hetero atom (n = 1 to 3)
	n = 4 – outer plus at 1 position
	n = 5 – outer plus at 2 position
	n = 6 – outer plus at 3 position
{0+}	plus at the center of a cyclopropane ring

The argument ⟨atomlist⟩ takes a usual format with respect to hetero atoms attached to *n* = 1 to 3, *e.g.*, 1==N for a nitrogen atom at 1-position. The argument ⟨subslist⟩ describes each substituent with a locant number and a bond modifier shown in Table 3.2, in which *n* is an Arabic numeral between 1 and 3.

Examples for `\oxiranev` etc.:

```
\oxiranev{2Sa==COOH;2Sb==COOH}\qquad
\aziridinev{1==H;2Sa==COOCH$_{3}$;2Sb==COOCH$_{3}$}\qquad\qquad
\thiiranev{3Sa==H$_{3}$C;3Sb==H$_{3}$C}
```

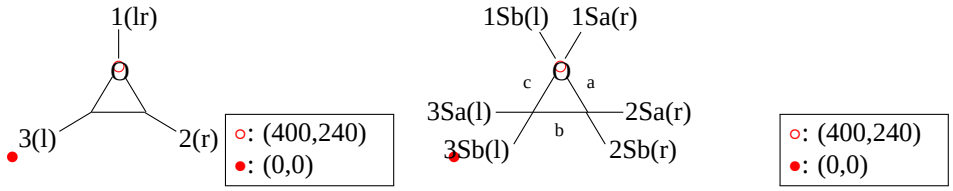
produce the following structures:



The X$\mathfrak{Z}$MTEX command `\oxiranevi` and related macros typeset three-membered heterocyclic compounds of inverse vertical type (hetarom.sty). The formats of these commands are as follows:

```
\oxiranevi[⟨bondlist⟩]{⟨subslist⟩}
\aziridinevi[⟨bondlist⟩]{⟨subslist⟩}
\thiiranevi[⟨bondlist⟩]{⟨subslist⟩}
```

The locant numbering is common as shown in the following diagram of `\oxiranevi`:

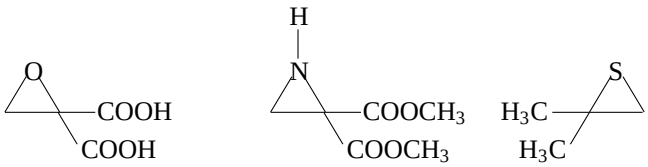


The arguments ⟨bondlist⟩ and ⟨subslist⟩ have the same formats as above (Tables 15.3 and 3.2). The following examples show the effect of changing the suffix '`v`' into '`vi`' by using the corresponding inverse commands.

Examples for `\oxiranevi` etc.:

```
\oxiranevi{2Sa==COOH;2Sb==COOH}\qquad
\aziridinevi{1==H;2Sa==COOCH$_{3}$;2Sb==COOCH$_{3}$}\qquad\qquad
\thiiranevi{3Sa==H$_{3}$C;3Sb==H$_{3}$C}
```

produce the following structures:



The locant numbers and alphabets of the X^^MTEX commands with the suffix ‘v’ are compared with those of their inverse macros with the suffix ‘vi’ (Fig. 15.4). The first row of Fig. 15.4 collects X^^MTEX commands with suffix ‘v’, while the second row collects the inverse commands with suffix ‘vi’.

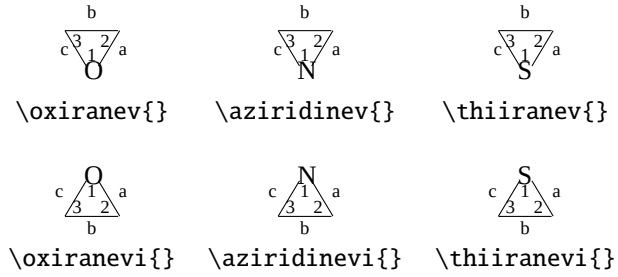


Figure 15.4. Locant numbers and alphabets of X^^MTEX commands of vertical type for specific use of drawing three--membered heterocycles. The first row collects X^^MTEX commands with suffix ‘v’ and the second row collects the inverse commands with suffix ‘vi’.

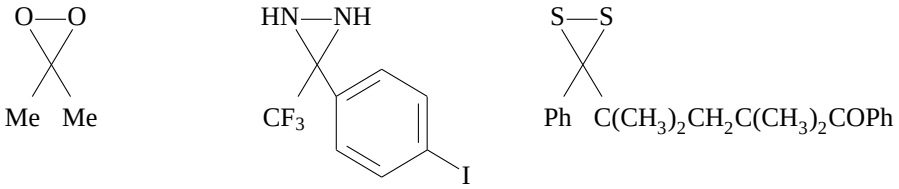
The numbering in X^^MTEX commands with suffix ‘v’ collected in Fig. 15.4 is selected to be anti-clockwise, while the numbering in X^^MTEX commands with suffix ‘vi’ is selected to be clockwise.

15.4.2 Using Commands for General Use

As already described in Subsection 3.4.1, the X^^MTEX commands `\threeheterov` and `\threeheterovi` for general use serve as general macros for drawing three-membered heterocyclic derivatives (hetarom.sty). They are especially useful to draw a broader range of heterocyclic compounds.

For example, three-membered hetrocycles with two hetero atoms can be drawn by using the X^^MTEX command `\threeheterov`, e.g., dimethyldioxirane (derived from acetone), a commercially available diaziridine, and the first isolable dithiirane [5].

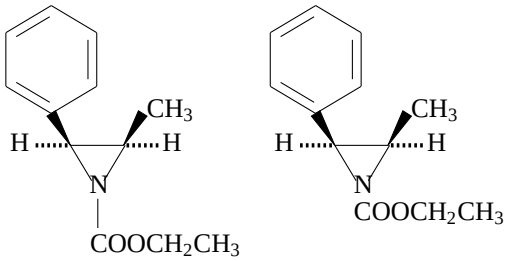
```
\threeheterov{2==O;3==O}{1Sa==Me;1Sb==Me} \qquad
\threeheterov{2==NH;3==HN}{1Sb==CF$_{3}$;%
1Sa==\benzenev{6==(yl);3==I}} \qquad
\threeheterov{2==S;3==S}{%
1Sb==Ph;1Sa==\ChemForm{C(CH_3)_2CH_2C(CH_3)_{2}COPh}}
```



An aziridine-1-carbonate [6] is drawn in two different ways with and without a linking bond between a nitrogen atom and a carbethoxy group, where the former applies the substitution technique to the ⟨subslist⟩ of `\aziridinev`, while the latter applies the replacement technique to the ⟨atimslist⟩ of `\threeheterov`.

```
\aziridinev{3SB==\benzenev{4==(yl)};3SA==H;
```

```
2SA==H;2SB==CH$_{3}$;1==COOCH$_{2}$CH$_{3}$}
\threeheterov{1==\downnobond{N}{COOCH$_{2}$CH$_{3}$}}
{3SB==\benzenev{4==(yl)};3SA==H;2SA==H;2SB==CH$_{3}$}
```



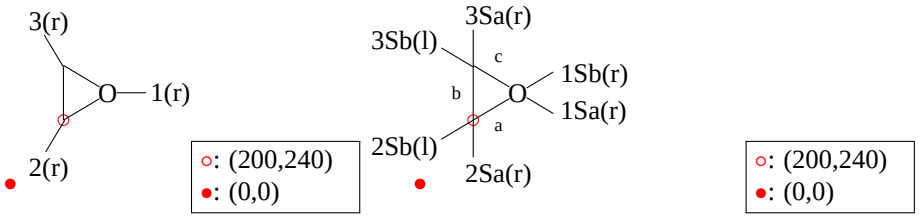
15.5 Drawing Horizontal Forms of Three-Membered Heterocycles

15.5.1 Using Commands for Specific Use

The XƎMTEX command `\oxiraneh` and related macros typeset three-membered heterocyclic compounds of horizontal type (hetaromh.sty). The formats of these commands are as follows:

```
\oxiraneh[⟨bondlist⟩]{⟨subslist⟩}
\aziridineh[⟨bondlist⟩]{⟨subslist⟩}
\thiiraneh[⟨bondlist⟩]{⟨subslist⟩}
```

The locant numbering is common as shown in the following diagram of `\oxiraneh`:

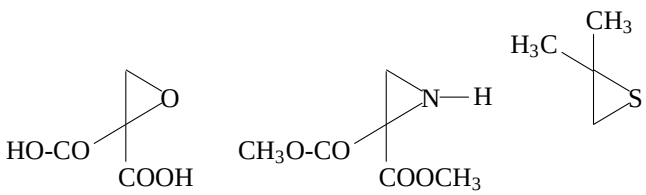


The handedness for each oriented or double-sided position is shown with a character set in parentheses. The optional argument ⟨bondlist⟩ specifies double bonds as shown in Table 15.3. The default setting is to produce a fully saturated ring. The argument ⟨subslist⟩ has the same format as above (Table 3.2).

Examples for `\oxiraneh` etc.:

```
\oxiraneh{2Sa==COOH;2Sb==HO-CO}\qquad \qquad
\aziridineh{1==H;2Sa==COOCH$_{3}$;2Sb==CH$_{3}$O-CO}\qquad
\thiiraneh{3Sa==CH$_{3}$;3Sb==H$_{3}$C}
```

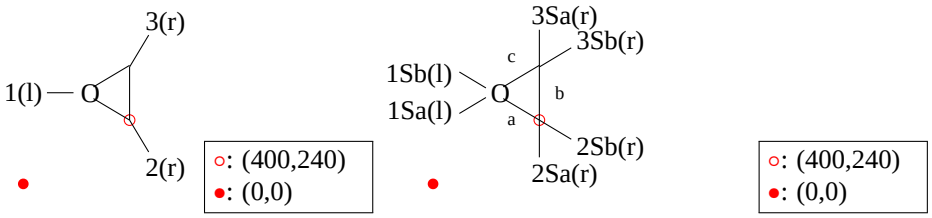
produce the following structures:



The XƎMTEX command `\oxiranehi` and related macros typeset three-membered heterocyclic compounds of inverse vertical type (hetaromh.sty). The formats of these commands are as follows:

```
\oxiranehi[⟨bondlist⟩]{⟨subslist⟩}
\aziridinehi[⟨bondlist⟩]{⟨subslist⟩}
\thiiranehi[⟨bondlist⟩]{⟨subslist⟩}
```

The locant numbering is common as shown in the following diagram of `\oxiranehi`:

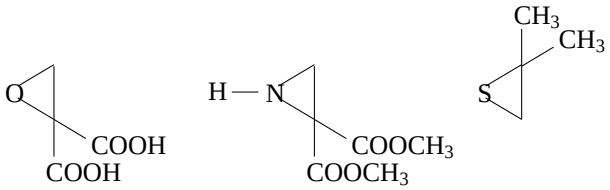


The handedness for each oriented or double-sided position is shown with a character set in parentheses. The arguments ⟨bondlist⟩ and ⟨subslist⟩ have the same formats as above (Tables 15.3 and 3.2). The default setting is to produce a fully saturated ring. The following examples show the effect of changing the suffix '`h`' into '`hi`' by using the corresponding inverse commands.

Examples for `\oxiranehi` etc.:

```
\oxiranehi{2Sa==COOH;2Sb==COOH}\qquad \qquad
\aziridinehi{1==H;2Sa==COOCH$_{3}$;2Sb==COOCH$_{3}$}\qquad
\thiiranehi{3Sa==CH$_{3}$;3Sb==CH$_{3}$}
```

produce the following structures:



The locant numbers and alphabets of the X$\mathfrak{H}$MTEX commands with the suffix '`h`' are compared with those of their inverse macros with the suffix '`hi`' (Fig. 15.5). The first row of Fig. 15.5 collects X$\mathfrak{H}$MTEX commands with suffix '`h`', while the second row collects the inverse commands with suffix '`hi`'.

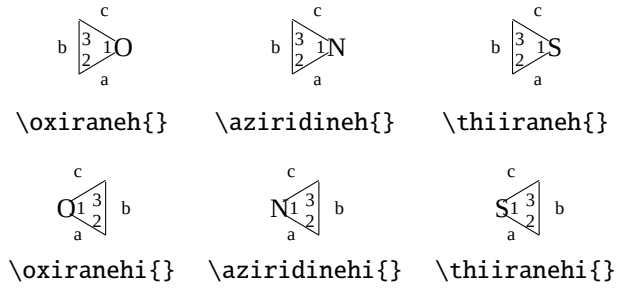


Figure 15.5. Locant numbers and alphabets of X$\mathfrak{H}$MTEX commands of vertical type for specific use of drawing three--membered heterocycles. The first row collects X$\mathfrak{H}$MTEX commands with suffix '`h`' and the second row collects the inverse commands with suffix '`hi`'.

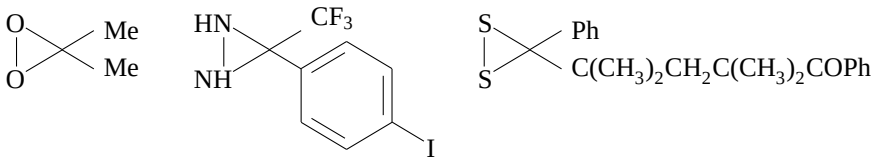
The numbering in X$\mathfrak{H}$MTEX commands with suffix '`h`' collected in Fig. 15.5 is selected to be clockwise, while the numbering in X$\mathfrak{H}$MTEX commands with suffix '`hi`' is selected to be anti-clockwise.

15.5.2 Using Commands for General Use

As already described in Subsection 3.4.1, the X$\mathfrak{H}$MTEX commands `\threeheteroh` and `\threeheterohi` for general use serve as general macros for drawing three-membered heterocyclic derivatives (hetaromh.sty). They are especially useful to draw a broader range of heterocyclic compounds.

For example, three-membered hetrocycles with two hetero atoms can be drawn by using the XƎMTEX command `\threeheterov`, e.g., The derivatives drawn by the XƎMTEX command `\threeheterov`, i.e., dimethyldioxirane (derived from acetone), a commercially available diaziridine, and the first isolable dithiirane [5], are redrawn here by using `\threeheteroh` as follows:

```
\threeheterov{2==O;3==O}{1Sa==Me;1Sb==Me} \qquad
\threeheterov{2==NH;3==HN}{1Sb==\raisebox{5pt}{CF$_{3}$};%
1Sa==\benzenev{6==(yl);3==I}} \qquad\qquad
\threeheterov{2==S;3==S}{%
1Sb==Ph;1Sa==\ChemForm{C(CH_3)_2CH_2C(CH_3)_{2}COPh}}
```



Note that the setting `1Sb==\raisebox{5pt}{CF$_{3}$}` in the command `\threeheteroh` of the second example is to avoid the superposition on the phenyl group.

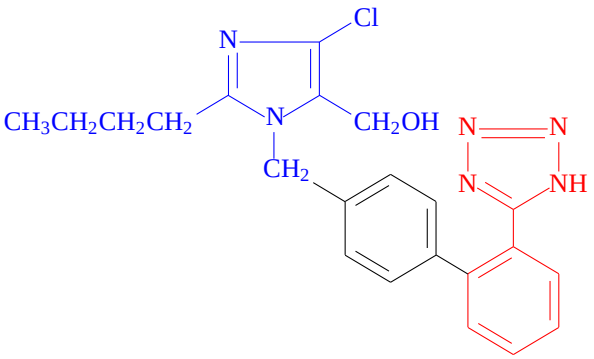
15.6 Illustrative Examples of Drawing Five- or Smaller-Membered Heterocycles

15.6.1 Generation of Substituents by (yl)-Functions

The XƎMTEX commands described in this chapter are able to generate substituents by using the (yl)-function technique. The resulting substituents can participate in substitution due to the substitution technique.

Example 15.1. The structure **15-1** of losartan developed by Merck as an angiotensin II receptor antagonist is drawn by dual application of the substitution technique. One red-colored substituent is drawn by declaring a (yl)-function in the ⟨subslist⟩ of the command `\fiveheterov`, which is further included in the ⟨subslist⟩ of the inner command `\benzenev` (the red-colored code). The other blue-colored substituent, which is generated by declaring a (yl)-function in the ⟨subslist⟩ of the command `\fiveheterov`, is further included in the `\lyl` command to add a linking divalent unit (CH_2) (the blue-colored code). The two substituents are declared in the ⟨subslist⟩ of the outer command `\benzenev`, which prints out the parent structure.

```
\benzenev{%
3==\benzenev{6==(yl);1==\fiveheterov[ce]{2==NH;3==N;4==N;5==N}{1==(yl)}};%
6==\lyl(6==CH$_{2}$){0==\fiveheterov[bd]{1==N;4==N}{1==(yl);2==CH$_{2}$OH;3==Cl;
5==CH$_{3}$CH$_{2}$CH$_{2}$CH$_{2}$}}}
```

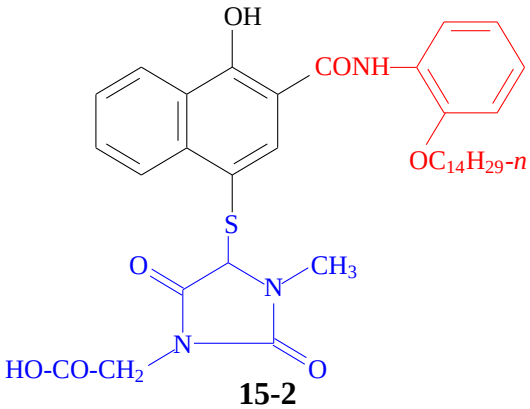


15-1 □

Example 15.2. The structure **15-2** of a bleach-accelerator-releasing coupler used in color photography [4, page 306] is drawn by the substitution technique, where a (yl)-function declared in the command

`\fiveheterovi` (or the command `\benzeneh`) along with the command `\ryl` plays an important role. Note that the two substituents at the positions 2 and 4 of a naphthalene parent structure drawn by `\naphthalenev` are generated by using the respective colored codes, i.e., a red-colored code for a substituent at the position 2 and a blue-colored code for a substituent at the position 4. The code for the hydroxyl group at the position 1 is shown in black.

```
\naphthalenev{1==OH;%
2==\ryl(5==CONH){4==\benzeneh{1==(yl);6==OC$_{14}$H$_{29}$-\textit{n}}};%
4==\ryl(0==S){8==\fiveheterovi{2==N;4==N}%
{1==(yl);2==CH$_{3}$;3D==O;4==HO-CO-CH$_{2}$;5D==O}}}
```

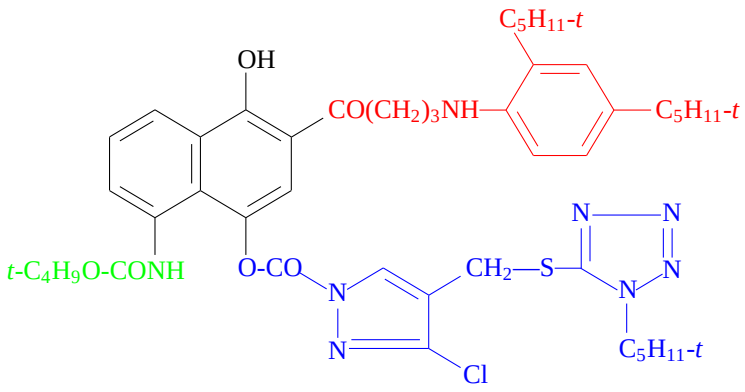


15-2

□

Example 15.3. The structure **15-3** of a multi-timing development-inhibitor-releasing coupler [4, page 302] is drawn by the multiple substitution technique in a nested fashion. The two five-membered rings are drawn by declaring (yl)-functions in `\fiveheterovi` and `\fiveheterov`. Note that the three substituents at the positions 2, 4, and 5 of a naphthalene parent structure drawn by `\naphthalenev` are generated by using the respective colored codes, i.e., a red-colored code for a substituent at the position 2, a blue-colored code for a substituent at the position 4, and a green-colored code for a substituent at the position 5. The code for the hydroxyl group at the position 1 is shown in black.

```
\naphthalenev{1==OH;%
2==\ryl(5==CO{(CH$_{2}$)}$_{3}$NH){4==\benzeneh{1==(yl);%
2==C$_{5}$H$_{11}$-\textit{t};4==C$_{5}$H$_{11}$-\textit{t}}};%
4==\ryl(0==O-CO){5==\fiveheterovi[ac]{4==N;5==N}{5==(yl);3==Cl;%
2==\ryl(5==CH$_{2}$---S){4==\fiveheterov[bd]{1==N;2==N;3==N;4==N}%
{5==(yl);1==C$_{5}$H$_{11}$-\textit{t}}}}};%
5==\lmoiety{\textit{t}-C$_{4}$H$_{9}$O-CON\rlap{H}}}
```

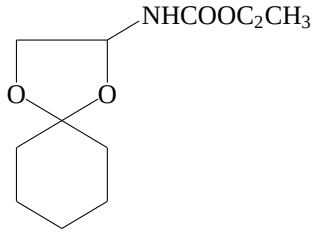


15-3

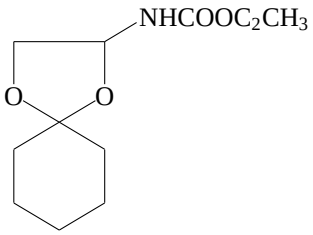
□

Example 15.4. The structure **15-4** of a derivative of cyclohexanone ethylene acetal [7] is drawn by the replacement technique. Thus, the setting of a (yl)-function in the command `\fiveheterov` generates a 1,3-dioxolane ring as an attached component, which is declared in the ⟨atomlist⟩ of `\sixheterov`.

```
\sixheterov{1s==\fiveheterov{2==O;5==O}%
{1==(yl);3==NHCOOC$_{2}$CH$_{3}$}}{}
```



15-4



15-4′

On the other hand, an apparently equivalent structure **15-4′** is drawn by an alternative code:

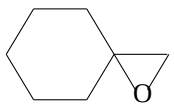
```
\fiveheterov{2==O;5==O;
1s==\cyclohexanev{1==(yl)}}{3==NHCOOC$_{2}$CH$_{3}$}
```

where the setting of a (yl)-function in the command `\cyclohexanev` generates a cyclohexane ring as an attached component, which is declared in the ⟨atomlist⟩ of `\fiveheterov` for drawing a 1,3-dioxolane ring as a parent structure. □

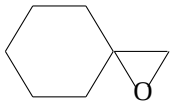
Example 15.5. Two diagrams **15-5** and **15-5′** for the structure of 1-oxaspiro[2.5]octane are drawn in two ways of different modes of the replacement technique:

```
\sixheteroh{4s==\oxiranev{3==(yl)}}{}
\threeheterov{1==O;3s==\cyclohexaneh{4==(yl)}}{}
```

where the former adopts a (yl)-function of the command `\oxiranev` for specific use, while the latter adopts a (yl)-function of the command `\cyclohexaneh` for specific use. The commands of general use, `\sixheteroh` and `\threeheterov`, are used to draw the parent structures. These codes produce the following diagrams respectively:



15-5



15-5′

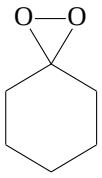
Note that the the command `\oxiranev` for drawing oxirane derivatives is available as a command for specific use in the XƎMTEX system. □

Example 15.6. Because no command of specific use for drawing dioxirane derivatives is unavailable in the standard distribution of the XƎMTEX system, the command `\threeheterov` of general use should be used to draw a dioxirane structure as a parent structure (for the purpose of the replacement technique and of the addition technique) and as a substituent due to a (yl)-function (for the purpose of the substitution technique and of the replacement technique).

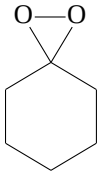
The command `\threeheterov` of general use is used to draw two diagrams **15-6** and **15-6′** for the structure of 1,2-dioxaspiro[2.5]octane, where the replacement technique is applied to the command `\threeheterov` in two different ways.

```
\threeheterov{2==O;3==O;1s==\cyclohexanev{1==(yl)}}{}
\sixheterov{1s==\threeheterov{2==O;3==O}{1==(yl)}}{}
```

The first code uses the command `\threeheterov` to draw a parent structure, while the second code uses the command `\threeheterov` to generate a substituent by means of a (yl)-function. These codes produce the following diagrams, which are apparently the same except their control points:



15-6



15-6′

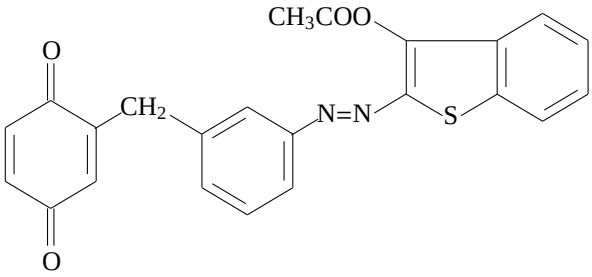
□

15.6.2 As Parent Structures for Ring Fusion

The XyMTEX commands described in this chapter are able to serve as parent structures for ring fusion in the addition technique.

Example 15.7. For the purpose of drawing the structure **15-7** of an azo dye having a quinone moiety [8,9], the thiophene ring is regarded as a parent structure, which is drawn by the `\thiophenev` command. On one hand, the addition technique brings about ring fusion between the thiophene ring and a six-membered fusion component due to `\sixfusev` so as to give a 6-5 fused ring. On the other hand, the left-hand azo group having a quinone moiety, which is generated by using a (yl)-function and two nested `\lyl` commands, is attached to the thiophene ring according to the substitution technique.

```
\thiophenev[d%
{b\sixfusev[ace]{}{}{e}}]%
{4==CH$_{3}$COO;5==\lyl(4==N=N){5==%
\benzenev{2==(yl);6==\lyl(5==CH$_{2}$){5==%
\benzenev[pa]{2==(yl);1D==O;4D==O}%
}}}}
```

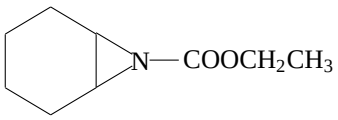


15-7

□

Example 15.8. The structure **15-8** of *N*-ethoxycarbonyl-7-azabicyclo[4.1.0]heptane [10,11] is drawn by regarding the aziridine ring as a parent structure, which is depicted by using `\aziridineh`. The attached component is derived by using `\sixfusev` and then attached to the aziridine ring by the addition technique.

```
\aziridineh[{b\sixfusev{}{}{B}}]{1==COOCH$_{2}$CH$_{3}$}
```

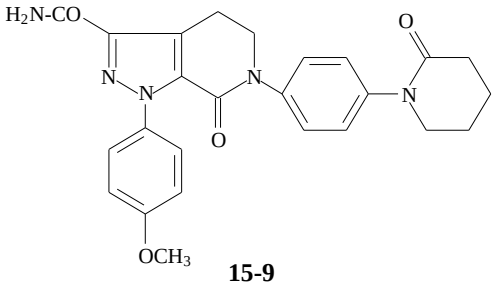


15-8

□

Example 15.9. The structure **15-9** of apixaban (Eliquis®) developed by Pfizer and Bristol-Myers Squibb is drawn by the addition technique applied to `\fiveheterov`. The fusing component based on `\sixheterov` has a substituent generated by the substitution technique due to nested (yl)-functions, which are declared in `\benzeneh` and `\sixheterov`.

```
\fiveheterov[bd%
{b\sixfusev{3==N}{4D==O;%
3==\benzeneh{1==(yl);4==\sixheteroh{1==N}{1==(yl);2D==O}}}{e}}]%
{1==N;5==N}{4==H$_{2}$N-CO;1==\benzenev{1==(yl);4==OCH$_{3}$}}
```



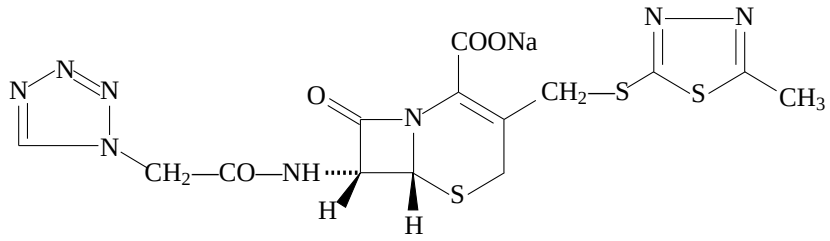
15-9

□

Example 15.10. To draw the structure **15-10** of cefazolin sodium (Sefmazon®, Cefazolin Na®), the general command `\fourhetero` is used in place of the specific command `\azetidine`. The addition technique is applied to `\fourhetero` by using a fusing unit `\sixfusev` (4 ← 6):

```
\begin{XyMcompd}(3000,900)(-900,0){cpd:cefazolinNa}{}
\fourhetero[%
{b\sixfusev[a]{4==S;6==\null}{1==COONa;5FB==H;%
2==\ryl(5==CH$_{2}$---S){3==%
\fiveheterov[bd]{1==S;3==N;4==N}{5==(yl);2==CH$_{3}$}}}{e}}%
]{3==N}{1SB==H;4D==O;%
1SA==\lyl(4==CH$_{2}$---CO---NH){3==%
\fiveheterovi[ad]{1==N;2==N;3==N;5==N}{3==(yl)}}}
\end{XyMcompd}
```

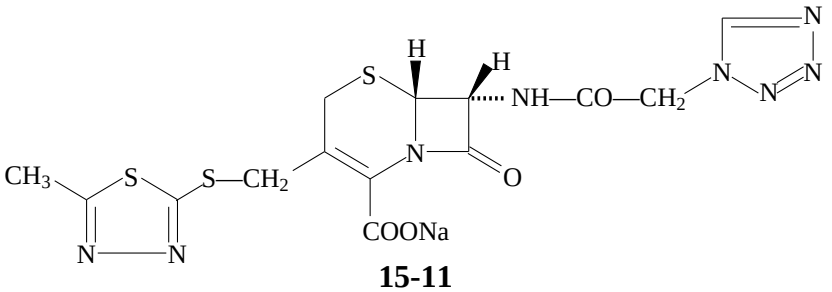
The four-membered ring due to `\fourhetero` has a side-chain generated by the substitution technique (`\lyl` and a (yl)-function declared in `\fiveheterovi`). The six-membered ring due to `\sixfusev` has a side-chain generated by the substitution technique (`\ryl` and a (yl)-function declared in `\fiveheterov`).



15-10

If you want to use `\azetidine` as a parent structure, the structural formula **15-11** rotated by 180° should be drawn by inputting the code:

```
\begin{XyMcompd}(3000,950)(-1100,-150){cpd:cefazolinNaZ}{}
\azetidine[%
{d\sixfusevi[f]{4==S;2==\null}{1==COONa;3FB==H;%
6==\lyl(3==S---CH$_{2}$){5==%
\fiveheterovi[bd]{1==S;3==N;4==N}{2==(yl);5==CH$_{3}$}}}{B}}%
]{3SB==H;2D==O;%
3SA==\ryl(4==NH---CO---CH$_{2}$){3==%
\fiveheterov[ac]{1==N;2==N;3==N;5==N}{5==(yl)}}}
\end{XyMcompd}
```

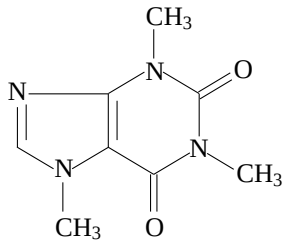


15-11

For a related structural formula, see the structural formula of cephalosporin C (**3-57**) with a four-to-six fused ring of another direction. □

Example 15.11. The structure **14-9** of caffeine has been drawn by the addition technique, where the scheme 5 → 6 has been applied. The inverse application of the addition technique is possible to give an equivalent structure **15-12**, where the command `\fiveheterov` is used to draw a five-membered parent structure, which is attached by a fusing unit generated by `\sixfusev` (5 ← 6).

```
\fiveheterov[d%
{b\sixfusev[e]{1==N;3==N}{1==CH$_{3}$;3==CH$_{3}$;2D==O;4D==O}{e}}
]{1==N;4==N}{1==CH$_{3}$}
\end{XyMcompd}
```



15-12

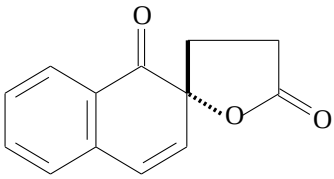
Compare this drawing with those of **2-35** and **14-9**. □

15.6.3 As Parent Structures for Spiro Ring Fusion

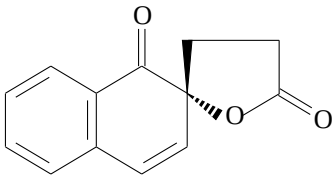
The XƎMTEX commands for general use for drawing five- or lower-membered heterocycles (Subsections 3.4.1–3.4.3) are able to serve as parent structures for spiro ring fusion in the replacement technique.

Example 15.12. The structure **15-13** of a spirolactone [12] is drawn by regarding a five-membered lactone as a parent structure, which is depicted by using `\fiveheterov`. The ⟨skelbdlist⟩ of the command `\fiveheterov` is used to generate a bold line and a bold dashed line. Compare this structure with **3-69**.

```
% use of skeletal bond list
\fiveheterov({dB}{eA}){1==O;%
5s==\decalinev[cfhk]{2==(yl);1D==O}%
}{2D==O}
% combination of bond deletion with the replacement technique
\fiveheterov{1==O;%
5s==\decalinev[cfhk]{2==(yl);1D==O};%
5s==\WedgeAsSubst(0,0)(0,1){200};%
5s==\HashWedgeAsSubst(0,0)(3,-2){120}%
}{2D==O}[de]
```



15-13

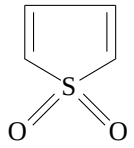


15-14

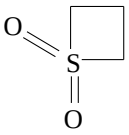
The combination of bond deletion with the replacement technique described in Subsection 3.5.4 can be applied to this case. Thereby, we obtain another code which generates a structure **15-14** with a wedge and a hashed wedge. Compare between **15-13** and **15-14**. Compare the latter structure **15-14** also with **3-85**, which is the counterpart of **3-69**. □

Example 15.13. The replacement technique is applicable to draw thiophene 1,1-dioxide **15-15**, thietane 1,1-dioxde **15-16**, and thiirane 1,1-dioxide **15-17**, where a SO_2 moiety is regarded as an attached component.

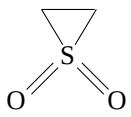
```
\fiveheterov[bd]{1h==\dtrigonal{1==(yl);0==S;2D==O;3D==O}}{}
\fourhetero{1h==\put(20,40){\Utrigonal{2==(yl);0==S;1D==O;3D==O}}}{}
\threeheterov{1h==\dtrigonal{1==(yl);0==S;2D==O;3D==O}}{}
```



15-15



15-16



15-17

The command `\put`, which is a command defined for the LATEX picture environment, can be used to adjust the position of an attached component. Note that `\put(20,40)` means that the control point (0,0) is shifted to (20, 40), where the values are determined by the unit length of the XƎMTEX system (`\unitlength` = 0.1pt). □

References

[1] IUPAC Chemical Nomenclature and Structure Representation Division, *Provisional Recommendations. Nomenclature of Organic Chemistry* (2004). http://www.iupac.org/reports/provisional/abstract04/favre_310305.html.

[2] T. Hiyama, S. Fujita, and H. Nozaki, *Yuki Gosei Kagaku Kyokai-Shi*, **31**, 623 (1973).

[3] S. Fujita, *Yuki Gosei Kagaku Kyokai-Shi*, **39**, 331–344 (1981).

[4] S. Fujita, "Organic Chemistry of Photography," Springer-Verlag, Berlin-Heidelberg (2004).

[5] A. Ishii, T. Maruta, J. Nakayama, M. Hoshino, and M. Shiro, *Angew. Chem. Intrn. Ed. Eng.*, **33**, 777–779 (1994).

[6] S. Fujita, T. Hiyama, and H. Nozaki, *Tetrahedron*, **26**, 4347–4352 (1970).

[7] T. Hiyama, S. Fujita, and H. Nozaki, *Bull. Chem. Soc. Jpn.*, **45**, 3500–3501 (1972).

[8] S. Fujita, *Yuki Gosei Kagaku Kyokai-Shi*, **37**, 960–966 (1979).

[9] S. Fujita and K. Sano, *J. Org. Chem.*, **44**, 2647–2651 (1979).

[10] T. Hiyama, S. Fujita, and H. Nozaki, *Yuki Gosei Kagaku Kyokai-Shi*, **31**, 624 (1973).

[11] T. Hiyama, H. Koide, S. Fujita, and H. Nozaki, *Tetrahedron*, **29**, 3137–3139 (1973).

[12] M. Uyanik and K. Ishihara, *Yuki Gosei Kagaku Kyokai-Shi*, **70**, 1116–1121 (2012).

Heterocycles with Fused Six-to-Six-Membered Rings. Commands for Specific Use

This chapter is devoted to introduce commands for drawing heterocyclic compounds with 6-6 fused rings. These commands are short-cut commands of `\decaheterov` etc. for general use (cf. Section 3.1 for the syntax).

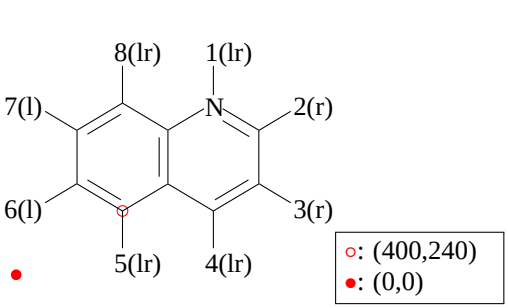
16.1 Drawing Vertical Forms

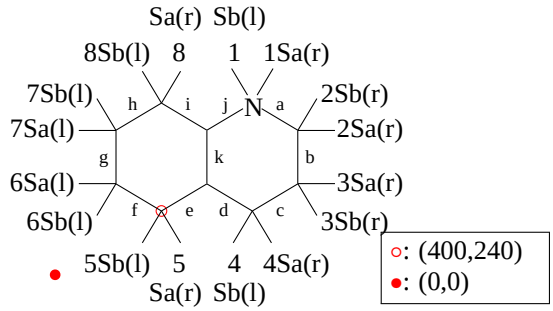
16.1.1 Using Commands for Specified Use

The X$\hat{}$MTEX command `\quinolinev` for specific use is used to draw quinoline derivatives of vertical type (hetarom.sty). Commands for drawing other fused 6-6 heterocycles are also defined. The formats of these commands are as follows:

```
\quinolinev[⟨bondlist⟩]{⟨subslist⟩}
\isoquinolinev[⟨bondlist⟩]{⟨subslist⟩}
\quinoxalinev[⟨bondlist⟩]{⟨subslist⟩}
\quinazolinev[⟨bondlist⟩]{⟨subslist⟩}
\cinnolinev[⟨bondlist⟩]{⟨subslist⟩}
\pteridinev[⟨bondlist⟩]{⟨subslist⟩}
```

Locant numbers for designating substitution positions as well as bond descriptors (locant alphabets) for setting double bonds are shown in the following diagrams of `\quinolinev` as representatives:





The handedness for each oriented or double-sided position is shown with a character set (r, l, or lr) in parentheses. Each character in the optional argument ⟨bondlist⟩ specifies an inner (endocyclic) double bond as shown in Table 16.1.

Table 16.1. Argument ⟨bondlist⟩ for Commands `\quinolinev` and the Related Commands

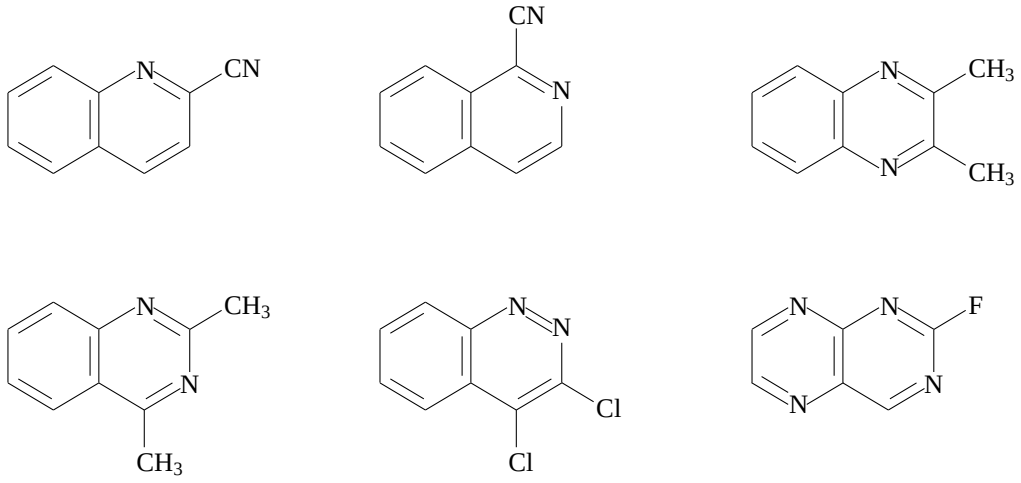
Character	Printed structure	Character	Printed structure
none or r	right-handed mancude-ring system	l	left-handed mancude-ring system
H or [ ]	fully saturated form		
a	1,2-double bond	b	2,3-double bond
c	4,3-double bond	d	4,4a-double bond
e	4a,5-double bond	f	5,6-double bond
g	6,7-double bond	h	7,8-double bond
i	8,8a-double bond	j	1,8a-double bond
k	4a,8a-double bond		
A	aromatic circle	B	aromatic circle
{*n*+}	plus at the *n*-nitrogen atom (*n* = 1 to 10)		

The argument ⟨subslist⟩ is employed to specify each substituent with a locant number and a bond modifier shown in Table 3.2, in which *n* is an Arabic numeral between 1 and 8. Substitution on 9 (4a position) or 10 (8a position) can be assigned in the usual way.

Examples for `\quinolinev` etc.:

```
\quinolinev{2==CN} \qquad
\isoquinolinev{1==CN}\qquad
\quinoxalinev{2==CH$_{3}$;3==CH$_{3}$} \par
\quinazolinev{2==CH$_{3}$;4==CH$_{3}$}\qquad
\cinnolinev{4==Cl;3==Cl} \qquad
\pteridinev{2==F}
```

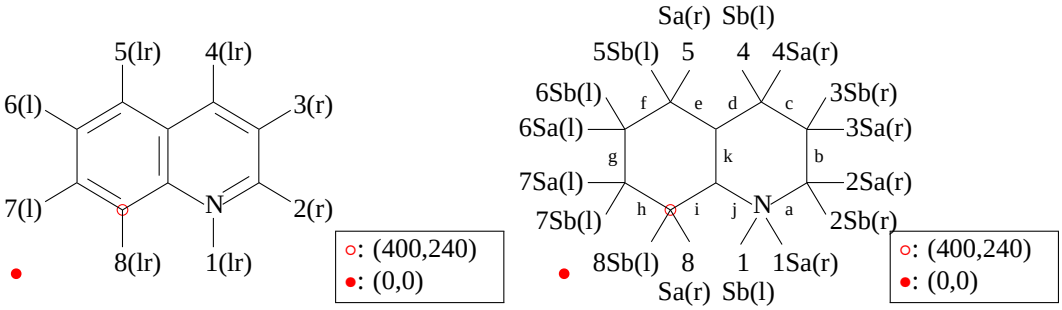
produce the following structures:



The X$\mathrm{\Xi}$MTEX command `\quinolinevi` for specific use is used to draw quinoline derivatives of inverse vertical type (hetarom.sty). Commands for depicting other fused heterocycles are also defined. The formats of these commands are as follows:

```
\quinolinevi[⟨bondlist⟩]{⟨subslist⟩}
\isoquinolinevi[⟨bondlist⟩]{⟨subslist⟩}
\quinoxalinevi[⟨bondlist⟩]{⟨subslist⟩}
\quinazolinevi[⟨bondlist⟩]{⟨subslist⟩}
\cinnolinevi[⟨bondlist⟩]{⟨subslist⟩}
\pteridinevi[⟨bondlist⟩]{⟨subslist⟩}
```

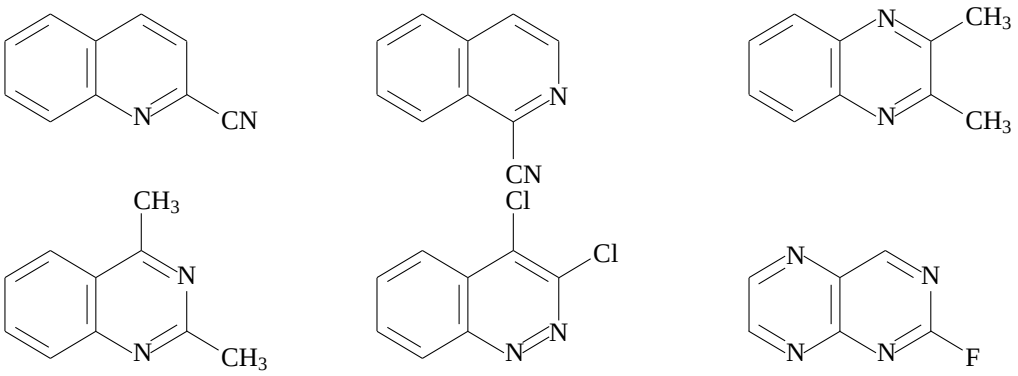
Locant numbers for designating substitution positions along with bond descriptors are represented by the following diagrams of `\quinolinevi` as representatives:



Examples for `\quinolinevi`:

```
\quinolinevi{2==CN} \qquad
\isoquinolinevi{1==CN}\qquad
\quinoxalinevi{2==CH$_{3}$;3==CH$_{3}$} \par
\quinazolinevi{2==CH$_{3}$;4==CH$_{3}$} \qquad
\cinnolinevi{4==Cl;3==Cl} \qquad
\pteridinevi{2==F}
```

produce the following structures:



The locant numbers and alphabets of the XƎMTEX commands with the suffix ‘`v`’ are compared with those of their inverse macros with the suffix ‘`vi`’ (Fig. 16.1).

The numbering in XƎMTEX commands with suffix ‘`v`’ collected in Fig. 16.1 is selected to be clockwise, while the numbering in XƎMTEX commands with suffix ‘`vi`’ is selected to be anti-clockwise.

Example 16.1. The structure **16-1** of bosutinib (Bosulif®) developed by Pfizer as a tyrosine kinase inhibitor is drawn by using the command `\quinolinev` for special use. Among the four substituents of the quinoline ring as a parent structure, one substituent at the 4-position is based on `\ryl` and a (yl)-function, The other substituent at the 7-position is based on the dual application of (yl)-functions, where the replacement technique in the inner `\pentamethylenei` command is used together with the substitution technique in the outer `\quinolinev` command.

```
\quinolinev{3==CN;6==CH$_{3}$O;%
4==\ryl(0==\llap{H}N){5==\benzenev{6==(yl);2==OCH$_{3}$;3==Cl;5==Cl}};%
7==\pentamethylenei{5==O;1==\sixheterov{3==N;6==N}{3==(yl);6==CH$_{3}$}}{5==(yl)}}
```

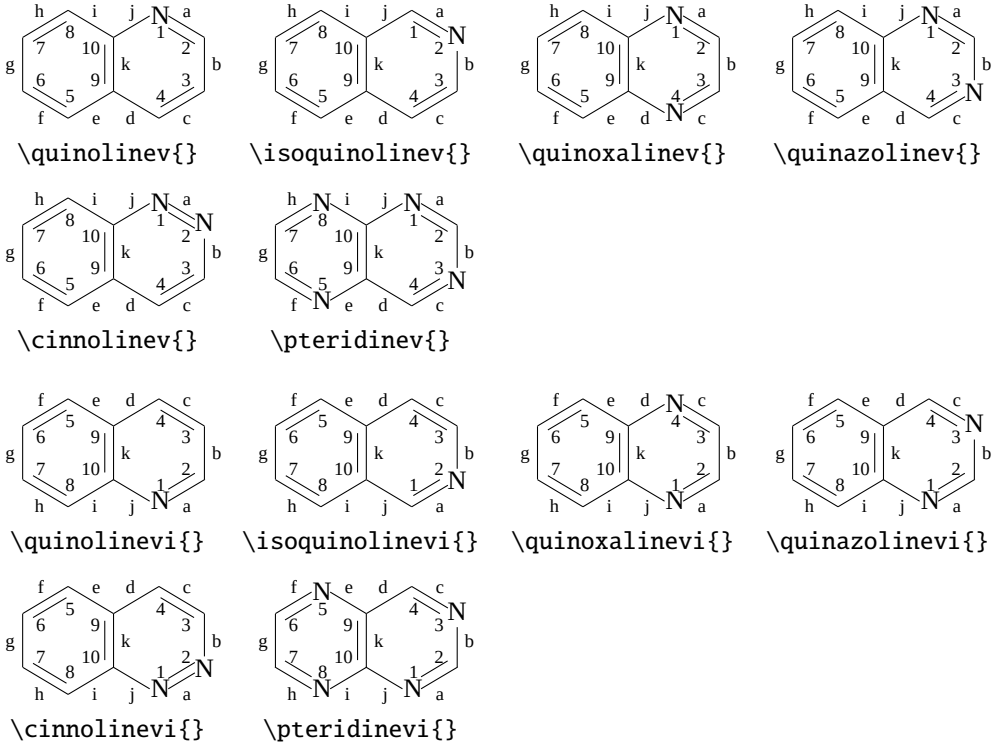
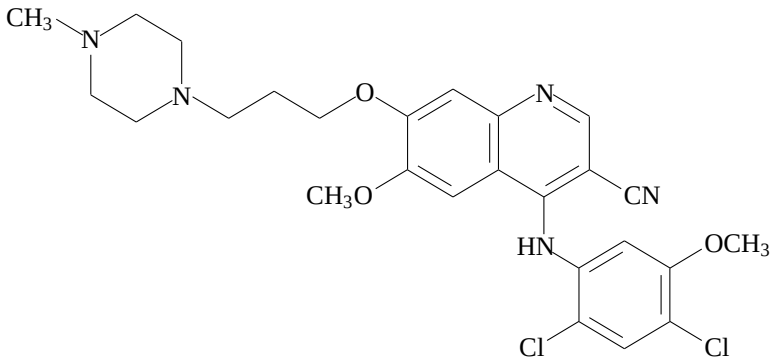


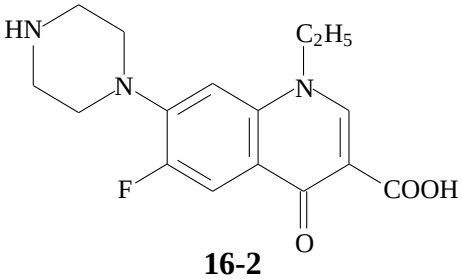
Figure 16.1. Locant numbers and alphabets of XyMTEX commands of vertical type for specific use of drawing fused six-six-membered heterocycles. The first and second rows collect XyMTEX commands with suffix 'v' and the third and fourth rows collect the corresponding commands with suffix 'vi'.



16-1 □

Example 16.2. The structure **16-2** of norfloxacin (Noroxin®) as an antibiotic is drawn by using the command `\quinolinev` for specific use, where a quinoline nucleus is regarded as a parent skeleton. The heterocyclic group is generated by a (yl)-function and attached by the substitution technique. Note that the expression of $N–C_2H_5$ at the 1-position explicitly shows the presence of a linking bond.

```
\quinolinev[bfhk]{1==C$_{2}$H$_{5}$;3==COOH;4D==O;6==F;%
7==\sixheterov{3==N;6==HN}{3==(yl)}}
```

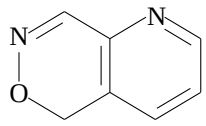


16-2 □

16.1.2 Using Commands for General Use

As already described in Subsection 3.4.6, the X$\mathfrak{Z}$MTEX commands `\decaheterov` and `\decaheterovi` for general use serve as general macros for drawing fused six-to-six-membered heterocyclic derivatives of vertical type (hetarom.sty). It is especially useful to draw heterocyclic compounds having combinations of skeletal atoms other than nitrogen atoms.

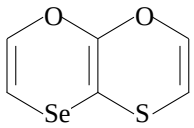
The following structures are cited from Chapter 2 (P-25) of IUPAC nomenclature [1] in order to demonstrate a variety of heterocyclic compounds accessible by using the X$\mathfrak{Z}$MTEX command `\decahetrov` for general use.



16-3

IUPAC name: 5*H*-pyrido[2.3-*d*][1.2]oxazine
X$\mathfrak{Z}$MTEX command:

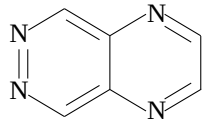
```
\decaheterov[achk]{1==N;6==O;7==N}{}
```



16-4

IUPAC name: [1.4]oxaselenino[2.3-*b*]oxathiine
X$\mathfrak{Z}$MTEX command:

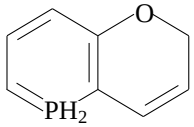
```
\decaheterov[bgk]{1==O;4==S;%
5==\SetTwoAtoms{Se};8==O}{}
```



16-5

IUPAC name: pyrazino[2,3-*d*]pyridazine
X$\mathfrak{Z}$MTEX command:

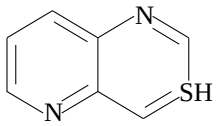
```
\decaheterov[acegi]{1==N;4==N;6==N;7==N}{}
```



16-6

IUPAC name: 2*H*-5λ^5-phosphinino[3.2-*b*]pyran
X$\mathfrak{Z}$MTEX command:

```
\decaheterov[cfhk]{1==O;%
5==\SetTwoAtoms{PH$_{2}$}}{}
```



16-7

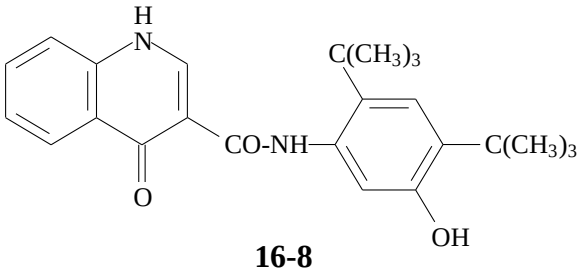
IUPAC name: 3-λ^4-pyrido[3.2-*d*][1.3]thiazine
X$\mathfrak{Z}$MTEX command:

```
\decaheterov[acegi]{1==N;3==SH;5==N}{}
```

The length of the vacant space produced by the truncation of each vertex is preset to accommodate a one-character atom (e.g., O, N, and S), so that an atom of two or more characters (e.g., Si and Se) or a group of two or more atoms (e.g., PH_2) is superposed onto the truncated bond line. The macro `\SetTwoAtoms` is used to avoid such an undesirable superposition, as found in the structures **16-4** and **16-6**.

Example 16.3. The structure **16-8** of ivacaftor (Kalydeco®) developed Vertex Pharmaceuticals as a cystic fibrosis transmembrance conductance regulator (CFTR) potentiator is drawn by using `\decaheterov`, where a quinoline ring is regarded as a parent structure. The substituent is generated by the combination of the `\ryl` command with a (yl)-function declared in `\benzeneh`. Note that the expression of NH at the 1-position shows the omission of a linking bond (cf. **16-2**).

```
\decaheterov[bfhk]{1==\upnobond{N}{H}}{4D==O;%
3==\ryl(3==CO-NH){%
4==\benzeneh{1==(yl);2==C(CH$_{3}$)$_{3}$;4==C(CH$_{3}$)$_{3}$;5==OH}}
```



16-8

□

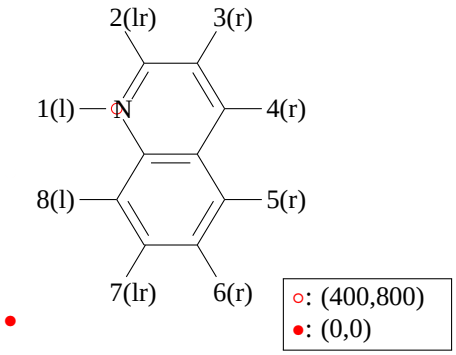
16.2 Drawing Horizontal Forms

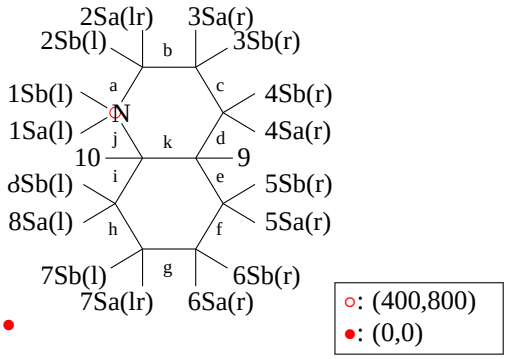
16.2.1 Using Commands for Specified Use

The horizontal counterparts of the commands of vertical type (`\quinolinev`, etc.) are defined similarly in the package file, hetaromh.sty.

```
\quinolineh[⟨bondlist⟩]{⟨subslist⟩}
\isoquinolineh[⟨bondlist⟩]{⟨subslist⟩}
\quinoxalineh[⟨bondlist⟩]{⟨subslist⟩}
\quinazolineh[⟨bondlist⟩]{⟨subslist⟩}
\cinnolineh[⟨bondlist⟩]{⟨subslist⟩}
\pteridineh[⟨bondlist⟩]{⟨subslist⟩}
```

Locant numbers (1–10) for designating substitution positions and bond descriptors (a–k) are found in the following diagram of `\quinolineh`:



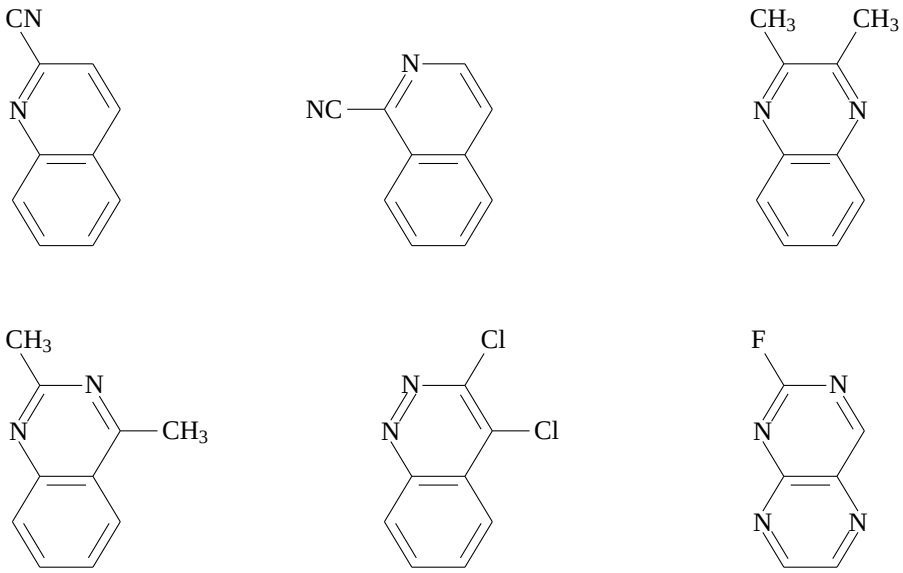


The handedness for each oriented or double-sided position is shown with a character set (r, l, or lr) in parentheses. The optional argument ⟨bondlist⟩ specifies double bonds to be typeset, as shown in Table 16.1.

Examples of `\quinolineh` etc.:

```
\quinolineh{2==CN} \qquad
\isoquinolineh{1==NC}\qquad
\quinoxalineh{2==CH$_{3}$;3==CH$_{3}$} \par
\quinazolineh{2==CH$_{3}$;4==CH$_{3}$}\qquad
\cinnolineh{4==Cl;3==Cl} \qquad
\pteridineh{2==F}
```

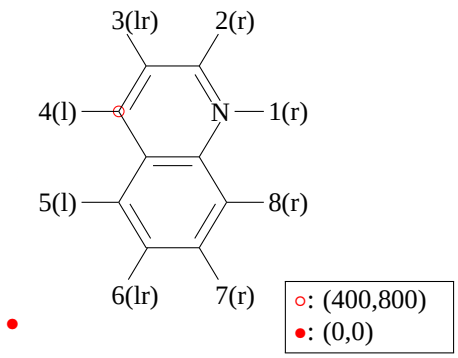
produce the following structures:

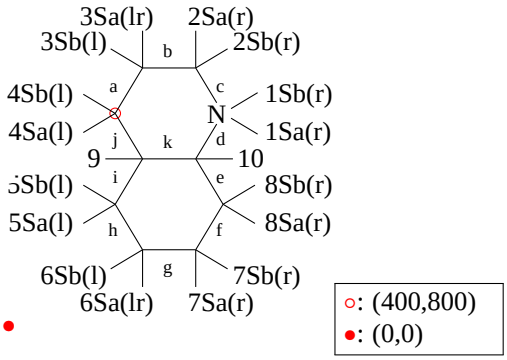


The X$\mathrm{\lambda}$MTEX command `\quinolinehi` defined in the package hetaromh.sty is used to draw quinoline derivatives of inverse horizontal type. Macros for drawing other fused heterocycles are also defined in the package hetaromh.sty. The formats of these commands are as follows:

```
\quinolinehi[⟨bondlist⟩]{⟨subslist⟩}
\isoquinolinehi[⟨bondlist⟩]{⟨subslist⟩}
\quinoxalinehi[⟨bondlist⟩]{⟨subslist⟩}
\quinazolinehi[⟨bondlist⟩]{⟨subslist⟩}
\cinnolinehi[⟨bondlist⟩]{⟨subslist⟩}
\pteridinehi[⟨bondlist⟩]{⟨subslist⟩}
```

Locant numbers for designating substitution positions and characters (a–f) for designating double bonds are shown in the following diagram of `\quinolinehi`:

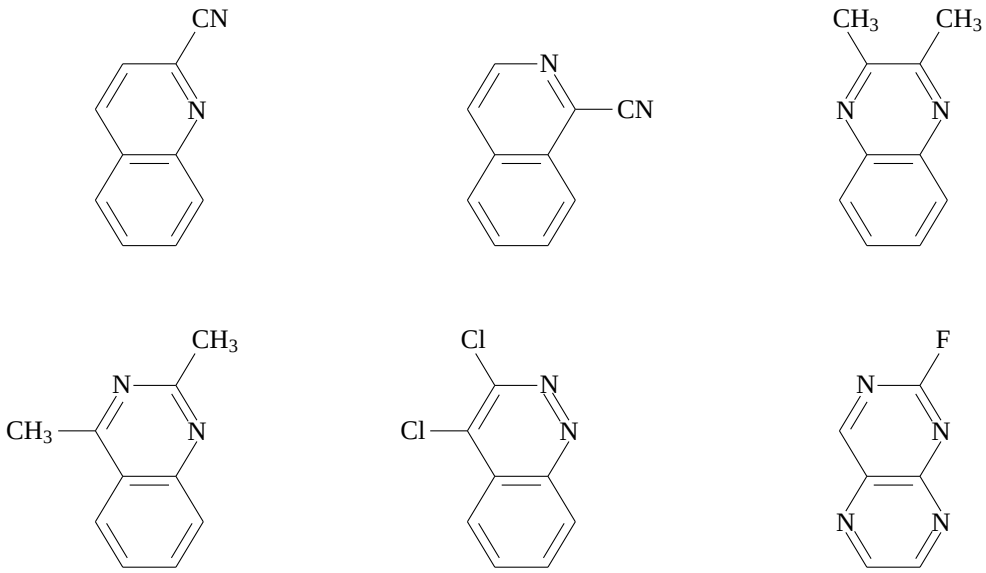




Examples of `\quinolinehi` etc.:

```
\quinolinehi{2==CN} \qquad
\isoquinolinehi{1==CN}\qquad
\quinoxalineh{2==CH$_{3}$;3==CH$_{3}$} \par
\quinazolinehi{2==CH$_{3}$;4==CH$_{3}$} \qquad
\cinnolinehi{4==Cl;3==Cl} \qquad
\pteridinehi{2==F}
```

produce the following structures:



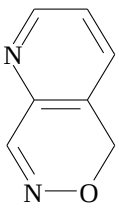
The locant numbers and alphabets of the XƎMTEX commands with the suffix ‘h’ are compared with those of their inverse macros with the suffix ‘hi’ (Fig. 16.2).

The numbering in XƎMTEX commands with suffix ‘h’ collected in Fig. 16.2 is selected to be clockwise, while the numbering in XƎMTEX commands with suffix ‘hi’ is selected to be anti-clockwise.

16.2.2 Using Commands for General Use

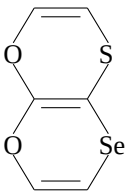
As already described in Subsection 3.4.6, the XƎMTEX commands `\decaheteroh` and `\decaheterohi` for general use serve as general macros for drawing fused six-to-six-membered heterocyclic derivatives of horizontal type (hetaromh.sty). It is especially useful to draw heterocyclic compounds having combinations of skeletal atoms other than nitrogen atoms.

The structures **16-3**–**16-7** depicted above by using the command `\decaheterov` are redrawn by using the horizontal counterpart `\decaheteroh`.



16-9

IUPAC name: 5*H*-pyrido[2.3-*d*][1.2]oxazine
XƎMTEX command:
`\decaheteroh[achk]{1==N;6==O;7==N}{}`



16-10

IUPAC name: [1.4]oxaselenino[2.3-*b*]oxathiine
XƎMTEX command:
`\decaheteroh[bgk]{1==O;4==S;5==Se;8==O}{}`

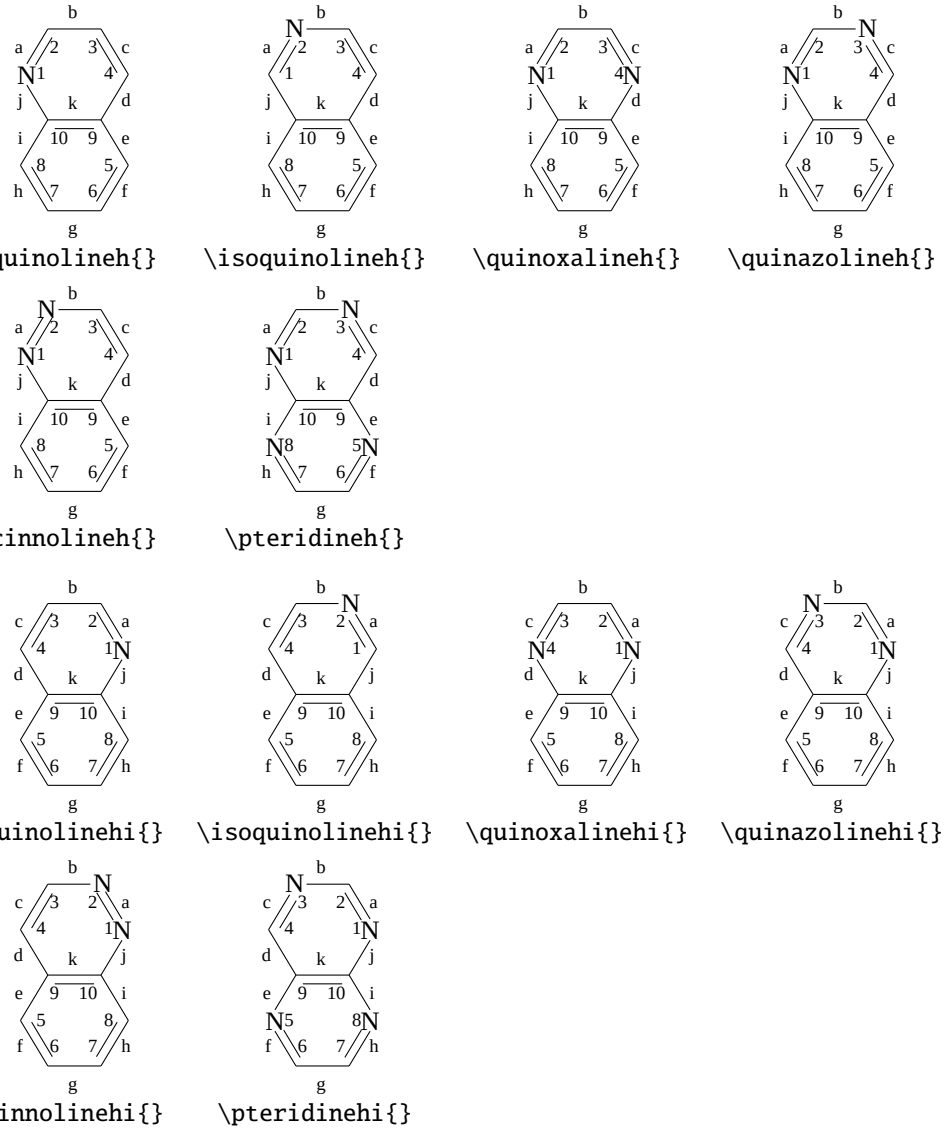
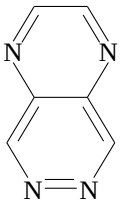
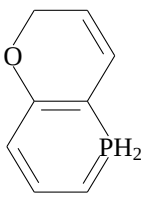


Figure 16.2. Locant numbers and alphabets of XeTeX commands of horizontal type for specific use of drawing fused six-six-membered heterocycles. The first and second rows collect XeTeX commands with suffix '`h`' and the third and fourth rows collect the corresponding commands with suffix '`hi`'.



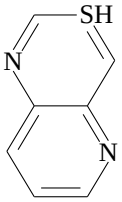
IUPAC name: pyrazino[2,3-*d*]pyridazine
XeTeX command:
`\decaheteroh[acegi]{1==N;4==N;6==N;7==N}{}`

16-11



IUPAC name: 2*H*-5λ^5-phosphinino[3.2-*b*]pyran
XeTeX command:
`\decaheteroh[cfhk]{1==O;5==PH$_{2}$}{}`

16-12

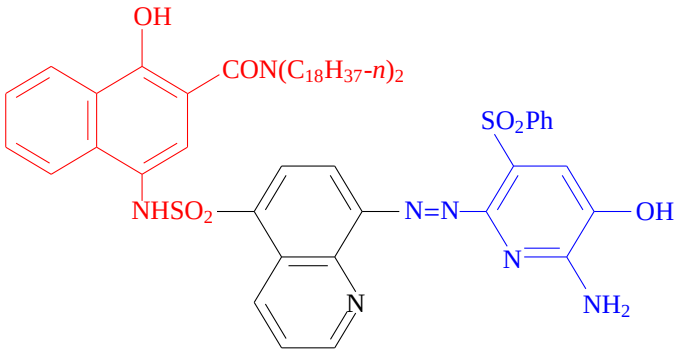


IUPAC name: 3-λ^4-pyrido[3.2-*d*][1.3]thiazine
XeTeX command:
```
\decaheteroh[acegi]{1==N;3==SH;5==N}{}
```

16-13

Example 16.4. The structure **16-14** of a *p*-sulfoamidonaphthol dye releaser [2, page 438] is regarded as a derivative of quinoline with two substituents, as depicted in color (red and blue). The quinoline structure is drawn by using the command `\decaheteroh` for general use, because the command `\quinolineh` or `\quinolinehi` for specific use has a skeletal nitrogen at an undesirable position.

```
\decaheteroh[acfhk]{5==N}{%
1==\lyl(4==NHSO$_{2}$){0==\naphthalenev{%
4==(yl);1==OH;2==CON(C$_{18}$H$_{37}$-\textit{n})$_{2}$}};%
4==\ryl(4==N=N){4==\sixheteroh[ace]{6==N}%
{1==(yl);2==SO$_{2}$Ph;4==OH;5==NH$_{2}$}}}
```



16-14

The two substituents are depicted by means of the substitution technique applied to the ⟨subslist⟩ of the `\decaheteroh`. The substituent at locant no. 1 (the 5-position of quinoline) is generated by the combination of `\lyl` with a (yl)-function declared in `\naphthalenev` (the red-colored code). The other substituent at locant no. 4 (the 8-position of quinoline) is generated by the combination of `\ryl` with a (yl)-function declared in `\sixheteroh` (the blue-colored code). □

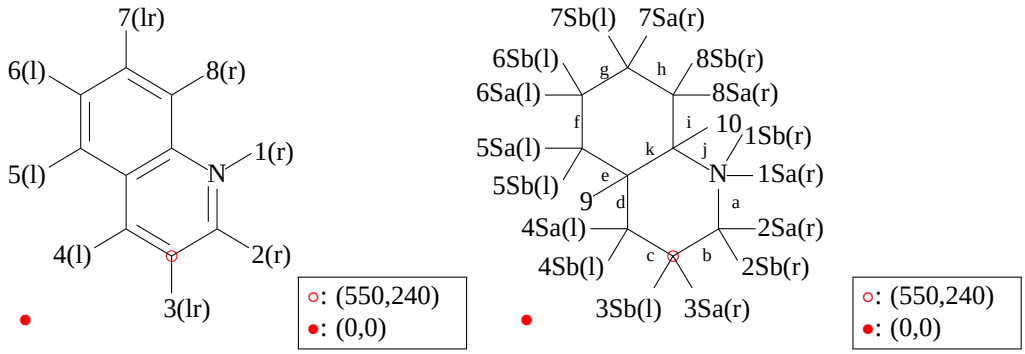
16.3 Drawing Diagonal Forms

16.3.1 Using Commands for Specified Use

The right-downward diagonal counterparts of the commands of vertical type (`\quinolinev`, etc.) are defined similarly in the package file, hetarom.sty. They have the suffix '`vb`' in common.

```
\quinolinevb[⟨bondlist⟩]{⟨subslist⟩}
\isoquinolinevb[⟨bondlist⟩]{⟨subslist⟩}
\quinoxalinevb[⟨bondlist⟩]{⟨subslist⟩}
\quinazolinevb[⟨bondlist⟩]{⟨subslist⟩}
\cinnolinevb[⟨bondlist⟩]{⟨subslist⟩}
\pteridinevb[⟨bondlist⟩]{⟨subslist⟩}
```

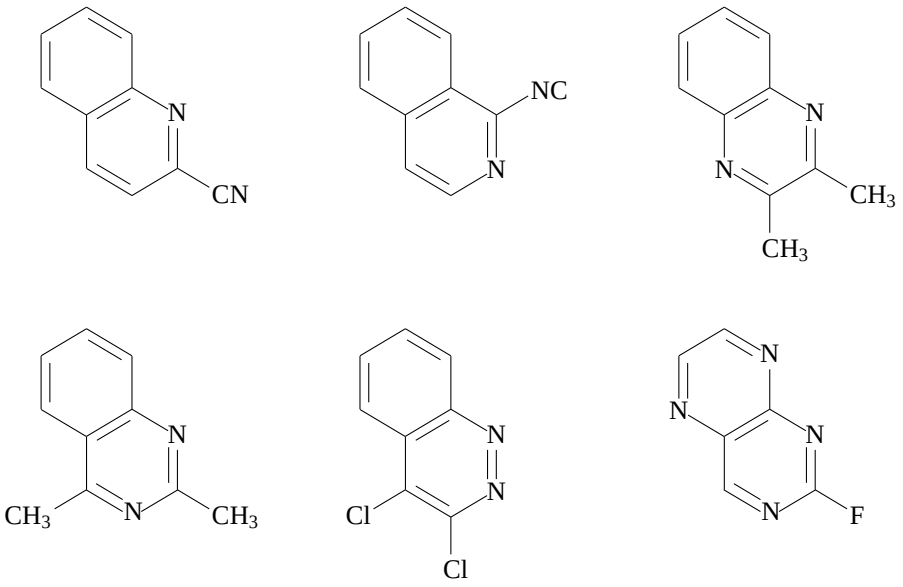
Locant numbers for designating substitution positions as well as bond descriptors (locant alphabets) for setting double bonds are shown in the following diagrams of `\quinolinevb` as representatives:



Examples of \quinolinevb etc.:

```
\quinolinevb{2==CN} \qquad
\isoquinolinevb{1==NC}\qquad
\quinoxalinevb{2==CH$_{3}$;3==CH$_{3}$} \par
\quinazolinevb{2==CH$_{3}$;4==CH$_{3}$}\qquad
\cinnolinevb{4==Cl;3==Cl} \qquad
\pteridinevb{2==F}
```

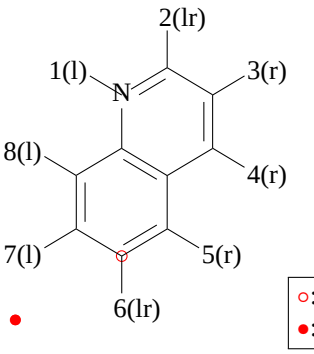
produce the following structures:

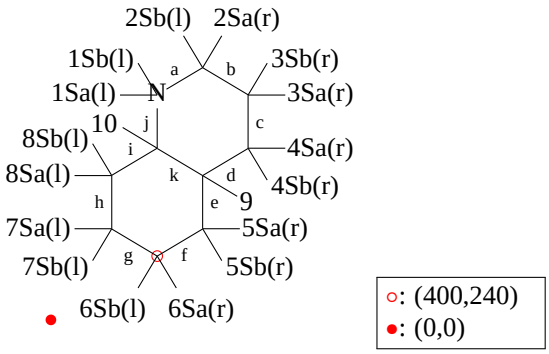


The right-upward diagonal counterparts of the commands of vertical type (\quinolinev, etc.) are defined similarly in the package file, hetarom.sty. They have the suffix 'vt' in common.

```
\quinolinevt[⟨bondlist⟩]{⟨subslist⟩}
\isoquinolinevt[⟨bondlist⟩]{⟨subslist⟩}
\quinoxalinevt[⟨bondlist⟩]{⟨subslist⟩}
\quinazolinevt[⟨bondlist⟩]{⟨subslist⟩}
\cinnolinevt[⟨bondlist⟩]{⟨subslist⟩}
\pteridinevt[⟨bondlist⟩]{⟨subslist⟩}
```

Locant numbers for designating substitution positions as well as bond descriptors (locant alphabets) for setting double bonds are shown in the following diagrams of \quinolinevt as representatives:

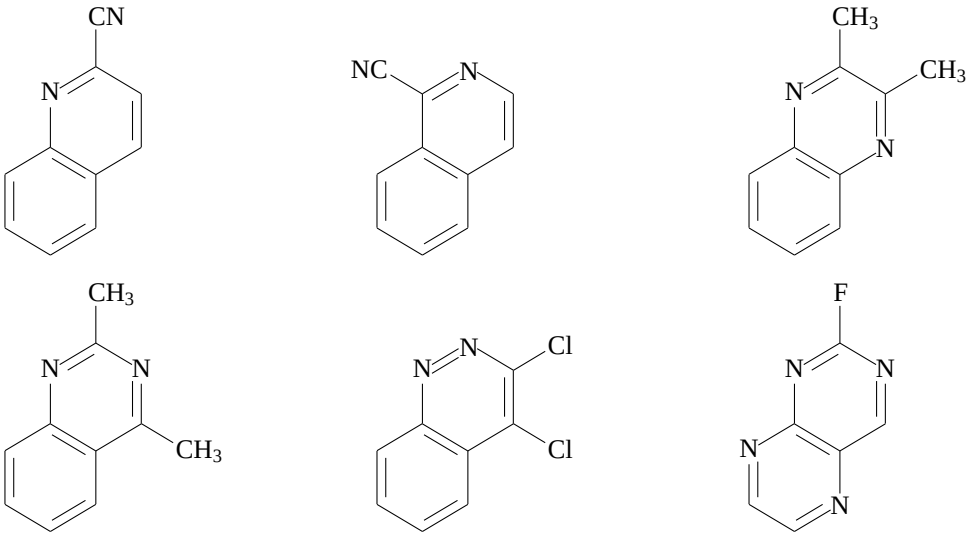




Examples of `\quinolinevt` etc.:

```
\quinolinevt{2==CN} \qquad
\isoquinolinevt{1==NC}\qquad
\quinoxalinevt{2==CH$_{3}$;3==CH$_{3}$} \par
\quinazolinevt{2==CH$_{3}$;4==CH$_{3}$}\qquad
\cinnolinevt{4==Cl;3==Cl} \qquad
\pteridinevt{2==F}
```

produce the following structures:



The locant numbers and alphabets of the XƎMTEX commands with the suffix ‘`vb`’ are compared with those of their related macros with the suffix ‘`vt`’ (Fig. 16.3).

The numbering in XƎMTEX commands with suffixes ‘`vb`’ and ‘`vt`’ collected in Fig. 16.3 is selected to be clockwise.

16.3.2 Using Commands for General Use

As already described in Subsection 3.4.6, the XƎMTEX commands `\decaheterovb` and `\decaheterobt` for general use serve as general macros for drawing fused six-to-six-membered heterocyclic derivatives of diagonal type (hetarom.sty). It is especially useful to draw heterocyclic compounds having combinations of skeletal atoms other than nitrogen atoms.

The structures **16-3**–**16-7** (depicted by using the command `\decaheterov`) and the counterpart structures **16-9**–**16-13** (depicted by using the command `\decaheteroh`) are redrawn by using the diagonal counterpart `\decaheterovb`.

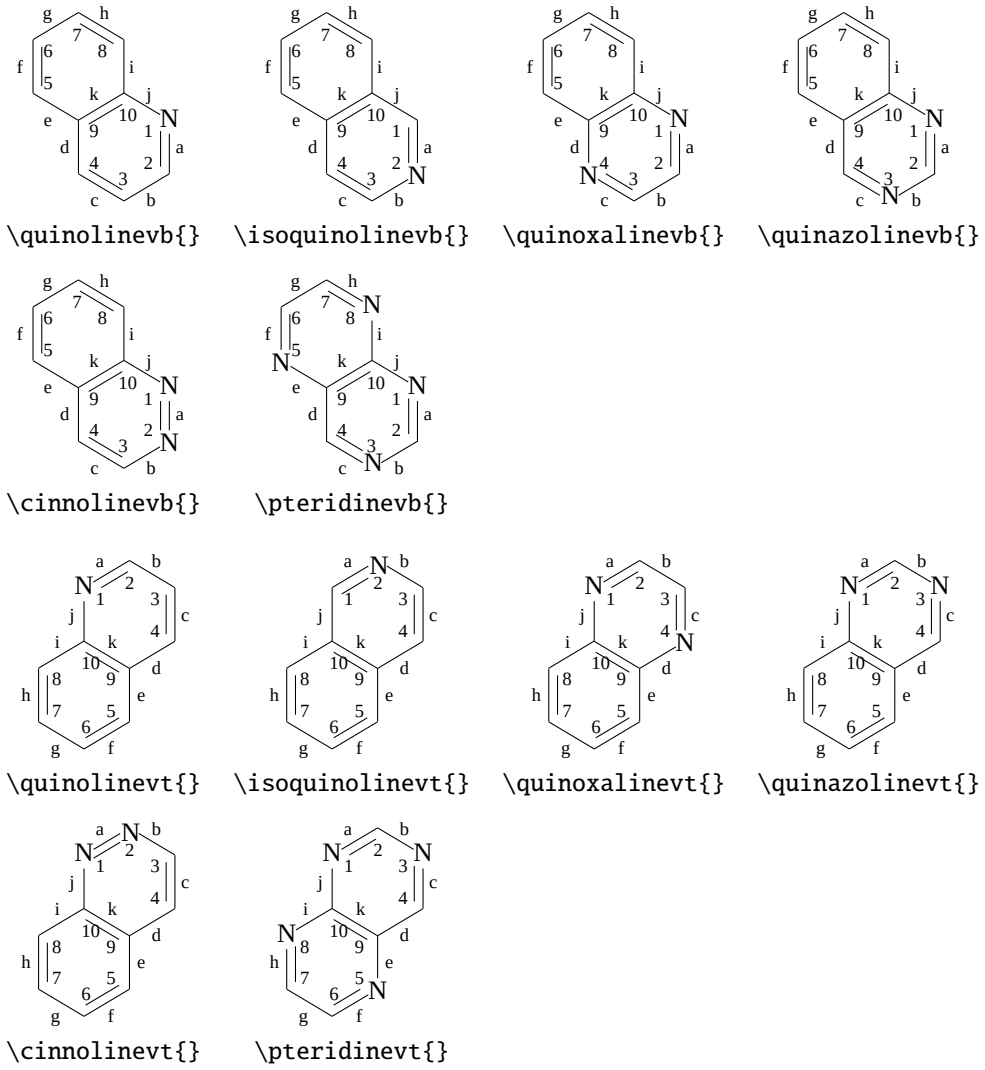
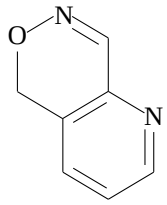
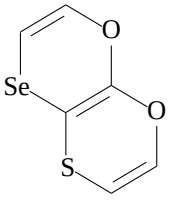


Figure 16.3. Locant numbers and alphabets of XeLaTeX commands of diagonal type for specific use of drawing fused six-six-membered heterocycles. The first and second rows collect XeLaTeX commands with suffix '`vb`' and the third and fourth rows collect the related commands with suffix '`vt`'.



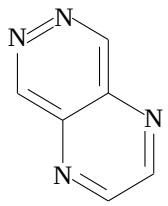
IUPAC name: 5*H*-pyrido[2.3-*d*][1.2]oxazine
XeLaTeX command:
`\decaheterovb[achk]{1==N;6==O;7==N}{}`

16-15



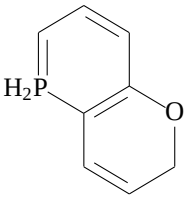
IUPAC name: [1.4]oxaselenino[2.3-*b*]oxathiine
XeLaTeX command:
`\decaheterovb[bgk]{1==O;4==S;5==Se;8==O}{}`

16-16



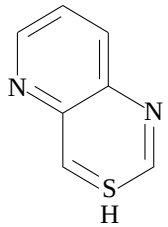
IUPAC name: pyrazino[2,3-*d*]pyridazine
XƎMTEX command:
```
\decaheterovb[acegi]{1==N;4==N;6==N;7==N}{}
```

16-17



IUPAC name: 2*H*-5λ^5-phosphinino[3.2-*b*]pyran
XƎMTEX command:
```
\decaheterovb[cfhk]{1==O;5==H$_{2}$P}{}
```

16-18

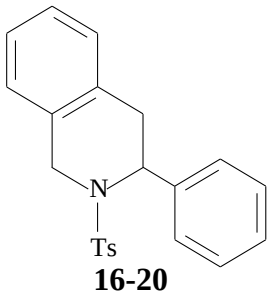


IUPAC name: 3-λ^4-pyrido[3.2-*d*][1.3]thiazine
XƎMTEX command:
```
\decaheterovb[acegi]{1==N;%
3==\downnobond{S}{H};5==N}{}
```

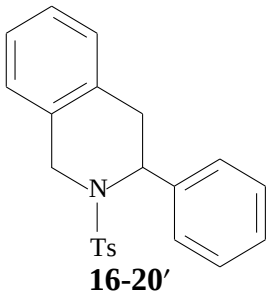
16-19

Example 16.5. The structure **16-20** of a tetrahydroisoquinoline derivative [3] is drawn by using the XƎMTEX command `\decaheterovb` for general use. The position of the fused double bond can be switched by changing the locant alphabet '`k`' into the uppercase letter '`K`' as shown in **16-20′**.

```
\decaheterovb[fhk]{3==N}{3==Ts;2==\benzenev{6==(yl)}}
\decaheterovb[fhK]{3==N}{3==Ts;2==\benzenev{6==(yl)}}
```



16-20



16-20′

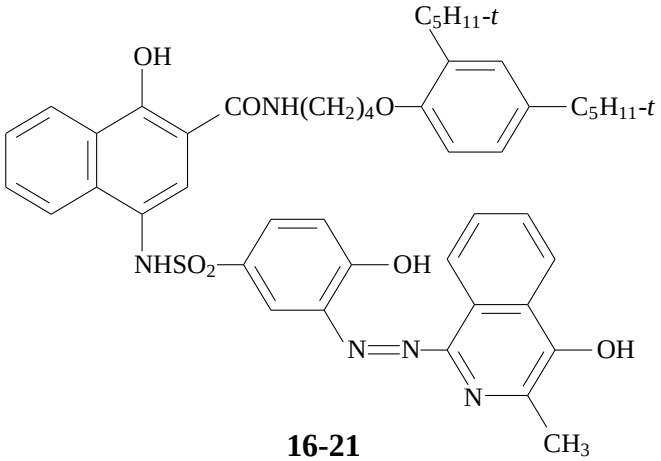
□

16.4 Illustrative Examples of Drawing 6-6 Fused Derivatives

16.4.1 Substituents Derived by (yl)-Functions

Example 16.6. The structure **16-21** of a *p*-sulfoamidonaphthol dye releaser [2, page 438] is regarded as a derivative of naphthalene with three substituents. The naphthalene structure is drawn by using the command `\naphthalenev` for specific use.

```
\naphthalenev{1==OH;
2==\ryl(5==CONH{(CH$_{2}$)$_{4}$}O){4==\benzeneh{1==(yl);%
2==C$_{5}$H$_{11}$-\textit{t};4==C$_{5}$H$_{11}$-\textit{t}}};%
4==\ryl(0==NHSO$_{2}$){4==\benzeneh{1==(yl);4==OH;%
5==\ryl(3==N\dblbond N){4==%
\decaheteroh[acfhk]{7==N}{8==(yl);5==OH;6==CH$_{3}$}}}}}
```



16-21

□

Example 16.7. Among the three substituents of the naphthalene ring of **16-21**, the 1-hydroxyl group is typeset by inputting a character string OH. The remaining two substituents are typeset by the substitution technique. The substituent at locant no. 2 is generated by the combination of `\ryl` with a (yl)-function declared in `\benzeneh`. On the other hand, the substituent at locant no. 4 is generated by multiple combinations of `\ryl` and (yl)-functions in a nested fashion represented schematically as follows: $NHSO_2$ (`\ryl`) → `\benzeneh` (yl) → N=N (`\ryl`) → `\decaheteroh` (yl).

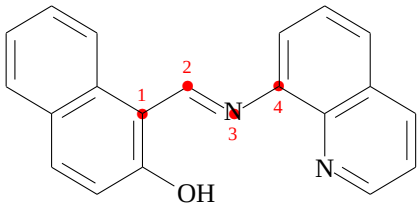
To avoid the superposition of the group OH onto the quinoline ring, the double bond of an azo group is drawn by declaring `N\bdlbond N` in place of `N=N`, where the command `\dblbond` is defined as follows to give a slightly long double bond.

```
%a double bond
\def\dblbond{\leavevmode\kern.4pt\raisebox{.3ex}{%
\hbox{\vbox{\hrule height0.4pt width1.2em\kern.6ex
\hrule height0.4pt width1.2em}}}\hskip.6pt}
```

□

Example 16.8. The structure **16-22** of a Schiff-base ligand derived from 8-aminoquinoline [4] is drawn by the replacement technique, where a four-atom zig-zag unit (1•—2•=3•—4•) as the parent skeleton is generated by the command `\tetramethylene`. The terminal positions (locant numbers 1 and 4) accommodate a naphthyl group generated by declaring a (yl)-function in `\naphthalenevb` and a quinoline group generated by declaring a (yl)-function in `\decaheterovb`, where the replacement technique is applied to the argument ⟨atomlist⟩ of `\tetramethylene`, just as the 3-position accommodates a nitrogen atom by the usual replacement operation.

```
\tetramethylene[b]{3==N;%
4s==\decaheterovb[acfhk]{4==N}{5==(yl)};%
1s==\naphthalenevb{1==(yl);2==OH}}{}
```



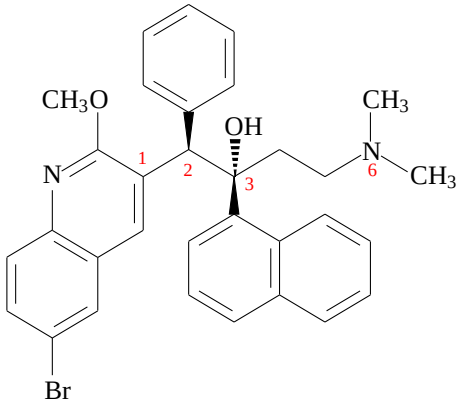
16-22

□

Example 16.9. The structure **16-23** of bedaquiline (Sirturo®) marketed by Johnson & Johnson as an diarylquinoline anti-tuberculosis drug is drawn by the replacement technique, where a six-atom zig-zag unit as the parent skeleton is generated by the command `\hexamethylene`. The terminal position (locant number 1) accommodates a quinoline group generated by declaring a (yl)-function in `\decaheterovt`, where the replacement technique is applied to the argument ⟨atomlist⟩ of `\hexamethylene`. The 2-position is substituted by a phenyl group, which is generated by declaring a (yl)-function in `\benzenev`, where the

substitution technique is applied to the argument ⟨subslist⟩ of `\hexamethylene`. The 3-position is substituted by a naphthyl group, which is generated by declaring a (yl)-function in `\naphthalenev`, where the substitution technique is applied to the argument ⟨subslist⟩ of `\hexamethylene`. In order to indicate the configuration at the 3-position, the hydroxyl group (OH) is drawn by the command `\put` and combined with a wedged bond generated by `\HashWedgeAsSubst`, where they are placed by means of the replacement technique. The 6-position accommodates a nitrogen atom by the usual replacement operation.

```
\hexamethylene{6==N;%
1s==\quinolinevt{3==(yl);2==\lmoiety{CH$_{3}$O};6==Br};
3==\put(0,180){OH};%
3s==\HashWedgeAsSubst(0,0)(0,1){140}}%
{2B==\benzenev{4==(yl)};
3B==\naphthalenev{8==(yl)};%
6==CH$_{3}$;6W==CH$_{3}$}
```

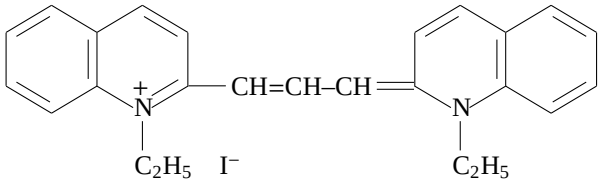


16-23

□

Example 16.10. The structure **16-24** of pinacyanol for photography [2, page 114] is drawn by using `\divalenth` to generate a divalent unit CH=CH–CH as a parent structure. The left terminal of the divalent unit accommodates a 6-6 fused ring generated by declaring a (yl)-function in `\quinolinevi`. The right terminal of the divalent unit accommodates another 6-6 fused ring generated by declaring a (yl)-function in `\decaheterov`. Both the substituents are placed by the replacement technique due to the second argument of `\divalenth`.

```
\divalenth{0==CH=CH--CH}{%
1==\quinolinevi[acfhk{1+}]{2==(yl);1==C$_{2}$H$_{5}$\kern10pt I$^{-}$};%
2D==\decaheterov[achk]{5==N}{6==(yl);5==C$_{2}$H$_{5}$}}
```



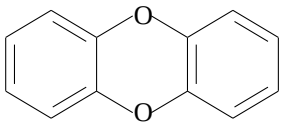
16-24

□

16.4.2 As Parent Structures for Ring Fusion

The argument ⟨bondlist⟩ of `\decaheterov` or related commands is capable of setting ring fusion due to the addition technique.

Example 16.11. The structure **16-25** of oxanthrene [1, P-25.2.2.2] is drawn by applying the addition technique to 1,4-benzodioxane, which is regarded as a parent structure.



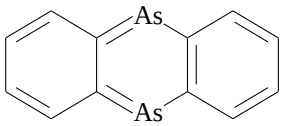
16-25

IUPAC name: oxanthrene
XƎMTEX command:

```
\decaheterov[egi%
{b\sixfusev[ace]{}{}{E}}]{1==O;4==O}{}
```

□

Example 16.12. The structure of **16-26** of arsanthrene [1, P-25.2.2.2] is drawn by applying the addition technique to 1,4-diarsanaphathalene, which is regarded as a parent structure. The command `\SetTwoAtoms` is used to avoid the undesirable superposition of the two-character atom 'As' onto a skeletal bond.



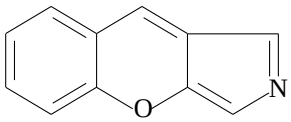
16-26

IUPAC name: arsanthrene
XƎMTEX command:

```
\decaheterov[dfhj%
{b\sixfusev[ace]{}{}{E}}%
]{1==\SetTwoAtoms{As};4==\SetTwoAtoms{As}}{}
```

□

Example 16.13. The structure **16-27** of chromeno[2.3-*c*]pyrrole [1, P-25.3.2.4] is drawn by applying the addition technique to chromene, which is regarded as a parent structure.



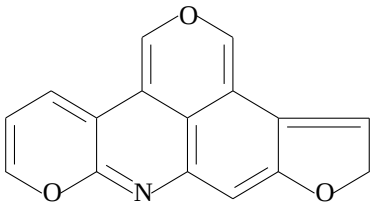
16-27

IUPAC name: chromeno[2.3-*c*]pyrrole
XƎMTEX command:

```
\decaheterovi[cegi%
{b\fivefusev[be]{2==N}{}{D}}%
]{1==O}{}
```

□

Example 16.14. The structure **16-28** of 5*H*-furo[2,3-*g*]dipyrano[2,3-*b*:3′,4′,5′-*d*,*e*]quinoline [1, P-25.3.4.1.2] is drawn by applying the addition technique to an oxaazanaphthalene, which is regarded as a parent structure.



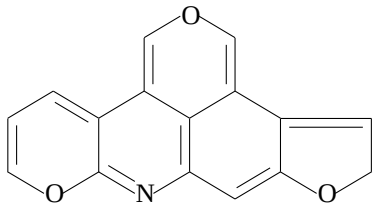
16-28

IUPAC name: 5*H*-furo[2,3-*g*]dipyrano-
[2,3-*b*:3′,4′,5′-*d*,*e*]-quinoline
XƎMTEX command:

```
\decaheterov[dgi%
{b\sixfusev[ce%
{b\fivefusev[c]{1==O}{}{d}}]{}{}{E}}%
{a\sixfusev[be]{1==O}{}{D}[c]}]%
{4==N;5==O}{}
```

□

Example 16.15. The construction of the IUPAC name 5*H*-furo[2,3-*g*]dipyrano[2,3-*b*:3′,4′,5′-*d*,*e*]quinoline [1, P-25.3.4.1.2] corresponds to an alternative way, in which the addition technique is applied to a quinoline as a parent structure, as shown in the code for drawing **16-28′**



16-28′

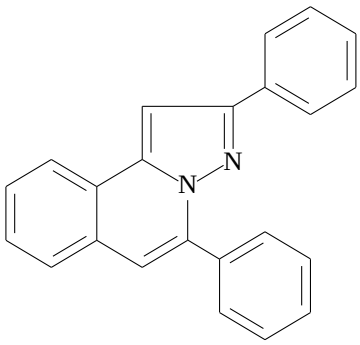
IUPAC name: 5*H*-furo[2,3-*g*]dipyrano-
[2,3-*b*:3′,4′,5′-*d*,*e*]-quinoline
XƎMTEX command:

```
\decaheterov[cfk%
{b\fivefusev[c]{1==O}{}{d}}%
{g\sixfusev[ae]{4==O}{}{B}}%
{i\sixfusev[be]{1==O}{}{D}[c]}%
]{5==N}{}
```

□

Example 16.16. The structure **16-29** of a fused isoquinoline [5] is drawn by applying the addition technique to a isoquinoline nucleus generated by `\decaheterov`, where an attached component is generated by `\fiveheterov`. Each of the isoquinoline nucleus and the attached component is substituted by a phenyl group generated by a (yl)-function.

```
\decaheterov[cegi%
{a\fivefusev[bd]{1==\null;2==N}{3==\benzenev{5==(yl)}}{e}}%
]{2==N}{3==\benzenev{6==(yl)}}
```



16-29

□

References

[1] IUPAC Chemical Nomenclature and Structure Representation Division, *Provisional Recommendations. Nomenclature of Organic Chemistry* (2004). http://www.iupac.org/reports/provisional/abstract04/favre_310305.html.

[2] S. Fujita, "Organic Chemistry of Photography," Springer-Verlag, Berlin-Heidelberg (2004).

[3] P. A. Vadola, I. Carrera, and D. Sames, *J. Org. Chem.*, **77**, 6689 (2012).

[4] K. Takano, M. Takahashi, T. Fukushima, M. Takezaki, T. Tominaga, H. Akashi, H. Takagi, and T. Shibahara, *Bull. Chem. Soc. Jpn.*, **85**, 1210–1221 (2012).

[5] P. Juang, Q. Yang, Z. Chen, Q. Ding, J. Xu, and Y. Peng, *J. Org. Chem.*, **77**, 8092 (2012).

Heterocycles with Fused Six-to-Five-Membered Rings. Commands for Specific Use

This chapter is devoted to introduce commands for drawing heterocyclic compounds with 6-5 fused rings. These commands are short-cut commands of `\nonaheterov` etc. for general use (cf. Section 3.1 for the syntax).

17.1 Drawing Vertical Forms

17.1.1 Using Commands for Specific Use

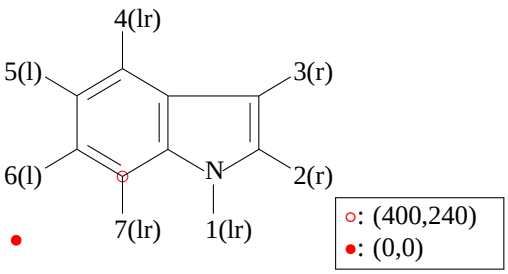
The XyMTEX system involves macros for drawing representative fused N-heterocycles that consist of a six- and a five-membered ring. These macros have the following formats (hetarom.sty).

```
\indolev[⟨bondlist⟩]{⟨subslist⟩}
\isoindolev[⟨bondlist⟩]{⟨subslist⟩}
\purinev[⟨bondlist⟩]{⟨subslist⟩}
```

Macros for drawing fused O- and N,O-heterocycles are also available (hetarom.sty). They are the same formats of arguments.

```
\benzofuranev[⟨bondlist⟩]{⟨subslist⟩}
\isobenzofuranev[⟨bondlist⟩]{⟨subslist⟩}
\benzoxazolev[⟨bondlist⟩]{⟨subslist⟩}
```

The locant numbering is common in these commands as shown in the following diagrams of `\indolev`:



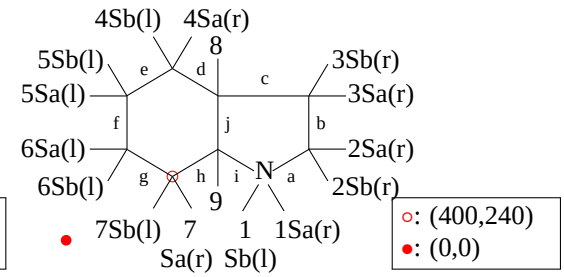


Table 17.1. Argument ⟨bondlist⟩ for Commands `\indolev` and Related Commands

Character	Printed structure	Character	Printed structure
none or r	aromatic six-membered ring	H or []	fully saturated form
a	1,2-double bond	b	2,3-double bond
c	3,3a-double bond	d	4,3a-double bond
e	4,5-double bond	f	5,6-double bond
g	6,7-double bond	h	7,7a-double bond
i	1,7a-double bond	j	3a,4a-double bond
A	aromatic circle (six-membered ring)		
B	aromatic circle (five-membered ring)		
{*n*+}	plus at the *n*-nitrogen atom (*n* = 1 to 9)		

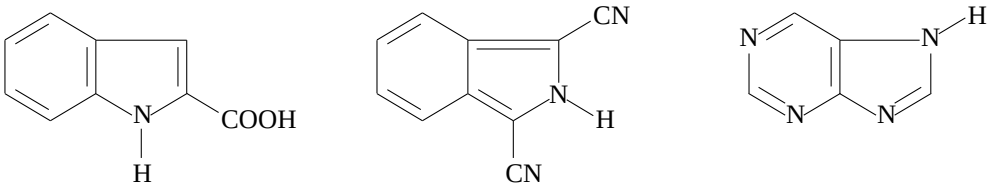
The handedness for each oriented or double-sided position is shown with a character set (r or l) in parentheses. The optional argument ⟨bondlist⟩ specifies edges with a double bond (Table 17.1).

The argument ⟨subslist⟩ is used to specify each substituent with a locant number and a bond modifier shown in Table 3.2, in which *n* is an Arabic numeral between 1 and 7. Substitution on 8 (3a position) or 9 (7a position) can be assigned in the usual way of specifying bridgehead positions.

Examples of `\indolev` etc.:

```
\indolev{1==H;2==COOH}\qquad
\isoindolev{2==H;1==CN;3==CN}\qquad
\purinev{3==H}
```

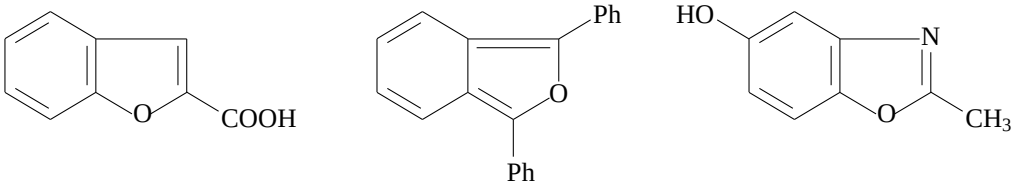
produce the following structures:



Examples of `\benzofuranev` etc.:

```
\benzofuranev{2==COOH}\qquad
\isobenzofuranev{1==Ph;3==Ph}\qquad
\benzoxazolev{2==CH$_{3}$;5==HO}
```

produce the following structures:



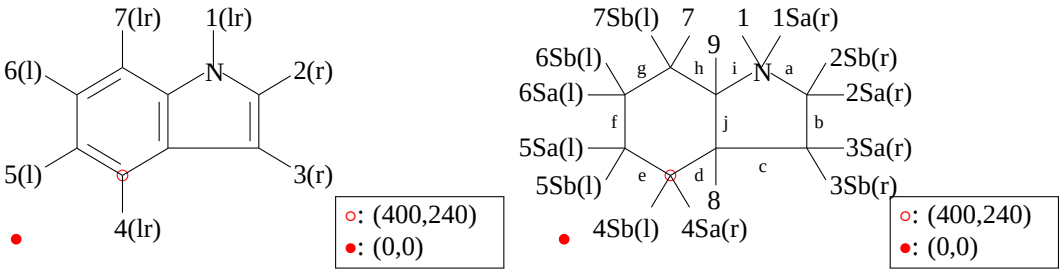
The package hetarom.sty also involves macros for drawing fused N-heterocycles of inverse vertical type. They have the following formats:

```
\indolevi[⟨bondlist⟩]{⟨subslist⟩}
\isoindolevi[⟨bondlist⟩]{⟨subslist⟩}
\purinevi[⟨bondlist⟩]{⟨subslist⟩}
```

Macros for drawing fused O- and N,O-heterocycles of inverse vertical type have the following formats. They are also contained in the package file hetarom.sty.

```
\benzofuranevi[⟨bondlist⟩]{⟨subslist⟩}
\isobenzofuranevi[⟨bondlist⟩]{⟨subslist⟩}
\benzoxazolevi[⟨bondlist⟩]{⟨subslist⟩}
```

They are the counterparts of the commands without suffix ‘i’ described above. The locant numbering is common in these commands as shown in the following diagrams of `\indolevi`:

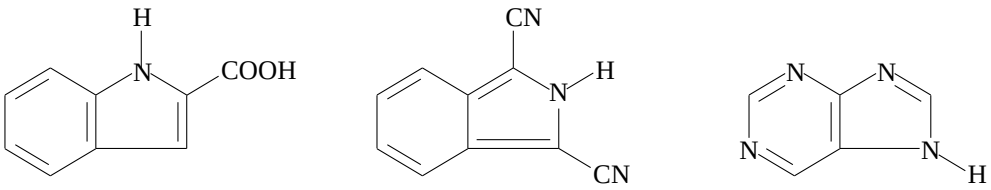


The handedness for each oriented or double-sided position is shown with a character set (l, r, or lr) in parentheses. The optional argument ⟨bondlist⟩ is used in a usual way (Table 17.1).

Examples of `\indolevi` etc.:

```
\indolevi{1==H;2==COOH}\qquad
\isoindolevi{2==H;1==CN;3==CN}\qquad
\purinevi{3==H}
```

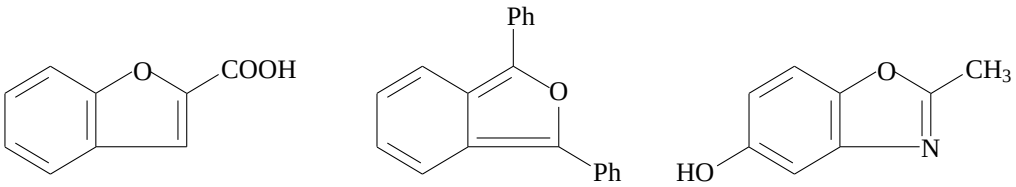
produce the following structures:



Examples of `\benzofuranevi` etc.:

```
\benzofuranevi{2==COOH}\qquad
\isobenzofuranevi{1==Ph;3==Ph}\qquad
\benzoxazolevi{2==CH$_{3}$;5==HO}
```

produce the following structures:



The locant numbers and alphabets of the XƎMTEX commands with the suffix ‘`v`’ are compared with those of their inverse macros with the suffix ‘`vi`’ (Fig. 17.1).

The numbering in XƎMTEX commands with suffix ‘`v`’ collected in Fig. 17.1 is selected to be anti-clockwise, while the numbering in XƎMTEX commands with suffix ‘`vi`’ is selected to be clockwise.

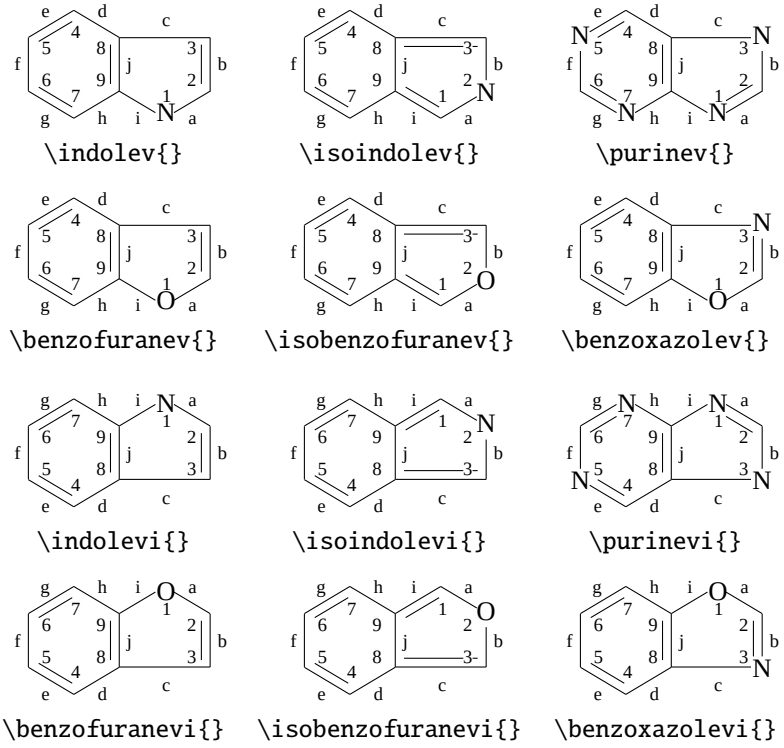
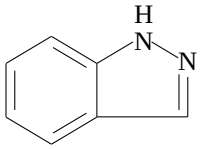


Figure 17.1. Locant numbers and alphabets of XƎMTEX commands of vertical type for specific use of drawing fused six-five-membered heterocycles. The first and second rows collect XƎMTEX commands with suffix '`v`' and the third and fourth rows collect the corresponding commands with suffix '`vi`'.

17.1.2 Using Commands for General Use

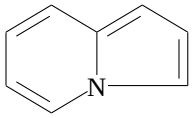
Macros for specific use such as `\indolev` and `\indolevi` are short-cut commands defined on the basis of general commands `\nonaheterov` and `\nonaheterovi`, which have already been discussed in Subsection 3.4.5. Such general commands enables us to draw a further variety of heterocyclic compounds.

The following structures are cited from Chapter 2 (P-25) of IUPAC nomenclature [1] in order to demonstrate a variety of heterocyclic compounds accessible by using the XƎMTEX command `\nonahetrovi` for general use.



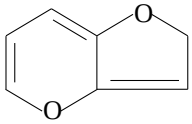
17-1

IUPAC name: 1*H*-indazole
XƎMTEX command:
```
\nonaheterovi[bdfh]{1==\upnobond{N}{H};2==N}{}
```



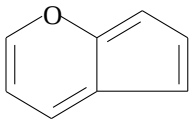
17-2

IUPAC name: indolizine
XƎMTEX command:
```
\nonaheterovi[begi]{8==N}{}
```



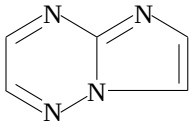
17-3

IUPAC name: 2*H*-furo[3,2-*b*]pyran
XƎMTEX command:
```
\nonaheterovi[cfh]{1==O;4==O}{}
```



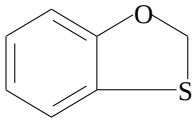
17-4

IUPAC name: cyclopenta[b]pyran
XeLaTeX command:
`\nonaheterovi[bdfi]{7==O}{}`



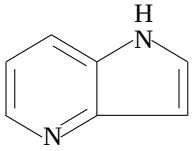
17-5

IUPAC name: imidazo[1,2-*b*][1,2,4]triazine
XeLaTeX command:
`\nonaheterovi[begi]{1==N;4==N;7==N;8==N}{}`



17-6

IUPAC name: 2*H*-1,3-benzoxathiole
XeLaTeX command:
`\nonaheterovi[dfh]{1==O;3==S}{}`

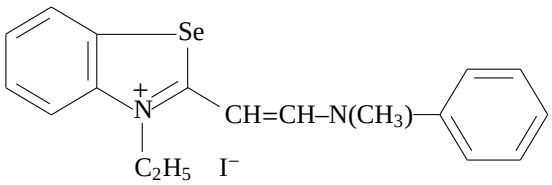


17-7

IUPAC name: 1*H*-pyrrolo[3,2-*b*]pyridine
XeLaTeX command:
`\nonaheterovi[bdfh]{1==\upnobond{N}{H};4==N}{}`

Example 17.1. The structure **17-8** of a hemicyanine dye for photography [2, page 115] is drawn by using `\nonaheterov`, where the substituent at the 2-position is generated by `\ryl` and a (yl)-function declared in the command `\benzeneh`.

```
\nonaheterov[aegj{1+}]{1==N;3==Se}{1==C$_{2}$H$_{5}$\kern10pt I$^{-}$;%
2==\ryl(3==CH=CH--{N(CH$_{3}$)}){4==\benzeneh{1==(yl)}}}
```



17-8

□

17.2 Drawing Horizontal Forms

17.2.1 Using Commands for Specific Use

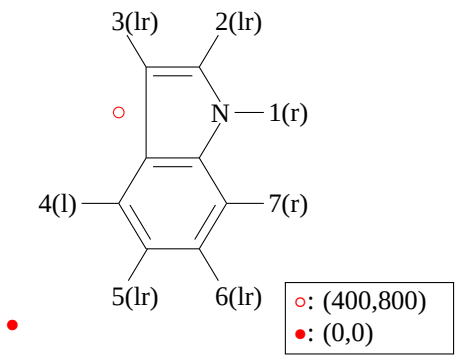
Macros for drawing N-heterocycles of horizontal type have the following formats (hetaromh.sty).

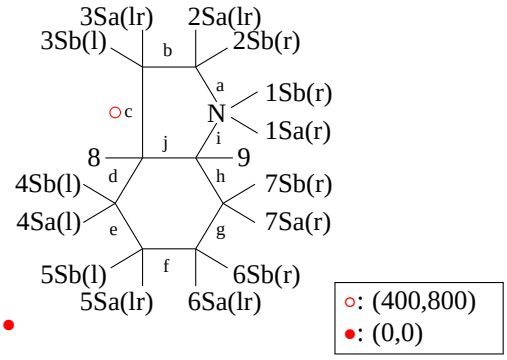
```
\indoleh[⟨bondlist⟩]{⟨subslist⟩}
\isoindoleh[⟨bondlist⟩]{⟨subslist⟩}
\purineh[⟨bondlist⟩]{⟨subslist⟩}
```

Macros for drawing O- and N,O-heterocycles are available by setting the package file hetaromh.sty. They have the following formats.

```
\benzofuraneh[⟨bondlist⟩]{⟨subslist⟩}
\isobenzofuraneh[⟨bondlist⟩]{⟨subslist⟩}
\benzoxazoleh[⟨bondlist⟩]{⟨subslist⟩}
```

Locant numbers for designating substitution positions are represented by the following diagrams of `\indoleh`:



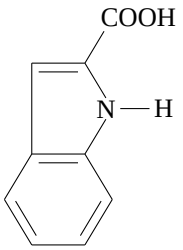


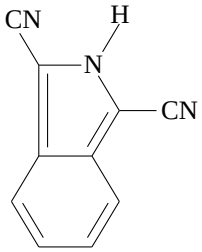
The handedness for each oriented or double-sided position is shown with a character set in parentheses. The optional argument ⟨bondlist⟩ specifies double bonds by using characters selected from Table 17.1.

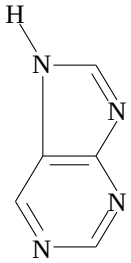
Examples of `\indoleh` etc.:

```
\indoleh{1==H;2==COOH}\qquad
\isoindoleh{2==H;1==CN;3==CN}\qquad
\purineh{3==H}
```

produce the following structures:



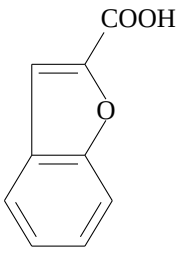


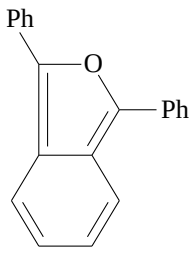


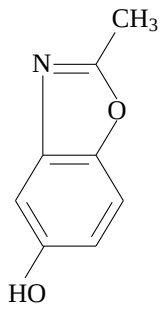
Examples of `\benzofuraneh` etc.:

```
\benzofuraneh{2==COOH}\qquad
\isobenzofuraneh{1==Ph;3==Ph}\qquad
\benzoxazoleh{2==CH$_{3}$;5==HO}
```

produce the following structures:



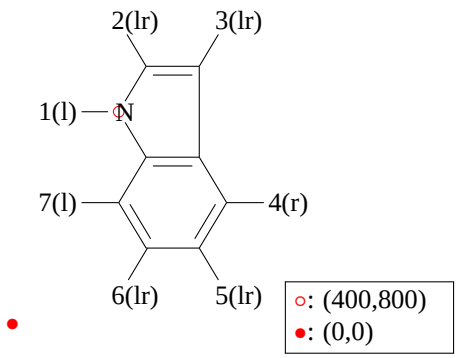


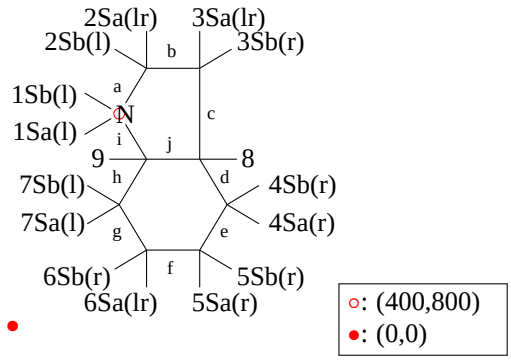


The macro `\indolehi` is used to draw inodele derivatives of inverse horizontal type (hetaromh.sty). Macros for drawing other fused heterocycles are also defined in the package hetaromh.sty. The format of these commands is as follows:

```
\indolehi[⟨bondlist⟩]{⟨subslist⟩}
\isoindolehi[⟨bondlist⟩]{⟨subslist⟩}
\purinehi[⟨bondlist⟩]{⟨subslist⟩}
\benzofuranehi[⟨bondlist⟩]{⟨subslist⟩}
\isobenzofuranehi[⟨bondlist⟩]{⟨subslist⟩}
\benzoxazolehi[⟨bondlist⟩]{⟨subslist⟩}
```

Locant numbers for designating substitution positions and characters for describing bonds to be doubled are shown in the following diagrams of `\indolehi`:

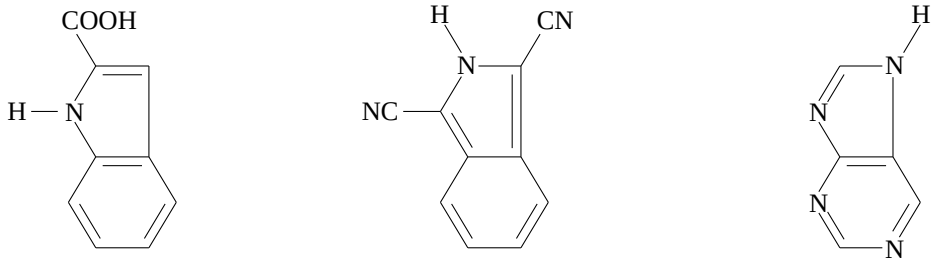




Examples of `\indolehi` etc:

```
\indolehi{1==H;2==COOH}\qquad
\isoindolehi{2==H;1==NC;3==CN}\qquad
\purinehi{3==H}
```

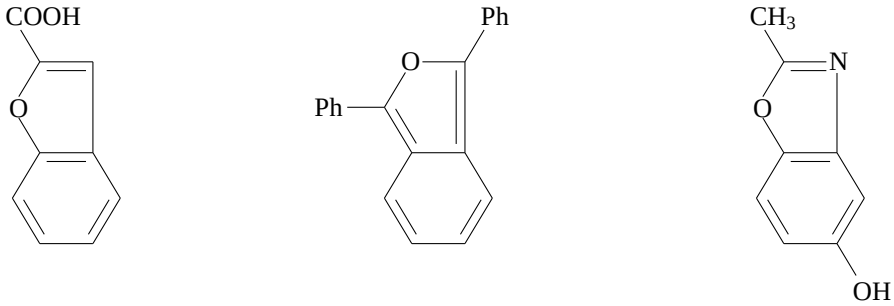
produce the following structures:



Examples of `\benzofuranehi` etc.:

```
\benzofuranehi{2==COOH}\qquad
\isobenzofuranehi{1==Ph;3==Ph}\qquad
\benzoxazolehi{2==CH$_{3}$;5==OH}
```

produce the following structures:



The locant numbers and alphabets of the XeLaTeX commands with the suffix ‘h’ are compared with those of their inverse macros with the suffix ‘hi’ (Fig. 17.2).

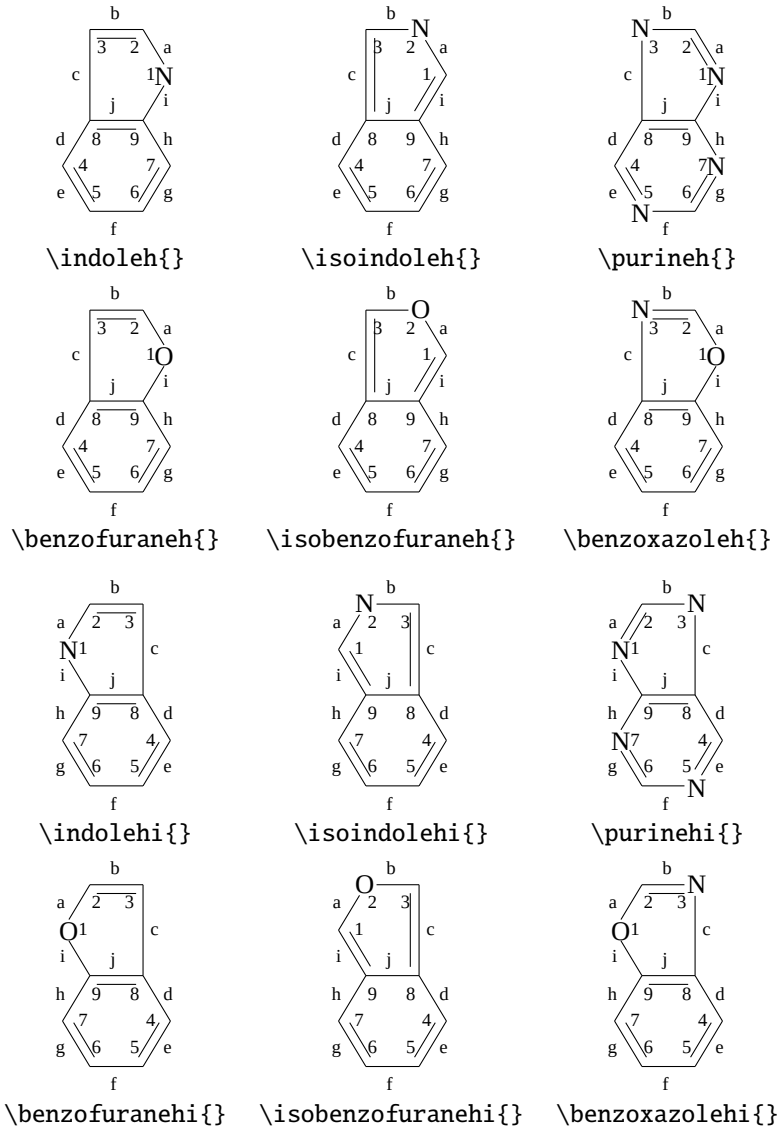


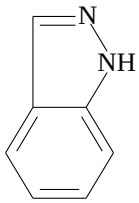
Figure 17.2. Locant numbers and alphabets of XeLaTeX commands of horizontal type for specific use of drawing fused six-five-membered heterocycles. The first and second rows collect XeLaTeX commands with suffix ‘h’ and the third and fourth rows collect the corresponding commands with suffix ‘hi’.

The numbering in XeLaTeX commands with suffix ‘h’ collected in Fig. 17.2 is selected to be anti-clockwise, while the numbering in XeLaTeX commands with suffix ‘hi’ is selected to be clockwise.

17.2.2 Commands for General Use

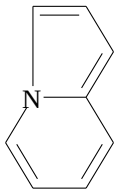
Macros for specific use such as `\indoleh` and `\indolehi` are based on general commands `\nonaheteroh` and `\nonaheterohi`, which have already been discussed in Subsection 3.4.5. These commands enable us to draw a further variety of heterocyclic compounds.

The structures **17-1**–**17-7** are redrawn by using the XƎMTEX command `\nonahetroh` for general use in order to demonstrate a variety of heterocyclic compounds accessible by the XƎMTEX system.



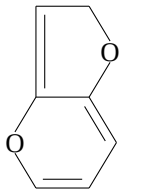
IUPAC name: 1*H*-indazole
XƎMTEX command:
`\nonaheteroh[bdfh]{1==NH;2==N}{}`

17-9



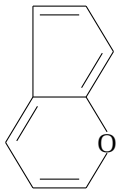
IUPAC name: indolizine
XƎMTEX command:
`\nonaheteroh[begi]{8==N}{}`

17-10



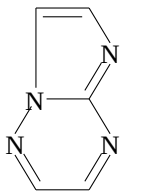
IUPAC name: 2*H*-furo[3,2-*b*]pyran
XƎMTEX command:
`\nonaheteroh[cfh]{1==O;4==O}{}`

17-11



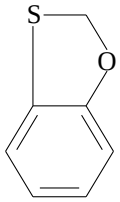
IUPAC name: cyclopenta[b]pyran
XƎMTEX command:
`\nonaheteroh[bdfi]{7==O}{}`

17-12



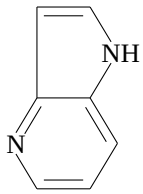
IUPAC name: imidazo[1,2-*b*][1,2,4]triazine
XƎMTEX command:
`\nonaheteroh[begi]{1==N;4==N;7==N;8==N}{}`

17-13



IUPAC name: 2*H*-1,3-benzoxathiole
XeLaTeX command:
`\nonaheteroh[dfh]{1==O;3==S}{}`

17-14



IUPAC name: 1*H*-pyrrolo[3,2-*b*]pyridine
XeLaTeX command:
`\nonaheteroh[bdfh]{1==NH;4==N}{}`

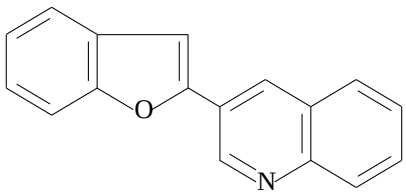
17-15

17.3 Illustrative Examples of Drawing 6-5 Fused Derivatives

17.3.1 Substituents Derived by (yl)-Functions

Example 17.2. The structure **17-16** of a quinoline having a benzofuran moiety [3] is drawn by the substitution technique, where the quinoline nucleus is regarded as a parent skeleton and the benzofuran moiety is generated by declaring a (yl)-function in `\benzofuranev`.

```
\decaheterov[acfhk]{5==N}{7==\benzofuranev{2==(yl)}}
```

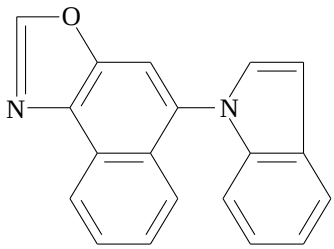


17-16

□

Example 17.3. The structure **17-17** of a photodegradation product [4] is drawn by the substitution technique, where an indole substituent is generated by declaring a (yl)-function in `\indolehi`.

```
\decalineh[acfhk{a\fivefuseh[c]{2==O;4==N}{}{e}}]{4==\indolehi{1==(yl)}}
```



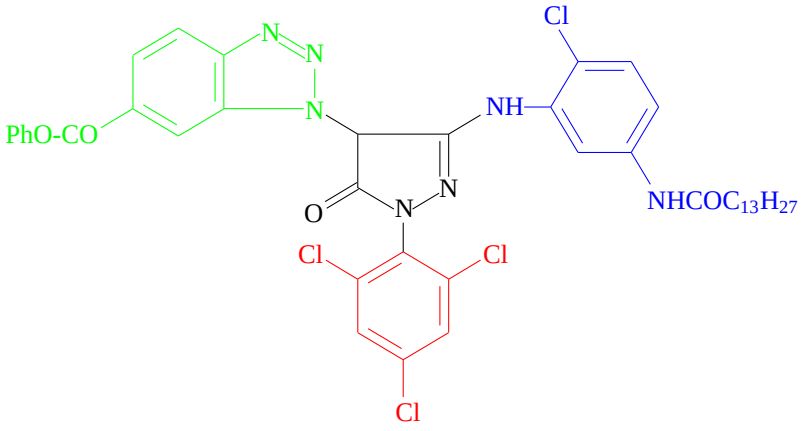
17-17

□

Example 17.4. The structure **17-18** of a development-inhibitor-releasing coupler for color photography [2, page290] is drawn by regarding a pyrazolone ring as a parent structure, which is generated by the command `\fiveheterov`. Among the four substituents, the exocyclic carbonyl group is placed by the ordinary substitution operation. The substituent at the 1-position (colored in red) is generated by declaring a (yl)-function in `benzenev` (the red-colored code). The substituent at the 3-position (colored in blue) is generated by the command `\ryl` and a (yl)-function declared in `\benzeneh` (the blue-colored code). The substituent

at the 4-position (colored in green) is generated by declaring a (yl)-function in \nonaheterovi (the green-colored code). The three generated substituents are placed by means of the substitution technique, where they are declared in the ⟨subslist⟩ of the outer \fiveheterov command.

```
\fiveheterov[b]{1==N;2==N}{5D==O;%
1==\benzenev{1==(yl);2==Cl;4==Cl;6==Cl};%
3==\ryl(5==NH){4==\benzeneh{1==(yl);2==Cl;5==NHCOC$_{13}$H$_{27}$}};%
4==\nonaheterovi[aegj]{1==N;2==N;3==N}{3==(yl);5==PhO-CO}}
```

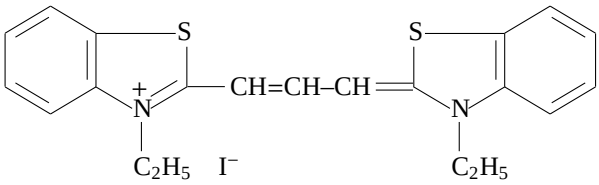


17-18

□

Example 17.5. The structure **17-19** of a hemicyanine dye for photography [2, page 115] is drawn by using \divalenth to generate a divalent unit CH=CH–CH as a parent structure. The left terminal of the divalent unit accommodates a 6-5 fused ring generated by declaring a (yl)-function in \nonaheterov, where the replacement technique is adopted in the second argument of \divalenth. The right terminal of the divalent unit accommodates a five-membered ring generated by declaring a (yl)-function in \fiveheterov, which is in turn fused by a six-membered ring due to \sixfusev. In the light of resonance, the right substituent is the same as the left substituent.

```
\divalenth{0==CH=CH--CH}{%
1==\nonaheterov[aegj{1+}]{1==N;3==S}{2==(yl);1==C$_{2}$H$_{5}$\kern10pt I$^{-}$};%
2D==\fiveheterov[b{b\sixfusev[ac]{}{}{e}}]{1==N;4==S}{5==(yl);1==C$_{2}$H$_{5}$}}
```



17-19

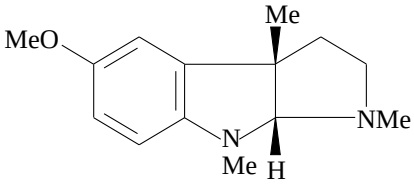
□

17.3.2 As Parent Structures for Ring Fusion

The argument ⟨bondlist⟩ of \nonaheterov or related commands is capable of setting ring fusion due to the addition technique.

Example 17.6. The structure **17-20** of (-)-esermethole synthesized by an enantioselective Ni catalyst [5] is drawn by the addition technique, where an indole nucleus generated by \nonaheterov is regarded as a parent structure and fused by a pyrrole ring due to \fiveheterovi.

```
\nonaheterov[egj%
{b\fivefusevi{3==NMe}{}{d}}%
]{1==\downnobond{N}{Me}}{5==MeO;2GB==H;3FB==Me}
```

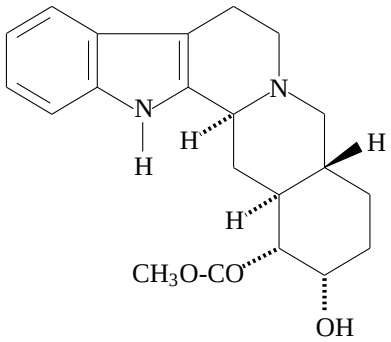


17-20

□

Example 17.7. The structure **17-21** of yohimbine as an indole alkaloid is drawn by the addition technique, where an indole nucleus generated by `\indolev` is regarded as a parent structure and fused by six-membered rings generated successively by `\sivfusev` in a nested fashion.

```
\indolev[begj%
{b\sixfusev[%
{c\sixfusev[%
{c\sixfusev{}{4A==OH;5A==CH$_{3}$O-CO}{F}}%
]{1==\null}{3FB==H;4GA==H}{F}}%
]{3==N}{4GA==H}{e}}%
]{1==H}
```

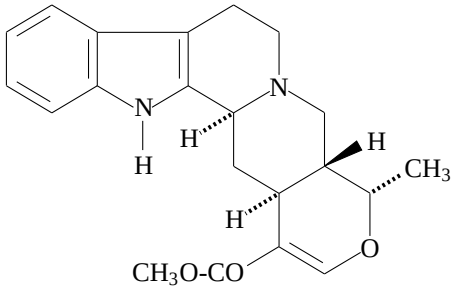


17-21

□

Example 17.8. The structure **17-22** of ajmalicine as an indole alkaloid is drawn in a similar way to yohimbine **17-21**.

```
\indolev[begj%
{b\sixfusev[%
{c\sixfusev[%
{c\sixfusev[d]{3==O}{5==CH$_{3}$O-CO;2A==CH$_{3}$}{F}}%
]{1==\null}{3FB==H;4GA==H}{F}}%
]{3==N}{4GA==H}{e}}%
]{1==H}
```

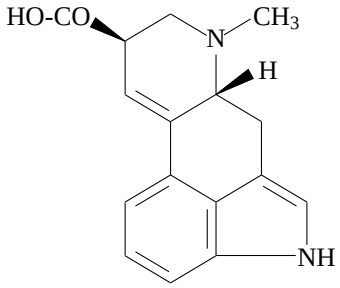


17-22

□

Example 17.9. The structure **17-23** of (+)-lysergic acid, which is a precursor for a wide range of ergoline alkaloids, is drawn by the addition technique, where an indole nucleus generated by `\nonaheterovi` is regarded as a parent structure and fused by six-membered rings generated successively by `\sivfusev` in a nested fashion.

```
\nonaheterovi[aegj%
{i\sixfusev[%
{f\sixfusev[d]{2==N}{2==CH$_{3}$;6B==HO-CO;3FB==H}{C}}%
]{}{}{C}[d]}%
]{3==NH}{}
```



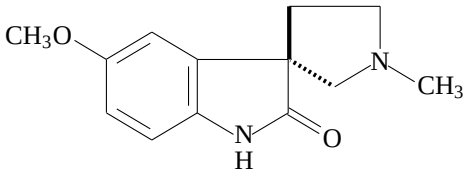
17-23 □

17.3.3 As Parent Structures for Spiro Ring Fusion

The ⟨atomlist⟩ of `\nonaheterov` or related XYMTEX commands for general use is capable of accommodating an attached component generated by a (yl) function, where there emerges a spiro fusion by means of the replacement technique.

Example 17.10. The structure **17-24** of horsfiline as an oxindole alkaloid [6] is drawn by the replacement technique, where an indole nucleus as parent structure is generated by `\nonaheterov` and a pyrrolidine nucleus as an attached component is generated by declaring a (yl)-function in `\fiveheterov`. The two skeletal bonds of the pyrrolidine nucleus are expressed to be a bold line and a dashed line by means of the ⟨skelbdlist⟩ '`{dB}{eA}`' surrounded by a pair of parenthesis.

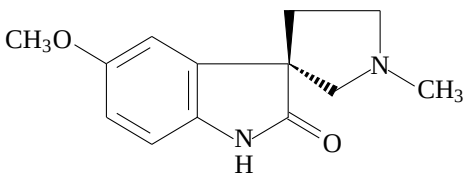
```
\nonaheterov[egj]%
{1==\downnobond{N}{H};%
3s==\fiveheterov({dB}{eA}){2==N}{5==(yl);2==CH$_{3}$}%
}{2D==O;5==CH$_{3}$O}
```



17-24 □

Example 17.11. The bold-lined bond and the dash-lined one in the pyrrolidine nucleus of **17-24** can be respectively changed into a wedge and a dashed wedge by using `\WedgeAsSubst` and `\HashWedgeAsSubst`, as shown in the structure **17-25**.

```
\nonaheterov[egj]
{1==\downnobond{N}{H};%
3s==\fiveheterov{2==N}{5==(yl);2==CH$_{3}$}[de];%
3s==\WedgeAsSubst(0,0)(0,1){200};%
3s==\HashWedgeAsSubst(0,0)(5,-3){171};%
}{2D==O;5==CH$_{3}$O}
```



17-25 □

References

[1] IUPAC Chemical Nomenclature and Structure Representation Division, *Provisional Recommendations. Nomenclature of Organic Chemistry* (2004). http://www.iupac.org/reports/provisional/abstract04/favre_310305.html.

[2] S. Fujita, "Organic Chemistry of Photography," Springer-Verlag, Berlin-Heidelberg (2004).

[3] Y. Monguchi and H. Sajiki, *Yuki Gosei Kagaku Kyokai-Shi*, **70**, 711–721 (2012).

[4] A. Alberti, C. Aubert, M. Campredon, and R. Demadrille, *Bull. Chem. Soc. Jpn.*, **85**, 1048–1052 (2012).

[5] Y. Nakao, *Bull. Chem. Soc. Jpn.*, **85**, 731–745 (2012).

[6] A. Jossang, P. Jossang, H. A. Hadi, T. Sevenet, and B. B. Horsfiline, *J. Org. Chem.*, **56**, 6527–6530 (1991).

Pyranoses and Furanoses

18.1 Drawing Pyranoses

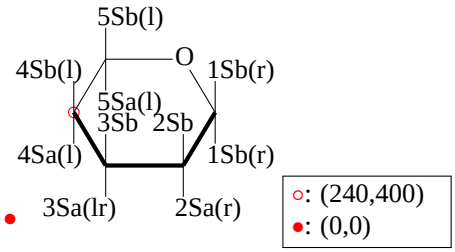
18.1.1 Using Commands for Specific Use

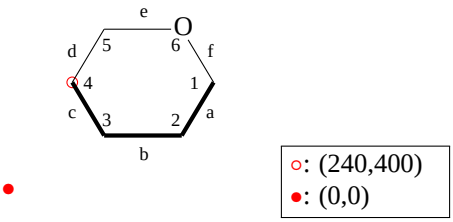
According to the IUPAC nomenclature [1, 2-Carb-5.4], cyclic carbohydrates are frequently represented by perspective diagrams named *the Haworth representation*.

For drawing pyranoses according to the Haworth representation, the command `\pyranose` or `\Pyranose` for specific is used. The format of these commands are as follows:

```
\pyranose[⟨bondlist⟩]{⟨subslist⟩}
\Pyranose[⟨bondlist⟩]{⟨subslist⟩}
```

Locant numbers for designating substitution positions and locant alphabets for designating unsaturation are represented by the following diagrams of `\pyranose`:





Each character set in parentheses represents the handedness of the corresponding position, which is fixed in this type of macros.

The two commands `\pyranose` and `\Pyranose` are different only in their output sizes. The optional argument ⟨bondlist⟩ is an character string in a pair of square brackets, where each character indicates the presence of a double bond at the corresponding edge (Table 18.1).

The argument ⟨subslist⟩ for this macro takes a general format, in which the modifiers listed in Table 3.2 are used.

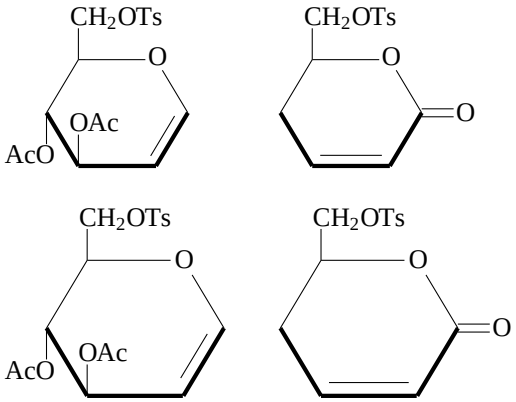
Examples for `\pyranose` and `\Pyranose`:

```
\pyranose[a]{3Sb==OAc;4Sa==AcO;5Sb==CH$_{2}$OTs}
\pyranose[b]{1D==O;5Sb==CH$_{2}$OTs} \\
\Pyranose[a]{3Sb==OAc;4Sa==AcO;5Sb==CH$_{2}$OTs}
\Pyranose[b]{1D==O;5Sb==CH$_{2}$OTs}
```

Table 18.1. Argument ⟨bondlist⟩ for commands \pyranose, \Pyranose, and Related Commands

Character	Printed structure
none	mother skeleton
a	1,2-double bond
b	2,3-double bond
c	4,3-double bond
d	4,5-double bond
e	5,6-double bond
f	6,1-double bond

produce the following diagrams:



For the purpose of drawing another type of expressions based on the Haworth representation, the command \pyranosew or \Pyranosew for specific can be used, when the PostScript-compatible mode or the PDF-compatible mode is selected. The format of these commands are as follows:

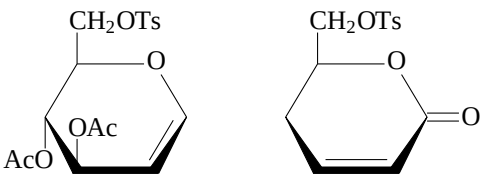
```
\pyranosew[⟨bondlist⟩]{⟨subslist⟩}
\Pyranosew[⟨bondlist⟩]{⟨subslist⟩}
```

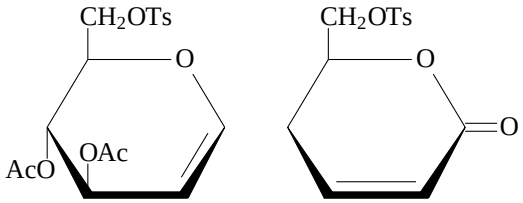
The specification of ⟨bondlist⟩ and ⟨subslist⟩ is identical with the command pyranose.

Examples for \pyranosew and \Pyranosew:

```
\pyranosew[a]{3Sb==OAc;4Sa==AcO;5Sb==CH$_{2}$OTs}
\pyranosew[b]{1D==O;5Sb==CH$_{2}$OTs} \\
\Pyranosew[a]{3Sb==OAc;4Sa==AcO;5Sb==CH$_{2}$OTs}
\Pyranosew[b]{1D==O;5Sb==CH$_{2}$OTs}
```

produce the following diagrams:



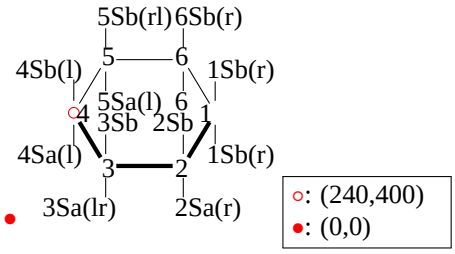


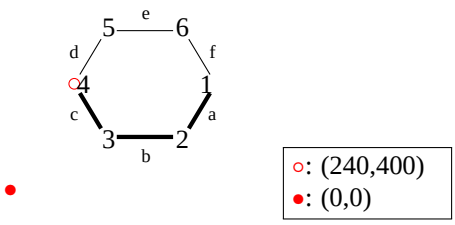
18.1.2 Using Commands for General Use

The commands `\sixsugarh` and `\SixSugarh` for general use are defined to draw six-membered rings of pyranose derivatives. According to the specification of `\ComGen` (cf. Section 3.1), they have the following formats:

```
\sixsugarh(⟨skelbdlist⟩)[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}[⟨delbdlist⟩]
\SixSugarh(⟨skelbdlist⟩)[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}[⟨delbdlist⟩]
```

Locant numbers for designating substitution positions and locant alphabets for designating unsaturation are represented by the following diagrams of `\sixsugarh`:





The specifications of required arguments, i.e., ⟨atomlist⟩ and ⟨subslist⟩, are based on those described in Section 3.2. The specifications of optional arguments, ⟨skelbdlist⟩, ⟨bondlist⟩, and ⟨delbdlist⟩ are based on those described in Section 3.3.

1. The first ⟨skelbdlist⟩ argument is an optional argument, which contains pairs of two alphabets in parentheses, e.g., (`{bA}{fB}`). Each pair contains a lowercase character selected from bond specifiers '`a`' to '`f`' and a uppercase character '`A`' or '`B`'. This means that the bond with a locant alphabet 'a' is printed out in a dashed line and the bond with 'f' is printed out in a bold line.

2. The second argument ⟨bondlist⟩ is an optional argument, which specifies bonds to be doubled as shown in Table 18.1.

3. The third ⟨atomlist⟩ argument is a required argument, which contains one or more hetero atom descriptors which are separated from each other by a semicolon. Each hetero atom descriptor consists of a locant number and a hetero atom, where these are separated with a double equality symbol.

4. The fourth ⟨subslist⟩ argument is a required argument, which contains one or more substitution descriptors which are separated from each other by a semicolon. Each substitution descriptor has a locant number with a bond modifier and a substituent, where these are separated with a double equality symbol.

5. The fifth argument ⟨delbdlist⟩ is an optional argument, which represents one or more bonds (edges) to be omitted. The omitted edges may be regarded as both fused and non-fused positions.

If we use `\sixsugarh` or `\SixSugarh`, we are able to draw β-D-Glucose in the twelve possible Haworth representations, as shown in Fig. 18.1.

The first row of Fig. 18.1 (**18-1**–**18-3**) are depicted by using `\sixsugarh`, where the ring is drawn in other orientations. The codes for drawing them are listed as follows:

```
\sixsugarh{6==O}{1Sa==H;1Sb==OH;2Sa==OH;2Sb==H;%
3Sa==H;3Sb==OH;4Sa==HO;4Sb==H;5Sa==H;5Sb==CH$_{2}$OH}
```

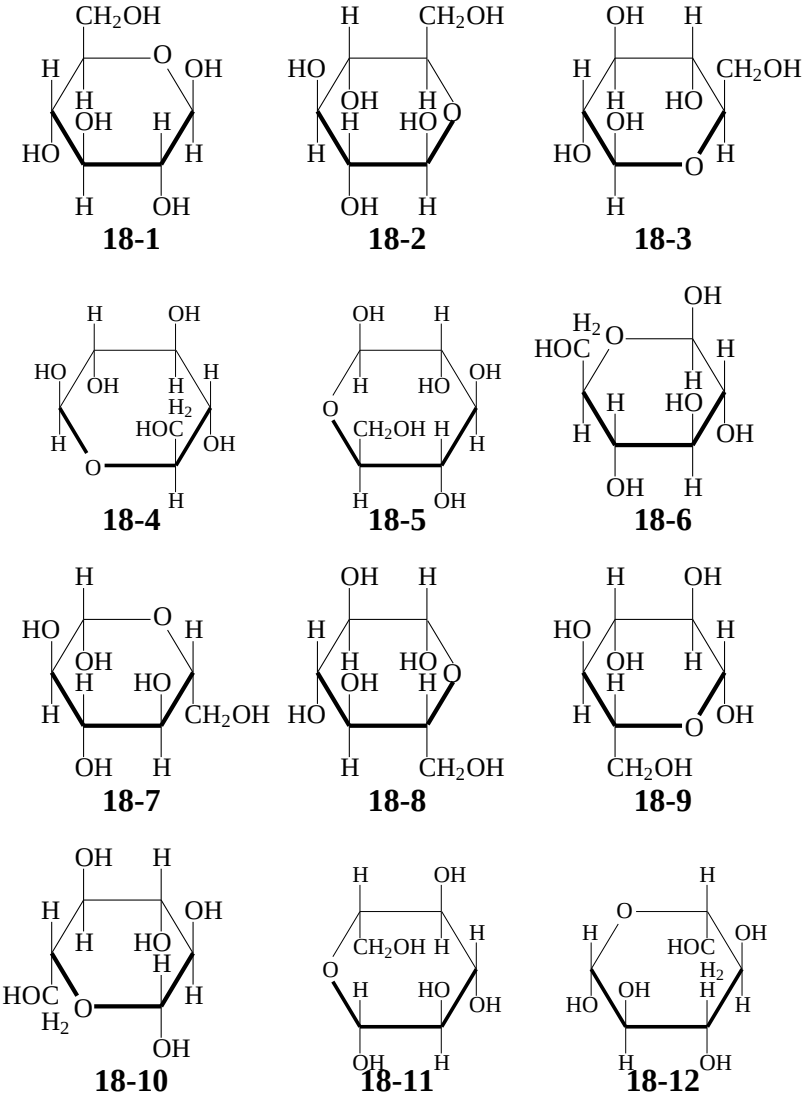


Figure 18.1. β-D-Glucose in the twelve possible Haworth representations

```
\sixsugarh{1==O}{2Sa==H;2Sb==\lmoiety{HO};3Sa==OH;3Sb==H;%
4Sa==H;4Sb==HO;5Sa==OH;5Sb==H;6Sa==H;6Sb==CH$_{2}$OH}
\sixsugarh{2==O}{3Sa==H;3Sb==OH;4Sa==HO;4Sb==H;%
5Sa==H;5Sb==OH;6Sa==\lmoiety{HO};6Sb==H;1Sa==H;1Sb==CH$_{2}$OH}
```

The formulas **18-4** and **18-5** of the second row of Fig. 18.1 are depicted by using `\SixSugarh`, where `\upnobond`, `rlap`, and/or `\lmoiety` are declared if there are undesirable superpositions. The sizes of the resulting diagrams are reduced by using `\scalebox`. The rightmost formula **18-6** is drawn by `\sixsugarh`, where `\upnobond`, `rlap`, and/or `\lmoiety` are declared. The codes for drawing them are listed as follows:

```
\scalebox{0.85}{%
\SixSugarh{3==O}{4Sa==H;4Sb==HO;5Sa==OH;5Sb==H;%
6Sa==H;6Sb==OH;1Sa==OH;1Sb==H;2Sa==H;2Sb==%
\lmoiety{HO\upnobond{C}{H\rlap{$_{2}$}}}}}}
\scalebox{0.85}{%
\SixSugarh{4==O}{5Sa==H;5Sb==OH;6Sa==\lmoiety{HO};6Sb==H;%
1Sa==H;1Sb==OH;2Sa==OH;2Sb==H;3Sa==H;3Sb==CH$_{2}$OH}}
\sixsugarh{5==O}{6Sa==H;6Sb==OH;1Sa==OH;1Sb==H;%
2Sa==H;2Sb==\lmoiety{HO};3Sa==OH;3Sb==H;%
4Sa==H;4Sb==HO\upnobond{C}{H\rlap{$_{2}$}}}
```

The third row of Fig. 18.1 (**18-7**–**18-9**) are depicted by using `\sixsugarh`, where the ring is drawn in inverse orientations. The codes for drawing them are listed as follows:

```
\sixsugarh{6==O}{5Sb==H;5Sa==OH;4Sb==HO;4Sa==H;%
3Sb==H;3Sa==OH;2Sb==\lmoiety{HO};2Sa==H;1Sb==H;1Sa==CH$_{2}$OH}
\sixsugarh{1==O}{6Sb==H;6Sa==\lmoiety{HO};5Sb==OH;5Sa==H;%
4Sb==H;4Sa==HO;3Sb==OH;3Sa==H;2Sb==H;2Sa==CH$_{2}$OH}
\sixsugarh{2==O}{1Sb==H;1Sa==OH;6Sb==OH;6Sa==H;%
5Sb==H;5Sa==OH;4Sb==HO;4Sa==H;3Sb==H;3Sa==CH$_{2}$OH}
```

The leftmost formula **18-10** of the fourth row of Fig. 18.1 is depicted by using `\sixsugarh`, where `\upnobond`, `rlap`, and/or `\lmoiety` are declared. The last two formulas **18-11** and **18-12** are drawn by `\SixSugarh`, where `\upnobond`, `rlap`, and/or `\lmoiety` are declared to avoid undesirable overlapping. The sizes of the resulting diagrams are reduced by using `\scalebox`. The codes for drawing them are listed as follows:

```
\noalign{\vskip10pt}
\sixsugarh{3==O}{2Sb==H;2Sa==OH;1Sb==OH;1Sa==H;%
6Sb==H;6Sa==\lmoiety{HO};5Sb==OH;5Sa==H;4Sb==H;4Sa==%
\lmoiety{HO\downnobond{C}{H\rlap{$_{2}$}}}}
\scalebox{0.85}{%
\SixSugarh{4==O}{3Sb==H;3Sa==OH;2Sb==\lmoiety{HO};2Sa==H;%
1Sb==H;1Sa==OH;6Sb==OH;6Sa==H;5Sb==H;5Sa==CH$_{2}$OH}}
\scalebox{0.85}{%
\SixSugarh{5==O}{4Sb==H;4Sa==HO;3Sb==OH;3Sa==H;%
2Sb==H;2Sa==OH;1Sb==OH;1Sa==H;6Sb==H;6Sa==%
\lmoiety{HO\downnobond{C}{H\rlap{$_{2}$}}}}}
```

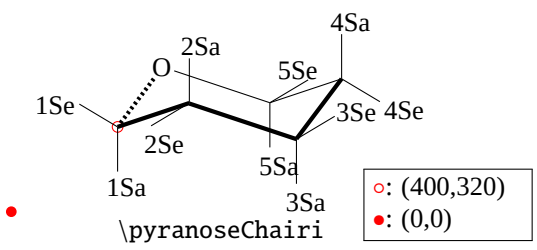
18.1.3 Chair Forms of Pyranose Rings

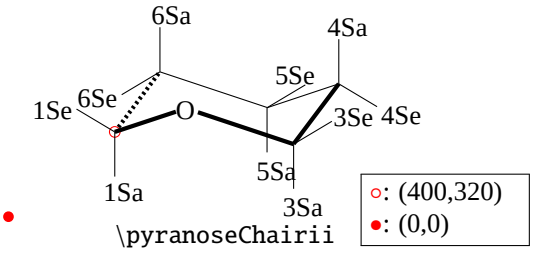
The steroid package of the XeLaTeX system supports commands of specific use for drawing chair forms of pyranose rings, which aim mainly at being incorporated in steroid ring systems (cf. Subsection 13.5.1).

For drawing chair form of pyranoses, the command `\pyranoseChairi` or `\pyranoseChairii` for specific is used. The format of these commands are as follows:

```
\pyranoseChairi[⟨bondlist⟩]{⟨subslist⟩}
\pyranoseChairii[⟨bondlist⟩]{⟨subslist⟩}
```

These commands have restricted abilities for the setting of ⟨subslist⟩, where the bond modifiers are restricted to ‘`Sa`’ for assigning an axial substituent, ‘`Se`’ for assigning an equatorial substituent, ‘`U`’ for assigning an unknown configuration (a wavy bond), and ‘`D`’ for assigning a double bond. The locant numbering for ⟨bondlist⟩ is set in a anti-clockwise fashion around the vertical axis of the chair form. The locant alphabets for their ⟨bondlist⟩ are selected from ‘`a`’ (the bond between 1 and 2) to ‘`f`’ (the bond between 6 and 1).

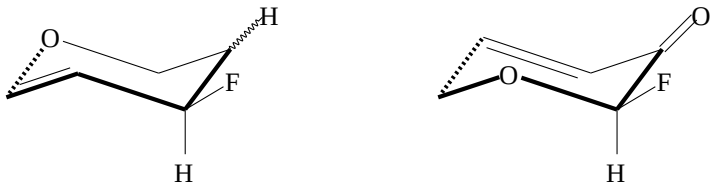




Examples for `\pyranoseChairi` and `\pyranoseChairii`:

```
\pyranoseChairi[a]{3Sa==H;3Se==F;4U==H}
\pyranoseChairii[e]{3Sa==H;3Se==F;4D==O}
```

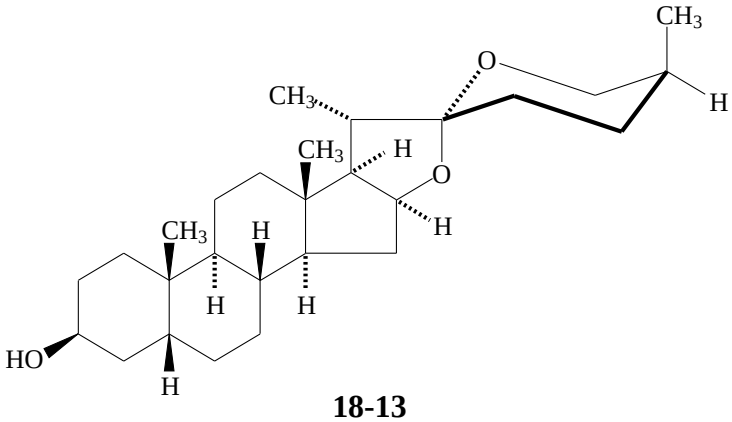
produce the following diagrams:



Example 18.1. The structure **18-13** of sarsasapogenin is drawn by using `\pyranoseChairi` after declaring a (yl)-function, where the spiro union is based on the replacement technique applied to the ⟨subslist⟩ of the command `\fivefusev`. Then the furan moiety due to `\fivefusev` is placed at the bond '`s`' in the ⟨bondlist⟩ of `\steroid` according to the addition technique for ring fusion. Thereby, the code:

```
\steroid[%
{s{\fivefusev{2==O;%
3s==\pyranoseChairi{1==(yl);4Sa==CH$_{3}$;4Se==H}}{4A==CH$_{3}$}{e}%
}}]{3B==HO;5B==H;{10}B==CH$_{3}$;8B==H;9A==H;{13}B==CH$_{3}$;
{14}A==H;{17}GA==H;{16}GA==H}
```

generates the following structure:



18-13 □

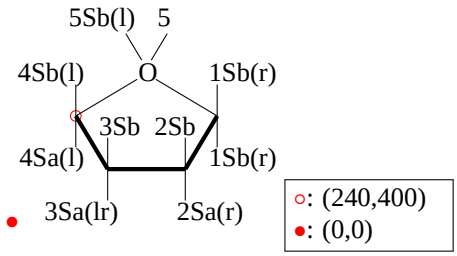
18.2 Drawing Furanoses

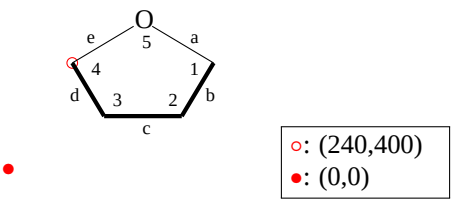
18.2.1 Using Commands for Specific Use

For drawing furanoses, the command `\furanose` or `\Furanose` is used. The formats of these command are as follows:

```
\furanose[⟨bondlist⟩]{⟨subslist⟩}
\Furanose[⟨bondlist⟩]{⟨subslist⟩}
```

Locant numbers for designating substitution positions and bond descriptors are represented by the following diagrams of `\furanose`:





Each character set in parentheses represents the handedness of the corresponding position, which is fixed in this type of macros.

The optional argument ⟨bondlist⟩ is an character string in a pair of brackets, where each character indicates the presence of a double bond at the edge corresponding to the character (Table 18.2).

Table 18.2. Argument ⟨bondlist⟩ for commands `\furanose`, `\Furanose, and Related Commands`

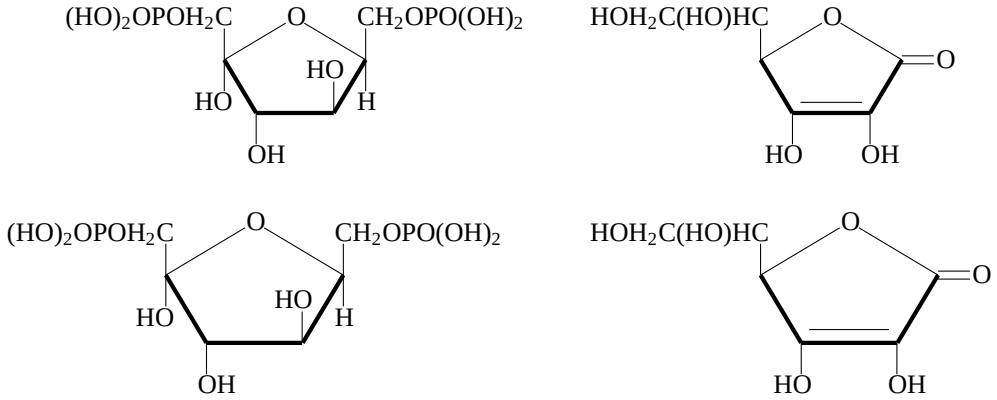
Character	Printed structure
none	mother skeleton
a	1,2-double bond
[h] b	2,3-double bond
c	4,3-double bond
d	4,5-double bond
e	5,1-double bond

The argument ⟨subslist⟩ for this macro takes a general format, in which the modifiers listed in Table 3.2 are used.

Examples of `\furanose` and `\Furanose`:

```
\furanose{1Sa==H;1Sb==CH$_{2}$OPO(OH)$_{2}$;2Sb==\lmoiety{HO};3Sa==OH;%
4Sb==(HO)$_{2}$OPOH$_{2}$C;4Sa==HO}\hskip4cm
\furanose[b]{1D==O;2Sa==OH;3Sa==\lmoiety{HO};4Sb==HOH$_{2}$C(HO)HC} \\
\Furanose{1Sa==H;1Sb==CH$_{2}$OPO(OH)$_{2}$;2Sb==\lmoiety{HO};3Sa==OH;%
4Sb==(HO)$_{2}$OPOH$_{2}$C;4Sa==HO}\hskip4cm
\Furanose[b]{1D==O;2Sa==OH;3Sa==\lmoiety{HO};4Sb==HOH$_{2}$C(HO)HC}
```

produce the following diagrams:



For the purpose of drawing another type of expressions based on the Haworth representation, the command `\furanosew` or `\Furanosew` for specific can be used, when the PostScript-compatible mode or the PDF-compatible mode is selected. The format of these commands are as follows:

```
\furanosew[⟨bondlist⟩]{⟨subslist⟩}
\Furanosew[⟨bondlist⟩]{⟨subslist⟩}
```

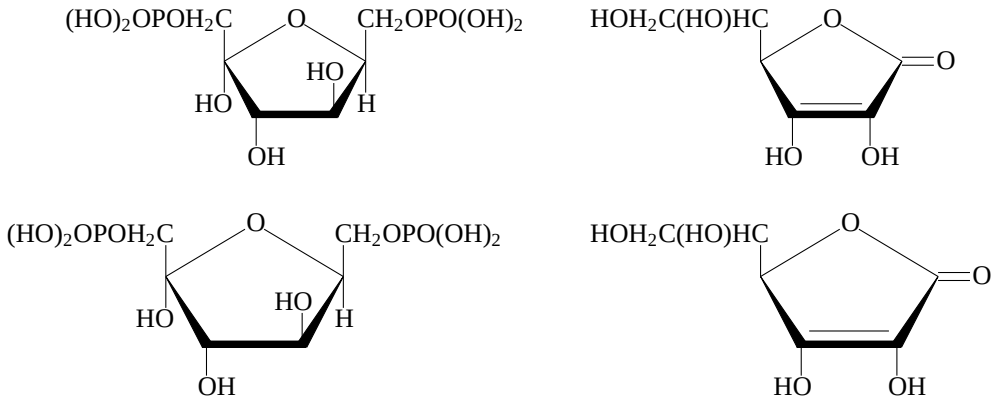
The specification of ⟨bondlist⟩ and ⟨subslist⟩ is identical with the command `\furanose`.

Examples of `\furanosew` and `\Furanosew`:

```
\furanosew{1Sa==H;1Sb==CH$_{2}$OPO(OH)$_{2}$;2Sb==\lmoiety{HO};3Sa==OH;%
4Sb==(HO)$_{2}$OPOH$_{2}$C;4Sa==HO}\hskip4cm
\furanosew[b]{1D==O;2Sa==OH;3Sa==\lmoiety{HO};4Sb==HOH$_{2}$C(HO)HC} \\
\Furanosew{1Sa==H;1Sb==CH$_{2}$OPO(OH)$_{2}$;2Sb==\lmoiety{HO};3Sa==OH;%
```

```
4Sb==(HO)$_{2}$OPOH$_{2}$C;4Sa==HO}\hskip4cm
\Furanosew[b]{1D==O;2Sa==OH;3Sa==\lmoiety{HO};4Sb==HOH$_{2}$C(HO)HC}
```

produce the following diagrams:

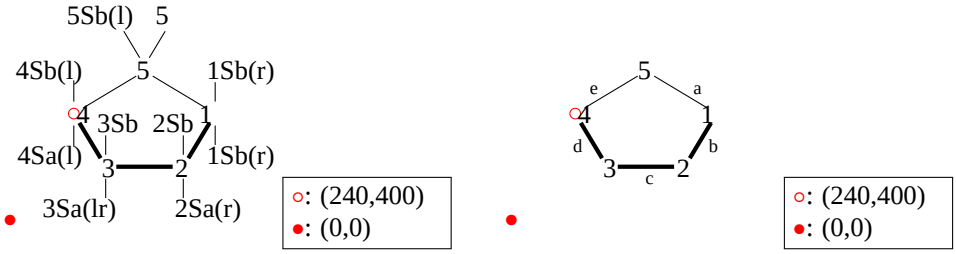


18.2.2 Using Commands for General Use

The commands `\fivesugarh` and `\FixSugarh` for general use are defined to draw five-membered rings of furanose derivatives. According to the specification of `\ComGen` (cf. Section 3.1), they have the following formats:

```
\fivesugarh(⟨skelbdlist⟩)[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}[⟨delbdlist⟩]
\FiveSugarh(⟨skelbdlist⟩)[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}[⟨delbdlist⟩]
```

Locant numbers for designating substitution positions and bond descriptors are represented by the following diagrams of `\fivesugarh`:

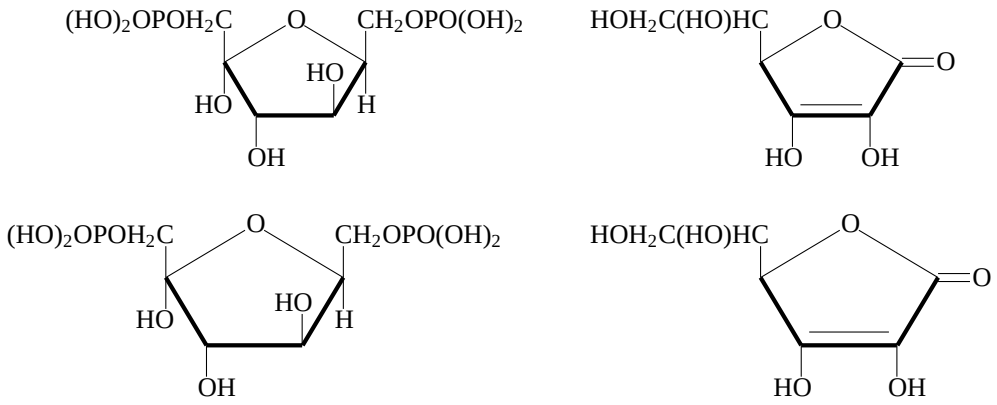


The specifications of required arguments, i.e., ⟨atomlist⟩ and ⟨subslist⟩, are based on those described in Section 3.2. The specifications of optional arguments, ⟨skelbdlist⟩, ⟨bondlist⟩, and ⟨delbdlist⟩ are based on those described in Section 3.3. They are the same as itemized in page 293 for `\sixsugarh`.

Examples of `\fivesugarh` and `\FiveSugarh`:

```
\fivesugarh{5==O}{1Sa==H;1Sb==CH$_{2}$OPO(OH)$_{2}$;2Sb==\lmoiety{HO};3Sa==OH;%
4Sb==(HO)$_{2}$OPOH$_{2}$C;4Sa==HO}\hskip4cm
\fivesugarh[b]{5==O}{1D==O;2Sa==OH;3Sa==\lmoiety{HO};4Sb==HOH$_{2}$C(HO)HC} \\
\FiveSugarh{5==O}{1Sa==H;1Sb==CH$_{2}$OPO(OH)$_{2}$;2Sb==\lmoiety{HO};3Sa==OH;%
4Sb==(HO)$_{2}$OPOH$_{2}$C;4Sa==HO}\hskip4cm
\FiveSugarh[b]{5==O}{1D==O;2Sa==OH;3Sa==\lmoiety{HO};4Sb==HOH$_{2}$C(HO)HC}
```

produce the following diagrams:



18.3 Illustrative Examples of Drawing Sugar Derivatives

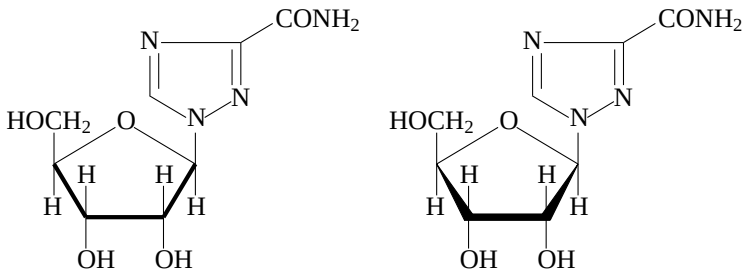
18.3.1 Wedged Skeletal Bonds

Furanoses

The default expression of a furanose skeleton drawn by `\furanose` has three front skeletal bonds of bold lines, while the counterpart drawn by `\furanosew` has a central bold line and two wedged lines.

Example 18.2. For example, the structural formula of ribavirin is drawn in two ways (**18-14** and **18-15**) by using the following codes:

```
\furanose{1Sa==H;2Sb==H;2Sa==OH;3Sb==H;3Sa==OH;4Sa==H;4Sb==HOC\rlap{H$_{2}$};%
1Sb==\fiveheterov[bd]{1==N;2==N;4==N}{1==(yl);3==CONH$_{2}$}}
\furanosew{1Sa==H;2Sb==H;2Sa==OH;3Sb==H;3Sa==OH;4Sa==H;4Sb==HOC\rlap{H$_{2}$};%
1Sb==\fiveheterov[bd]{1==N;2==N;4==N}{1==(yl);3==CONH$_{2}$}}
```



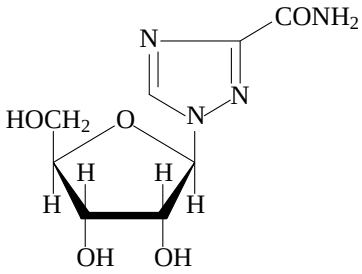
18-14 **18-15**

□

Example 18.3. The drawing of **18-15** by using `\furanosew` is based on a special mode of setting, where the command `\WedgeAsSubst` as well as the command `\PutBondLine` are declared in the ⟨atomlist⟩ of `\fivesugarh`, as shown in the following code:

```
\fivesugarh{5==O;1s==\WedgeAsSubst(0,0)(-3,-5){120};%
4s==\WedgeAsSubst(0,0)(3,-5){120};%
3s==\PutBondLine(-17,0)(307,0){2.8pt}%
}{1Sa==H;2Sb==H;2Sa==OH;3Sb==H;3Sa==OH;4Sa==H;4Sb==HOC\rlap{H$_{2}$};
1Sb==\fiveheterov[bd]{1==N;2==N;4==N}{1==(yl);3==CONH$_{2}$}%
}[abc]
```

which generates the same structure as **18-15**:



18-16 (=18-15)

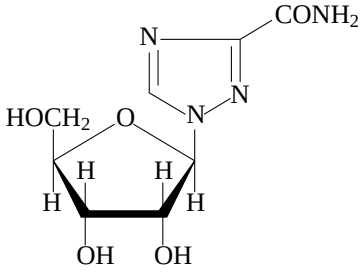
□

Example 18.4. This input code can be simplified by making a tentative macro named `\myfuranose` as follows:

```
\makeatletter
\def\myfuranose{\@ifnextchar[{\@myfuranose}{\@myfuranose[]}}
\def\@myfuranose[#1]#2{%
\fivesugarh[#1]{5==O;1s==\WedgeAsSubst(0,0)(-3,-5){120};%
4s==\WedgeAsSubst(0,0)(3,-5){120};%
3s==\PutBondLine(-17,0)(307,0){2.8pt}%
}{#2}[abc]}
\makeatother
```

Thereby, the same formula can be typeset by writing a more simplified code:

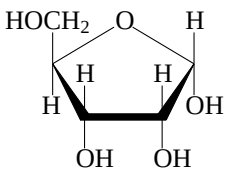
```
\myfuranose{1Sa==H;2Sb==H;2Sa==OH;3Sb==H;3Sa==OH;%
4Sa==H;4Sb==HOC\rlap{H$_{2}$};%
1Sb==\fiveheterov[bd]{1==N;2==N;4==N}{1==(yl);3==CONH$_{2}$}}
```



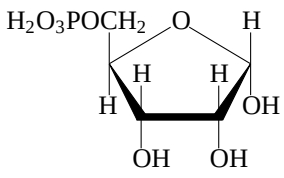
□

Example 18.5. Because the tentative macro `\myfuranose` is convenient to draw various furanoses, it is renamed to be `\furanosew`, which has been stored in the hcycle package of the X$\mathfrak{H}$MTEX system, as described above. Thereby, the structures of α-D-ribofuranose and its 5-phosphoric acid are drawn by using `\furanosew` (= `\myfuranose`) as follows:

```
\furanosew{1Sa==OH;1Sb==H;2Sb==H;2Sa==OH;3Sb==H;3Sa==OH;4Sa==H;%
4Sb==HOC\rlap{H$_{2}$}}
\furanosew{1Sa==OH;1Sb==H;2Sb==H;2Sa==OH;3Sb==H;3Sa==OH;4Sa==H;%
4Sb==H$_{2}$O$_{3}$POC\rlap{H$_{2}$}}
```



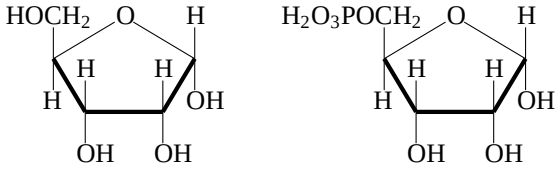
18-17



18-18

Simply by converting `\furanosew` (= `\myfuranose`) into `\furanose`, the corresponding default expressions can be obtained. Thus, the default structural formulas of α-D-ribofuranose and its 5-phosphoric acid are obtained by inputting the following codes:

```
\furanose{1Sa==OH;1Sb==H;2Sb==H;2Sa==OH;3Sb==H;3Sa==OH;4Sa==H;%
4Sb==HOC\rlap{H$_{2}$}}
\furanose{1Sa==OH;1Sb==H;2Sb==H;2Sa==OH;3Sb==H;3Sa==OH;4Sa==H;%
4Sb==H$_{2}$O$_{3}$POC\rlap{H$_{2}$}}
```



□

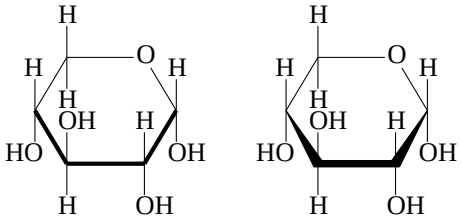
Pyranoses

The same situations as described for furanose hold true for pyranoses.

Example 18.6. Thus, two expressions of α-D-xylose are obtained by the following codes:

```
\pyranose{1Sa==OH;1Sb==H;2Sb==H;2Sa==OH;3Sb==OH;3Sa==H;%
4Sa==HO;4Sb==H;5Sa==H;5Sb==H}
\sixsugarh{6==O;1s==\WedgeAsSubst(0,0)(-3,-5){120};%
4s==\WedgeAsSubst(0,0)(3,-5){120};%
3s==\PutBondLine(-17,0)(307,0){2.8pt}%
}{1Sa==OH;1Sb==H;2Sb==H;2Sa==OH;3Sb==OH;3Sa==H;%
4Sa==HO;4Sb==H;5Sa==H;5Sb==H}[abc]
```

which generate the following formulas:



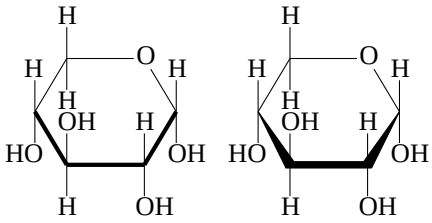
□

Example 18.7. Let us make a macro named `\mypyranose` as follows:

```
\makeatletter
\def\mypyranose{\@ifnextchar[{\@mypyranose}{\@mypyranose[]}}
\def\@mypyranose[#1]#2{%
\sixsugarh[#1]{6==O;1s==\WedgeAsSubst(0,0)(-3,-5){120};%
4s==\WedgeAsSubst(0,0)(3,-5){120};%
3s==\PutBondLine(-17,0)(307,0){2.8pt}%
}{#2}[abc]}
\makeatother
```

The tentative macro `\mypyranose` is renamed to be `\pyranosew`, which has been stored in the hcycle package of the XƎMTEX system, as described above. Hence, the same argument declared in `\pyranose` and `\pyranosew` (= `\mypyranose`) generates alternative expressions as follows:

```
\pyranose{1Sa==OH;1Sb==H;2Sb==H;2Sa==OH;3Sb==OH;3Sa==H;%
4Sa==HO;4Sb==H;5Sa==H;5Sb==H}
\pyranosew{1Sa==OH;1Sb==H;2Sb==H;2Sa==OH;3Sb==OH;3Sa==H;%
4Sa==HO;4Sb==H;5Sa==H;5Sb==H}
```



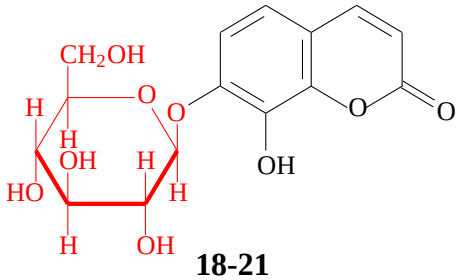
18-19 **18-20**

□

18.3.2 Substituents Derived by (yl)-Functions

Glycosides

Example 18.8. The structure **18-21** of daphnin as a toxic glycoside is drawn by declaring a (yl)-function in `\pyranose` to generate the β-D-glucopyranosyloxy moiety (colored in red), which is placed in the ⟨subslist⟩ of the command `\decaheterov` in terms of the substitution technique. Note that this substitution technique regards the 8-hydroxycoumarin skeleton as a parent structure.



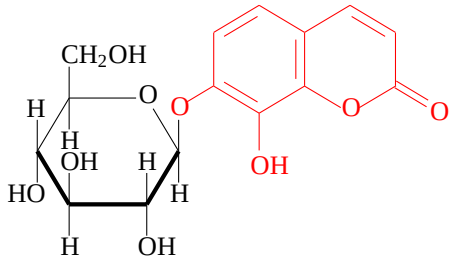
18-21

trivial name: daphnin
IUPAC name: 7-(β-D-Glucopyranosyloxy)-8-hydroxycoumarin
XyMTEX command:

```
\decaheterovi[cfhk]{1==O}{2D==O;8==OH;%
7==\lyl(3==O){8==%
\pyranose{1Sb==(yl);1Sa==H;2Sb==H;2Sa==OH;3Sb==OH;3Sa==H;4Sa==HO;%
4Sb==H;5Sa==H;5Sb==CH$_{2}$OH}}}
```

□

Example 18.9. If we regard the β-D-glucopyranose skeleton as a parent skeleton, we find another way of the application of the substitution technique, where the 8-hydroxycoumarin aglycone serves as a substituent (colored in red). Thereby we are able to draw the structure **18-22**, which is the same as **18-21**.



18-22 (= **18-21**)

trivial name: daphnin
IUPAC name: 7-(β-D-Glucopyranosyloxy)-8-hydroxycoumarin
XyMTEX command:

```
\pyranose{1Sa==H;2Sb==H;2Sa==OH;3Sb==OH;3Sa==H;4Sa==HO;%
4Sb==H;5Sa==H;5Sb==CH$_{2}$OH;%
1Sb==\ryl(8==O){3==\decaheterovi[cfhk]{1==O}{7==(yl);2D==O;8==OH}}}
```

□

Example 18.10. The structural formula **18-23** of adonitoxin as another toxic glycoside (Fig. 18.2) is drawn by the code defined as follows:

```
\def\adonitoxin{%
\begin{XyMcompd}(2200,1800)(-550,-300){}{}
\steroid{{{10}}==\lmoiety{OHC};{{14}}==OH;%
{{13}}==\lmoiety{H$_{3}$C};{{16}}==OH;%
{{17}}==\fiveheterov[e]{3==O}{4D==O;1==(yl)};%
3==\lyl(3==O){8==%
\pyranosew{1Sb==(yl);1Sa==H;2Sb==H;2Sa==OH;3Sb==H;3Sa==OH;4Sb==HO;%
4Sa==H;5Sb==H;5Sa==CH$_{3}$}}}
\end{XyMcompd}}
```

A pyranose component at the 3-position of the steroid ring is generated by combining a `\lyl` with a (yl)-function declared in the command `\pyranosew` (colored in red). A lactone component at the 17-position

is generated by declaring a (yl)-function in `\fiveheterov` (colored in blue). These two components are placed in the ⟨subslist⟩ of the command `steroid` according to the substitution technique.

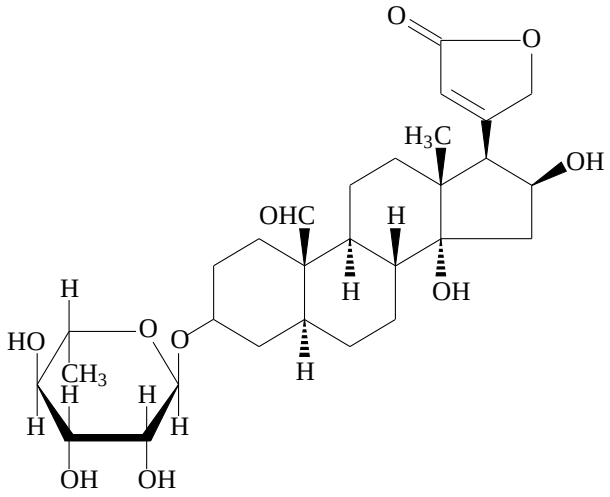
Then, we write down the defined command `\adonitoxin`. If it is necessary to reduce the size of a formula, the command `\changeunitlength` is declared. The resulting formulas are depicted in Fig. 18.2.

Note that the drawing shown in Fig. 18.2 is based on the viewpoint that the steroid skeleton is a parent structure. □

Example 18.11. The structural formula **18-24** of adonitoxin can be drawn in an alternative way by regarding the pyranose skeleton as a parent structure, where the command `\pyranosew` (the same as `\mypyranose` described above) is used to generate the pyranose skeleton.

```
\wedgehashedwedge
\pyranosew{1Sa==H;2Sb==H;2Sa==OH;3Sb==H;3Sa==OH;4Sb==HO;%
4Sa==H;5Sb==H;5Sa==CH$_{3}$;%
1Sb==\ryl(8==O){3==%
\steroid{3==(yl);5A==H;8B==H;9A==H;{{10}B}==\lmoiety{OHC};{{14}A}==OH;%
{{13}B}==\lmoiety{H$_{3}$C};{{16}B}==OH;%
{{17}B}==\fiveheterov[e]{3==O}{4D==O;1==(yl)}}}}
```

This code typesets the following formula:



18-24

□

Disaccharides

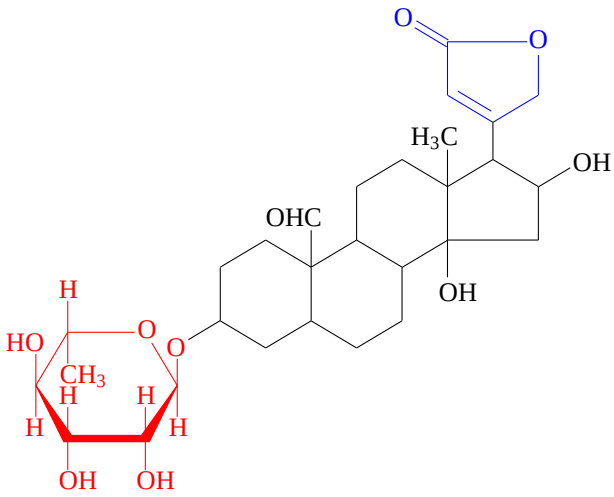
The substitution technique is effective to draw the structures of disaccharides.

Example 18.12. The structure of sucrose as a disaccharide with pyranose and furanose rings are drawn in two ways, where the divalent oxygen drawn by `\utrigonal` is selected as a parent skeleton. The left diagram **18-25** adopts `\furanose` and `\pyranose` for drawing two substituent components after declaring a (yl)-function, where the resulting sugar rings have three front skeletal bonds of bold lines. On the other hand, the right diagram **18-26** adopts `\furanosew` and `\pyranosew` for drawing two substituent components after declaring a (yl)-function, where the resulting sugar rings have a central bold line and two wedged lines.

```
%bold-lined bonds
\utrigonal{0==O;%
2==\furanose{4==(yl);1Sa==CH$_{2}$OH;2Sb==\lmoiety{HO};%
2Sa==H;3Sb==H;3Sa==OH;4Sb==HOC\rlap{H$_{2}$}};%
3==\pyranose{1==(yl);2Sa==OH;3Sb==OH;4Sa==HO;5Sb==CH$_{2}$OH}}
%wedged bonds and a bold-line bond
\utrigonal{0==O;%
2==\furanosew{4==(yl);1Sa==CH$_{2}$OH;2Sb==\lmoiety{HO};%
2Sa==H;3Sb==H;3Sa==OH;4Sb==HOC\rlap{H$_{2}$}};%
3==\pyranosew{1==(yl);2Sa==OH;3Sb==OH;4Sa==HO;5Sb==CH$_{2}$OH}}
```

—0.1pt

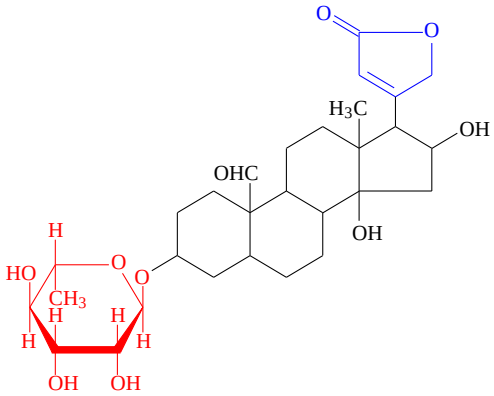
```
\adonitoxin
```



18-23

—0.08pt

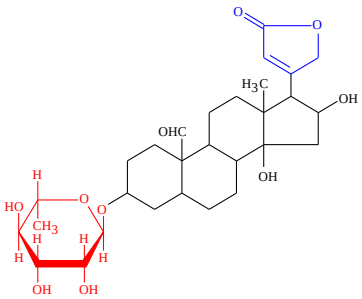
```
{\changeunitlength{0.08pt}\adonitoxin}
```



18-23′

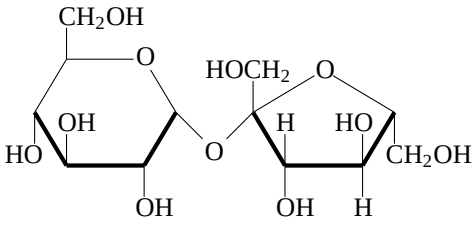
—0.06pt

```
{\changeunitlength{0.06pt}\adonitoxin}
```

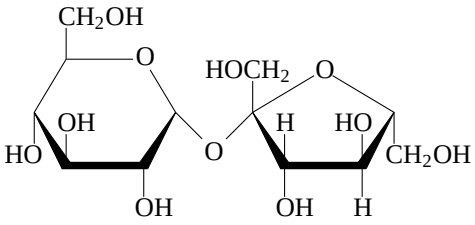


18-23″

Figure 18.2. Adonitoxin in various sizes



18-25

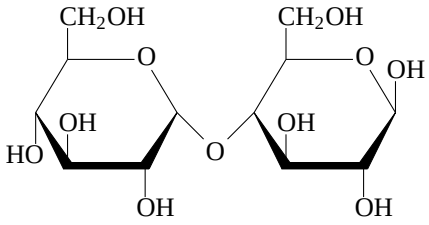


18-26

□

Example 18.13. The structure **18-27** of maltose as a disaccharide with two pyranose rings is drawn by the substitution technique in a similar way.

```
\utrigonal{0==O;%
2==\pyranosew{4==(yl);1Sb==OH;2Sa==OH;3Sb==OH;5Sb==CH$_{2}$OH};%
3==\pyranosew{1==(yl);2Sa==OH;3Sb==OH;4Sa==HO;5Sb==CH$_{2}$OH}}
```



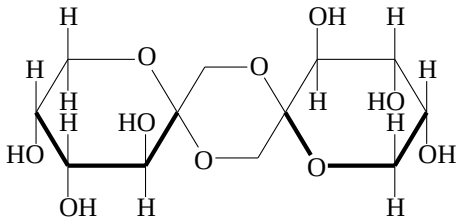
18-27

□

18.3.3 Spiro Fusion Based on (yl)-Functions

The cyclic product of condensation of two monosaccharide molecules with the elimination of two molecules of water is called an intermolecular anhydride. Such an intermolecular anhydride, which is named by placing 'dianhydride' according to the IUPAC nomenclature [1, 2-Carb-27], has a two spiro linkage, as exemplified by **18-28**.

Example 18.14. The spiro components generated by declaring a (yl)-function undergo spiro fusion by means of the replacement technique using the ⟨atomlist⟩ of the command `\sixheteroh`.



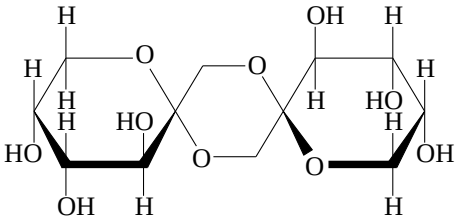
18-28

IUPAC name: α-D-Fructopyranose β-D-fructopyranose 1,2′:1′,2-dianhydride
XƎMTEX command:

```
\sixheteroh{3==O;6==O;%
1s==\sixsugarh{6==O}{1==(yl);2Sa==H;2Sb==\lmoiety{HO};%
3Sa==OH;3Sb==H;4Sa==HO;4Sb==H;5Sa==H;5Sb==H};%
4s==\sixsugarh{3==O}{4==(yl);1Sa==OH;1Sb==H;2Sa==H;%
2Sb==H;5Sa==H;5Sb==OH;6Sa==\lmoiety{HO};6Sb==H}}{}
```

□

Example 18.15. If we want to draw a pyranose ring with wedged bonds, the code `1s==\sixsugarh{6==O}{...}` for drawing the left sugar ring of **18-28** can be replaced by the command `1s==\pyranosew{...}` (the same as `\mypyranose`). The right sugar ring should be drawn by adding `\WedgeAsSubst` and `\PutBondLine` in a similar way to the definition of `\mypyranose` described above. Thereby the following code for drawing **18-29** is obtained.



18-29

IUPAC name: α-D-Fructopyranose β-D-fructopyranose 1,2′:1′,2-dianhydride

XyMTEX command:

```
\sixheteroh{3==O;6==O;%
1s==\pyranosew{1==(yl);2Sa==H;2Sb==\lmoiety{HO};%
3Sa==OH;3Sb==H;4Sa==HO;4Sb==H;5Sa==H;5Sb==H};%
4s==\sixsugarh{3==O;%
1s==\WedgeAsSubst(0,0)(-3,-5){120};%
4s==\WedgeAsSubst(0,0)(3,-5){93};%
3s==\PutBondLine(50,0)(307,0){2.8pt}%
}{4==(yl);1Sa==OH;1Sb==H;2Sa==H;%
2Sb==H;5Sa==H;5Sb==OH;6Sa==\lmoiety{HO};6Sb==H}[abc]}{}
```

□

References

[1] A. D. McNaught and IUPAC and International Union of Biochemistry Joint Commission on Biochemical Nomenclature, *Pure Appl. Chem.*, **68**, 1919–2008 (1986).

Part IV

Aliphatic Compounds

Aliphatic Compounds of Lower Carbon Contents. Commands for Specific Use

This chapter is devoted to depict tetrahedral and trigonal structures as well as their related structures. These commands for specific use have no general commands, so that they lack ⟨atomlist⟩. Instead, each central atom is declared to be `0==...` in the ⟨subslist⟩. On the other hand, the commands for drawing ethylene derivatives have ⟨atomlist⟩ and ⟨subslist⟩, where central atoms are declared in the ⟨atomlist⟩.

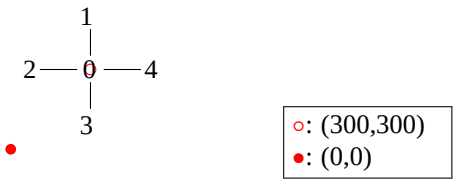
19.1 Drawing Planar Forms of Tetrahedral Compounds

19.1.1 Tetragonal Skeleton with One Central Atom

The X$\tilde{\text{a}}$MTEX command `\tetrahedral` is used to draw the planar form of a tetrahedral unit (aliphat.sty). The format of this command is as follows:

```
\tetrahedral[⟨bondlist⟩]{⟨subslist⟩}
```

The following diagram shows the numbering for designating substitution positions:



in which the same macro is used to typeset both saturated and unsaturated derivatives.

The optional argument ⟨bondlist⟩ has a restricted format, where the declaration of locant alphabets is not permitted but the specification of a charge on the central atom is permitted: i.e., `{0+}` represents a + charge (or another one character) on the center.

The argument ⟨subslist⟩ is used to specify each substituent with a locant number and a bond modifier shown in Table 19.1, in which *n* is an Arabic numeral between 1 and 4.

The central carbon atom is assigned by writing 0==C in the ⟨subslist⟩. The structural formula of an ammonium ion can also be obtained with this command.

Examples of `\tetrahedral`:

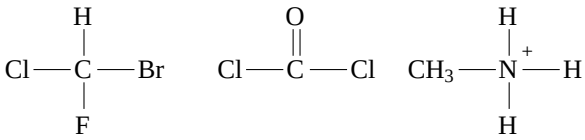
```
\tetrahedral{0==C;1==H;2==Cl;3==F;4==Br}\qquad
```

Table 19.1. ⟨subslist⟩ for `\tetrahedral`

Character	Structures printed
*n*T	triple bond at *n*-atom
*n*D	double bond at *n*-atom
n or *n*S	single bond at *n*-atom
*n*A	alpha single bond at *n*-atom
*n*B	beta single bond at *n*-atom

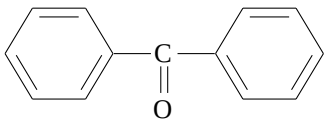
```
\tetrahedral{0==C;1D==O;2==Cl;4==Cl}\qquad
\tetrahedral[{0+}]{0==N;1==H;2==CH$_{3}$;3==H;4==H}\qquad
```

produce the following structures:

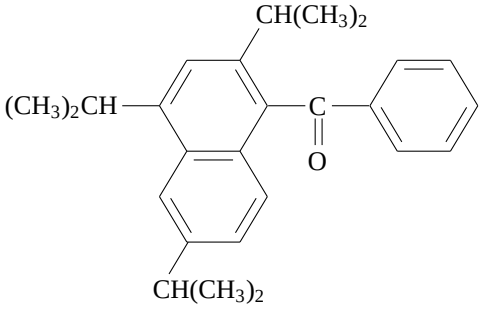


Example 19.1. The structure **19-1** of benzophenenoen is drawn by regarding the tetrahedral skeleton as a parent structure (–CO–), where two phenyl groups are generated by declaring a (yl)-function in the `\benzeneh` command and participate in the substitution technique.

```
\tetrahedral{0==C;2==\benzeneh{4==(yl)};3D==O;4==\benzeneh{1==(yl)}}
\tetrahedral{0==C;%
2==\naphthaleneh{4==(yl);1==(CH$_{3}$)$_{2}$CH;3==CH(CH$_{3}$)$_{2}$;%
7==CH(CH$_{3}$)$_{2}$;};3D==O;
4==\benzeneh{1==(yl)}}
```



19-1



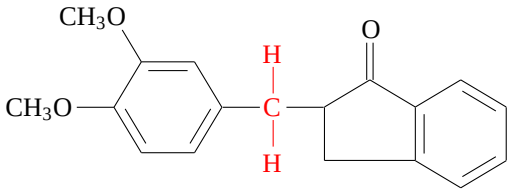
19-2

□

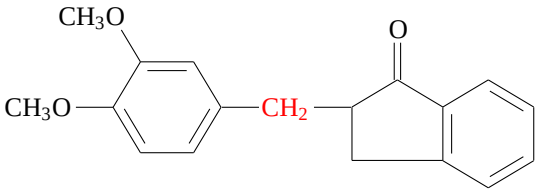
Example 19.2. In a similar way, the substitution technique can be applied to draw the structure **19-2** of 2,4,6-triisopropyl-α-naphthophenone, where the tetrahedral skeleton is regarded as a parent structure (–CO–). The phenyl group and the naphthyl group are generated by declaring a (yl)-function in the `\beneneh` and `\naththaleneh` command respectively and they are placed the ⟨subslist⟩ of the command `\tetrahedral`.

A methylene linkage in a cyclization product by an intramolecular Friedel-Crafts acylation [1, page 613] can be expressed as a full format of a tetrahedral skeleton (**19-3**) or as a simplified format (**19-4**). These two expressions are drawn commonly by using the command `\tetrahedral`, where the red-colored codes correspond to the two alternative expressions of the methylene linkage:

```
\tetrahedral{0==C;1==H;3==H;%
2==\benzeneh{4==(yl);1==CH$_{3}$O;2==\lmoiety{CH$_{3}$O}};%
4==\cyclopentanevi[{b\sixfusev[ace]{}{}{E}}]%
{1D==O;5==(yl)}}
\tetrahedral{0==CH$_{2}$;%
2==\benzeneh{4==(yl);1==CH$_{3}$O;2==\lmoiety{CH$_{3}$O}};%
4==\cyclopentanevi[{b\sixfusev[ace]{}{}{E}}]%
{1D==O;5==(yl)}}
```



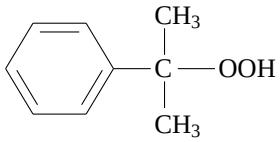
19-3



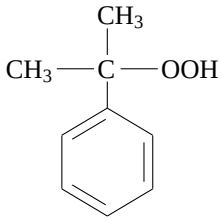
19-4 □

Example 19.3. The structure **19-5** of cumene hydroperoxide is drawn by declaring a (yl)-function in the command `\tetrahedral`, where a benzene skeleton due to `\benzeneh` is regarded as a parent structure. On the other hand, an alternative drawing of **19-6** is available by declaring a (yl)-function in the command `\benzenev`, where a planar tetragonal skeleton due to `\tetrahedral` is regarded as a parent structure.

```
\benzeneh{4==\tetrahedral{2==(yl);0==C;1==CH$_{3}$;3==CH$_{3}$;4==OOH}}
\tetrahedral{0==C;1==CH$_{3}$;2==CH$_{3}$;4==OOH;3==\benzenev{1==(yl)}}
```



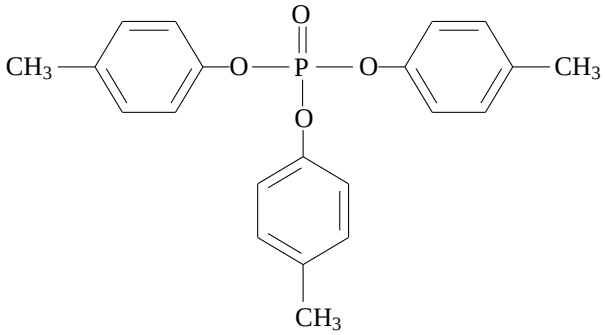
19-5



19-6 □

Example 19.4. The structure **19-7** of tri(*p*-tolyl) phosphate used as a solvent for color photographic film [2, page 21] is drawn by applying the substitution technique. Thus, a tetrahedral skeleton drawn by the command `\tetrahedral` is regarded as a parent structure, while three *p*-tolyloxy groups as substituents are generated by the combination of the command `\ryl` or `\lyl` with a (yl)-function declared in `\benzeneh` or `\benzenev` and then placed in the ⟨bondlist⟩ of the command `\tetrahedral`.

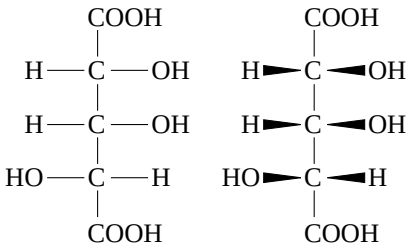
```
\tetrahedral{0==P;1D==O;
2==\lyl(4==O){4==\benzeneh{4==(yl);1==CH$_{3}$}};%
4==\ryl(4==O){4==\benzeneh{1==(yl);4==CH$_{3}$}};%
3==\ryl(0==O){8==\benzenev{1==(yl);4==CH$_{3}$}}}
```



19-7 □

Example 19.5. The Fischer projection **19-8** of a stereoisomer of 2,3,4-trihydroxyglutaric acid is drawn by regarding the central carbon at the 3-position as a parent structure, which is generated by the command `\tetrahedral`. The 2-carbon center and the 4-carbon center are regarded as substituents, each of which is generated by declaring a (yl)-function in the command `\tetrahedral`. The substituents are placed in the ⟨subslist⟩ according to the substitution technique.

```
\tetrahedral{0==C;2==H;4==OH;%%3
3==\tetrahedral{0==C;1==(yl);3==COOH;2==HO;4==H};%%4
1==\tetrahedral{0==C;3==(yl);1==COOH;2==H;4==OH}%%2
}%%3
```



19-8 **19-9**

On the other hand, the corresponding expression **19-9** with wedged bonds is also drawn in a similar way according to the substitution technique.

```
\tetrahedral{0==C;2B==H;4B==OH;%%3
3==\tetrahedral{0==C;1==(yl);3==COOH;2B==HO;4B==H};%%4
1==\tetrahedral{0==C;3==(yl);1==COOH;2B==H;4B==OH}%%2
}%%3
```

The structural formulas **19-8** and **19-9** have been further modified by adding locant numbers and the *RS*-stereodescriptors of the CIP (Cahn-Ingold-Prelog) system to respective carbon centers [3]. □

19.1.2 Automatic Adjustment for Two- or More-Character Central Atoms of Tetrahedral Molecules

The specification of the command `\tetrahedral` in X$\mathfrak{Z}$MTEX Versions 3.00 (published) and 4.00 (private) allows us to draw a one-character central atom only, which is output in the centralized position of the domain of the central atom. This means that an atom represented by two characters (Si, Zn, etc.) or a group such as CH and CH_2 cannot be placed properly as a central atom, where the central atom and an incident bond may overlap each other. The command `\tetrahedral` in X$\mathfrak{Z}$MTEX Version 4.01 and later is improved to allow a length-variable central atoms.

1. Examples of Metal Complexes:

which are drawn by the following codes:

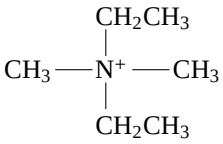
```
\tetrahedral{0==Si;4==CH$_{3}$;2==CH$_{3}$;1==OCH$_{3}$;3==OCH$_{3}$}
\hskip3cm
\tetrahedral{0==Sn;1==C$_{4}$H$_{9}$-$n$;%
3==C$_{4}$H$_{9}$-$n$;2==$n$-C$_{4}$H$_{9}$;4==Cl}
```

2. As for quaternary ammonium salts, e.g.,

the specification of X$\mathfrak{Z}$MTEX Versions 3.00 and 4.00 has forced us to write the following codes:

```
\tetrahedral{0==N\rlap{$^{^{+}}$};4==CH$_{3}$;2==CH$_{3}$;%
1==CH$_{2}$CH$_{3}$;3==CH$_{2}$CH$_{3}$}
\hskip 3cm
\tetrahedral[{0+}]{0==N;4==CH$_{3}$;2==CH$_{3}$;%
1==CH$_{2}$CH$_{3}$;3==CH$_{2}$CH$_{3}$}
```

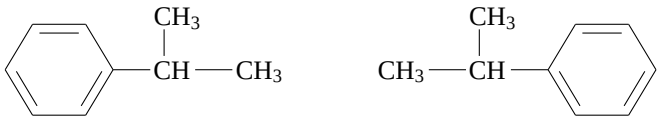
On the other hand, the version 4.01 can draw a quaternary salt in the following way:



by inputting as follows:

```
\tetrahedral{0==N$^{+}$;4==CH$_{3}$;2==CH$_{3}$;%
1==CH$_{2}$CH$_{3}$;3==CH$_{2}$CH$_{3}$}
```

3. Cumene (isopropylbenzene or 2-propylbenzene) can be drawn as follows:



They are drawn by the following codes containing a “yl function”:

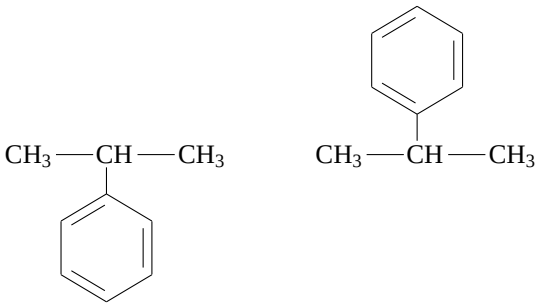
```
\bzdrh{4==\tetrahedral{2==(yl);0==CH;1==CH$_{3}$;4==CH$_{3}$}}
\hskip4cm
\bzdrh{1==\tetrahedral{4==(yl);0==CH;1==CH$_{3}$;2==CH$_{3}$}}
```

Cumene can be drawn as a derivative of propane, i.e., 2-phenylpropane. Thus, we have:

These formulas are drawn by inputting following codes:

```
\tetrahedral{2==\bzdrh{4==(yl)};0==CH;1==CH$_{3}$;4==CH$_{3}$}
\hskip3cm
\tetrahedral{4==\bzdrh{1==(yl)};0==CH;1==CH$_{3}$;2==CH$_{3}$}
```

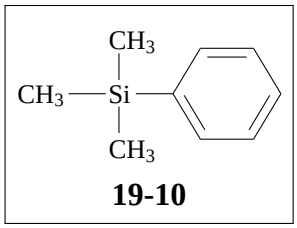
The direction of a phenyl group can be changed:



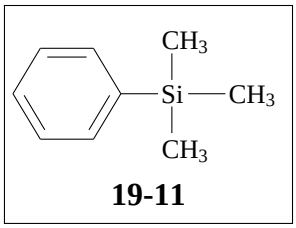
These formulas are drawn by inputting following codes:

```
\tetrahedral{3==\bzdrv{1==(yl)};0==CH;2==CH$_{3}$;4==CH$_{3}$}
\hskip2cm
\tetrahedral{1==\bzdrv{4==(yl)};0==CH;2==CH$_{3}$;4==CH$_{3}$}
```

4. The formulas of trimethylsilylbenzene (**19-10** and **19-11**) represented by:



19-10



19-11

are drawn by the following codes

```
\fbox{%
\begin{XyMcompd}(900,600)(-300,100){cpd:2}{}
\bzdrh{1==\tetrahedral{4==(yl);0==Si;1==CH$_{3}$;2==CH$_{3}$;3==CH$_{3}$}}
\end{XyMcompd}}
\hskip1cm
\fbox{%
\begin{XyMcompd}(900,600)(300,100){cpd:3}{}
\bzdrh{4==\tetrahedral{2==(yl);0==Si;1==CH$_{3}$;4==CH$_{3}$;3==CH$_{3}$}}
\end{XyMcompd}}
```

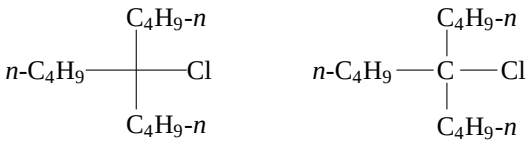
in which the `XyMcompd` environment is used to specify the drawing domain of each structural formula (surrounded by the `\fbox` command). Moreover, the cross references of the formulas can be accomplished by using `\cref` or `\ref`.

19.1.3 Omission of Central Atoms

A central atom could not be omitted in the old version of the `\tetrahedral` command so that a vacancy was resulted if the central atom is not specified. In XƎMTEX Version 4.01 and later, the `\tetrahedral` command allows the omission of such a central atom, where a vacancy is deleted. For example, the codes

```
\tetrahedral{1==C$_{4}$H$_{9}$-$n$;%
3==C$_{4}$H$_{9}$-$n$;2==$n$-C$_{4}$H$_{9}$$;4==Cl}
\hskip2cm
\tetrahedral{0==C;1==C$_{4}$H$_{9}$-$n$;%
3==C$_{4}$H$_{9}$-$n$;2==$n$-C$_{4}$H$_{9}$$;4==Cl}
```

produce the following structures:



The `\tetrahedral` command can be used in another command in a nested fashion. The following examples show the use of the `\tetrahedral` command in the argument of the `\bzdrh` command. Thus, the codes:

```
\bzdrh{4==%
\tetrahedral{2==(yl);1==C$_{4}$H$_{9}$-$n$;%
3==C$_{4}$H$_{9}$-$n$;4==Cl}}
\hskip3cm
\bzdrh{4==%
\tetrahedral{2==(yl);0==C;1==C$_{4}$H$_{9}$-$n$;%
3==C$_{4}$H$_{9}$-$n$;4==Cl}}
```

produce the following structures:

Note: In XeLaTeX Version 4.01 and later, the `\trigonal` command etc. do not support this function, so that a vacancy was resulted if the central atom is not specified.

19.1.4 Variable Bond Lengths

In XeLaTeX Version 4.01 and later, the `\tetrahedral` command takes an additional optional argument ⟨lengthlist⟩, which specifies the bond length of each horizontal or vertical bond by the unit `\unitlength` (= 0.1pt for the standard situation). The ⟨lengthlist⟩ is surrounded by a pair of angle brackets as shown in the full specification of the `\tetrahedral` command:

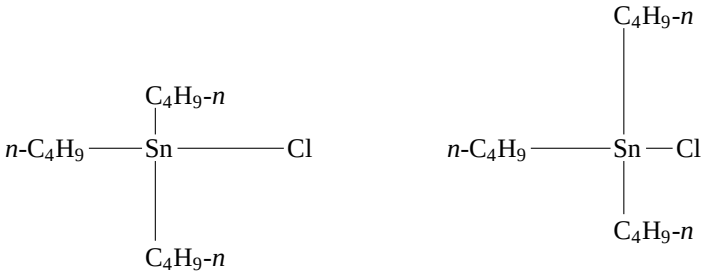
```
\tetrahedral[⟨bondlist⟩]{⟨subslist⟩}<⟨lengthlist⟩>
```

The ⟨lengthlist⟩ contains four values punctuated with commas, which successively indicate the bond lengths of 0–1, 0–2, 0–3, and 0–4 bonds. When a value is omitted, the corresponding bond is printed out by using a default value.

For example, the codes

```
\tetrahedral{0==Sn;1==C$_{4}$H$_{9}$-$n$;%
3==C$_{4}$H$_{9}$-$n$;2==$n$-C$_{4}$H$_{9}$$;4==Cl}<100,200,300,400>
\hskip2cm
\tetrahedral{0==Sn;1==C$_{4}$H$_{9}$-$n$;%
3==C$_{4}$H$_{9}$-$n$;2==$n$-C$_{4}$H$_{9}$$;4==Cl}<400,300,200,100>
```

produce the following structures:



Example 19.6. In 2004, I have published a monograph entitled “Organic Chemistry of Photography” [2]. In this book, I have extensively used XeLaTeX (Version 4.00) for typesetting chemical structural formulas. However, a direct method has been applied as follows, because the version 4.00 did not support the function of variable bond lengths. Thus, I have first defined a command `\methineunitCA` for drawing the methine unit:

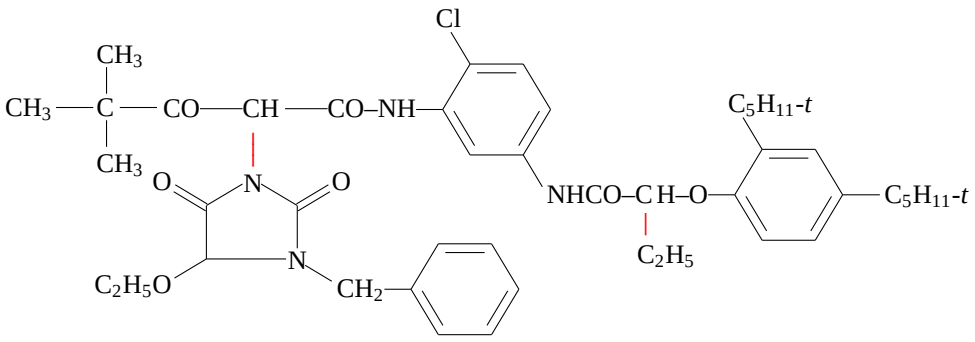
```
\makeatletter
\begingroup
\def\methineunitCA#1{\vtop{%
\hbox to0.8em{CH\hss}\nointerlineskip
\hbox to0.8em{\hss
$\big|$\rule[-1.7ex]{0pt}{5ex}%
\hss}\nointerlineskip
\hbox to0.8em{\hss\kern#1%
\fiveheterovi{1==N;3==N}{1==(yl);2D==O;5D==O;4==C$_{2}$H$_{5}$O;%
```

```
3==\ryl(3==CH$_{2}$){4==\bzdrh{1==(yl)}}}\hss}\nointerlineskip
\hbox to1.6em{}%
}}
```

The command \methineunitCA contains layout data of a vertical bond in the form of \rule in the vertical TEX-box (\vtop). Then this methine unit is incorporated to the main skeleton of a yellow coupler to be drawn:

```
%EX-Y yellow coupler
%\fbox{%
\begin{tabular}{c}
\begin{XyMcompd}(3600,1500)(-100,-700){}{}
\tetrahedral{0==C;1==CH$_{3}$;2==CH$_{3}$;3==CH$_{3}$;%
4==\raisebox{.5ex}{\ryl(4=={CO\sbond\methineunitCA{1pt}\sbond CO--NH}){%%
4==\bzdrh{1==(yl);2==Cl;5==%
\ryl(3==NHCO--%
\vtop{\hbox{C}\nointerlineskip
\hbox to0.8em{\hss\rule[-1.2ex]{0pt}{3.5ex}$|$\hss}\nointerlineskip
\hbox to0.8em{\hss C\rlap{$_{2}$H$_{5}$}\hss}%
}%
H--O){4==\bzdrh{1==(yl);2==C$_{5}$H$_{11}$-$t$;%
4==C$_{5}$H$_{11}$-$t$}}};%
}}%%
}%
\end{XyMcompd} \\
\compd\label{cpd:ch1-00LL1a} \\
\end{tabular}
%}
\endgroup
\makeatother
```

The command \ryl contains a vertical bond of —C_2C_5 in the form of \rule in the vertical TEX-box (\vtop). The above codes produce the following structure of a two-equivalent yellow coupler:



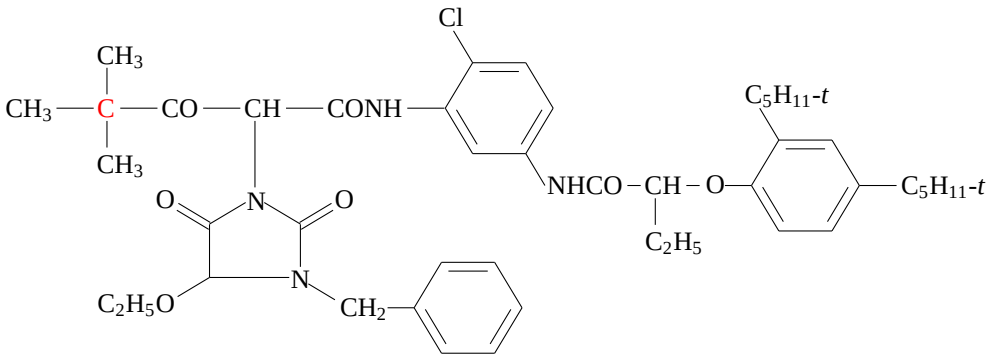
19-12

This direct method contains layout data in the form of the command \methineunitCA etc., as colored in red. Such layout data should be concealed from the source list of the book for the consistency of the XƒMTEX methodology. □

Example 19.7. The function of variable bond lengths supported by XƒMTEX (Version 4.01 or later) provides us with a more elegant solution to draw this type of compounds. The same structure as **19-12** can be drawn by using the redefined command \tetrahedral. Thus, the codes:

```
%\fbox{%
\begin{XyMcompd}(3800,1500)(-100,-700){cpd:06}{}
\tetrahedral{0==C;%
1==CH$_{3}$;2==CH$_{3}$;3==CH$_{3}$;%
4==\tetrahedral{0==CO;2==(yl);%
4==\tetrahedral{0==CH;2==(yl);%
3==\fiveheterovi{1==N;3==N}{1==(yl);2D==O;5D==O;4==C$_{2}$H$_{5}$O;%
3==\ryl(3==CH$_{2}$){4==\bzdrh{1==(yl)}}};%
4==\tetrahedral{0==CONH;2==(yl);%
4==\bzdrh{1==(yl);2==Cl;%
5==\tetrahedral{0==NHCO;2==(yl);%
4==\tetrahedral{0==CH;2==(yl);3==C$_{2}$H$_{5}$;%
4==\ryl(4==O){4==\bzdrh{1==(yl);2==C$_{5}$H$_{11}$-$t$;%
4==C$_{5}$H$_{11}$-$t$}%
}}<,,,50>}<,,,50>}}}<,,250,>}}%
\end{XyMcompd}%
%}
```

typeset the following structure:



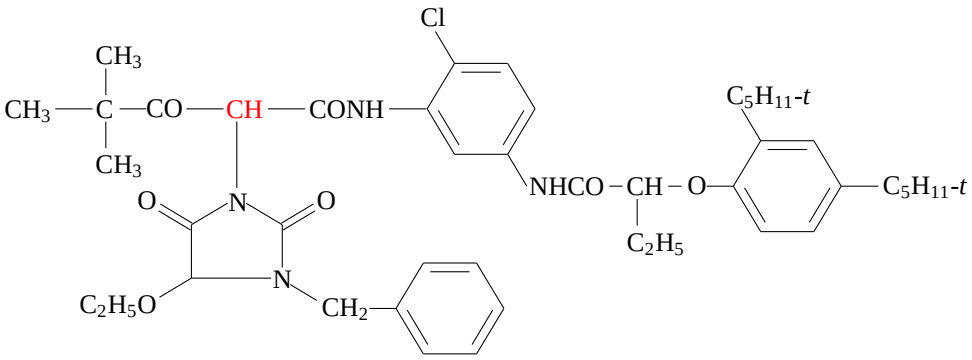
19-13

It should be noted that this drawing is started at the red-colored carbon by using the redefined command `\tetrahedral`. □

Example 19.8. The start of drawing at another carbon is possible. For example, the following codes:

```
%\fbox{%
\begin{XyMcompd}(3800,1500)(-600,-700){cpd:07}{}
\tetrahedral{0==CH;%
2==\lyl(4==CO){%
4==\tetrahedral{4==(yl);0==C;1==CH$_{3}$;2==CH$_{3}$;3==CH$_{3}$}};%
3==\fiveheterovi{1==N;3==N}{1==(yl);2D==O;5D==O;4==C$_{2}$H$_{5}$O;%
3==\ryl(3==CH$_{2}$){4==\bzdrh{1==(yl)}}};%
4==\tetrahedral{0==CONH;2==(yl);%
4==\bzdrh{1==(yl);2==Cl;%
5==\tetrahedral{0==NHCO;2==(yl);%
4==\tetrahedral{0==CH;2==(yl);3==C$_{2}$H$_{5}$;%
4==\ryl(4==O){4==\bzdrh{1==(yl);2==C$_{5}$H$_{11}$-$t$;%
4==C$_{5}$H$_{11}$-$t$}%
}}<,,,50>}<,,,50>}}}<,,250,>
\end{XyMcompd}%
%}
```

produce almost the same structure:



19-14

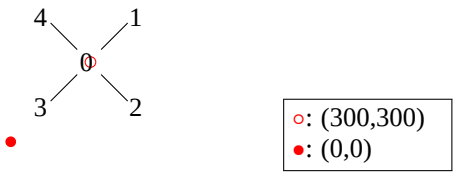
where the starting carbon atom is designated by red color. □

19.2 Drawing Square Planar Compounds

The XƎMTEX command `\squareplanar` is used to draw a tetrahedral unit of another type (aliphat.sty). The format of this command is as follows:[a]

```
\squareplanar[⟨bondlist⟩]{⟨subslist⟩}
```

The following diagram shows the numbering for designating substitution positions:



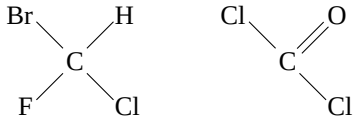
The optional argument ⟨bondlist⟩ has a restricted format, where the declaration of locant alphabets is not permitted but the specification of a charge on the central atom is permitted: i.e., `{0+}` represents a + charge (or another one character) on the center.

The argument ⟨subslist⟩ is used to specify each substituent with a locant number and a bond modifier shown in Table 19.1, in which *n* is an Arabic numeral between 1 and 4.

Examples of `\squareplanar`:

```
\squareplanar{0==C;1==H;2==Cl;3==F;4==Br}\qquad
\squareplanar{0==C;1D==O;2==Cl;4==Cl}
```

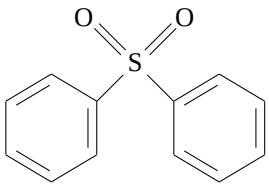
produce the following structures:



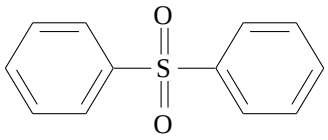
[a] The old command `\square` has been replaced by the `\squareplanar`, because the former is in conflict with the command of the same name defined in the amssymb package.

Example 19.9. The structure of diphenyl sulfone is drawn in two different ways, i.e., **19-15** by using `\squareplanar` and **19-16** by using `\tetrahedral`.

```
\squareplanar{0==S;1D==O;4D==O;%
2==\benzenev{6==(yl)};3==\benzenev{2==(yl)}}
\tetrahedral{0==S;1D==O;3D==O;%
2==\benzeneh{4==(yl)};4==\benzeneh{1==(yl)}}
```



19-15



19-16

□

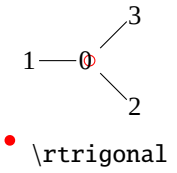
19.3 Drawing Trigonal Units

19.3.1 Right- and Left-Handed Trigonal Units

The XeLaTeX commands `\rtrigonal` and `\ltrigonal` are used to draw right-handed and left-handed trigonal units (aliphat.sty). The formats of these commands are as follows:

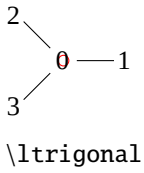
```
\rtrigonal[⟨bondlist⟩]{⟨subslist⟩}
\ltrigonal[⟨bondlist⟩]{⟨subslist⟩}
```

The bond angles of 2–0–3 are 90° in the trigonal units printed with these commands. The arguments ⟨bondlist⟩ and ⟨subslist⟩ are the same as those of `\tetrahedral`. The following diagram shows the numbering for designating substitution positions:



\rtrigonal

○: (300,300)
●: (0,0)



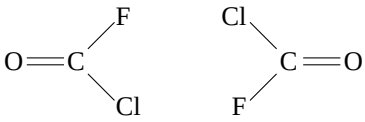
\ltrigonal

○: (300,300)
●: (0,0)

Examples of `\rtrigonal` and `\ltrigonal`:

```
\rtrigonal{0==C;1D==O;2==Cl;3==F}\qquad
\ltrigonal{0==C;1D==O;2==Cl;3==F}
```

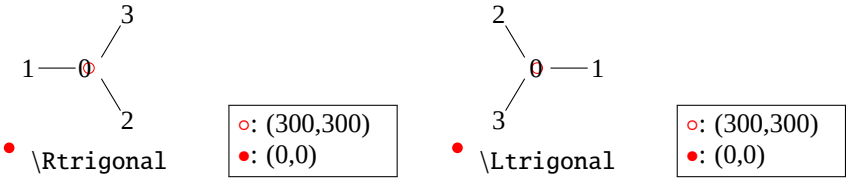
produce the following structures:



The XeLaTeX commands `\Rtrigonal` and `\Ltrigonal` are used to draw right-handed and left-handed trigonal units (aliphat.sty). The formats of these commands are as follows:

```
\Rtrigonal[⟨bondlist⟩]{⟨subslist⟩}
\Ltrigonal[⟨bondlist⟩]{⟨subslist⟩}
```

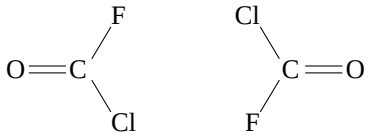
The bond angles of 2–0–3 are 120° in the trigonal units printed with these commands. The arguments ⟨bondlist⟩ and ⟨subslist⟩ are the same as those of `\tetrahedral`. The following diagram shows the numbering for designating substitution positions:



Examples of `\rtrigonal` and `\ltrigonal`:

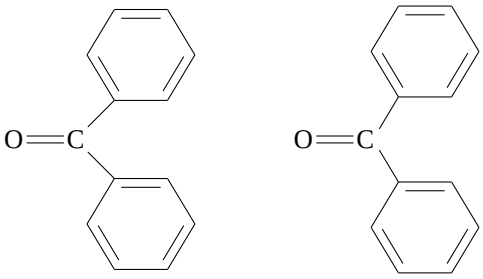
```
\Rtrigonal{0==C;1D==O;2==Cl;3==F}\qquad
\Ltrigonal{0==C;1D==O;2==Cl;3==F}
```

produce the following structures:



Example 19.10. For the purpose of comparing between `\rtrigonal` and `\Rtrigonal`, the structure of benzophenone is drawn by using these commands, which generate **19-17** and **19-18** respectively. See also **19-1** drawn by using `\tetrahedral`.

```
\rtrigonal{0==C;1D==O;%
2==\benzeneh{2==(yl)};3==\benzeneh{6==(yl)}}
\Rtrigonal{0==C;1D==O;%
2==\benzeneh{2==(yl)};3==\benzeneh{6==(yl)}}
```



19-17
`\rtrigonal`

19-18
`\Rtrigonal`

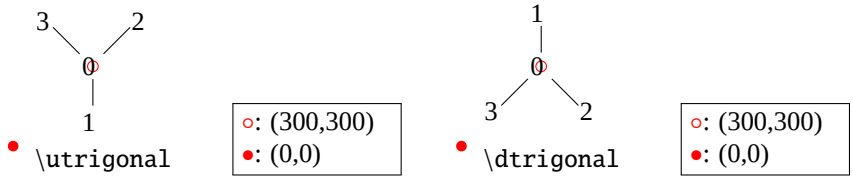
□

19.3.2 Up- and Downward Trigonal Units

The XeLaTeX commands `\utrigonal` and `\dtrigonal` are used to draw right-handed and left-handed trigonal units (aliphat.sty). The formats of these commands are as follows:

```
\utrigonal[⟨bondlist⟩]{⟨subslist⟩}
\dtrigonal[⟨bondlist⟩]{⟨subslist⟩}
```

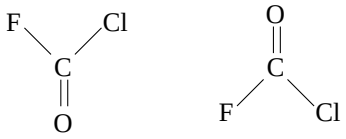
The bond angles of 2–0–3 are 90° in the trigonal units printed with these commands. The arguments ⟨bondlist⟩ and ⟨subslist⟩ are the same as those of `\tetrahedral`. The following diagram shows the numbering for designating substitution positions:



Examples of `\utrigonal` and `\dtrigonal`:

```
\utrigonal{0==C;1D==O;2==Cl;3==F}\qquad
\dtrigonal{0==C;1D==O;2==Cl;3==F}
```

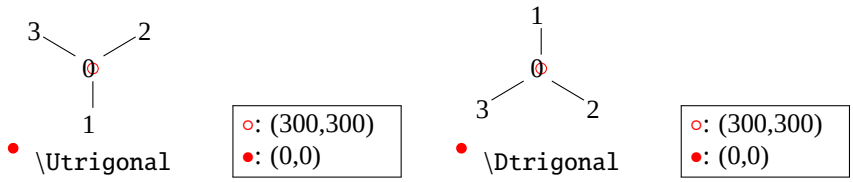
produce the following structures:



The XƎMTEX commands `\Utrigonal` and `\Dtrigonal` are used to draw right-handed and left-handed trigonal units (aliphat.sty). The formats of these commands are as follows:

```
\Utrigonal[⟨bondlist⟩]{⟨subslist⟩}
\Dtrigonal[⟨bondlist⟩]{⟨subslist⟩}
```

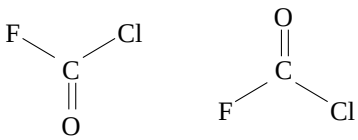
The bond angles of 2–0–3 are 120° in the trigonal units printed with these commands. The arguments ⟨bondlist⟩ and ⟨subslist⟩ are the same as those of `\tetrahedral`. The following diagram shows the numbering for designating substitution positions:



Examples of `\Utrigonal` and `\Dtrigonal`:

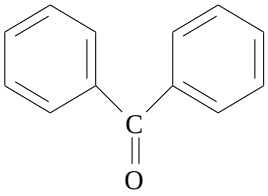
```
\Utrigonal{0==C;1D==O;2==Cl;3==F}\qquad
\Dtrigonal{0==C;1D==O;2==Cl;3==F}
```

produce the following structures:

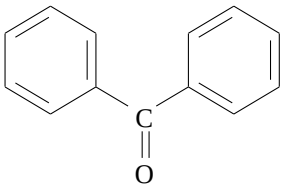


Example 19.11. For the purpose of comparing between `\utrigonal` and `\Utrigonal`, the structure of benzophenone is drawn by using these commands, which generate **19-19** and **19-20** respectively. See also **19-1** drawn by using `\tetrahedral`.

```
\utrigonal{0==C;1D==O;%
2==\benzenev{5==(yl)};3==\benzenev{3==(yl)}}
\Utrigonal{0==C;1D==O;%
2==\benzenev{5==(yl)};3==\benzenev{3==(yl)}}
```



19-19
`\utrigonal`



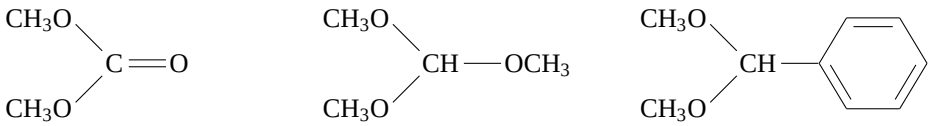
19-20
`\Utrigonal`

□

19.3.3 Variable Bond Lengths

The same situation as described in Subsection 19.1.4 (for `\tetrahedral`) occurred in the use of the commands `\ltrigonal` and `Ltrigonal` of the previous versions of X$\widehat{\text{M}}$TEX (< Version 4.01). These commands have been also improved to allow a length-variable central atoms in X$\widehat{\text{M}}$TEX Version 4.01 and later.

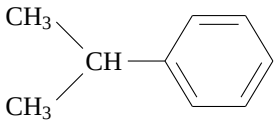
1. For example, the command `\ltrigonal` is used to draw structural formulas having a two-character group (CH) as follows:



where the first formula is drawn as a reference formula with a centeral atom of a single character (C). These formulas are drawn by the following codes:

```
\ltrigonal{0==C;2==CH$_{3}$O;1D==O;3==CH$_{3}$O}
\hskip 2cm
\ltrigonal{0==CH;2==CH$_{3}$O;1==OCH$_{3}$;3==CH$_{3}$O}
\hskip2cm
\ltrigonal{0==CH;2==CH$_{3}$O;1==\bzdrh{1==(yl)};3==CH$_{3}$O}
```

The following formula (**19-21**) is drawn by regarding cumene as 2-propenylbenzene:

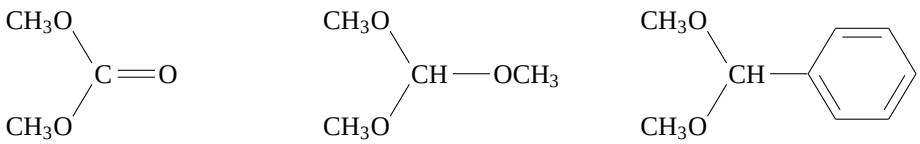


19-21

which is drawn by the code:

```
\begin{XyMcompd}(1000,500)(-400,200){cpd:4}{}
\bzdrh{1==\ltrigonal{1==(yl);0==CH;2==CH$_{3}$;3==CH$_{3}$}}
\end{XyMcompd}
```

2. The command `\Ltrigonal` is defined in the same guideline as `\ltrigonal` described above. The command is used to draw the same formulas having a two-character group (CH) as follows:

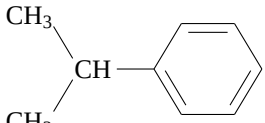


These formulas are drawn by the following codes:

```
\Ltrigonal{0==C;2==CH$_{3}$O;1D==O;3==CH$_{3}$O}
\hskip 2cm
\Ltrigonal{0==CH;2==CH$_{3}$O;1==OCH$_{3}$;3==CH$_{3}$O}
```

```
\hskip2cm
\Ltrigonal{0==CH;2==CH$_{3}$O;1==\bzdrh{1==(yl)};3==CH$_{3}$O}
```

The following formula (**19-22**) is drawn by regarding cumene as 2-propenylbenzene:



19-22

which is drawn by the code:

```
\begin{XyMcompd}(1000,500)(-400,200){cpd:5}{}
\bzdrh{1==\Ltrigonal{1==(yl);0==CH;2==CH$_{3}$;3==CH$_{3}$}}
\end{XyMcompd}
```

3. On the other hand, the previous definitions of the commands `\rtrigonal` and `\Rtrigonal` remain unchanged in XƎMTEX version 4.01 and later, because even a group of two or more characters can be accommodated as a central atom.


```
\bzdrh{4==\rtrigonal{0==CH;3==CH$_3$;2==CH$_3$;1==(yl)}}
\hskip3cm
\bzdrh{4==\Rtrigonal{0==CH;3==CH$_3$;2==CH$_3$;1==(yl)}}
```

4. On the same line, the previous definitions of the commands `\utrigonal` and `\Utrigonal` remain unchanged in XƎMTEX version 4.01 and later.


```
\utrigonal{1==\bzdrv{1==(yl)};0==CH;2==CH$_{3}$;3==CH$_{3}$}
\hskip3cm
\Utrigonal{1==\bzdrv{1==(yl)};0==CH;2==CH$_{3}$;3==CH$_{3}$}
```

5. The previous definitions of the commands `\dtrigonal` and `\Dtrigonal` remain also unchanged in XƎMTEX version 4.01 and later.


```
\dtrigonal{1==\bzdrv{4==(yl)};0==CH;2==CH$_{3}$;3==CH$_{3}$}
\hskip3cm
\Dtrigonal{1==\bzdrv{4==(yl)};0==CH;2==CH$_{3}$;3==CH$_{3}$}
```

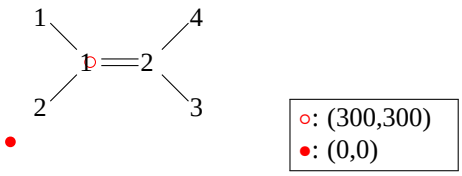
19.4 Drawing Ethylene Derivatives

19.4.1 Horizontal Forms

The XeLaTeX command `\ethyleneh` (or equivalently `\ethylene`) is used to draw ethylene derivatives with angles 90° (aliphat.sty). The format of this command is as follows:

```
\ethyleneh[⟨bondlist⟩]{⟨atomlist⟩}{ ⟨subslist⟩}
\ethylene[⟨bondlist⟩]{⟨atomlist⟩}{ ⟨subslist⟩}
```

The following diagram shows the numbering for designating substitution positions:



The argument ⟨bondlist⟩ is used to assign a double or triple bond to the central bond, as collected in Table 19.2. The bond angles of 1–(1)–2 are 90° in the trigonal units printed with these commands. The argument

Table 19.2. ⟨bondlist⟩ for `\ethyleneh` or `\ethylene`

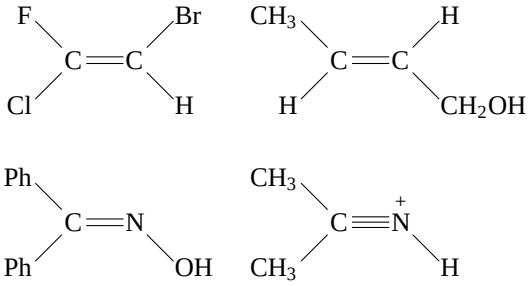
Character	Structures printed
{*n*+}	+ charge (or another one character) on *n*-atom
d	inner double bond (between centers 1 and 2)
t	inner triple bond (between centers 1 and 2)

⟨atomlist⟩ is used for giving central atoms. The argument ⟨subslist⟩ is the same as that of `\tetrahedral`.

Examples or `\ethyleneh`:

```
\ethyleneh{1==C;2==C}{1==F;2==Cl;3==H;4==Br}\qquad
\ethyleneh{1==C;2==C}{1==CH$_{3}$;2==H;3==CH$_{2}$OH;4==H}\par
\ethyleneh{1==C;2==N}{1==Ph;2==Ph;3==OH}\qquad
\ethyleneh[t{2+}]{1==C;2==N}{1==CH$_{3}$;2==CH$_{3}$;3==H}
```

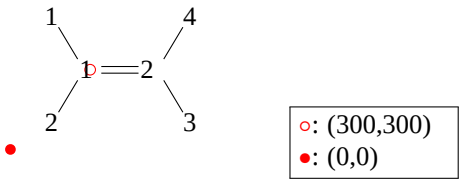
produce the following structures:



The XeLaTeX command `\Ethyleneh` (or equivalently `\Ethylene`) is used to draw ethylene derivatives with angles 120° (aliphat.sty). The format of this command is as follows:

```
\Ethyleneh[⟨bondlist⟩]{⟨atomlist⟩}{ ⟨subslist⟩}
\Ethylene[⟨bondlist⟩]{⟨atomlist⟩}{ ⟨subslist⟩}
```

The following diagram shows the numbering for designating substitution positions:

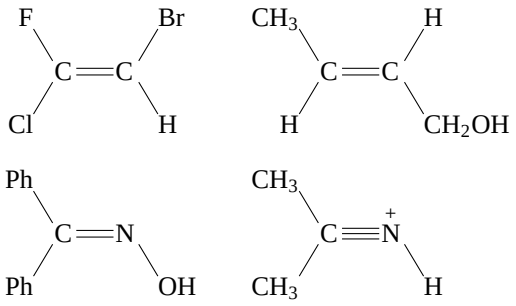


The bond angles of 1–(1)–2 are 120° in the trigonal units printed with these commands. The argument ⟨bondlist⟩ is used to assign a double or triple bond to the central bond, as collected in Table 19.2. The argument ⟨atomlist⟩ is used for giving central atoms. The argument ⟨subslist⟩ is the same as that of `\tetrahedral`.

Examples or `\Ethyleneh`:

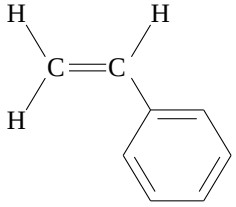
```
\Ethyleneh{1==C;2==C}{1==F;2==Cl;3==H;4==Br}\qquad
\Ethyleneh{1==C;2==C}{1==CH$_{3}$;2==H;3==CH$_{2}$OH;4==H}\par
\Ethyleneh{1==C;2==N}{1==Ph;2==Ph;3==OH}\qquad
\Ethyleneh[t{2+}]{1==C;2==N}{1==CH$_{3}$;2==CH$_{3}$;3==H}
```

produce the following structures:

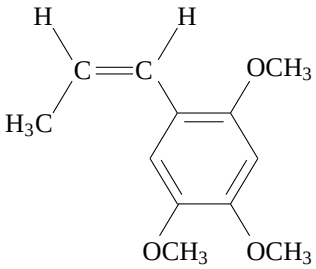


Example 19.12. The structure **19-23** of styrene is drawn by using `\Ethyleneh`, which generates a ethylenic skeleton as a parent structure. The structure **19-24** of *cis*-2,4,5-trimethyl-1-propenylbenzene is also drawn by using `\Ethyleneh`, which generates a ethylenic skeleton as a parent structure. Each phenyl substituent is generated by a (yl)-function declared in `\benzeneh` and then placed in the ⟨subslist⟩ of the `\Ethyleneh` according to the substitution technique.

```
\Ethyleneh{1==C;2==C}{1==H;2==H;4==H;3==\benzeneh{2==(yl)}}
\Ethyleneh{1==C;2==C}{1==H;2==H$_{3}$C;4==H;%
3==\benzeneh{2==(yl);3==OCH$_{3}$;5==OCH$_{3}$;6==OCH$_{3}$;}}
```



19-23

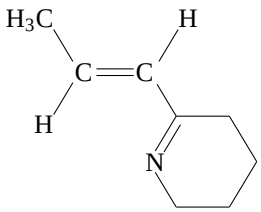


19-24

□

Example 19.13. An olefinic moiety generated by declaring a (yl)-function in `\Ethyleneh` etc. can be placed in the ⟨susblist⟩ of another command according to the substitution technique. For example, the structure **19-25** of 2-(1-propenyl)-3,4,5,6-tetrahydropyridine is drawn by this procedure as follows:

```
\sixheteroh[a]{1==N}{2==\Ethyleneh{1==C;2==C}{3==(yl);1==H$_{3}$C;2==H;4==H}}
```



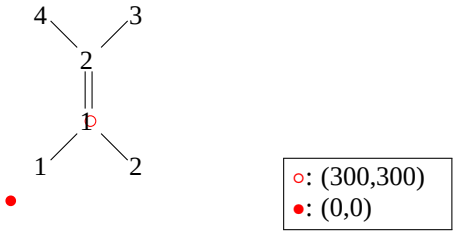
19-25 □

19.4.2 Vertical Forms

The XeLaTeX command `\ethylenev`, which is the vertical counterpart of `\ethyleneh` (or equivalently `\ethylene`), is used to draw ethylene derivatives with angles 90° (aliphat.sty). The format of this command is as follows:

```
\ethylenev[⟨bondlist⟩]{⟨atomlist⟩}{ ⟨subslist⟩}
```

The following diagram shows the numbering for designating substitution positions:

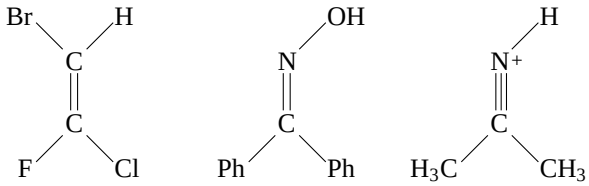


The bond angles of 1–(1)–2 are 90° in the trigonal units printed with these commands. The argument ⟨bondlist⟩ is used to assign a double or triple bond to the central bond, as collected in Table 19.2. The argument ⟨atomlist⟩ is used for giving central atoms. The argument ⟨subslist⟩ is the same as that of `\tetrahedral`.

Examples of `\ethylenev`:

```
\ethylenev{1==C;2==C}{1==F;2==Cl;3==H;4==Br}\qquad
\ethylenev{1==C;2==N}{1==Ph;2==Ph;3==OH}\qquad
\ethylenev[t{2+}]{1==C;2==N}{1==H$_{3}$C;2==CH$_{3}$;3==H}
```

produce the following structures:

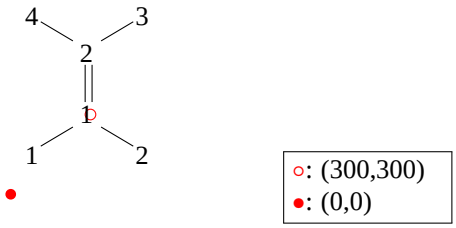


The bond angles of 1–(1)–2 etc. are 90° in the trigonal units printed with these commands.

The macro `\Ethylenev` is used to draw ethylene derivatives with angles 120° (aliphat.sty). It is the vertical counterpart of `\Ethyleneh`. The format of the command is as follows:

```
\Ethylenev[⟨bondlist⟩]{⟨atomlist⟩}{ ⟨subslist⟩}
```

The following diagram shows the numbering for designating substitution positions:

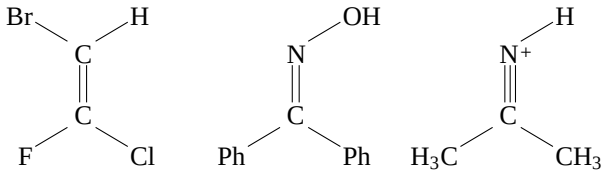


The bond angles of 1–(1)–2 are 120° in the trigonal units printed with these commands. The argument ⟨bondlist⟩ is used to assign a double or triple bond to the central bond, as collected in Table 19.2. The argument ⟨atomlist⟩ is used for giving central atoms. The argument ⟨subslist⟩ is the same as that of `\tetrahedral`.

Example:

```
\Ethylenev{1==C;2==C}{1==F;2==Cl;3==H;4==Br}\qquad
\Ethylenev{1==C;2==N}{1==Ph;2==Ph;3==OH}\qquad
\Ethylenev[t{2+}]{1==C;2==N}{1==H$_{3}$C;2==CH$_{3}$;3==H}
```

produce the following structures:

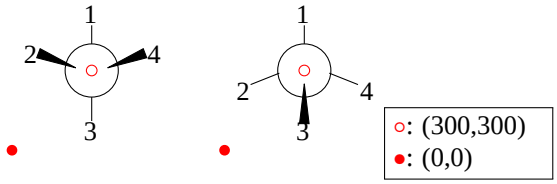


19.5 Drawing Configurations

The macros `tetrastereo` and `dtetrastereo` typset fragments which show actual configuration of a tetrahedral carbon in different modes of projections. The formats of these commands are as follows:

```
\tetrastereo[⟨bondlist⟩]{⟨subslist⟩}
\dtetrastereo[⟨bondlist⟩]{⟨subslist⟩}
```

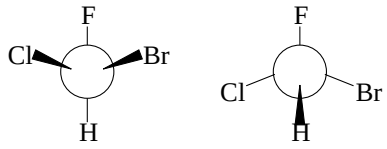
The arguments ⟨bondlist⟩ and ⟨subslist⟩ are the same as those of `\tetrahedral`.
The following diagram shows the numbering for designating substitution positions:



Examples of `\tetrastereo` and `\dtetrastereo`:

```
\tetrastereo{1==F;2==Cl;3==H;4==Br}\qquad
\dtetrastereo{1==F;2==Cl;3==H;4==Br}
```

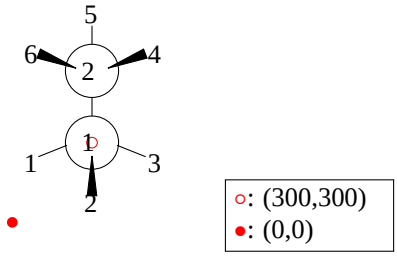
produce the following structures:



The configuration of ethane is typeset by the macro `\ethanestereo`. The format of the command is as follows:

```
\ethanestereo[⟨bondlist⟩]{⟨atomlist⟩}{ ⟨subslist⟩}
```

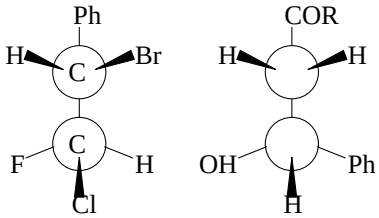
The arguments ⟨bondlist⟩ and ⟨subslist⟩ are the same as those of `\tetrahedral`. The argument ⟨atomlist⟩ is used for giving central atoms.



Examples of `\ethanestereo`:

```
\ethanestereo{1==C;2==C}{1==F;2==Cl;3==H;4==Br;6==H;5==Ph}\qquad
\ethanestereo{}{1==OH;2==H;3==Ph;4==H;5==COR;6==H}
```

produce the following structures:



Further examples of typesetting the configurations of ethane derivatives have been described in an article concerning stereochemistry [4].

References

[1] F. A. Carey and R. J. Sundberg, “Advanced Organic Chemistry. Part B: Reactions and Syntheses,” 3rd ed., Prenum Press, New York-London (1990).

[2] S. Fujita, “Organic Chemistry of Photography,” Springer-Verlag, Berlin-Heidelberg (2004).

[3] S. Fujita, *Tetrahedron*, **65**, 1581–1592 (2009).

[4] S. Fujita, *J. Chem. Inf. Comput. Sci.*, **32**, 354–363 (1992).

Tetrahedral Units with Wedged Bonds

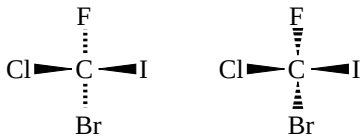
This chapter is devoted to various tetrahedral units, which are intended mainly to depict absolute configurations.

20.1 Various Tetrahedral Units

The macro `\tetrahedral` is supported to draw a tetrahedral methane derivative, as described in Chapter 19. Because XeLaTeX version 4.02 or later is capable of drawing wedged bonds, the codes:

```
\tetrahedral{0==C;1A==F;2B==Cl;3A==Br;4B==I}
{\wedgehashedwedge \qquad
\tetrahedral{0==C;1A==F;2B==Cl;3A==Br;4B==I}}
```

now generate the following formulas:



These expressions are acceptable according to the IUPAC Recommendations 2006 [1, ST-0.2, ST-1.1.3].

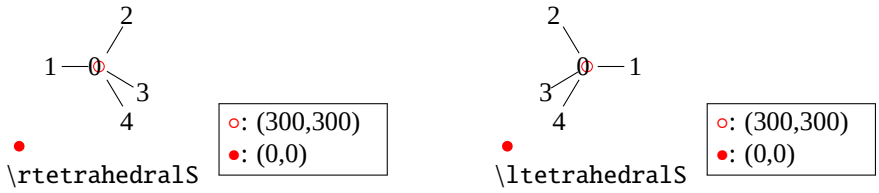
In addition, the XeLaTeX version 4.02 or later (aliphat.sty) provides us with commands to draw various tetrahedral derivatives with wedged bonds:

```
\rtetrahedralS[⟨bondlist⟩]{⟨subslist⟩}
\RtetrahedralS[⟨bondlist⟩]{⟨subslist⟩}
\ltetrahedralS[⟨bondlist⟩]{⟨subslist⟩}
\LtetrahedralS[⟨bondlist⟩]{⟨subslist⟩}
\utetrahedralS[⟨bondlist⟩]{⟨subslist⟩}
\UtetrahedralS[⟨bondlist⟩]{⟨subslist⟩}
\dtetrahedralS[⟨bondlist⟩]{⟨subslist⟩}
\DtetrahedralS[⟨bondlist⟩]{⟨subslist⟩}
\htetrahedralS[⟨bondlist⟩]{⟨subslist⟩}
```

where the end letter ‘S’ is the abbreviation of the word ‘stereo’. The prefix ‘r’ or ‘R’ indicates that the triangle formed by 2-3-4 is placed in the right of the principle axis (1—0). These commands generate right-

type tetrahedrons. On the other hand, the prefix ‘l’ or ‘L’ indicates that the triangle formed by 2-3-4 is placed in the left of the principle axis (0—1). These commands generate left-type tetrahedrons. The prefix ‘u’ or ‘U’ indicates that the triangle formed by 2-3-4 is placed in the upward direction of the principle axis (0—1), so that these commands generate up-type tetrahedrons. On the other hand, the prefix ‘d’ or ‘D’ indicates that the triangle formed by 2-3-4 is placed in the downward direction of the principle axis (1—0), so that these commands generate down-type tetrahedrons.

For example, a pair of commands `\rtetrahedralS` and `\ltetrahedralS` give the following diagrams of right-type and of left-type:



The argument ⟨bondlist⟩ designates a character on the central atom of the formula drawn by this macro. It is incapable of assigning locant alphabets, so that it only assigns a plus or minus charge on the center:

⟨bondlist⟩ = {`0+`} : `+ charge (or another one character) on the center`

The ⟨subslist⟩ is used to specify a central atom and substituents. Although any bond modifiers can be used, positions 1 and 2 are designed to have no bond modifier (a single thin line), while positions 3 and 4 are considered to take a bond modifier (B or A) so that a bold wedged bond (or bold bond) or a hashed wedged bond (or hashed dash bond) is generated. These features are exemplified by the pair of commands `\rtetrahedralS` and `\ltetrahedralS` as follows:

`\rtetrahedralS{1==1;2==2;3A==3;4B==4;0==0}` for right-type
`\ltetrahedralS{1==1;2==2;3A==3;4B==4;0==0}` for left-type

(right-type) (left-type)

In other words, the positions 1 and 2 and the central atom (0) are presumed to be coplanar so as to be placed in the plane of a page; the bond to the position 3 is an α-bond; and the bond to the position 4 is a β-bond. Total features of the commands supported by the XeTeX system for drawing various tetrahedral units are summarized in Fig. 20.1.

20.2 Right- and Left-Types

The bond from the central atom to the position 1 of an tetrahedral unit of the right- or left-type is drawn as a horizontal thin line, which shows an east (rightward) or a west (leftward) bond.

20.2.1 Right-Type Tetrahedrons by `\rtetrahedralS`

In a structural formula depicted by the command `\rtetrahedralS`, position 1, position 2, and the central atom are placed in the plane of a page, where the bond from the central atom to the position 1 is a horizontal west (leftward) bond. For example, the command `\rtetrahedralS` used in the codes:

```
\rtetrahedralS{0==C;1==F;2==Cl;3A==Br;4B==I}
\rtetrahedralS{1==F;2==Cl;3A==Br;4B==I}
```

gives the following formulas:

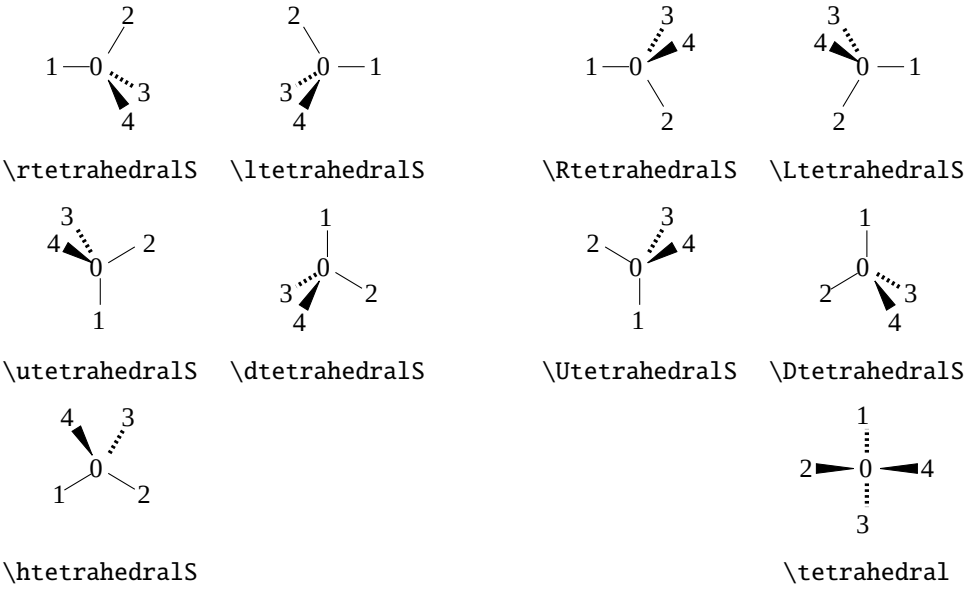
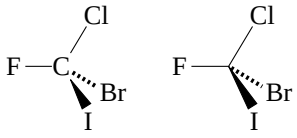


Figure 20.1. Locant Numbers for Various Tetrahedral Units



where the presence or absence of `0==C` decides the appearance of generated bonds. The codes:

```
\rtetrahedralS{0==C;1==\bzdrh{4==(yl)};2==Cl;3A==Br;4B==I} \hskip1cm
\rtetrahedralS{1==\bzdrh{4==(yl)};2==Cl;3A==Br;4B==I} \hskip1cm
\rtetrahedralS{0==C;1==F;2==\bzdrh{6==(yl)};3A==Br;4B==I}
\rtetrahedralS{1==F;2==\bzdrh{6==(yl)};3A==Br;4B==I} \par
\vskip1cm
{\wedgehashedwedge
\rtetrahedralS{0==C;1==\bzdrh{4==(yl)};2==Cl;3A==Br;4B==I} \hskip1cm
\rtetrahedralS{1==\bzdrh{4==(yl)};2==Cl;3A==Br;4B==I} \hskip1cm
\rtetrahedralS{0==C;1==F;2==\bzdrh{6==(yl)};3A==Br;4B==I}
\rtetrahedralS{1==F;2==\bzdrh{6==(yl)};3A==Br;4B==I} }\par
\vskip1cm
{\dashhasheddash
\rtetrahedralS{0==C;1==\bzdrh{4==(yl)};2==Cl;3A==Br;4B==I} \hskip1cm
\rtetrahedralS{1==\bzdrh{4==(yl)};2==Cl;3A==Br;4B==I} \hskip1cm
\rtetrahedralS{0==C;1==F;2==\bzdrh{6==(yl)};3A==Br;4B==I}
\rtetrahedralS{1==F;2==\bzdrh{6==(yl)};3A==Br;4B==I} }\par
```

generate the formulas collected in Fig. 20.2, where structural formulas shown as examples are respectively drawn by the default mode (the top row), the `\wedgehashedwedge` mode (the middle row), and the `\dashhasheddash` mode (the bottom row).

20.2.2 Left-Type Tetrahedrons by `\ltetrahedralS`

In order to draw the mirror-image formulas of those drawn by `\rtetrahedralS`, we can use the command `\ltetrahedralS`. In a structural formula depicted by this command, position 1, position 2, and the central atom are placed in the plane of a page, where the bond from the central atom to the position 1 is a horizontal east (rightward) bond. Thus the codes:

```
\ltetrahedralS{0==C;1==F;2==Cl;3A==Br;4B==I}
```

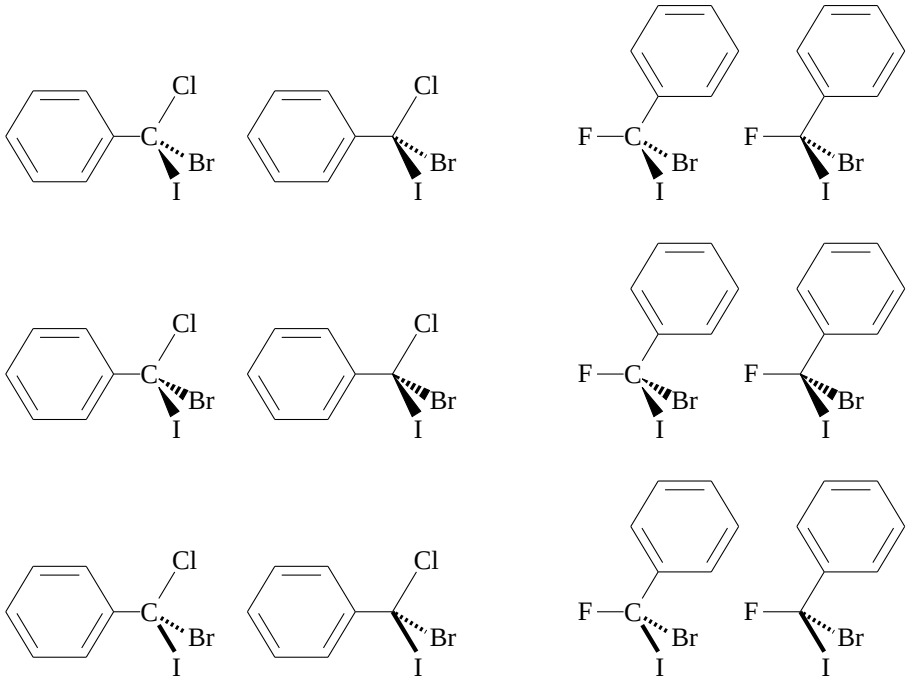
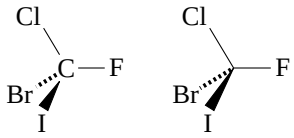


Figure 20.2. Examples of \rtetrahedralS. The top row shows the drawing due to the default mode, the middle row shows the drawing due to the \wedgehashedwedge mode, and the bottom row shows the drawing due to the \dashhasheddash mode.

```
\ltetrahedralS{1==F;2==Cl;3A==Br;4B==I}
```

give the following formulas:



where the presence or absence of 0==C decides the appearance of generated bonds. In addition, the codes:

```
\ltetrahedralS{0==C;1==\bzdrh{1==(yl)};2==Cl;3A==Br;4B==I} \hskip1cm
\ltetrahedralS{1==\bzdrh{1==(yl)};2==Cl;3A==Br;4B==I} \hskip1cm
\ltetrahedralS{0==C;1==F;2==\bzdrh{5==(yl)};3A==Br;4B==I}
\ltetrahedralS{1==F;2==\bzdrh{5==(yl)};3A==Br;4B==I} \par
\vskip1cm
{\wedgehashedwedge
\ltetrahedralS{0==C;1==\bzdrh{1==(yl)};2==Cl;3A==Br;4B==I} \hskip1cm
\ltetrahedralS{1==\bzdrh{1==(yl)};2==Cl;3A==Br;4B==I} \hskip1cm
\ltetrahedralS{0==C;1==F;2==\bzdrh{5==(yl)};3A==Br;4B==I}
\ltetrahedralS{1==F;2==\bzdrh{5==(yl)};3A==Br;4B==I} }\par
\vskip1cm
{\dashhasheddash
\ltetrahedralS{0==C;1==\bzdrh{1==(yl)};2==Cl;3A==Br;4B==I} \hskip1cm
\ltetrahedralS{1==\bzdrh{1==(yl)};2==Cl;3A==Br;4B==I} \hskip1cm
\ltetrahedralS{0==C;1==F;2==\bzdrh{5==(yl)};3A==Br;4B==I}
\ltetrahedralS{1==F;2==\bzdrh{5==(yl)};3A==Br;4B==I} }\par
```

generate the formulas collected in Fig. 20.3, where structural formulas shown as examples are respectively drawn by the default mode (the top row), the \wedgehashedwedge mode (the middle row), and the \dashhasheddash mode (the bottom row).

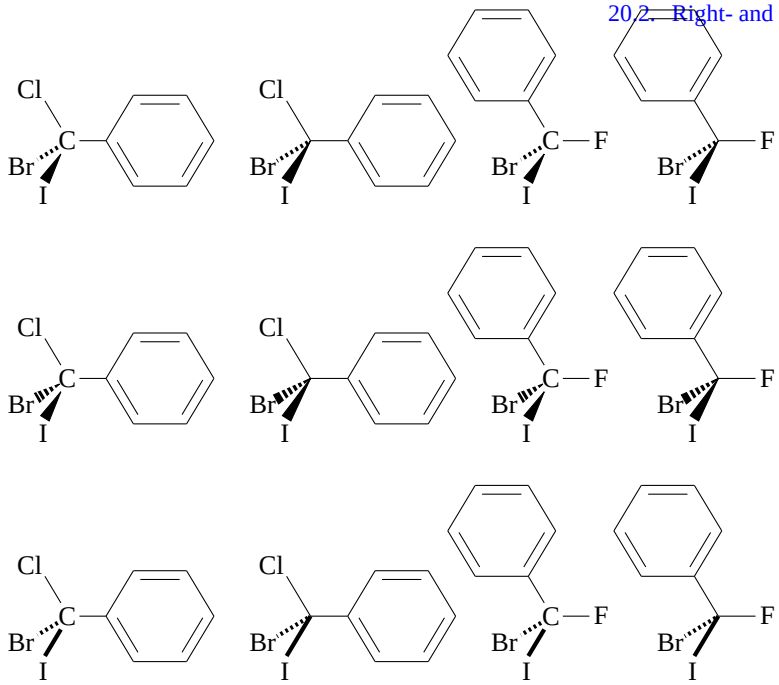


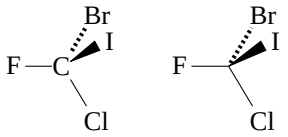
Figure 20.3. Examples of `\ltetrahedralS`. The top row shows the drawing due to the default mode, the middle row shows the drawing due to the `\wedgehashedwedge` mode, and the bottom row shows the drawing due to the `\dashhasheddash` mode.

20.2.3 Right-Type Tetrahedrons by `\RtetrahedralS`

A diagram generated by he command `\RtetrahedralS` is rotated by 180° around the axis through the central carbon and the position 1 so as to give a diagram generated by the command `\rtetrahedralS`. Thus, the codes:

```
\RtetrahedralS{0==C;1==F;2==Cl;3A==Br;4B==I}
\RtetrahedralS{1==F;2==Cl;3A==Br;4B==I}
```

give the following formulas:



where the presence or absence of `0==C` decides the appearance of generated bonds. The codes:

```
\RtetrahedralS{0==C;1==\bzdrh{4==(yl)};2==Cl;3A==Br;4B==I} \hskip1cm
\RtetrahedralS{1==\bzdrh{4==(yl)};2==Cl;3A==Br;4B==I} \hskip1cm
\RtetrahedralS{0==C;1==F;2==\bzdrh{2==(yl)};3A==Br;4B==I}
\RtetrahedralS{1==F;2==\bzdrh{2==(yl)};3A==Br;4B==I} \par
\vskip1cm
{\wedgehashedwedge
\RtetrahedralS{0==C;1==\bzdrh{4==(yl)};2==Cl;3A==Br;4B==I} \hskip1cm
\RtetrahedralS{1==\bzdrh{4==(yl)};2==Cl;3A==Br;4B==I} \hskip1cm
\RtetrahedralS{0==C;1==F;2==\bzdrh{2==(yl)};3A==Br;4B==I}
\RtetrahedralS{1==F;2==\bzdrh{2==(yl)};3A==Br;4B==I}} \par
\vskip1cm
{\dashhasheddash
\RtetrahedralS{0==C;1==\bzdrh{4==(yl)};2==Cl;3A==Br;4B==I} \hskip1cm
\RtetrahedralS{1==\bzdrh{4==(yl)};2==Cl;3A==Br;4B==I} \hskip1cm
\RtetrahedralS{0==C;1==F;2==\bzdrh{2==(yl)};3A==Br;4B==I}
\RtetrahedralS{1==F;2==\bzdrh{2==(yl)};3A==Br;4B==I}} \par
```

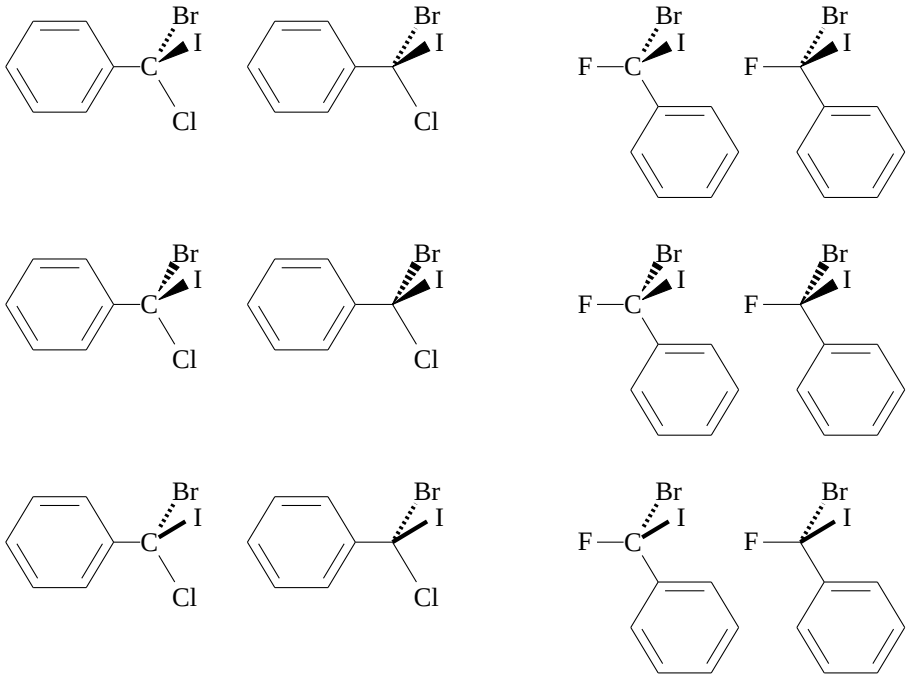


Figure 20.4. Examples of \RtetrahedralS. The top row shows the drawing due to the default mode, the middle row shows the drawing due to the \wedgehashedwedge mode, and the bottom row shows the drawing due to the \dashhasheddash mode.

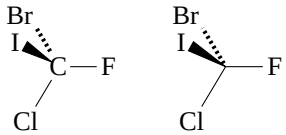
generate the formulas collected in Fig. 20.4, where structural formulas shown as examples are respectively drawn by the default mode (the top row), the \wedgehashedwedge mode (the middle row), and the \dashhasheddash mode (the bottom row).

20.2.4 Left-Type Tetrahedrons by \LtetrahedralS

In order to draw the mirror-image formulas of those depicted by \RtetrahedralS, we can use the command \LtetrahedralS as follows. Thus the codes:

```
\LtetrahedralS{0==C;1==F;2==Cl;3A==Br;4B==I}
\LtetrahedralS{1==F;2==Cl;3A==Br;4B==I}
```

give the following formulas:



where the presence or absence of 0==C decides the appearance of generated bonds. In addition, the codes:

```
\LtetrahedralS{0==C;1==\bzdrh{1==(yl)};2==Cl;3A==Br;4B==I} \hskip1cm
\LtetrahedralS{1==\bzdrh{1==(yl)};2==Cl;3A==Br;4B==I} \hskip1cm
\LtetrahedralS{0==C;1==F;2==\bzdrh{3==(yl)};3A==Br;4B==I}
\LtetrahedralS{1==F;2==\bzdrh{3==(yl)};3A==Br;4B==I} \par
\vskip1cm
{\wedgehashedwedge
\LtetrahedralS{0==C;1==\bzdrh{1==(yl)};2==Cl;3A==Br;4B==I} \hskip1cm
\LtetrahedralS{1==\bzdrh{1==(yl)};2==Cl;3A==Br;4B==I} \hskip1cm
\LtetrahedralS{0==C;1==F;2==\bzdrh{3==(yl)};3A==Br;4B==I}
\LtetrahedralS{1==F;2==\bzdrh{3==(yl)};3A==Br;4B==I}} \par
```

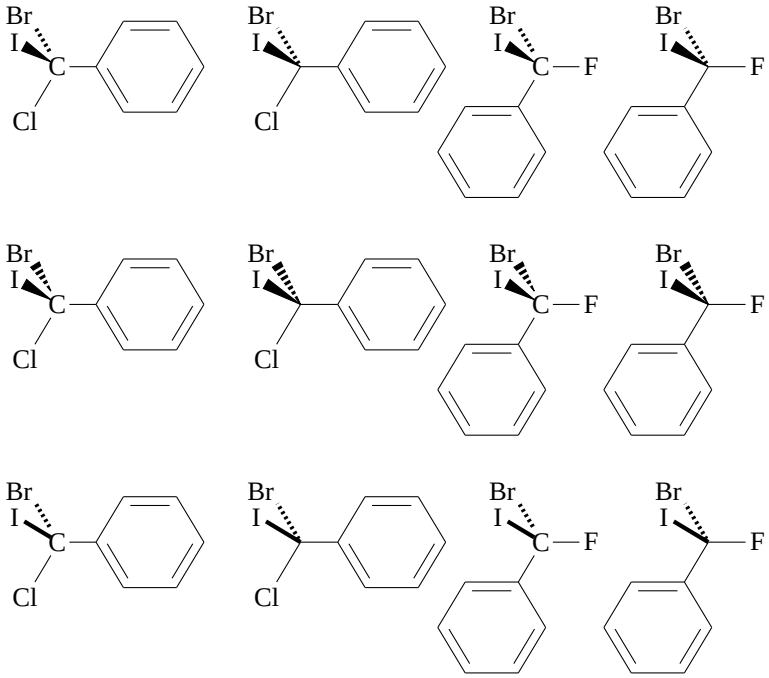


Figure 20.5. Examples of \LtetrahedralS. The top row shows the drawing due to the default mode, the middle row shows the drawing due to the \wedgehashedwedge mode, and the bottom row shows the drawing due to the \dashhasheddash mode.

```
\vskip1cm
{\dashhasheddash
\LtetrahedralS{0==C;1==\bzdrh{1==(yl)};2==Cl;3A==Br;4B==I} \hskip1cm
\LtetrahedralS{1==\bzdrh{1==(yl)};2==Cl;3A==Br;4B==I} \hskip1cm
\LtetrahedralS{0==C;1==F;2==\bzdrh{3==(yl)};3A==Br;4B==I}
\LtetrahedralS{1==F;2==\bzdrh{3==(yl)};3A==Br;4B==I}} \par
```

generate the formulas collected in Fig. 20.5, where structural formulas shown as examples are respectively drawn by the default mode (the top row), the \wedgehashedwedge mode (the middle row), and the \dashhasheddash mode (the bottom row).

20.3 Up- and Down-Types

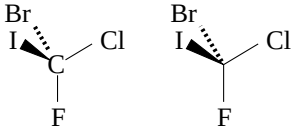
The bond from the central atom to the position 1 of an tetrahedral unit of the up- or down-type is drawn as a vertical thin line, which shows an north (upward) or a south (downward) bond.

20.3.1 Up-Type Tetrahedrons by \utetrahedralS

The bond to position 1 in a structural formula depicted by \utetrahedralS is a south (downward) bond. For example, the command \utetrahedralS used in the codes:

```
\utetrahedralS{0==C;1==F;2==Cl;3A==Br;4B==I}
\utetrahedralS{1==F;2==Cl;3A==Br;4B==I}
```

gives the following formulas:



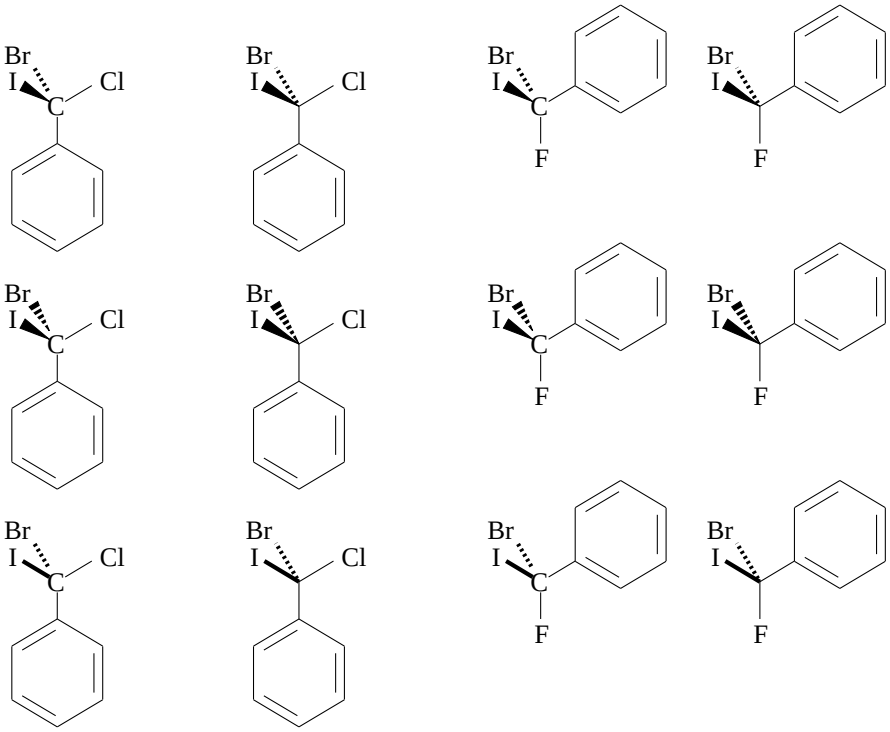


Figure 20.6. Examples of \utetrahedralS. The top row shows the drawing due to the default mode, the middle row shows the drawing due to the \wedgehashedwedge mode, and the bottom row shows the drawing due to the \dashhasheddash mode.

where the presence or absence of 0==C decides the appearance of generated bonds. The codes:

```
\utetrahedralS{0==C;1==\bzdrv{1==(yl)};2==Cl;3A==Br;4B==I} \hskip1cm
\utetrahedralS{1==\bzdrv{1==(yl)};2==Cl;3A==Br;4B==I} \hskip1cm
\utetrahedralS{0==C;1==F;2==\bzdrv{5==(yl)};3A==Br;4B==I} \qquad
\utetrahedralS{1==F;2==\bzdrv{5==(yl)};3A==Br;4B==I} \par
\vskip1cm
{\wedgehashedwedge
\utetrahedralS{0==C;1==\bzdrv{1==(yl)};2==Cl;3A==Br;4B==I} \hskip1cm
\utetrahedralS{1==\bzdrv{1==(yl)};2==Cl;3A==Br;4B==I} \hskip1cm
\utetrahedralS{0==C;1==F;2==\bzdrv{5==(yl)};3A==Br;4B==I} \qquad
\utetrahedralS{1==F;2==\bzdrv{5==(yl)};3A==Br;4B==I} }\par
\vskip1cm
{\dashhasheddash
\utetrahedralS{0==C;1==\bzdrv{1==(yl)};2==Cl;3A==Br;4B==I} \hskip1cm
\utetrahedralS{1==\bzdrv{1==(yl)};2==Cl;3A==Br;4B==I} \hskip1cm
\utetrahedralS{0==C;1==F;2==\bzdrv{5==(yl)};3A==Br;4B==I} \qquad
\utetrahedralS{1==F;2==\bzdrv{5==(yl)};3A==Br;4B==I} }\par
```

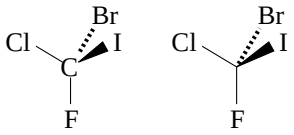
generate the formulas collected in Fig. 20.6, where structural formulas shown as examples are respectively drawn by the default mode (the top row), the \wedgehashedwedge mode (the middle row), and the \dashhasheddash mode (the bottom row).

20.3.2 Up-Type Tetrahedrons by \UtetrahedralS

The bond to position 1 in a structural formula depicted by \UtetrahedralS is a south (downward) bond. The formula is rotated by 180° around the bond so as to give a formula depicted by \utetrahedralS. For example, \UtetrahedralS used in the codes:

```
\UtetrahedralS{0==C;1==F;2==Cl;3A==Br;4B==I}
\UtetrahedralS{1==F;2==Cl;3A==Br;4B==I}
```

gives the following formulas:



where the presence or absence of `0==C` decides the appearance of generated bonds. The codes:

```
\UtetrahedralS{0==C;1==\bzdrv{1==(yl)};2==Cl;3A==Br;4B==I} \hskip1cm
\UtetrahedralS{1==\bzdrv{1==(yl)};2==Cl;3A==Br;4B==I} \hskip1cm
\UtetrahedralS{0==C;1==F;2==\bzdrv{3==(yl)};3A==Br;4B==I} \qquad
\UtetrahedralS{1==F;2==\bzdrv{3==(yl)};3A==Br;4B==I} \par
\vskip1cm
{\wedgehashedwedge
\UtetrahedralS{0==C;1==\bzdrv{1==(yl)};2==Cl;3A==Br;4B==I} \hskip1cm
\UtetrahedralS{1==\bzdrv{1==(yl)};2==Cl;3A==Br;4B==I} \hskip1cm
\UtetrahedralS{0==C;1==F;2==\bzdrv{3==(yl)};3A==Br;4B==I} \qquad
\UtetrahedralS{1==F;2==\bzdrv{3==(yl)};3A==Br;4B==I} }\par
\vskip1cm
{\dashhasheddash
\UtetrahedralS{0==C;1==\bzdrv{1==(yl)};2==Cl;3A==Br;4B==I} \hskip1cm
\UtetrahedralS{1==\bzdrv{1==(yl)};2==Cl;3A==Br;4B==I} \hskip1cm
\UtetrahedralS{0==C;1==F;2==\bzdrv{3==(yl)};3A==Br;4B==I} \qquad
\UtetrahedralS{1==F;2==\bzdrv{3==(yl)};3A==Br;4B==I} }\par
```

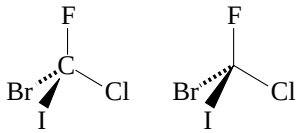
generate the formulas collected in Fig. 20.7, where structural formulas shown as examples are respectively drawn by the default mode (the top row), the `\wedgehashedwedge` mode (the middle row), and the `\dashhasheddash` mode (the bottom row).

20.3.3 Down-Type Tetrahedrons by `\dtetrahedralS`

The bond to position 1 in a structural formula depicted by `\dtetrahedralS` is a north (upward) bond. For example, `\dtetrahedralS` used in the codes:

```
\dtetrahedralS{0==C;1==F;2==Cl;3A==Br;4B==I}
\dtetrahedralS{1==F;2==Cl;3A==Br;4B==I}
```

gives the following formulas:



where the presence or absence of `0==C` decides the appearance of generated bonds. The codes:

```
\dtetrahedralS{0==C;1==\bzdrv{4==(yl)};2==Cl;3A==Br;4B==I} \hskip1cm
\dtetrahedralS{1==\bzdrv{4==(yl)};2==Cl;3A==Br;4B==I} \hskip1cm
\dtetrahedralS{0==C;1==F;2==\bzdrv{6==(yl)};3A==Br;4B==I} \qquad
\dtetrahedralS{1==F;2==\bzdrv{6==(yl)};3A==Br;4B==I} \par
\vskip1cm
{\wedgehashedwedge
\dtetrahedralS{0==C;1==\bzdrv{4==(yl)};2==Cl;3A==Br;4B==I} \hskip1cm
\dtetrahedralS{1==\bzdrv{4==(yl)};2==Cl;3A==Br;4B==I} \hskip1cm
\dtetrahedralS{0==C;1==F;2==\bzdrv{6==(yl)};3A==Br;4B==I} \qquad
```

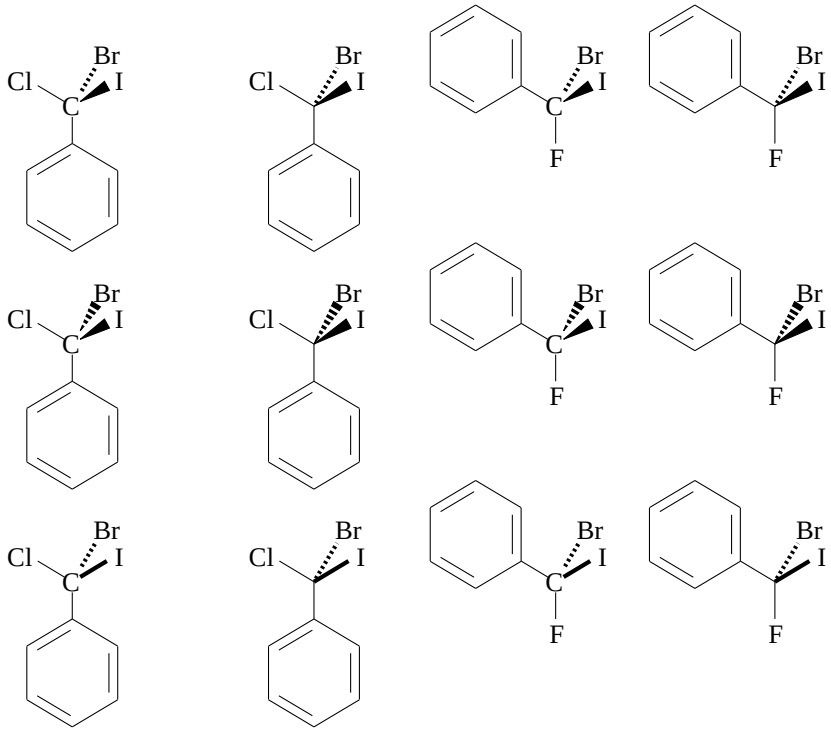


Figure 20.7. Examples of \UtetrahedralS. The top row shows the drawing due to the default mode, the middle row shows the drawing due to the \wedgehashedwedge mode, and the bottom row shows the drawing due to the \dashhasheddash mode.

```
\dtetrahedralS{1==F;2==\bzdrv{6==(yl)};3A==Br;4B==I} }\par
\vskip1cm
{\dashhasheddash
\dtetrahedralS{0==C;1==\bzdrv{4==(yl)};2==Cl;3A==Br;4B==I} \hskip1cm
\dtetrahedralS{1==\bzdrv{4==(yl)};2==Cl;3A==Br;4B==I} \hskip1cm
\dtetrahedralS{0==C;1==F;2==\bzdrv{6==(yl)};3A==Br;4B==I} \qquad
\dtetrahedralS{1==F;2==\bzdrv{6==(yl)};3A==Br;4B==I} }\par
```

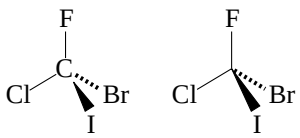
generate the formulas collected in Fig. 20.8, where structural formulas shown as examples are respectively drawn by the default mode (the top row), the \wedgehashedwedge mode (the middle row), and the \dashhasheddash mode (the bottom row).

20.3.4 Down-Type Tetrahedrons by \DtetrahedralS

The bond to position 1 in a structural formula depicted by \DtetrahedralS is a north (upward) bond. The formula is rotated by 180° around the bond so as to give a formula depicted by \dtetrahedralS. For example, \DtetrahedralS used in the codes:

```
\DtetrahedralS{0==C;1==F;2==Cl;3A==Br;4B==I}
\DtetrahedralS{1==F;2==Cl;3A==Br;4B==I}
```

gives the following formulas:



where the presence or absence of 0==C decides the appearance of generated bonds. The codes:

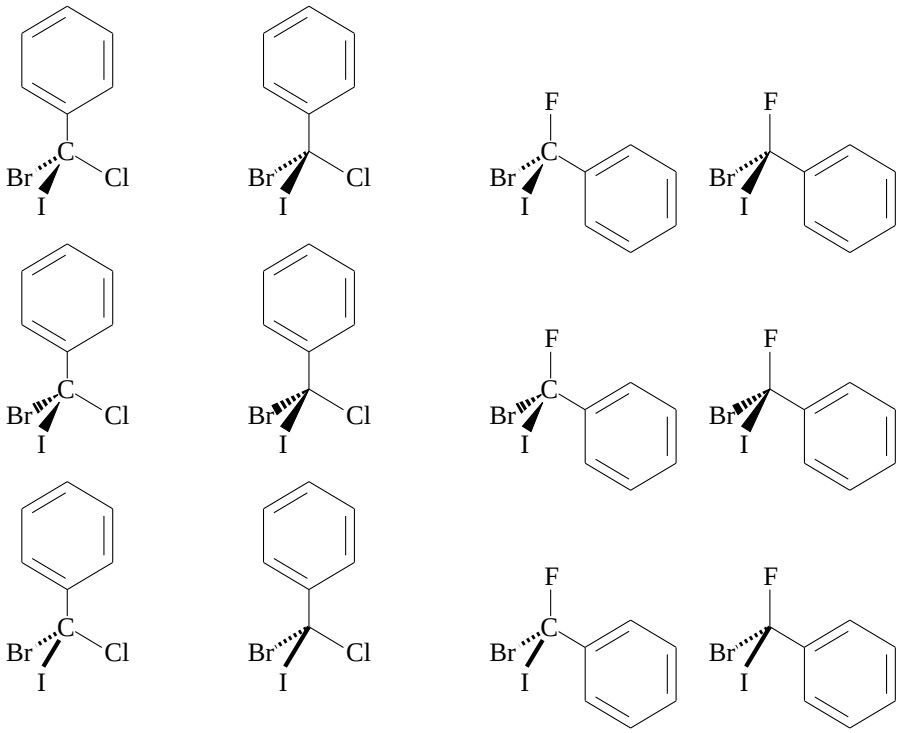


Figure 20.8. Examples of \dtetrahedralS. The top row shows the drawing due to the default mode, the middle row shows the drawing due to the \wedgehashedwedge mode, and the bottom row shows the drawing due to the \dashhasheddash mode.

```
\DtetrahedralS{0==C;1==\bzdrv{4==(yl)};2==Cl;3A==Br;4B==I} \hskip1cm
\DtetrahedralS{1==\bzdrv{4==(yl)};2==Cl;3A==Br;4B==I} \hskip1cm
\DtetrahedralS{0==C;1==F;2==\bzdrv{2==(yl)};3A==Br;4B==I} \qquad
\DtetrahedralS{1==F;2==\bzdrv{2==(yl)};3A==Br;4B==I} \par
\vskip1cm
{\wedgehashedwedge
\DtetrahedralS{0==C;1==\bzdrv{4==(yl)};2==Cl;3A==Br;4B==I} \hskip1cm
\DtetrahedralS{1==\bzdrv{4==(yl)};2==Cl;3A==Br;4B==I} \hskip1cm
\DtetrahedralS{0==C;1==F;2==\bzdrv{2==(yl)};3A==Br;4B==I} \qquad
\DtetrahedralS{1==F;2==\bzdrv{2==(yl)};3A==Br;4B==I} }\par
\vskip1cm
{\dashhasheddash
\DtetrahedralS{0==C;1==\bzdrv{4==(yl)};2==Cl;3A==Br;4B==I} \hskip1cm
\DtetrahedralS{1==\bzdrv{4==(yl)};2==Cl;3A==Br;4B==I} \hskip1cm
\DtetrahedralS{0==C;1==F;2==\bzdrv{2==(yl)};3A==Br;4B==I} \qquad
\DtetrahedralS{1==F;2==\bzdrv{2==(yl)};3A==Br;4B==I} }\par
```

generate the formulas collected in Fig. 20.9, where structural formulas shown as examples are respectively drawn by the default mode (the top row), the \wedgehashedwedge mode (the middle row), and the \dashhasheddash mode (the bottom row).

20.4 Horizontal-Type

20.4.1 Horizontal-Type Tetrahedrons by \htetrahedralS

The command \htetrahedralS of horizontal-type draws bonds to positions 1 and 2 to be diagonal thin lines (southeast and southwest bonds). For example, \htetrahedralS used in the codes:

```
\htetrahedralS{0==C;1==F;2==Cl;3A==Br;4B==I}
```

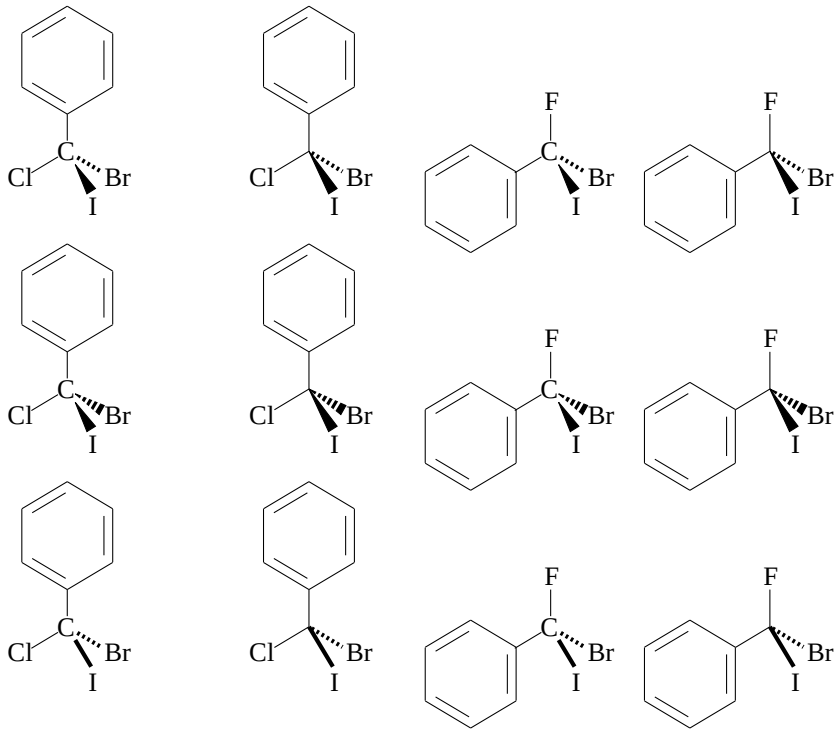
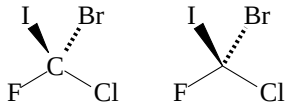


Figure 20.9. Examples of \DtetrahedralS. The top row shows the drawing due to the default mode, the middle row shows the drawing due to the \wedgehashedwedge mode, and the bottom row shows the drawing due to the \dashhasheddash mode.

```
\htetrahedralS{1==F;2==Cl;3A==Br;4B==I}
```

gives the following formulas:



where the presence or absence of 0==C decides the appearance of generated bonds. These expressions are preferred according to the IUPAC Recommendations 2006 [1, ST-0.2]. The codes:

```
\htetrahedralS{0==C;1==\bzdrv{2==(yl)};2==Cl;3A==Br;4B==I} \hskip1cm
\htetrahedralS{1==\bzdrv{2==(yl)};2==Cl;3A==Br;4B==I} \hskip1cm
\htetrahedralS{0==C;1==F;2==\bzdrv{6==(yl)};3A==Br;4B==I} \qquad
\htetrahedralS{1==F;2==\bzdrv{6==(yl)};3A==Br;4B==I} \par
\vskip1cm
{\wedgehashedwedge
\htetrahedralS{0==C;1==\bzdrv{2==(yl)};2==Cl;3A==Br;4B==I} \hskip1cm
\htetrahedralS{1==\bzdrv{2==(yl)};2==Cl;3A==Br;4B==I} \hskip1cm
\htetrahedralS{0==C;1==F;2==\bzdrv{6==(yl)};3A==Br;4B==I} \qquad
\htetrahedralS{1==F;2==\bzdrv{6==(yl)};3A==Br;4B==I} }\par
\vskip1cm
{\dashhasheddash
\htetrahedralS{0==C;1==\bzdrv{2==(yl)};2==Cl;3A==Br;4B==I} \hskip1cm
\htetrahedralS{1==\bzdrv{2==(yl)};2==Cl;3A==Br;4B==I} \hskip1cm
\htetrahedralS{0==C;1==F;2==\bzdrv{6==(yl)};3A==Br;4B==I} \qquad
\htetrahedralS{1==F;2==\bzdrv{6==(yl)};3A==Br;4B==I} }\par
```

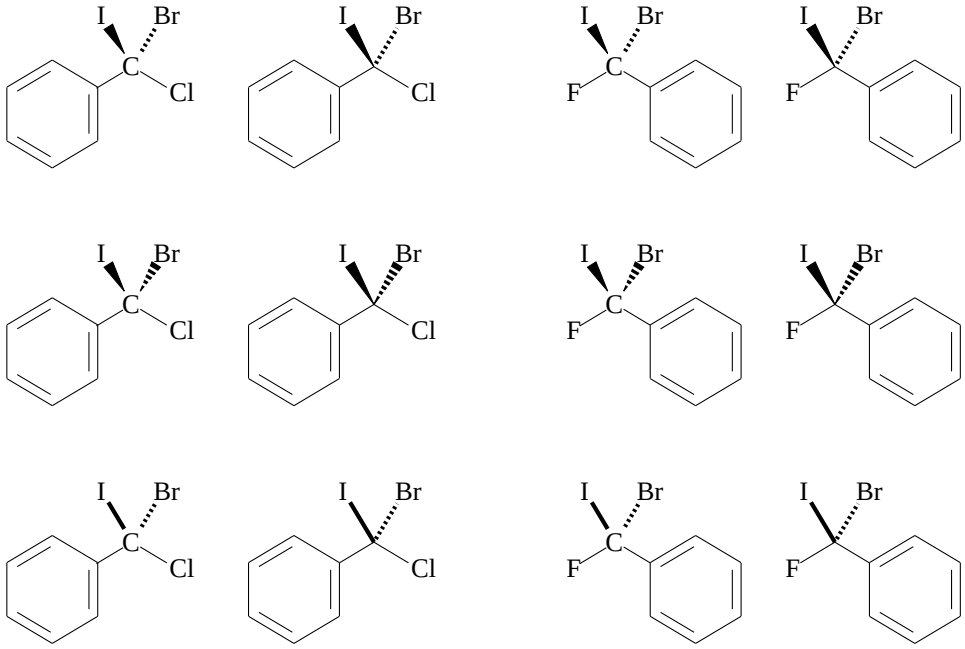


Figure 20.10. Examples of `\htetrahedralS`. The top row shows the drawing due to the default mode, the middle row shows the drawing due to the `\wedgehashedwedge` mode, and the bottom row shows the drawing due to the `\dashhasheddash` mode.

generate the formulas collected in Fig. 20.10, where structural formulas shown as examples are respectively drawn by the default mode (the top row), the `\wedgehashedwedge` mode (the middle row), and the `\dashhasheddash` mode (the bottom row).

20.5 Trigonal Bipyramidal Units

To draw transition states of reactions, we can use trigonal bipyramidal units.

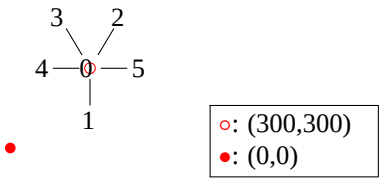
20.5.1 Up-Type Trigonal Bipyramids by \utrigpyramid

The XeTeX command `\utrigpyramid` for drawing up-type trigonal bipyramids has the following format:

```
\utrigpyramid[⟨bondlist⟩]{⟨subslist⟩}
```

The argument ⟨bondlist⟩ designates a character on the central atom of the formula drawn by this macro. It is incapable of assigning locant alphabets, so that it only assigns a plus or minus charge on the center, e.g., `[{0+}]`. The ⟨subslist⟩ is used to specify a central atom and substituents.

The bond to position 1 in a structural formula depicted by `\utrigpyramid` is a south (downward) bond. Locant numbers are assigned as follows:

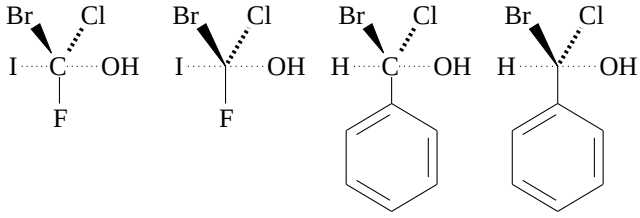


For example, `\utrigpyramid` used in the codes:

```
\utrigpyramid{0==C;1==F;2A==Cl;3B==Br;4A==I;5A==OH}
\utrigpyramid{1==F;2A==Cl;3B==Br;4A==I;5A==OH}
```

```
\utrigpyramid{0==C;5A==OH;2A==Cl;3B==Br;1==\bzdrv{1==(yl)};4A==H}
\utrigpyramid{5A==OH;2A==Cl;3B==Br;1==\bzdrv{1==(yl)};4A==H}
```

gives the following formulas:

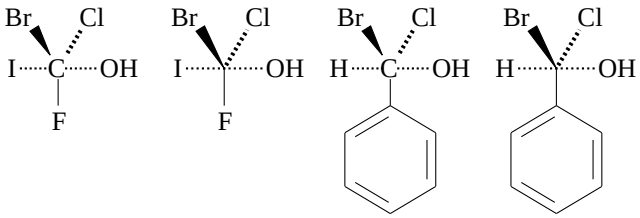


where the presence or absence of `0==C` decides the appearance of generated bonds. Because the dotted bond between the center (0) and locant 4 as well as between the center (0) and locant 5 is drawn by the command `\dottedline` of the epic package (via the XeLaTeX command `\d@t@rline`), the thickness of the dotted bond 0—4 or 0—5 depends on the default value of the epic package.

In order to thicken the dotted bonds 0—4 and 0–5, the command `\picsquare@bl` is redefined as follows, because the thickness of a dot stems from `\picsquare@bl` in the epic package.

```
{
\makeatletter
%redefinition of the epic package
\def\picsquare@bl{\vrule height 2.5\@wholewidth depth \z@  width 2.5\@wholewidth}
\makeatother
\utrigpyramid{0==C;1==F;2A==Cl;3B==Br;4A==I;5A==OH}
\utrigpyramid{1==F;2A==Cl;3B==Br;4A==I;5A==OH}
\utrigpyramid{0==C;5A==OH;2A==Cl;3B==Br;1==\bzdrv{1==(yl)};4A==H}
\utrigpyramid{5A==OH;2A==Cl;3B==Br;1==\bzdrv{1==(yl)};4A==H}
}
```

These codes give the following formulas:



where the presence or absence of `0==C` decides the appearance of generated bonds.

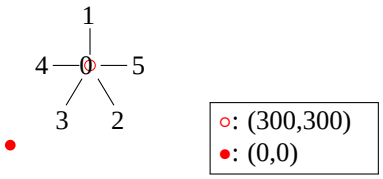
20.5.2 Down-Type Trigonal Bipyramids by \dtrigpyramid

The XeLaTeX command `\dtrigpyramid` for drawing up-type trigonal bipyramids has the following format:

```
\dtrigpyramid[⟨bondlist⟩]{⟨subslist⟩}
```

The argument ⟨bondlist⟩ designates a character on the central atom of the formula drawn by this macro. It is incapable of assigning locant alphabets, so that it only assigns a plus or minus charge on the center, e.g., `[{0+}]`. The ⟨subslist⟩ is used to specify a central atom and substituents.

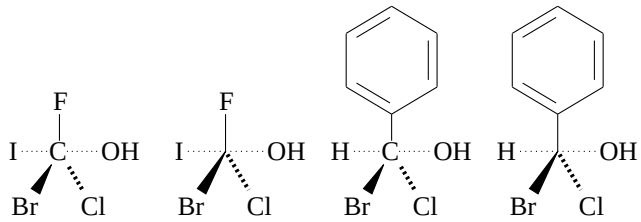
The bond to position 1 in a structural formula depicted by `\dtrigpyramid` is a north (upward) bond. Locant numbers are assigned as follows:



For example, `\dtrigpyramid` used in the codes:

```
\dtrigpyramid{0==C;1==F;2A==Cl;3B==Br;4A==I;5A==OH}
\dtrigpyramid{1==F;2A==Cl;3B==Br;4A==I;5A==OH}
\dtrigpyramid{0==C;5A==OH;2A==Cl;3B==Br;1==\bzdrv{1==(yl)};4A==H}
\dtrigpyramid{5A==OH;2A==Cl;3B==Br;1==\bzdrv{1==(yl)};4A==H}
```

gives the following formulas:

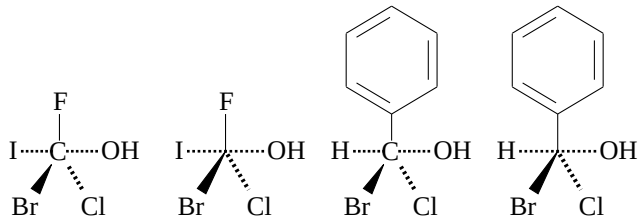


where the presence or absence of `0==C` decides the appearance of generated bonds.

In order to thicken the dotted bonds 0—4 and 0–5, the command `\picsquare@bl` is redefined as follows, because the thickness of a dot stems from `\picsquare@bl` in the epic package.

```
{
\makeatletter
%redefinition of the epic package
\def\picsquare@bl{\vrule height 10\unitlength depth \z@  width 10\unitlength}
\makeatother
\dtrigpyramid{0==C;1==F;2A==Cl;3B==Br;4A==I;5A==OH}
\dtrigpyramid{1==F;2A==Cl;3B==Br;4A==I;5A==OH}
\dtrigpyramid{0==C;5A==OH;2A==Cl;3B==Br;1==\bzdrv{4==(yl)};4A==H}
\dtrigpyramid{5A==OH;2A==Cl;3B==Br;1==\bzdrv{4==(yl)};4A==H}
}
```

These codes give the following formulas:



20.6 Illustrative Examples and Applications

20.6.1 Truncation at a Central Atom

The central atom at locant 0 is presumed to be a one-letter atom such as C, O, or N, so that two-letter atoms such Si, Ge, and Sn overlap the starting terminal of each bond.

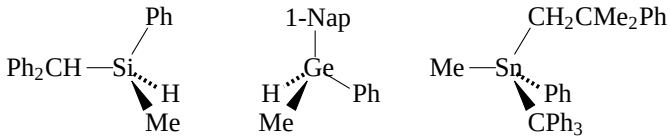
Example 20.1. If the command `\SetTwoAtomx` for truncation at the central atom is declared at an inappropriate position (at the top position of the ⟨subslist⟩), e.g.,

```
\rtetrahedralS{0==\SetTwoAtomx{Si};1==Ph$_{2}$CH;2==Ph;3A==H;4B==Me}
```

```
\dtetrahedralS{0==\SetTwoAtomx{Ge};1==\llap{1-}Nap;2==Ph;3A==H;4B==Me}
\rtetrahedralS{0==\SetTwoAtomx{Sn};1==Me;2==CH$_{2}$CMe$_{2}$Ph;%
3A==Ph;4B==CPh$_{3}$}
```

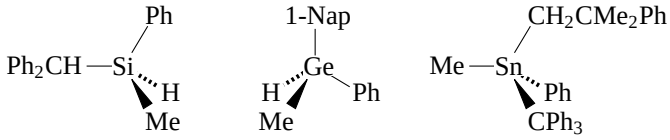
its effect is not fully realized, as found in **20-1**, **20-2**, and **20-3**.

(a) No effects of truncation:



20-1 **20-2** **20-3**

(b) Effective truncation:



20-1′ **20-2′** **20-3′**

By declaring `0==\SetTwoAtomx{Si}` at the last position of the ⟨subslist⟩, i.e.,

```
\rtetrahedralS{1==Ph$_{2}$CH;2==Ph;3A==H;4B==Me;0==\SetTwoAtomx{Si}}
\dtetrahedralS{1==\llap{1-}Nap;2==Ph;3A==H;4B==Me;0==\SetTwoAtomx{Ge}}
\rtetrahedralS{1==Me;2==CH$_{2}$CMe$_{2}$Ph;%
3A==Ph;4B==CPh$_{3}$$;0==\SetTwoAtomx{Sn}}
```

we are able to obtain **20-1′**, **20-2′**, and **20-3′**, in which efficient truncation is fulfilled. □

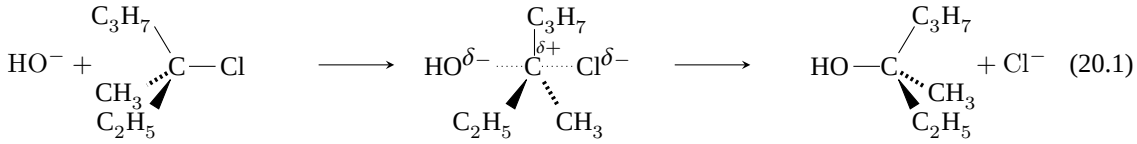
20.6.2 Reaction Schemes

By combining two or more commands defined in the present chapter, we can write an reaction scheme containing a transition-state diagram.

Example 20.2. For example, the code:

```
\begin{chemeqn}
HO^{-} +
\raisebox{-28pt}{%
\ltetrahedralS{0==C;1==Cl;2==C$_{3}$H$_{7}$;3A==CH$_{3}$;4B==C$_{2}$H$_{5}$}}
\qquad\reactrarrow{0pt}{1cm}{}{}\qquad
\raisebox{-28pt}{%
\dtrigpyramid[{0{~~$\delta+$}}]%
{0==C;4A==HO$^{\delta-}$;5A==Cl$^{\delta-}$;1==C$_{3}$H$_{7}$;%
2A==CH$_{3}$;3B==C$_{2}$H$_{5}$}}
\qquad\reactrarrow{0pt}{1cm}{}{}\qquad
\raisebox{-28pt}{%
\rtetrahedralS{0==C;1==HO;2==C$_{3}$H$_{7}$;3A==CH$_{3}$;4B==C$_{2}$H$_{5}$}}
+ Cl^{-}
\end{chemeqn}
```

generates the following scheme:



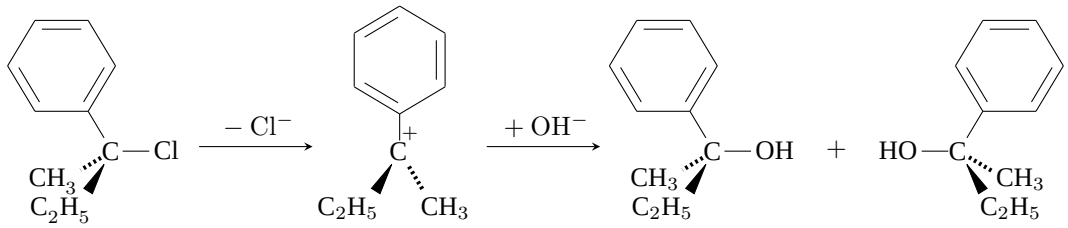
(20.1)

□

Example 20.3. Similarly, the code:

```
\begin{chemeqn}
\raisebox{-28pt}{%
\ltetrahedralS{0==C;1==Cl;2==\bzdrh{5==(yl)};3A==CH$_{3}$;4B==C$_{2}$H$_{5}$}}
\reactrarrow{0pt}{1.5cm}{\chemform{{}-Cl^{-}}}{\strut}
\raisebox{-28pt}{%
\dtrigpyramid[{0{~~$+$}}]%
{0==C;1==\bzdrv{4==(yl)};2A==CH$_{3}$;3B==C$_{2}$H$_{5}$}}
\reactrarrow{0pt}{1.5cm}{\chemform{{}+OH^{-}}}{\strut}\quad
\raisebox{-28pt}{%
\ltetrahedralS{0==C;1==OH;2==\bzdrh{5==(yl)};3A==CH$_{3}$;4B==C$_{2}$H$_{5}$}}
\quad +\quad
\raisebox{-28pt}{%
\rtetrahedralS{0==C;1==HO;2==\bzdrh{6==(yl)};3A==CH$_{3}$;4B==C$_{2}$H$_{5}$}}
\end{chemeqn}
```

produces the following scheme containing a carbocation intermediate:



(20.2)

□

Note: The chemeqn environment of the X$\mathfrak{Y}$MTEX system is based on the math version 'chem' defined in the chemist package, the chmst-ps package, or the chmst-pdf package, which is automatically loaded by the X$\mathfrak{Y}$MTEX system (`\usepackage{xymtex}`, `\usepackage{xymtexps}`, or `\usepackage{xymtexpdf}`). This math version may be in conflict with the math versions defined in the txfonts package. Hence, the X$\mathfrak{Y}$MTEX system (xymtexpdf or xymtexps) should be loaded after the txfonts package in order to assure the sufficient result of the chemeqn environment. For example, the order of loading in the preamble of a LATEX document should be as follows:

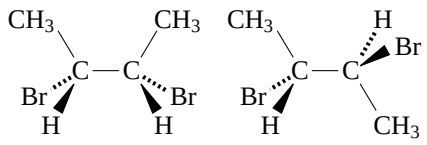
```
\usepackage{amsmath}
\usepackage{txfonts}%Times Roman
\usepackage[scaled]{helvet}%Helvetica 95%
\usepackage{xymtexpdf}
```

20.6.3 Conformations

Example 20.4. An eclipsed conformer and a staggered one are drawn by the codes:

```
\ltetrahedralS{0==C;1==\rtetrahedralS{1==(yl);0==C;2==CH$_{3}$;3A==Br;4B==H};%
2==CH$_{3}$;3A==Br;4B==H}
\qquad
\ltetrahedralS{0==C;1==\RtetrahedralS{1==(yl);0==C;2==CH$_{3}$;3A==H;4B==Br};%
2==CH$_{3}$;3A==Br;4B==H}
```

which generate the following formulas:

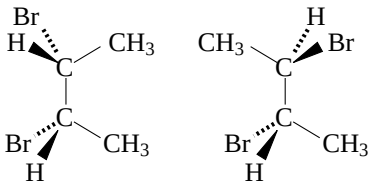


□

Example 20.5. The corresponding vertical diagrams are drawn by the codes:

```
\utetrahedralS{0==C;1==\dtetrahedralS{1==(yl);0==C;2==CH$_{3}$;3A==Br;4B==H};%
2==CH$_{3}$;3A==Br;4B==H}
\qquad
\UtetrahedralS{0==C;1==\dtetrahedralS{1==(yl);0==C;2==CH$_{3}$;3A==Br;4B==H};%
2==CH$_{3}$;3A==H;4B==Br}
```

which generate the following formulas:



□

References

[1] J. Brecher and IUPAC Chemical Nomenclature and Structure Representation Division, *Pure Appl. Chem.*, **78**, 1897–1970 (2006).

Chapter 21

Zigzag Polymethylene Chains

This chapter is devoted to introduce `\dimethylene`, `\trimethylene`, etc. for the purpose of drawing polymethylene chains of carbon contents 2 to 10. These macros can be used to generate polymethylene chains of carbon contents larger than 10 by the replacement technique or the substitution technique, because they have ⟨atomlist⟩ along with ⟨substlist⟩. They are also used to generate hetera (e.g., oxa and aza) derivatives by the replacement technique.

21.1 General Features of Commands for drawing Zigzag Chains

For the purpose of drawing zigzag polymethylene chains of carbon contents 2 to 10, the XyMTEX system supports the commands listed in Table 21.1. These commands have the following syntax:

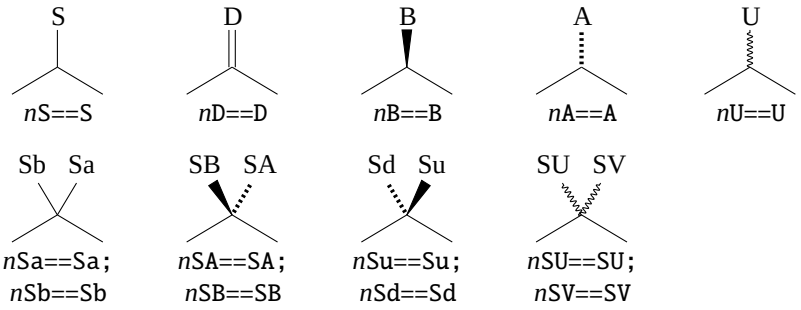
```
\ZigzagCom[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}
```

where `\ZigzagCom` represents the name of a command listed in Table 21.1. Note that the suffix '`i`' indicates a command for drawing a zigzag in an inverse direction.

Table 21.1. Commands for Drawing Zigzag Polymethylene Skeletons

carbon content	normal direction command (`\ZigzagCom`)	inverse direction command (`\ZigzagCom`)
Transoid zigzag polymethylenes		
2	`\dimethylene`	`\dimethylenei`
3	`\trimethylene`	`\trimethylenei`
4	`\tetramethylene`	`\tetramethylenei`
5	`\pentamethylene`	`\pentamethylenei`
6	`\hexamethylene`	`\hexamethylenei`
7	`\heptamethylene`	`\heptamethylenei`
8	`\octamethylene`	`\octamethylenei`
9	`\nonamethylene`	`\nonamethylenei`
10	`\decamethylene`	`\decamethylenei`
Cisoid zigzag polymethylenes		
4	`\tetramethylenecup`	`\tetramethylenecap`

(a) Upward bonds at inner positions



(b) Downward bonds at inner positions

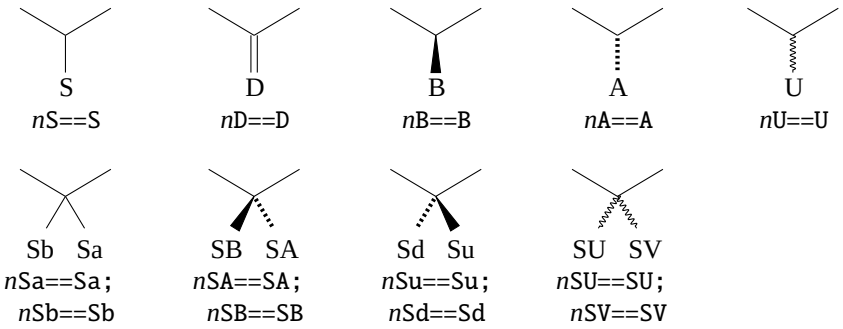


Figure 21.1. Bond modifiers for inner positions of zigzag polymethylene chains under the default setting of the XyMTEX system (`\wedgehasheddash`).

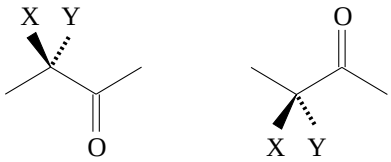
The argument ⟨bondlist⟩ of `\ZigzagCom` contains lowercase (or sometimes uppercase) locant alphabets, each of which indicates the presence of an inner double bond on the corresponding position (cf. Subsection 3.3.1). The argument ⟨atomlist⟩ of `\ZigzagCom` follows the convention of the XyMTEX system (cf. Section 3.2).

Although the argument ⟨subslist⟩ argument of `\ZigzagCom` also follows the convention of the XyMTEX system (cf. Section 3.2), several bond modifiers are added to specify bonds at the terminal positions.

Fig. 21.1 shows bond modifiers for inner positions of zigzag polymethylene chains under the default setting of the XyMTEX system (`\wedgehasheddash`). Upward bonds (a) or downward bonds (b) at inner positions of polymethylenes are automatically selected if a command and a locant number are given. For example, the codes:

```
\tetramethylene{}{2SB==X;2SA==Y;3D==O}
\tetramethylenei{}{2SB==X;2SA==Y;3D==O}
```

generate the following diagrams:



where the inner positions 2 and 3 of `\tetramethylene` (the left diagram) are characterized by upward bonds and downward bonds respectively, while the inverse directions of bonds are adopted in the case of `\tetramethylenei` (the right diagram).

Hashed bonds collected in Fig. 21.1 under the default setting of the XyMTEX system (`\wedgehasheddash`) can be changed into hashed wedged bonds by declaring `\wedgehashedwedge`. For example, the codes:

```
\wedgehashedwedge
\tetramethylene{}{2SB==X;2SA==Y;3D==O}
\tetramethylenei{}{2SB==X;2SA==Y;3D==O}
```

generate the following diagrams:

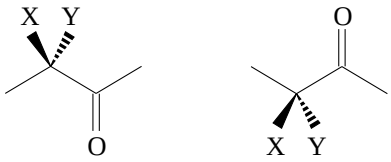
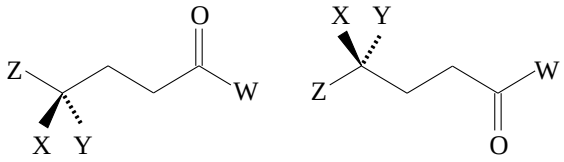


Fig. 21.2 shows bond modifiers for left terminal positions of zigzag polymethylene chains under the default setting of the XƎMTEX system (`\wedgehasheddash`). On the other hand, Fig. 21.3 shows bond modifiers for right terminal positions of zigzag polymethylene chains. Figs. 21.2 and 21.3 contain additional bond modifiers such as 'W', 'WB', 'WA', and 'WU' in comparison with Fig. 21.1.

Upward bonds (a) or downward bonds (b) as well as terminal bonds are automatically selected if a command and a locant number are given. For example, the codes:

```
\tetramethylene{}{1W==Z;1SB==X;1SA==Y;4D==O;4W==W} \qquad
\tetramethylenei{}{1W==Z;1SB==X;1SA==Y;4D==O;4W==W}
```

generate the following diagrams:

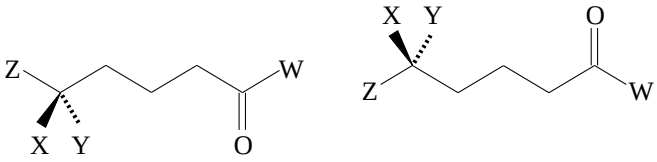


The terminal positions 1 and 4 of `\tetramethylene` (the left diagram) are characterized by downward bonds (and a related terminal bond) and upward bonds (and a related terminal bond), respectively. These features of outputs are common to polymethylene chains with even numbers of carbon content. On the other hand, the inverse directions of bonds are adopted in the case of `\tetramethylenei` (the right diagram).

When a carbon content is odd, the output of a right terminal turns out to be inverse. For example, the codes:

```
\pentamethylene{}{1W==Z;1SB==X;1SA==Y;5D==O;5W==W} \qquad
\pentamethylenei{}{1W==Z;1SB==X;1SA==Y;5D==O;5W==W}
```

generate the following diagrams:



The terminal positions 1 and 5 of `\pentamethylene` (the left diagram) are characterized by both downward bonds (and a related terminal bond). On the other hand, the inverse directions of bonds are adopted in the case of `\pentamethylenei` (the right diagram).

21.2 Dimethylenes

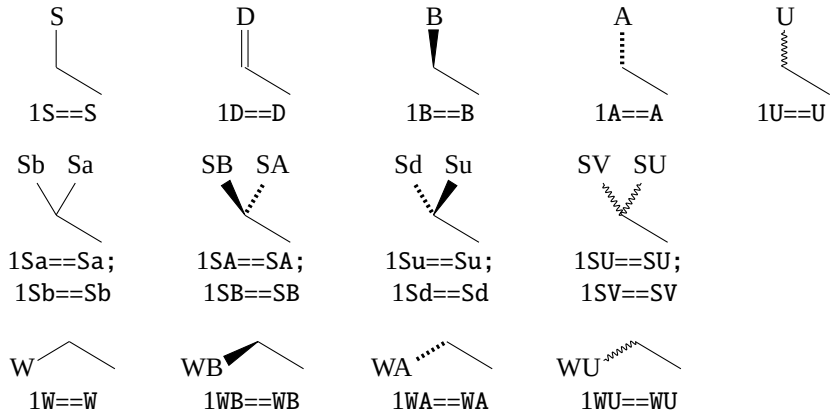
21.2.1 Drawing by `\dimethylene`

The XƎMTEX command `\dimethylene` for general use has two arguments ⟨atomlist⟩ and ⟨subslist⟩ as well as an optional argument ⟨bondlist⟩ (methylen.sty):

```
\dimethylene[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}
```

Note that this command has a simplified format, in which these arguments are selected from the full list of arguments for the XƎMTEX commands for general use (Section 3.1). The ⟨bondlist⟩ argument contains one character a or A, each of which indicates the presence of an inner (endo-chain) double bond on the

(a) Upward and terminal bonds at left terminal positions



(b) Downward and terminal bonds at left terminal positions

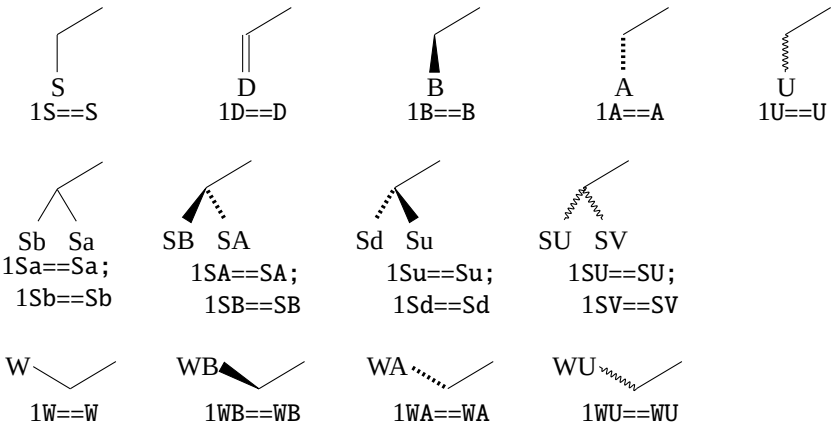
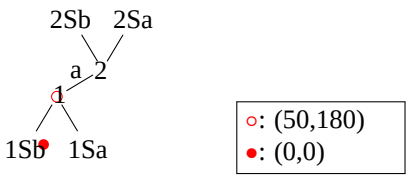


Figure 21.2. Bond modifiers for left terminal positions of zigzag polymethylene chains under the default setting of the X^ηMTEX system (`\wedgehasheddash`).

corresponding position (cf. Subsection 3.3.1). A lowercase letter is used to typeset a double bond at a lower-side of an outer skeletal bond, while an uppercase letter typesets a double bond at a upper-side of an outer skeletal bond (Note that the option 'A' represents an aromatic circle in commands `\sixheterov` etc.). The ⟨atomlist⟩ and ⟨subslist⟩ arguments follow the conventions of the X^ηMTEX system (cf. Section 3.2).

The following diagram shows the numbering for designating substitution positions:

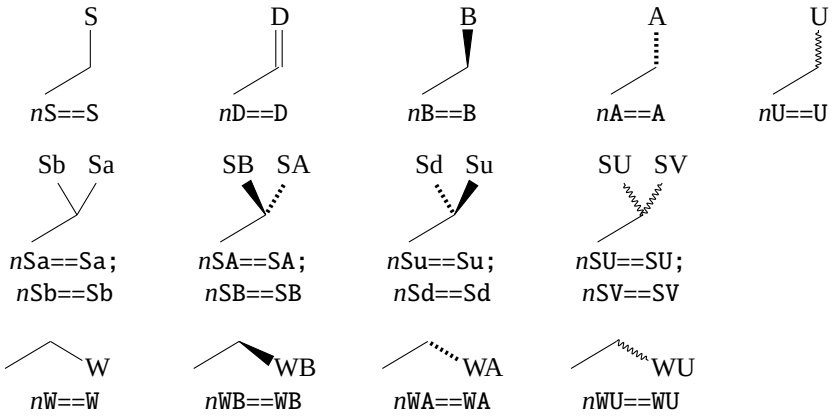


Lowercase vs. uppercase letters ('a' vs. 'A') in the ⟨bondlist⟩ of the `\dimethylene` command designate the position of an bond added to the bond 'a', as shown in the code,

```
\dimethylene[a]{}{1W==\bzdrv{3==(yl)};1==Cl;2W==H;2==F}
\hskip2cm
\bzdrv{3==\dimethylene[A]{}{1==(yl);1==Cl;2W==H;2==F}}
```

which typesets the following formulas:

(a) Upward and terminal bonds at right terminal positions



(b) Downward and terminal bonds at right terminal positions

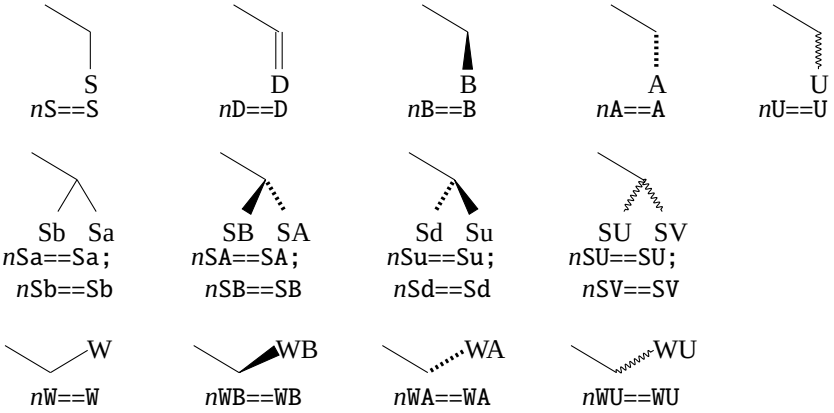
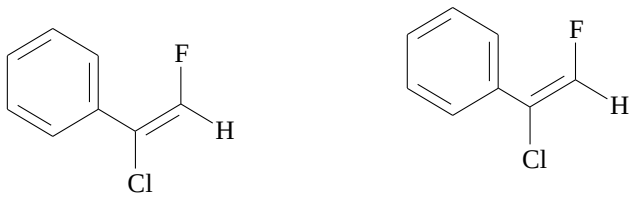


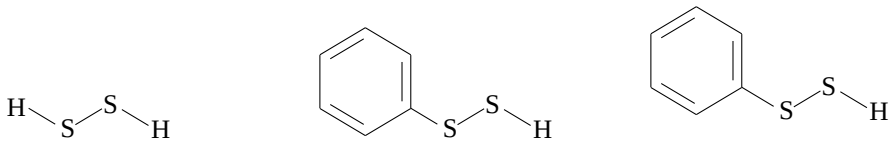
Figure 21.3. Bond modifiers for right terminal positions of zigzag polymethylene chains under the default setting of the XeTeX system (`\wedgehasheddash`).



In addition to the standard bond modifiers listed in Table 3.2, the terminal positions of the command `\dimethylene` can take a bond modifier 'W'. For example, the codes,

```
\dimethylene{1==S;2==S}{1W==H;2W==H}
\hskip4cm
\dimethylene{1==S;2==S}{1W==\bzdrv{3==(yl)};2W==H}
\hskip1cm
\bzdrv{3==\dimethylene{1==S;2==S}{1==(yl);2W==H}}
```

generate the following formulas:



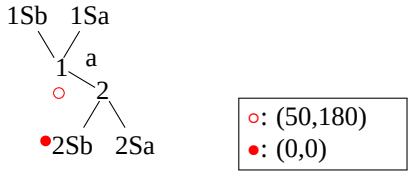
where the ⟨atomlist⟩ is used to set two sulfur atoms in the dimethylene chain.

21.2.2 Drawing by \dimethylenei

The XeLaTeX command `\dimethylenei` is the inverse counterpart of `\dimethylene`, where arguments ⟨atomlist⟩, ⟨subslist⟩, and ⟨bondlist⟩ take such common formats as found in the definition of the latter (methylen.sty):

```
\dimethylenei[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}
```

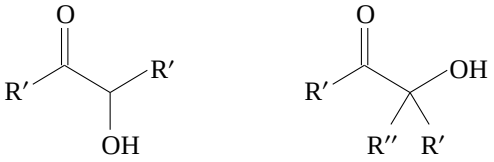
The following diagram shows the numbering for designating substitution positions:



Note that the coordinate of position no. 1 is (50, 283), where 180 + 103 = 283.

The following examples show a specification of the ⟨subslist⟩.

```
\dimethylenei{}{1W==R$^{\prime}$;2W==R$^{\prime}$;1D==O;2==OH}
\hskip3cm
\dimethylenei{}{1W==R$^{\prime}$;%
2Sa==R$^{\prime}$;2Sb==R$^{\prime\prime}$;1D==O;2W==OH}
```

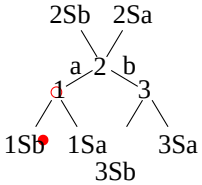


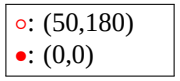
21.3 Trimethylenes

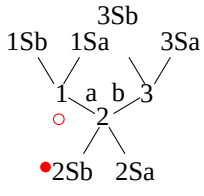
The XeLaTeX commands `\trimethylene` and `\trimethylenei` have two arguments ⟨atomlist⟩ and ⟨subslist⟩ as well as an optional argument ⟨bondlist⟩ (methylen.sty).

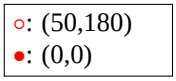
```
\trimethylene[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}
\trimethylenei[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}
```

The following diagrams show the numbering for designating substitution positions:



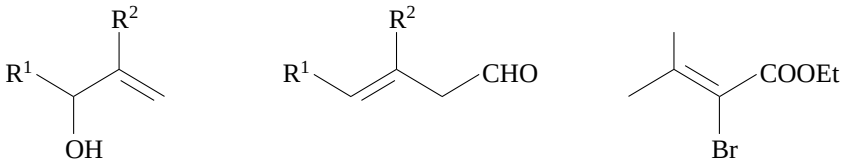






Examples:

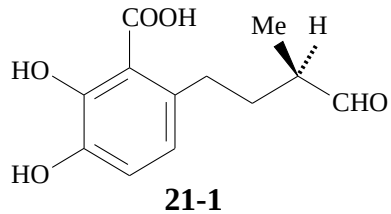
```
\trimethylene[b]{}{1W==R$^{1}$;1==OH;2==R$^{2}$}
\hskip2cm
\trimethylene[a]{}{1W==R$^{1}$;2==R$^{2}$;3W==CHO}
\hskip2cm
\trimethylene[B]{}{2==\null;3W==COOEt;3==Br}
```



Example 21.1. The substitution technique is applied to a trimethylene skeleton drawn by `\trimethylenei`, which is regarded as a parent structure. A phenyl group is generated by declaring a (yl)-function in the `\bzdrv` (= `\benzenev`) and placed in the ⟨subslist⟩.

```
\trimethylenei{}{1W==\bzdrv{2==(yl);1==COOH;5==HO;6==HO};%
3W==CHO;3SA==H;3SB==Me}
```

This code generates the following structural formula.

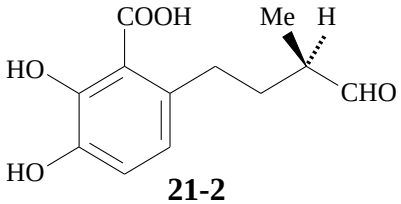


21-1

The bond linking the phenyl substituent with a trimethylene skeleton is shorter than the other methylene C—C bonds of the formula **21-1**, because it is generated by the substitution technique. The replacement technique is applicable to elongate the bond Ph—C, if we use the `\tetramethylene` command (see the next section). In the following code, a phenyl group generated by declaring a (yl)-function in the `\bzdrv` (= `\benzenev`) is placed in the ⟨atomlist⟩ of the command `\tetramethylene` according to the replacement technique.

```
\tetramethylene{1s==\bzdrv{2==(yl);1==COOH;5==HO;6==HO}}%
{4W==CHO;4SA==H;4SB==Me}
```

Thereby, we obtain the following structural formula.



21-2

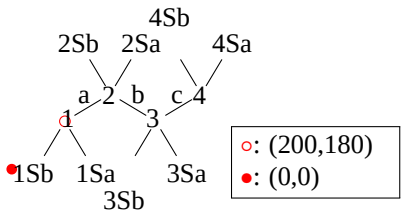
□

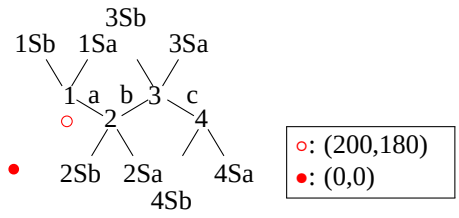
21.4 Tetramethylenes

The XeTeX commands `\tetramethylene` and `\tetramethylenei` have two arguments ⟨atomlist⟩ and ⟨subslist⟩ as well as an optional argument ⟨bondlist⟩ (methylen.sty).

```
\tetramethylene[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}
\tetramethylenei[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}
```

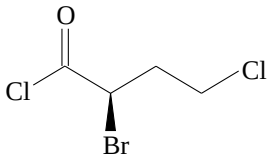
The following diagram shows the numbering for designating substitution positions:



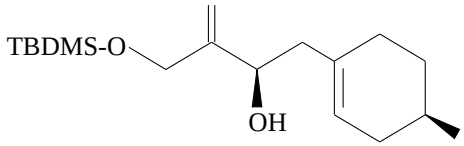


Examples:

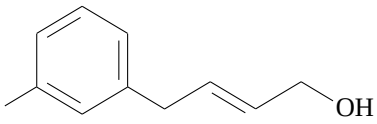
```
\tetramethylenei{}{1W==Cl;1D==O;2B==Br;4W==Cl}
```




```
\tetramethylene{}{1W==TBDMS-O;2D==\null;3B==OH;%
4W==\cyclohexanev[e]{6==(yl);3B==\null}}
```




```
\tetramethylene[b]{}{1W==\bzdrv{5==\null;3==(yl)};4W==OH}
```

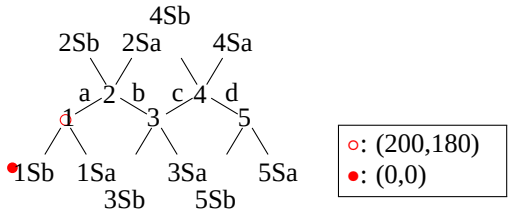


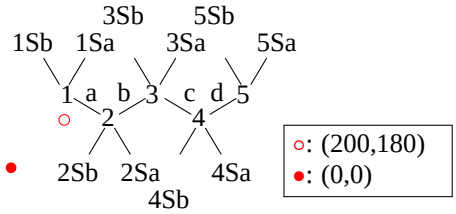
21.5 Pentamethylenes

The XeLaTeX commands `\pentamethylene` and `\pentamethylenei` have two arguments ⟨atomlist⟩ and ⟨subslist⟩ as well as an optional argument ⟨bondlist⟩ (methylen.sty).

```
\pentamethylene[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}
\pentamethylenei[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}
```

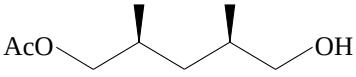
The following diagram shows the numbering for designating substitution positions:



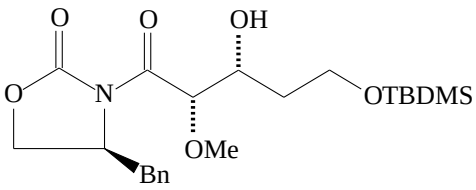


Examples:

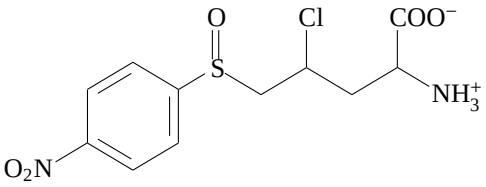
```
\pentamethylene{}{1W==AcO;2B==\null;4B==\null;5W==OH}
```



```
\pentamethylenei{}{1W==\fiveheterovi{2==N;5==O}{1D==O;2==(yl);3B==Bn};%
1D==O;2A==OMe;3A==OH;5W==OTBDMS}
```




```
\pentamethylenei{1==S}{1W==\bzdrv{2==(yl);5==O$_{2}$N};%
1D==O;3==Cl;5==COO$^{-}$;5W==NH$_{3}^{+}$}
```

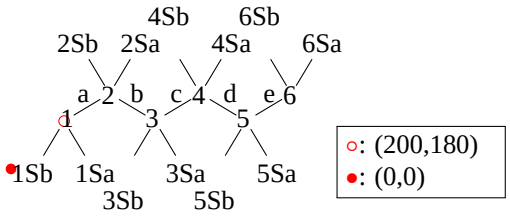


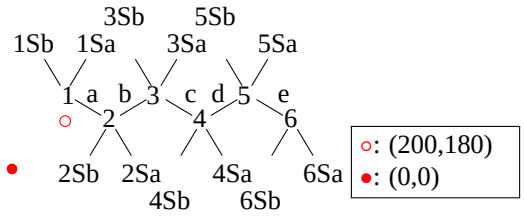
21.6 Hexamethylenes

The XeLaTeX commands `\hexamethylene` and `\hexamethylenei` have two arguments ⟨atomlist⟩ and ⟨subslist⟩ as well as an optional argument ⟨bondlist⟩ (methylen.sty).

```
\hexamethylene[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}
\hexamethylenei[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}
```

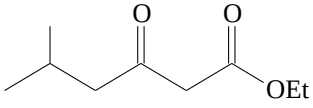
The following diagram shows the numbering for designating substitution positions:



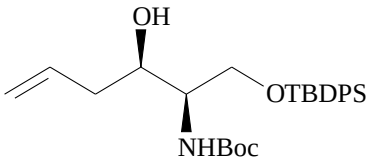


Examples:

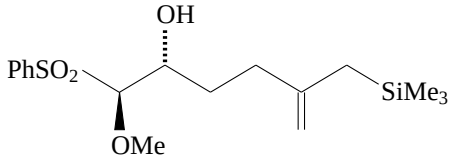
```
\hexamethylene{}{2==\null;4D==O;6D==O;6W==OEt}
```



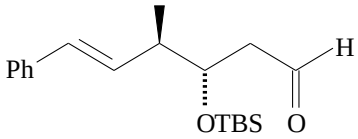

```
\hexamethylene[a]{}{4B==OH;5B==NHBoc;6W==OTBDPS}
```



```
\hexamethylene{}{1W==PhSO$_{2}$;1B==OMe;2A==OH;5D==\null;6W==SiMe$_{3}$}
```




```
\hexamethylenei[a]{}{1W==Ph;3B==\null;4A==OTBS;6D==O;6W==H}
```

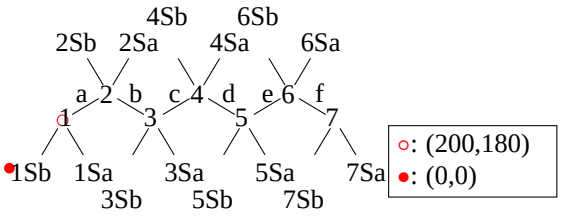


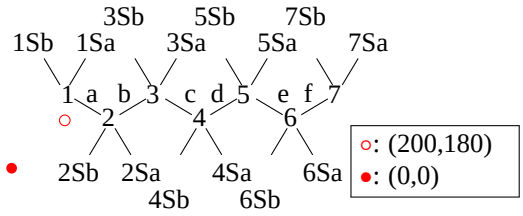
21.7 Heptamethylenes

The XyMTEX commands `\heptamethylene` and `\heptamethylenei` have two arguments ⟨atomlist⟩ and ⟨subslist⟩ as well as an optional argument ⟨bondlist⟩ (methylen.sty).

```
\heptamethylene[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}
\heptamethylenei[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}
```

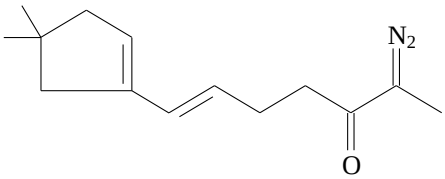
The following diagrams show the numbering for designating substitution positions:





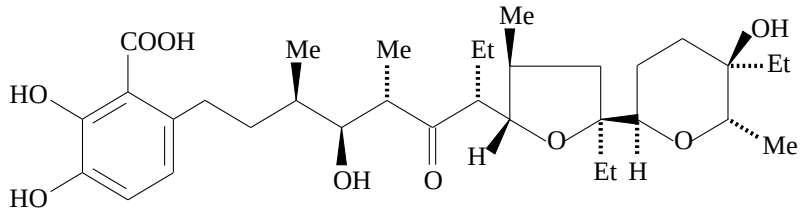
Examples:

```
\heptamethylene[a]{}{1W==\cyclopentanevi[b]{3==(yl);5Sa==\null;5Sb==\null};%
5D==O;6D==N$_{2}$}
```



Example 21.2. The terminal bonds due to `1W==\bzdrv{...}` and `7W==\fiveheterov{...}` are shorter than the other inner bonds of **21-3**, which is drawn by applying the substitution technique to the `\heptamethylenei` command.

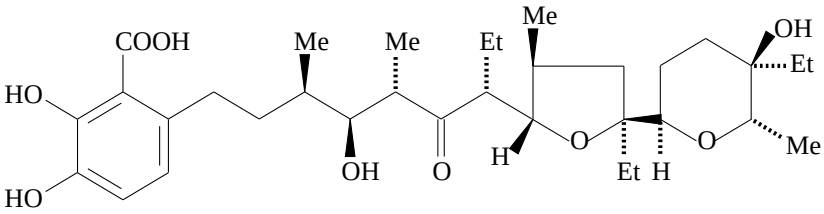
```
\heptamethylenei{}{1W==\bzdrv{1==COOH;2==(yl);5==HO;6==HO};%
3B==Me;4B==OH;5A==Me;6D==O;7A==Et;%
7W==\fiveheterov{1==O}{5==(yl);5SB==H;4GB==Me;2GA==Et;%
2Su==\sixheterovi{1==O}{6==(yl);6FA==H;3SB==OH;3SA==Et;2A==Me}}}
```



21-3

To elongate the terminal bonds described above, the structure **21-4** is drawn by applying the replacement technique to the `\nonamethylene` command.

```
\nonamethylene{%
1s==\bzdrv{1==COOH;2==(yl);5==HO;6==HO};%
9s==\fiveheterov{1==O}{5==(yl);5SB==H;4GB==Me;2GA==Et;%
2Su==\sixheterovi{1==O}{6==(yl);6FA==H;3SB==OH;3SA==Et;2A==Me}}
}{4B==Me;5B==OH;6A==Me;7D==O;8A==Et}
```



21-4

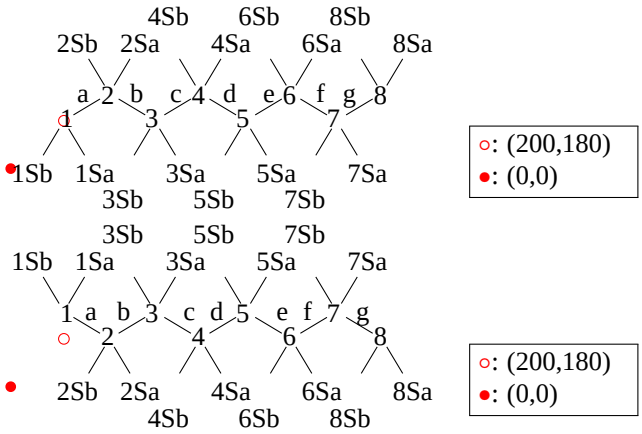
□

21.8 Octamethylenes

The XeLaTeX commands `\octamethylene` and `\octamethylenei` have two arguments ⟨atomlist⟩ and ⟨subslist⟩ as well as an optional argument ⟨bondlist⟩ (methylen.sty).

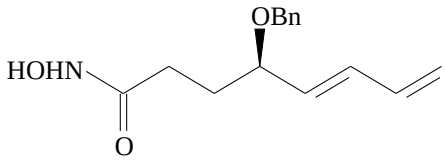
```
\octamethylene[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}
\octamethylenei[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}
```

The following diagrams show the numbering for designating substitution positions:

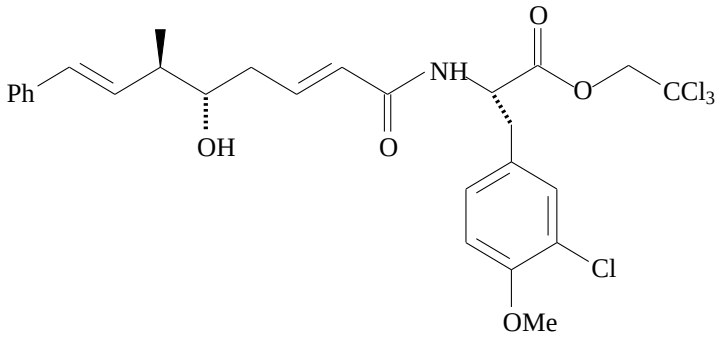


Examples:

```
\octamethylene[eg]{}{1W==HOHN;1D==O;4B==OBn}
```




```
\octamethylenei[af]{}{1W==Ph;3B==\null;4A==OH;8D==O;%
8W==\ryl(4==NH){%
5==\tetramethylene{3==O}{1==(yl);2D==O;4W==CCl$_{3}$;%
1SA==\ryl{8==\bzdrv{1==(yl);3==Cl;4==OMe}}}}}
```

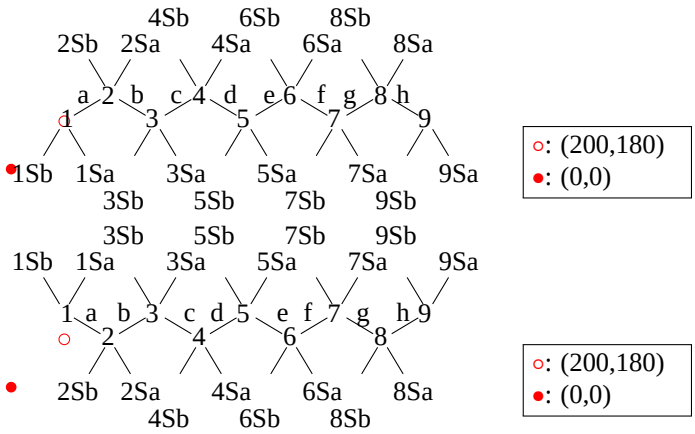


21.9 Nonamethylenes

The XeLaTeX commands `\nonamethylene` and `\nonamethylenei` have two arguments ⟨atomlist⟩ and ⟨subslist⟩ as well as an optional argument ⟨bondlist⟩ (methylen.sty).

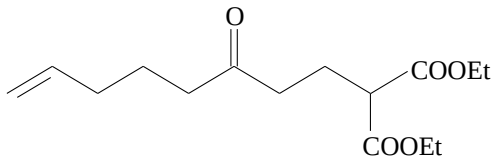
```
\nonamethylene[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}
\nonamethylenei[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}
```

The following diagrams show the numbering for designating substitution positions:

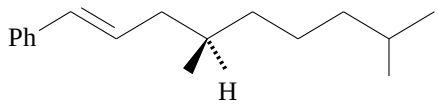


Examples:

```
\nonamethylene[a]{}{6D==O;9W==COOEt;9==COOEt}
```




```
\nonamethylenei[a]{}{1W==Ph;4SB==\null;4SA==H;8==\null}
```

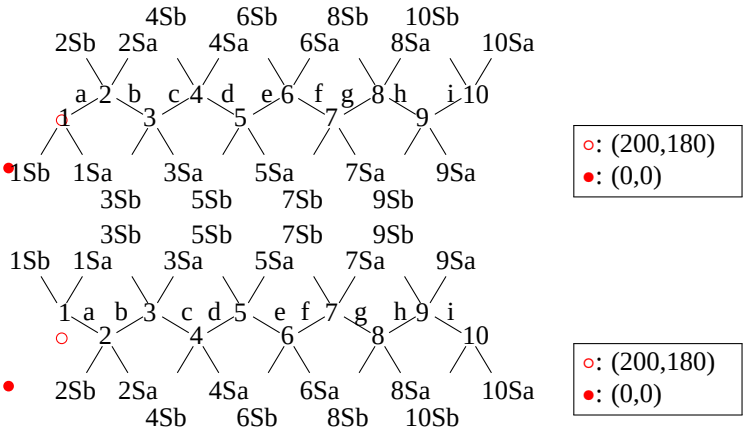


21.10 Decamethylenes

The XeLaTeX commands `\decamethylene` and `\decamethylenei` have two arguments ⟨atomlist⟩ and ⟨subslist⟩ as well as an optional argument ⟨bondlist⟩ (methylen.sty).

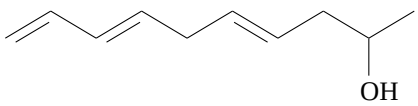
```
\decamethylene[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}
\decamethylenei[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}
```

The following diagrams show the numbering for designating substitution positions:



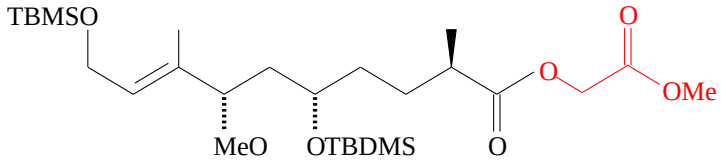
Example:

```
\decamethylene[acf]{}{9==OH}
```



Example 21.3. The terminal substituent of **21-5** is generated by the combination of `\ryl` and a (yl)-function declared in `\dimethylene` (colored in red).

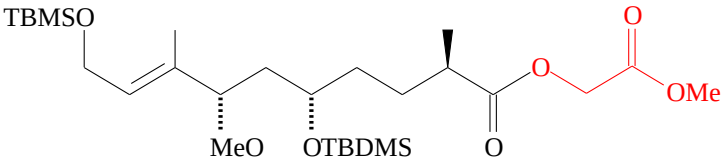
```
\decamethylenei[b]{}{1==\lmoiety{TBMSO};3==\null;4A==MeO;6A==OTBDMS;%
9B==\null;{10}D==O;%
{10}W==\ryl(4==O){5==\dimethylene{}{1==(yl);2D==O;2W==OMe}}}
```



21-5

On the other hand, the terminal substituent of **21-6** is generated by declaring a (yl)-function in `\trimethylenei` (colored in red). Compare the O—C bond in the red-colored substituent of **21-6** with the counterpart bond of **21-5**.

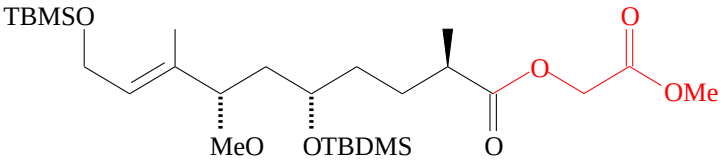
```
\decamethylenei[b]{}{1==\lmoiety{TBMSO};3==\null;4A==MeO;6A==OTBDMS;%
9B==\null;{10}D==O;%
{10}W==\trimethylenei{1==O}{1==(yl);3D==O;3W==OMe}}
```



21-6

The above-mentioned methods of drawing **21-5** and **21-6** are based on the substitution technique, where the red-colored substituents are placed in the ⟨subslist⟩ of `\decamethylenei`. A further way of drawing **21-7** is based on the replacement technique, where a (yl)-function is declared in `\tetramethylene`, which is placed in the ⟨atomlist⟩ of `\decamethylenei`, as colored in red.

```
\decamethylenei[b]{%
{10}s==\tetramethylene{2==O}{1==(yl);4D==O;4W==OMe}%
}{1==\lmoiety{TBMSO};3==\null;4A==MeO;6A==OTBDMS;%
9B==\null;{10}D==O}
```



21-7

□

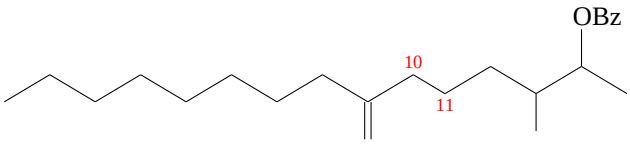
21.11 Longer Polymethylene Chains

A polymethylene chain longer than ten carbons should be written by combining two or more units selected from the above-mentioned di- to deca-methylenes.

To do this task, we regard one unit as a substituent of another unit according to the substitution technique. In this method, the code for the former unit is written in the ⟨subslist⟩ of the code for the latter. For example, the code,

```
\decamethylene{}{9D==\null;%
{10}W==\pentamethylene{}{1==(yl);3==\null;4==OBz}}
```

generates the following formula:



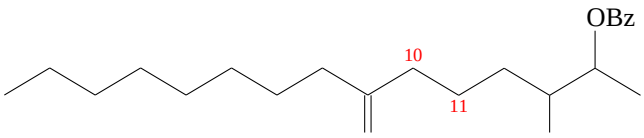
21-8

Note that the resulting structure **21-8** has a shorter bond (bond 10—11) than the remaining skeletal bonds.

Alternatively, we regard one unit as a replacement part of another unit according to the replacement technique, where the code for the former unit is written in the ⟨bondlist⟩ of the code for the latter (see spiro compounds). The same formula with slightly different appearance can be typeset by the code,

```
\decamethylene{{10}s==\hexamethylenei{}{1==(yl);4==\null;5==OBz}%
}{9D==\null}
```

which gives



21-9

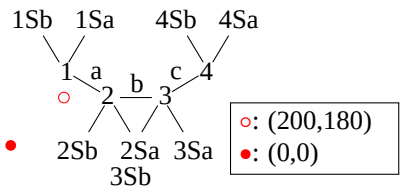
Note that the resulting structure **21-9** has the bond between 10—11 of the equal length to the remaining skeletal bonds.

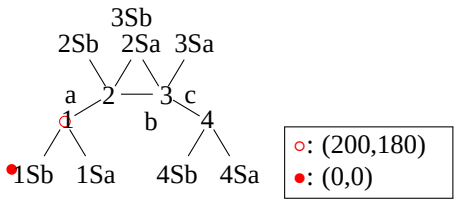
21.12 Cisoid Tetramethylenes

The XƎMTEX commands `\tetramethylenecup` and `\tetramethylenecap` have two arguments ⟨atomlist⟩ and ⟨subslist⟩ as well as an optional argument ⟨bondlist⟩ (methylen.sty).

```
\tetramethylenecup[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}
\tetramethylenecap[⟨bondlist⟩]{⟨atomlist⟩}{⟨subslist⟩}
```

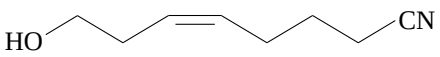
The following diagrams show the numbering for designating substitution positions:



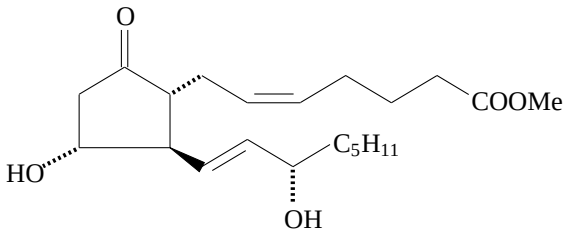


Examples:

```
\tetramethylenecap[b]{1s==\dimethylenei{}{1W==HO;2==(yl)};%
4s==\trimethylene{}{3W==CN;1==(yl)}}{}
```




```
\cyclopentanevi{1D==O;4A==HO;%
2A==\tetramethylenecup[b]{%
4s==\trimethylenei{}{1==(yl);3W==COOMe}}{1==(yl)};%
3B==\trimethylene[a]{}{1==(yl);3A==OH;3W==C$_{5}$H$_{11}$}}
```

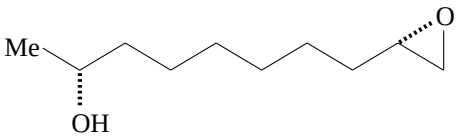


21.13 Ring Fusion to Polymethylenes

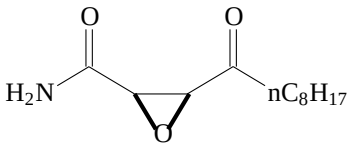
The ⟨bondlist⟩ of each “methylene” command described in Sections 21.2–21.10 is capable of accepting bond fusion by the addition technique.

Examples:

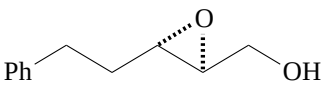
```
\nonamethylene[{h\threefusehi({cA}){3==O}{}{a}}]{}{1W==Me;1A==OH}
```




```
\tetramethylenecup[{b\threefusev({aB}{cB}){1==O}{}{B}}]%
{}{1D==O;1W==H$_{2}$N;4D==O;4W==nC$_{8}$H$_{17}$}
```




```
\pentamethylenei[{c\threefusehi({bA}{cA}){3==O}{}{a}}]{}{1W==Ph;5W==OH}
```

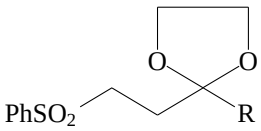


21.14 Ring Replacement to Polymethylenes

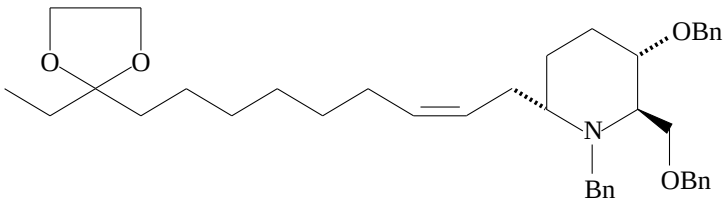
The ⟨atomlist⟩ of each “methylene” command described in Sections 21.2–21.10 is capable of accepting atom or ring replacement by the replacement technique.

Examples:

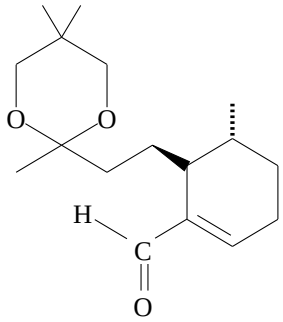
```
\trimethylenei{3s==\fiveheterov{2==O;5==O}{1==(yl)}}{1W==PhSO$_{2}$;3W==R}
```




```
\tetramethylenecup[b]{%
1s==\nonamethylenei{3s==\fiveheterov{2==O;5==O}{1==(yl)}}{9==(yl)};%
4s==\ryl{5A==\sixheterovi{1==N}{1==Bn;%
2B==\ryl{8==OBn};3A==OBn;6==(yl)}}}{}
```




```
\tetramethylene{%
2s==\sixheterovi{2==O;6==O}{4Sa==\null;4Sb==\null;1==(yl)};%
4s==\ryl{5B==\cyclohexanev[d]{6==(yl);1A==\null;%
5==\Utrigonal{0==C;1D==O;2==(yl);3==H}}}}{}
```



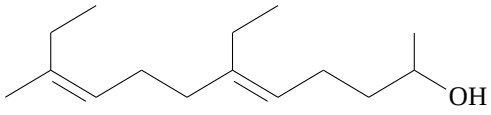
21.15 Branched Chains

21.15.1 Drawing by the Substitution Technique

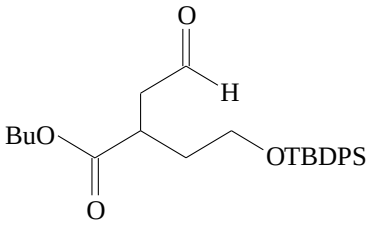
Branched chains can be drawn by using a “methylene” command with a (yl)-function according to the substitution technique. Each vertical bond due to the substitution technique is shorter than the remaining methylene bonds.

Examples:

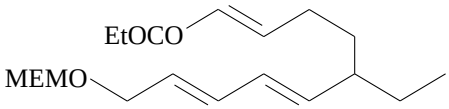
```
\decamethylene[bf]{}{%
2==\dimethylene{}{1==(yl)};6==\dimethylene{}{1==(yl)};%
{10}W==OH;{{10}}==\null}
```




```
\tetramethylene{}{1W==BuO;1D==O;4W==OTBDPS;%
2==\dimethylene{}{1==(yl);2D==O;2W==H}}
```




```
\octamethylene[bd]{}{1W==MEMO;%
6==\tetramethylenei[a]{}{4==(yl);1W==EtOCO}}
```

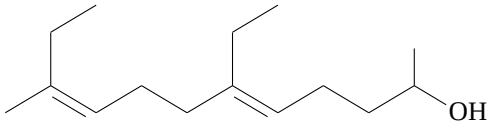


21.15.2 Drawing by the Replacement Technique

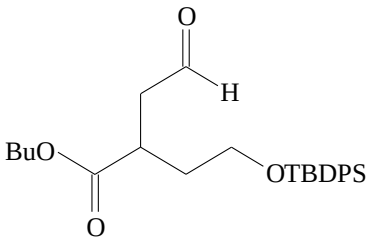
Branched chains can be alternatively drawn by the combination of `\BiFunc` with a (yl)-function declared in a "methylene" command. Each vertical bond due to this combination has a variable length, so that its length can be adjusted to be equal to those of the remaining methylene bonds by declaring `\BiFunc(0,1){200}{}{...}`.

Examples:

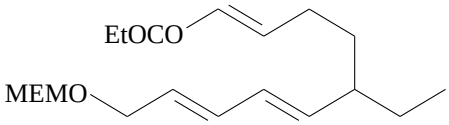
```
\decamethylene[bf]{%
2s==\BiFunc(0,1){200}{}{\dimethylene{}{1==(yl)}};%
6s==\BiFunc(0,1){200}{}{\dimethylene{}{1==(yl)}}%
}{{10}W==OH;{{10}}==\null}
```




```
\tetramethylene{%
2s==\BiFunc(0,1){200}{}{\dimethylene{}{1==(yl);2D==O;2W==H}}%
}{1W==BuO;1D==O;4W==OTBDPS}
```



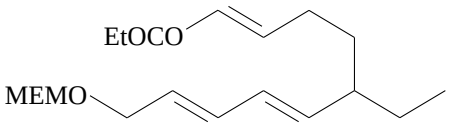

```
\octamethylene[bd]{%
6s==\BiFunc(0,1){200}{}{\tetramethylenei[a]{}{4==(yl);1W==EtOCO}}%
}{1W==MEMO}
```



The \BiFunc command is irregularly applied in the above examples, where a vacant argument {} is involved in the code \BiFunc(0,1){200}{}{...}.

Example 21.4. Because the XyMTEX system is flexible, there exist various ways to depict a target molecule. The regular application of the \BiFunc command is also capable of drawing branched chains. The last example can be drawn by the following code, where the \BiFunc command is regularly applied, as found in the code \BiFunc(0,1){200}{...}{...}.

```
\begin{XyMcompd}(1500,450)(-1250,-100){}{}
\BiFunc(0,1){200}{\octamethylene[bd]{}{6==(yl);1W==MEMO}}%
{\tetramethylenei[a]{}{4==(yl);1W==EtOCO}}%
\end{XyMcompd}
```



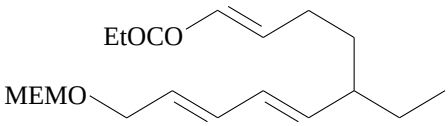
21-10

□

Example 21.5. An equivalent diagram can be drawn by doubly applying the replacement technique:

```
\begin{XyMcompd}(1550,450)(-200,150){}{}
\octamethylene[bd]{%
6s==\put(0,200){\tetramethylenei[a]{}{4==(yl);1W==EtOCO}};%
6s==\PutBondLine(0,0)(0,200){0.4pt}
}{1W==MEMO}
\end{XyMcompd}
```

where \PutBondLine is used to draw a vertical bond. This code generates the following diagram:



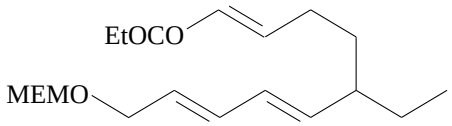
21-11

□

Example 21.6. There is another mode of depiction in which a hypothetical six-membered ring is considered:

```
\begin{XyMcompd}(1550,450)(-200,150){}{}
\octamethylene[bd%
{e\sixfusev{%
6s==\dimethylenei[a]{}{2==(yl);1W==EtOCO}%
}{}{C}[de]}%
]{}{1W==MEMO}
\end{XyMcompd}
```

The hypothetical ring is depicted by the addition technique, where the fusing unit `\sixfusev` is declared in the ⟨bondlist⟩ of the `\octamethylene`. The hypothetical ring corresponds to a part of the side chain to be drawn. The remaining part of the side chain is drawn by the replacement technique, where `\dimethylenei` is declared in the ⟨atomlist⟩ of the command `\sixfusev`. This code generates the following formula:



21-12

□

Part V

Other Building Blocks and Utilities

Polymers

22.1 Polymer Delimiters as Substituents

22.1.1 Usual Polymer Delimiters

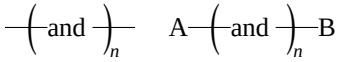
The commands `\leftpolymer` and `\rightpolymer` draw parentheses when used in the ⟨subslist⟩ of a XeLaTeX command:

```
\leftpolymer{⟨leftsubs⟩}
\rightpolymer{⟨rightsubs⟩}{⟨subscript⟩}
```

where the argument ⟨leftsubs⟩ represents a left moiety to be attached, the argument ⟨rightsubs⟩ represents a right moiety to be attached, and the argument ⟨subscript⟩ represents a subscript for designating a repetition number. These command are used in combination with the command `\sbond` or other commands for drawing appropriate bonds.

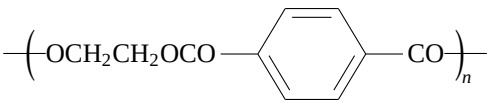
For example, they are combined the `\sbond` command (for drawing a single bond) to typeset a single bond crossed with a parenthesis:

```
\leftpolymer{}\sbond and \sbond\rightpolymer{}{n} \qquad
\leftpolymer{A}\sbond and \sbond\rightpolymer{B}{n}
```



Example 22.1. These commands are used pairwise to indicate a polymer unit, as shown in the following code for drawing poly-ethylene terephthalate.

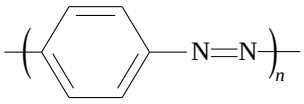
```
\bzdrh{1=={\leftpolymer{}\sbond OCH$_{2}$CH$_{2}$OCO};%
4=={CO\sbond\rightpolymer{}{n}}}
```



Note that the designation of the polymer is treated as the description of a substituent by the command `\bzdrh`. □

Example 22.2. A poly-azophenylene can be drawn in the light of the same methodology.

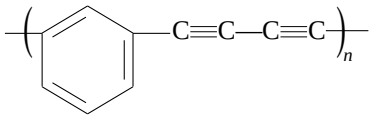
```
\bzdrh{1=={\leftpolymer{}};%
4=={N\dbond N\sbond \rightpolymer{}{n}}}
```



□

Example 22.3. The following example uses the `\bzdrv` command, where horizontal valences at the 2- and 6- positions are typeset by the bond modifier `Sa`.

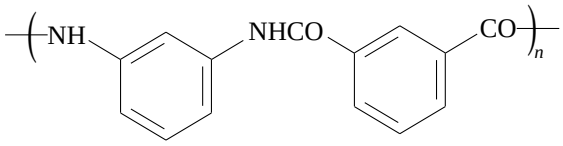
```
\bzdrv{6Sa=={\leftpolymer{}};%
2Sa=={C\tbond C---C\tbond C\sbond \rightpolymer{}{n}}}
```



□

Example 22.4. The following code for drawing poly-*m*-phenylene isophthalamide contains two successive `\bzdrv` commands in combination with `\ryl`.

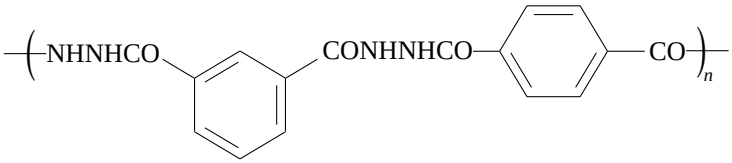
```
\bzdrv{6=={\leftpolymer{}\sbond NH};2=%
\ryl(5=NHCO~){5==\bzdrv{6==(yl);2=={CO\sbond\rightpolymer{}{n}}}}}
```



□

Example 22.5. The following code uses the commands `\bzdrv` and `\bzdrh` for drawing an aromatic polyhydrazide, where the command `\ryl` is used to insert the linking moiety CONHNHCO.

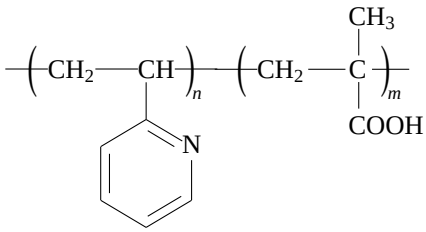
```
\bzdrv{6=={\leftpolymer{}\sbond NHNHCO};2=%
\ryl(5=CONHNHCO){4==\bzdrh{1==(yl);4=={CO\sbond\rightpolymer{}{n}}}}}
```



□

Example 22.6. The combination of `\sixheterov` and `\tetrahedral` in an outer picture environment enables us to draw 2-vinylpyridine-methacrylic acid block polymer, where `\leftpolymer` and `\rightpolymer` are used to show a polymer unit.

```
\begin{picture}(1700,900)(-200,-300)
\put(0,-535){\sixheterov[ace]{2==N}{1=={%
\hbox to0pt{\hss\leftpolymer{}\sbond CH$_{2}$\sbond}%
CH\sbond\rightpolymer{}{n}}}}
\put(900,0){\tetrahedral{0==C;1==CH$_{3}$;%
2=={\leftpolymer{}\sbond CH$_{2}$};%
3==COOH;4=={\rightpolymer{}{m}}}}
\end{picture}
```

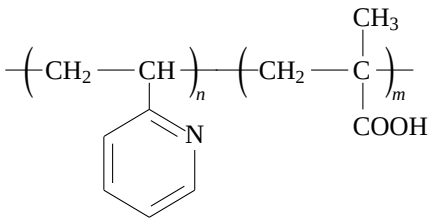


□

Example 22.7. The same block polymer can be drawn by the code:

```
\tetrahedral{0==CH$_{2}$;2==\leftpolymer{};4==%
\tetrahedral{0==CH;2==(yl);3==%
\sixheterov[ace]{2==N}{1==(yl)};4==\rightpolymer{%
\kern-2pt\leftpolymer{}\sbond\tetrahedral{0==CH$_{2}$;2==(yl);4==%
\tetrahedral{0==C;2==(yl);1==CH$_{3}$;3==COOH;4==\rightpolymer{}{m}}}%
}{n}}}
```

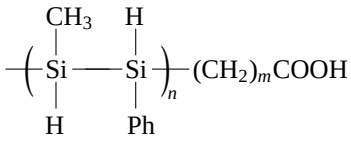
where the red inner code is the argument ⟨rightsubs⟩ of `\rightpolymer`. This code generates the following structure:



□

Example 22.8. The following example shows the use of two `\tetrahedral` commands in an outer picture environment.

```
\begin{picture}(1200,600)(150,0)
\put(0,0){\tetrahedral{%
 0==Si;1==CH$_3$;%
 2=={\leftpolymer{}};% no terminal atoms
 3==H;4==}}
\put(300,0){\tetrahedral{%
 0==Si;1==H;%
 4=={\rightpolymer{(CH$_{2}$)$_{m}$COOH}{n}};%
 2==;3==Ph}}
\end{picture}
```

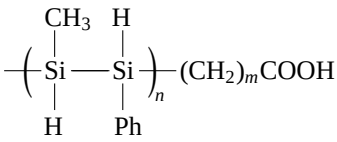


□

Example 22.9. The same polymer can be drawn by a simpler code without using the outer picture environment:

```
\tetrahedral{%
 0==Si;1==CH$_3$;2=={\leftpolymer{}};%
 3==H;4==\tetrahedral{0==Si;2==(yl);1==H;%
 4==\rightpolymer{(CH$_{2}$)$_{m}$COOH}{n};%
 2==;3==Ph}}
```

This code generates the following formula:



□

22.1.2 Changing Polymer Delimiters

The height of parentheses can be changed by using `\leftPolymer` and `\rightPolymer` in which a desired delimiter is designated as an argument.

```
\leftPolymer{⟨delimiter⟩}{⟨leftsubs⟩}
\rightPolymer{⟨delimiter⟩}{⟨leftsubs⟩}{⟨subscript⟩}
```

where the argument ⟨delimiter⟩ represents a delimiter to be used. For the other arguments, see the syntax of `\leftpolymer` or `\rightpolymer`.

Example 22.10. For example, an ethyenimine-succinimide copolymer is typeset by this technique, where parentheses are changed into brackets.

```
\leftPolymer{[}{}\sbond CH$_{2}$CH$_{2}$CONHCH$_{2}$CH$_{2}$NH%
\sbond\rightPolymer{]}{}{n}
```

□

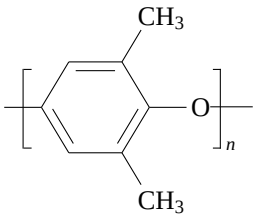
The parentheses can also be changed into brackets by using `\leftsqrpolymer` and `\rightsqrpolymer`.

```
\leftsqrpolymer{⟨leftsubs⟩}
\rightsqrpolymer{⟨rightsubs⟩}{⟨subscript⟩}
```

For the arguments, see the syntax of `\leftpolymer` or `\rightpolymer`

Example 22.11. The following example shows the usage of these commands.

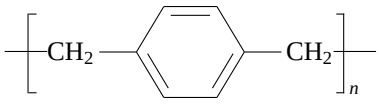
```
\bzdrh{%
1==\leftsqrpolymer{};%
3==CH$_{3}$;5==CH$_{3}$;%
4==O\sbond\rightsqrpolymer{}{n}}
```



□

Example 22.12. In a similar way, poly-*p*-xylylene is drawn as follows.

```
\bzdrh{%
1==\leftsqrpolymer{}\sbond CH$_{2}$;%
4==CH$_{2}$\sbond\rightsqrpolymer{}{n}}
```



□

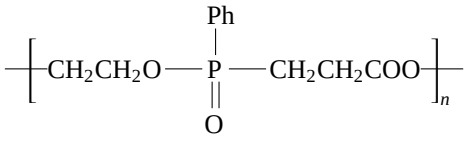
Thick-line brackets produced by `\leftSqrpolymer` and `\rightSqrpolymer` can be also used as polymer delimiters.

```
\leftSqrpolymer{⟨leftsubs⟩}
\rightSqrpolymer{⟨rightsubs⟩}{⟨subscript⟩}
```

For the arguments, see the syntax of `\leftpolymer` or `\rightpolymer`

Example 22.13. The following example uses the `\tetrahedral` command for drawing phenyldioxaphosphorane-acrylic acid copolymer, where thick-line brackets are used.

```
\tetrahedral{%
0==P;1==Ph;%
2=={\leftSqrpolymer{}\sbond CH$_{2}$CH$_{2}$O};%
3D==O;%
4=={CH$_{2}$CH$_{2}$COO\sbond\rightSqrpolymer{}{n}}}
```



□

22.2 Polymer Delimiters as Whole Enclosures

The command `\mpolymer` takes two arguments:

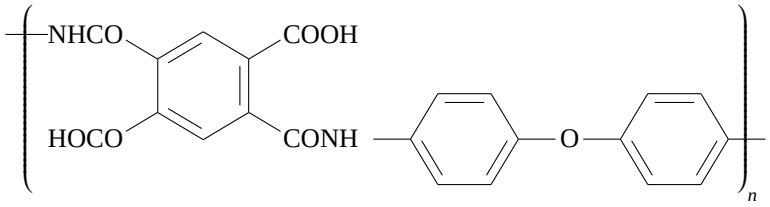
```
\mpolymer{⟨polymerunit⟩}{⟨subscript⟩}
```

where the first argument ⟨polymerunit⟩ is a polymer unit and the second ⟨subscript⟩ is a repeating number. It measures the height of the polymer unit and surrounds the unit with parentheses.

Example 22.14. To obtain a sufficient result of `\mpolymer`, the size of the monomer structure should be specified by using the LaTeX `picture` environment. Thus, the code:

```
\mpolymer{%
\begin{picture}(2650,700)(-240,200)
\put(0,158){\bzdrv{2==COOH;3==CONH;5==HOCO;6=={\sbond NHCO}}}
\put(940,0){\bzdrh{1==;4==O}}
\put(1730,0){\bzdrh{1==;4==}}
\end{picture}}{n}
```

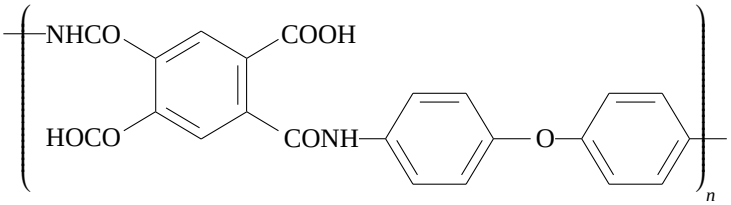
produces



□

Example 22.15. The same polymer can be drawn by a simpler code, in which the substitution technique due to (yl)-functions are applied:

```
\mpolymer{%
\begin{picture}(2500,700)(-240,42)
\put(0,0){%
\bzdrv{2==COOH;5==HOCO;6=={\sbond NHCO};3==\ryl(3==CONH){%
4==\bzdrh{1==(yl);4==\ryl(4==O){4==\bzdrh{1==(yl);4==\null}}}}}}
\end{picture}}{n}
```



where the left terminal is `6=={\sbond NHCO}` and the right terminal is `4==\null`. □

The command `\sqrpolymer` has the same function as `\mpolymer` except that it surrounds a polymer unit with thin-line brackets.

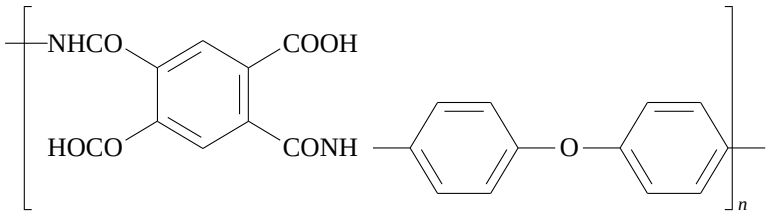
```
\sqrpolymer{⟨polymerunit⟩}{⟨subscript⟩}
```

where the first argument ⟨polymerunit⟩ is a polymer unit and the second ⟨subscript⟩ is a repeating number. The short declaration `\sqrpolymer{TEXT}{}` produces $\left[\text{TEXT}\right]$.

Example 22.16. The statement:

```
\sqrpolymer{%
\begin{picture}(2600,700)(-240,200)
\put(0,158){\bzdrv{2==COOH;3==CONH;5==HOCO;6=={\sbond NHCO}}}
\put(940,0){\bzdrh{1==;4==O}}
\put(1730,0){\bzdrh{1==;4==}}
\end{picture}}{n}
```

produces a polymer:



□

On the other hand, the command `\Sqrpolymer` surrounds a polymer unit with thick-line brackets.

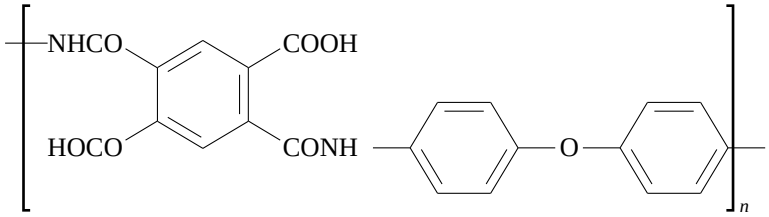
```
\Sqrpolymer{⟨polymerunit⟩}{⟨subscript⟩}
```

where the first argument ⟨polymerunit⟩ is a polymer unit and the second ⟨subscript⟩ is a repeating number.

Example 22.17. For example, the code:

```
\Sqrpolymer{%
\begin{picture}(2600,700)(-240,200)
\put(0,158){\bzdrv{2==COOH;3==CONH;5==HOCO;6=={\sbond NHCO}}}
\put(940,0){\bzdrh{1==;4==O}}
\put(1730,0){\bzdrh{1==;4==}}
\end{picture}}{n}
```

produces the following formula:



□

A scheme for preparing a polymer is typeset by combining the commands described above.

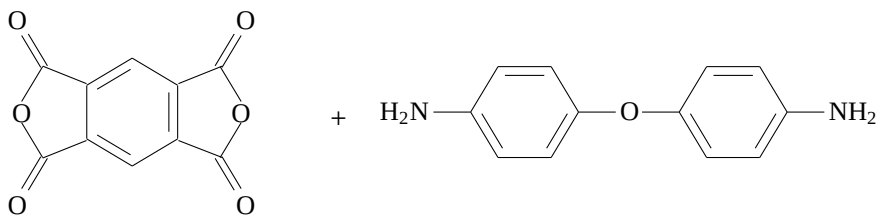
Example 22.18. Let us first prepare a macro `\pyromellitic` for drawing pyromellitic acid derivatives.

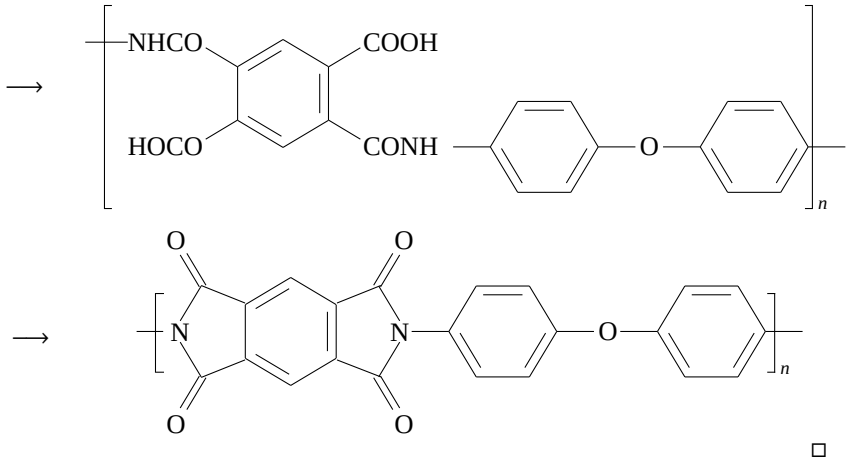
```
\def\pyromellitic#1#2#3#4{%
\begin{picture}(1200,0)(0,400)
\def\kktmp{#1}
\ifx\kktmp\empty
\put(0,0){\fiveheterohi{1==#3}{2D==O;5D==O}[bcd]}
\else
\put(0,0){\fiveheterohi{1==#3}{1==#1;2D==O;5D==O}[bcd]}
\fi
\PutBondLine(343,573)(508,507){0.4pt}%
\PutBondLine(343,227)(508,293){0.4pt}%
\put(280,-43){\bzdrv{}}%
\PutBondLine(1019,573)(854,507){0.4pt}%
\PutBondLine(1019,229)(854,293){0.4pt}%
\def\kktmp{#2}%
\ifx\kktmp\empty
\put(468,0){\fiveheteroh{1==#4}{2D==O;5D==O}[bcd]}
\else
\put(468,0){\fiveheteroh{1==#4}{1==#2;2D==O;5D==O}[bcd]}
\fi
\end{picture}}
```

The first and second arguments of the `\pyromellitic` show the presence of exocyclic valences for polymerization. The third and fourth arguments show the hetero atoms on the five-membered rings.

The preparation of a poly-pyromellitimide from pyromellitic anhydride and an diamine is illustrated as follows.

```
% the first line
\raisebox{400\unitlength}{\pyromellitic{}{}{O}{O}}
\qquad \raisebox{350\unitlength}{+} \qquad
\bzdrh{1==H$_{2}$N;4==O}
\hskip-120\unitlength
\bzdrh{1==;4==NH$_{2}$}
% the 2nd line
\begin{flushright}
\raisebox{400\unitlength}{$\longrightarrow$} \qquad
\sqrpolymer{%
\begin{picture}(2600,700)(-240,200)
\put(0,158){\bzdrv{2==COOH;3==CONH;5==HOCO;6=={\sbond NHCO}}}
\put(940,0){\bzdrh{1==;4==O}}
\put(1730,0){\bzdrh{1==;4==}}
\end{picture}}{n} \\[5pt]
% the 3rd line
\raisebox{350\unitlength}{$\longrightarrow$} \qquad
\raisebox{400\unitlength}{%
\pyromellitic{{\leftsqrpolymer{}}}{}{N}{N}}
\hskip-190\unitlength
\bzdrh{1==;4==O}
\hskip-120\unitlength
\bzdrh{1==;4=={\rightsqrpolymer{}{n}}}
\end{flushright}
```





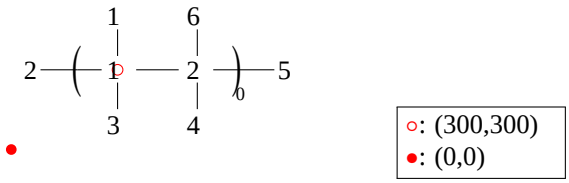
22.3 Polymer Units

22.3.1 Polyethylene Unit

The command `\polyethylene` is used to draw polyethylene derivatives, in which each substituent is designated by the ⟨subslist⟩. The syntax of this command is as follows:

```
\polyethylene[⟨auxlist⟩]{⟨centatmlist⟩}{⟨subslist⟩}
```

The following diagram shows the numbering for designating substituents and center-atom positions.



in which the same macro is used to typeset both saturated and unsaturated derivatives. The default subscript is decided to be 0 == *x*.

The optional argument ⟨auxlist⟩ is used to specify a charge on the central atoms, i.e., {*n*+} represents a + charge (or another one character) on the *n*-center.

The argument ⟨centatmlist⟩ indicates central atoms 1 and 2, *e.g.*, `1==C` and `2==Si`. A double bond and a triple bond between the central atoms can be designated by writing `0D==` an `0T==`, respectively.

The argument ⟨subslist⟩ is used to specify each substituent with a locant number and a bond modifier shown in Table 22.1, in which *n* is an Arabic numeral between 1 and 4.

Table 22.1. ⟨subslist⟩ for `\polyethylene`

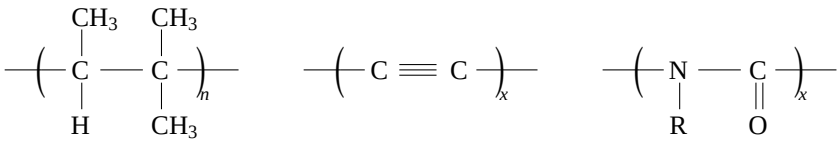
Character	Structures printed
*n*T	triple bond at *n*-atom
*n*D	double bond at *n*-atom
n or *n*S	single bond at *n*-atom
*n*A	alpha single bond at *n*-atom
*n*B	beta single bond at *n*-atom
0	the subscript of the right parenthesis

Example:

```
\polyethylene{1==C;2==C}%
```

```
 {1==CH$_{3}$;2==;3==H;4==CH$_{3}$;5==;6==CH$_{3}$;0==n}
\polyethylene{1==C;2==C;0T==}{2==;5==}
\polyethylene{1==N;2==C}{2==;5==;3==R;4D==O}
```

produce the following structures:



Note that the default subscript is decided to be *x*, as found in the last two examples. If the subscript is changed into *n* (or another character), the declaration of 0 = *n* (or another character) should be added to the ⟨subslist⟩, as found in the first example.

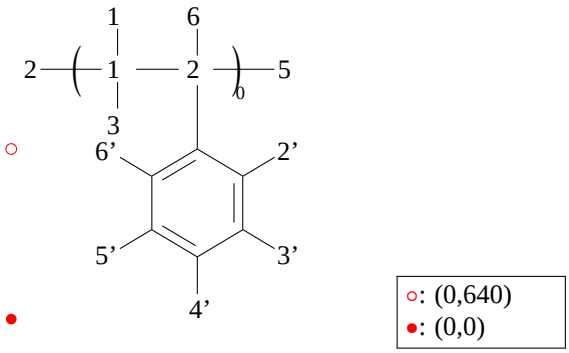
22.3.2 Polystyrene Unit

The command `\polystyrene` is used to draw polystyrene derivatives, in which substituents on both the polymer chain and the phenyl group are designated by the ⟨subslist⟩ and the ⟨phsubslist⟩, respectively.

The syntax of this command is as follows:

```
\polyethylene[⟨auxlist⟩]{⟨centatmlist⟩}{⟨subslist⟩}{⟨phsubslist⟩}
```

The following diagram shows the numbering for designating substituents and center-atom positions.



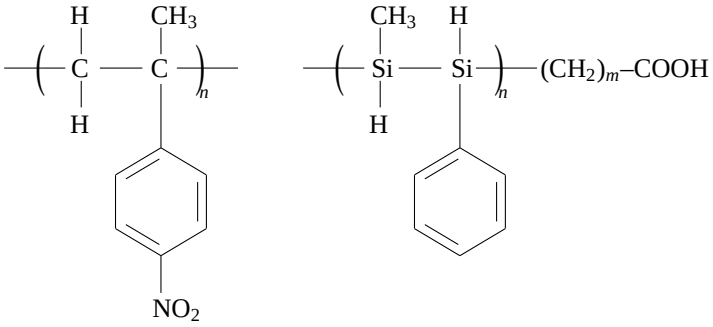
in which the same macro is used to typeset both saturated and unsaturated derivatives.

The arguments ⟨auxlist⟩, ⟨centatmlist⟩, and ⟨subslist⟩ have the same meanings as described for the command `\polyethylene` (see Table 22.1). The argument ⟨phsubslist⟩ is used to indicate substituents on the phenyl group. For example, `n` or `nS` shows the presence of a single bond at the *n*-atom of the phenyl group.

Example:

```
\polystyrene{}%
{1==H;2==;3==H;5==;6==CH$_{3}$;0==n}{4==NO$_{2}$}
\polystyrene{1==Si;2==Si}{6==H;2==;3==H;%
5=={(CH$_{2}$)$_{m}$--COOH};%
1==CH$_{3}$;0==n}{}
```

produce the following structures:


H
CH3
C
C
n
H
NO2
CH3
H
Si
Si
n
H
(CH2)m–COOH

Chapter 23

Lone Pairs and Radicals

The lewissturc package has been added to the XeLaTeX system version 4.05 and later in order to support new macros for drawing Lewis structures.

23.1 Basic Commands for Drawing Lone Pairs

The command `\overpair` supported by the lewisstruc package (included in the XeLaTeX system) draws a lone pair over an atom specified by its argument, while the command `\underpair` draws a lone pair under an atom specified by its argument ⟨atom⟩.

```
\overpair{⟨atom⟩}
\underpair{⟨atom⟩}
```

These commands can be nested freely, as follows:

```
single usage: \overpair{O} \underpair{N} \qquad
nested usage: \underpair{\overpair{O}} \overpair{\underpair{N}}
```

single usage: $\ddot{\mathrm{O}}\ \underset{\cdot\cdot}{\mathrm{N}}$ nested usage: $\ddot{\mathrm{O}}\ \underset{\cdot\cdot}{\ddot{\mathrm{N}}}$

The `\LewisSbond` command draws a lone pair in the form of a semicolon:

```
\LewisSbond
```

The Lewis structures of hydrogen fluoride and water are typeset as follows:

```
HF \qquad H\LewisSbond\overpair{\underpair{F}}\LewisSbond{} \qquad
H\sbond\overpair{\underpair{F}}\LewisSbond{} \\[5pt]
\chemform{H_{2}O} \qquad
H\LewisSbond\overpair{\underpair{O}}\LewisSbond{}H \qquad
H\sbond\overpair{\underpair{O}}\sbond{}H
```

HF H:$\underset{\cdot\cdot}{\ddot{\mathrm{F}}}$: H——$\underset{\cdot\cdot}{\ddot{\mathrm{F}}}$:

$\mathrm{H_2O}$ H:$\underset{\cdot\cdot}{\ddot{\mathrm{O}}}$:H H——$\underset{\cdot\cdot}{\ddot{\mathrm{O}}}$——H

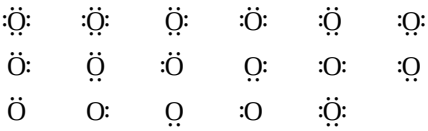
The command \lonepairA is capable of drawing at most four lone pairs, the positions of which are specified by its optional argument ⟨lonepairNo⟩.

```
\lonepairA[⟨lonepairNo⟩]{⟨atom⟩}
```

The argument ⟨atom⟩ indicates the central atom. The numbering of the four lone pairs in the argument ⟨lonepairNo⟩ is shown as follows:

where a set of numbers for drawing lone pairs (e.g., 124 etc. in an ascending order) is given as an optional argument. A list of such modes of numbering is summarized in the following example:

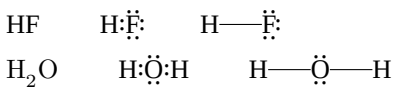
```
\lonepairA{0} \qquad
\lonepairA[1234]{0} \qquad \lonepairA[123]{0} \qquad
\lonepairA[124]{0} \qquad \lonepairA[134]{0} \qquad
\lonepairA[234]{0} \\[5pt]
\lonepairA[12]{0} \qquad \lonepairA[13]{0} \qquad
\lonepairA[14]{0} \qquad \lonepairA[23]{0} \qquad
\lonepairA[24]{0} \qquad \lonepairA[34]{0} \\[5pt]
\lonepairA[1]{0} \qquad\lonepairA[2]{0} \qquad
\lonepairA[3]{0} \qquad \lonepairA[4]{0} \qquad
\lonepairA[5]{0}
```



An element represented by two alphabets (e.g., Ne) can be attached by four lone pairs by using the \lonepairA command. Thus, the command \lonepairA[1234]{Ne} outputs Ne properly.

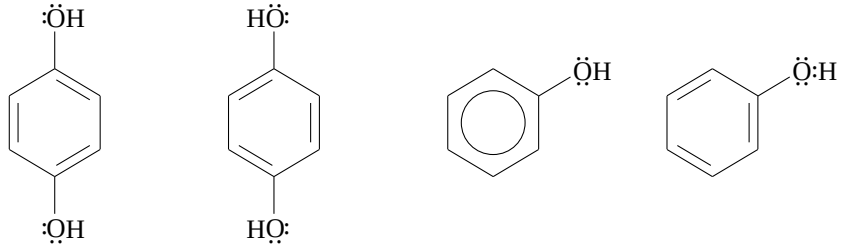
By using the command \lonepairA, the Lewis structures of hydrogen fluoride and water are alternatively typeset as follows:

```
HF \qquad H\LewisSbond\lonepairA[123]{F}
\qquad H\sbond\lonepairA[123]{F} \\[5pt]
\chemform{H_{2}O} \qquad
H\LewisSbond\lonepairA[13]{O}\LewisSbond{}H \qquad
H\sbond\lonepairA[13]{O}\sbond{}H
```



Example 23.1. An atom with lone pairs (drawn by \lonepairA) can be incorporated in a structural formula due to the XYMTEX system. The following example shows benzene derivatives with hydroxyl substituents, which contain lone pairs by means of \lonepairA.

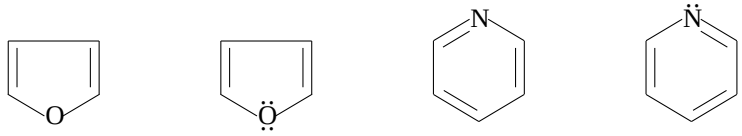
```
\bzdrv[l]{1==\lonepairA[14]{O}H;4==\lonepairA[34]{O}H}
\bzdrv[r]{1==\lmoiety{H\lonepairA[12]{O}};4==\lmoiety{H\lonepairA[23]{O}}}
\bzdrv[A]{2==\lonepairA[13]{O}H}
\bzdrv{2==\lonepairA[13]{O}\LewisSbond{}H}
```



□

Example 23.2. Although lone pairs of heterocyclic compounds are usually abbreviated in organic chemistry, they participate in nucleophilic reactions as nucleophiles. To show such participation explicitly, lone pairs are drawn by `\lonepairA` as follows:

```
\furanv{}
\fiveheterov[bd]{1==\lonepairA[13]{O}}{}
\pyridinev{}
\sixheterov[ace]{1==\lonepairA[1]{N}}{}
```



□

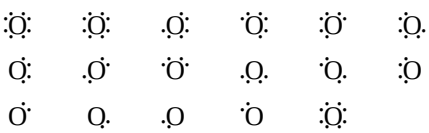
The command `\lonepairB` is capable of drawing at most four lone pairs in an alternative mode, where the positions of selected lone pairs are specified by its optional argument ⟨lonepairNo⟩.

```
\lonepairB[⟨lonepairNo⟩]{⟨atom⟩}
```

The numbering of the four lone pairs is shown as follows:

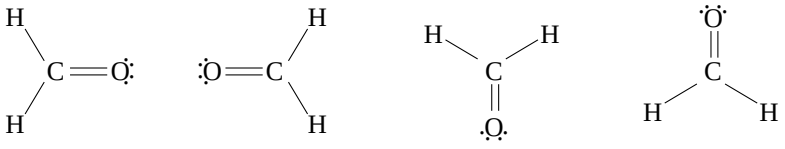
where a set of numbers for drawing lone pairs (e.g., 124 etc.) is given as an optional argument. A list of such modes of numbering is summarized in the following example:

```
\lonepairB{0} \qquad
\lonepairB[1234]{0} \qquad \lonepairB[123]{0} \qquad
\lonepairB[124]{0} \qquad \lonepairB[134]{0} \qquad
\lonepairB[234]{0} \\[5pt]
\lonepairB[12]{0} \qquad \lonepairB[13]{0} \qquad
\lonepairB[14]{0} \qquad \lonepairB[23]{0} \qquad
\lonepairB[24]{0} \qquad \lonepairB[34]{0} \\[5pt]
\lonepairB[1]{0} \qquad\lonepairB[2]{0} \qquad
\lonepairB[3]{0} \qquad \lonepairB[4]{0} \qquad
\lonepairB[5]{0}
```



Example 23.3. An atom with lone pairs (drawn by `\lonepairB`) can also be incorporated in a structural formula due to the XᵧMTEX system. The following example shows formaldehyde derivatives with a carbonyl oxygen, which contains lone pairs by means of `\lonepairB`.

```
\Ltrigonal{0==C;1D==\lonepairB[12]{O};2==H;3==H} \qquad
\Rtrigonal{0==C;1D==\lonepairB[34]{O};2==H;3==H} \qquad
\Utrigonal{0==C;1D==\lonepairB[23]{O};2==H;3==H} \qquad
\Dtrigonal{0==C;1D==\lonepairB[14]{O};2==H;3==H}
```



□

23.2 Basic Commands for Drawing Radicals

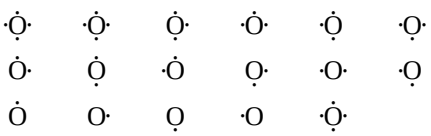
In analogy to the command `\lonepairA`, the command `\chemradicalA` is capable of drawing at most four electrons (dots), the positions of which are specified by its optional argument ⟨lonepairNo⟩.

```
\chemradicalA[⟨lonepairNo⟩]{⟨atom⟩}
```

The numbering of the four electrons is shown as follows:

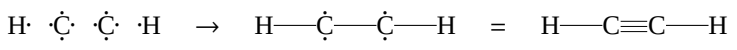
where a set of numbers for drawing unpaired electrons (e.g., 124 etc. in an ascending order) is given as an optional argument. A list of such modes of numbering is summarized in the following example:

```
\chemradicalA{O} \qquad \chemradicalA[1234]{O} \qquad
\chemradicalA[123]{O} \qquad \chemradicalA[124]{O} \qquad
\chemradicalA[134]{O} \qquad \chemradicalA[234]{O} \\[5pt]
\chemradicalA[12]{O} \qquad \chemradicalA[13]{O} \qquad
\chemradicalA[14]{O} \qquad \chemradicalA[23]{O} \qquad
\chemradicalA[24]{O} \qquad \chemradicalA[34]{O} \\[5pt]
\chemradicalA[1]{O} \qquad \chemradicalA[2]{O} \qquad
\chemradicalA[3]{O} \qquad \chemradicalA[4]{O} \qquad
\chemradicalA[5]{O} \qquad
```



Example 23.4. A Lewis structure of acetylene is drawn by using the `\chemradicalA` command.

```
\begin{ChemEquation}
\chemradicalA[2]{H} \quad \chemradicalA[1234]{C} \quad
\chemradicalA[1234]{C} \quad \chemradicalA[4]{H} \quad
\rightarrow \quad
H\sbond\chemradicalA[13]{C}\sbond\chemradicalA[13]{C}\sbond{}H
\quad = \quad H\sbond{}C\tbond{}C\sbond{}H
\end{ChemEquation}
```



(23.1)

Note the `ChemEquation` environment is supported by the chemist package of the XƎMTEX system. □

In analogy to the command `\lonepairB`, the command `\chemradicalB` is capable of drawing at most four electrons (dots), the positions of which are specified by its optional argument ⟨lonepairNo⟩.

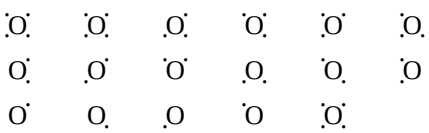
```
\chemradicalB[⟨lonepairNo⟩]{⟨atom⟩}
```

The numbering of the four electrons is shown as follows:

where a set of numbers for drawing electrons (e.g., 124 etc. in an ascending order) is given as an optional argument. A list of such modes of numbering is summarized in the following example:

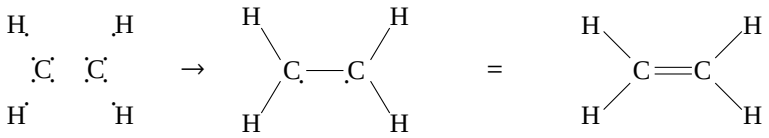
```
\chemradicalB{O} \qquad \chemradicalB[1234]{O} \qquad
\chemradicalB[123]{O} \qquad \chemradicalB[124]{O} \qquad
\chemradicalB[134]{O} \qquad \chemradicalB[234]{O} \\[5pt]
```

```
\chemradicalB[12]{O} \qquad \chemradicalB[13]{O} \qquad
\chemradicalB[14]{O} \qquad \chemradicalB[23]{O} \qquad
\chemradicalB[24]{O} \qquad \chemradicalB[34]{O} \\[5pt]
\chemradicalB[1]{O} \qquad \chemradicalB[2]{O} \qquad
\chemradicalB[3]{O} \qquad \chemradicalB[4]{O} \qquad
\chemradicalB[5]{O} \qquad
```



Example 23.5. A Lewis structure of ethylene is drawn by using the `\chemradicalB` command, where the first structure is drawn by using the picture environment of the native LaTeX 2_ε.

```
\begin{ChemEquation}
\raisebox{-18pt}{\unitlength=0.1pt
\begin{picture}(425,380)(-103,-171)
\put(-103,171){\chemradicalB[2]{H}}
\put(-103,-171){\chemradicalB[1]{H}}
\put(0,0){\chemradicalB{C}}
\put(200,0){\chemradicalB{C}}
\put(303,171){\chemradicalB[3]{H}}
\put(303,-171){\chemradicalB[4]{H}}
\end{picture}} \qquad
\rightarrow
\raisebox{-28pt}{%
\Ltrigonal{0==\chemradicalB[2]{C};2==H;3==H;%
1==\Rtrigonal{0==\chemradicalB[3]{C};1==(yl);2==H;3==H}}}
\qquad\qquad = \qquad
\raisebox{-28pt}{\ethylene{}{1==H;2==H;3==H;4==H}}
\end{ChemEquation}
```



(23.2)

□

23.3 Lewis Structures

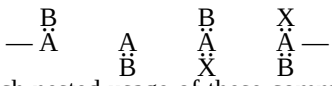
23.3.1 Atoms with an Atom through a Lone Pair

The command `\overpairover{A}{B}` is used to draw an atom (A) attached upward by another atom (B) through a lone pair, while the command `\underpairunder{A}{B}` is used to draw an atom (A) attached downward by another atom (B) through a lone pair.

```
\overpairover{⟨atomA⟩}{⟨atomB⟩}
\underpairunder{⟨atomA⟩}{⟨atomB⟩}
```

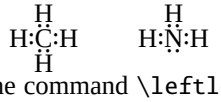
These commands can be nested freely.

```
--- \overpairover{A}{B} \qquad \underpairunder{A}{B} \qquad
\underpairunder{\overpairover{A}{B}}{X} \qquad
\overpairover{\underpairunder{A}{B}}{X} ---
```



Such nested usage of these commands allows us to draw Lewis structures of methane and ammonia, as follows:

```
H\LewisSbond\underpairunder{\overpairover{C}{H}}{H}\LewisSbond{}H \qquad
H\LewisSbond\overpairover{\underpair{N}}{H}\LewisSbond{}H
```

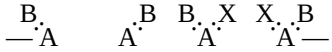


The command `\leftlonepairover{A}{B}` is used to draw an atom (A) attached by another atom (B) through a lone pair in the northwest direction, while the command `\rightlonepairover{A}{B}` is used to draw an atom (A) attached by another atom (B) through a lone pair in the northeast direction.

```
\leftlonepairover{⟨atomA⟩}{⟨atomB⟩}
\rightlonepairover{⟨atomA⟩}{⟨atomB⟩}
```

These commands can be nested freely.

```
--- \leftlonepairover{A}{B} \qquad
\rightlonepairover{A}{B} \qquad
\rightlonepairover{\leftlonepairover{A}{B}}{X} \qquad
\leftlonepairover{\rightlonepairover{A}{B}}{X} ---
```

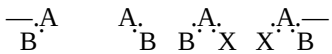


Downward counterparts of these commands are also supported by the lewisstruc package. Thus, the command `\leftlonepairunder{A}{B}` is used to draw an atom (A) attached by another atom (B) through a lone pair in the southwest direction, while the command `\rightlonepairunder{A}{B}` is used to draw an atom (A) attached by another atom (B) through a lone pair in the southeast direction.

```
\leftlonepairunder{⟨atomA⟩}{⟨atomB⟩}
\rightlonepairunder{⟨atomA⟩}{⟨atomB⟩}
```

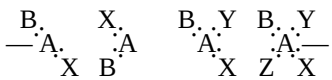
These commands can be nested freely.

```
--- \leftlonepairunder{A}{B} \qquad
\rightlonepairunder{A}{B} \qquad
\rightlonepairunder{\leftlonepairunder{A}{B}}{X} \qquad
\leftlonepairunder{\rightlonepairunder{A}{B}}{X} ---
```



These upward-type and downward-type commands can be nested freely, as exemplified by the following outputs:

```
--- \rightlonepairunder{\leftlonepairover{A}{B}}{X} \qquad
\leftlonepairover{\leftlonepairunder{A}{B}}{X} \qquad
\rightlonepairover{\rightlonepairunder{\leftlonepairover{A}{B}}{X}}{Y} \qquad
\leftlonepairunder{\rightlonepairover{%
\rightlonepairunder{\leftlonepairover{A}{B}}{X}}{Y}}{Z} ---
```



23.3.2 Tetrahedral Lewis Structures

The command `\Lewistetrahedral{A}` is capable of drawing at most four atoms through lone pairs, where the positions of selected atoms with lone pairs are specified by the argument ⟨subslist⟩.

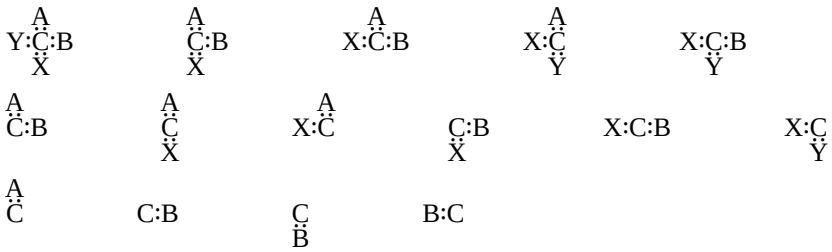
```
\LewistetrahedralA{⟨subslist⟩}
```

The numbering of the four atoms with lone pairs is shown as follows:

The argument ⟨subslist⟩ is in accord with the general syntax described in Subsection 3.2.1, where the inner argument ⟨locNo⟩ is selected from 0 to 4 as shown above and the inner argument ⟨bdmodifier⟩ is selected from none (Lewis single bond), D (Lewis double bond), T (Lewis triple bond), and N (normal single bond).

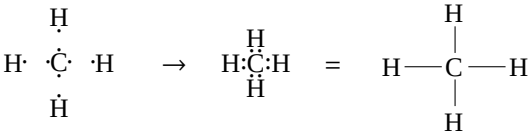
Following examples show the applicability of the command `\LewistetrahedralA`.

```
\LewistetrahedralA{0==C;1==A;2==B;3==X;4==Y} \qquad\qquad
\LewistetrahedralA{0==C;1==A;2==B;3==X} \qquad\qquad
\LewistetrahedralA{0==C;1==A;2==B;4==X} \qquad\qquad
\LewistetrahedralA{0==C;1==A;3==Y;4==X} \qquad\qquad
\LewistetrahedralA{0==C;2==B;3==Y;4==X} \\[15pt]
\LewistetrahedralA{0==C;1==A;2==B} \qquad\qquad
\LewistetrahedralA{0==C;1==A;3==X} \qquad\qquad
\LewistetrahedralA{0==C;1==A;4==X} \qquad\qquad
\LewistetrahedralA{0==C;2==B;3==X} \qquad\qquad
\LewistetrahedralA{0==C;2==B;4==X} \qquad\qquad
\LewistetrahedralA{0==C;3==Y;4==X} \\[15pt]
\LewistetrahedralA{0==C;1==A} \qquad\qquad
\LewistetrahedralA{0==C;2==B} \qquad\qquad
\LewistetrahedralA{0==C;3==B} \qquad\qquad
\LewistetrahedralA{0==C;4==B}
```



Example 23.6. A Lewis structure of methane is drawn by using the `\LewistetrahedralA` command. The first structure is drawn by using the array environment of the native LaTeX 2_ε, where `\chemradicalA` commands are used to draw component radical structures.

```
\begin{ChemEquation}
\begin{array}{ccc}
& \chemradicalA[3]{H} & \\[5pt]
\chemradicalA[2]{H} & \chemradicalA[1234]{C} & \chemradicalA[4]{H} \\[5pt]
& \chemradicalA[1]{H} & \\
\end{array}
\quad \rightarrow \quad
\LewistetrahedralA{0==C;1==H;2==H;3==H;4==H}
\quad = \quad
\raisebox{-28pt}{\tetrahedral{0==C;1==H;2==H;3==H;4==H}}
\end{ChemEquation}
```

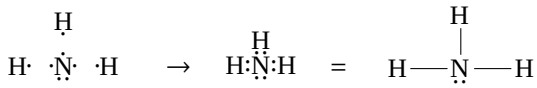


(23.3)

□

Example 23.7. A Lewis structure of ammonia is also drawn by using the `\LewistetrahedralA` command. The first structure is drawn by using the array environment of the native LaTeX 2_ε, where `\chemradicalA` commands are used to draw component radical structures. When inner math modes may cause troubles, the use of the `\mbox` command is sometimes useful as follows:

```
\begin{ChemEquation}
\raisebox{8pt}{%
$\begin{array}{ccc}
& \chemradicalA[3]{H} & \\[5pt]
\chemradicalA[2]{H} & \chemradicalA[124]{\underpair{N}} & \chemradicalA[4]{H} \\
\end{array}$}
\quad \rightarrow \quad
\LewistetrahedralA{0==N;1==H;2==H;3==\null;4==H}
\quad = \quad
\raisebox{-28pt}{\tetrahedral{0==\underpair{N};1==H;2==H;4==H}}
\end{ChemEquation}
```



(23.4)

□

The command `\LewistetrahedralB` is capable of drawing at most four atoms through lone pairs in an alternative mode, where the positions of selected atoms with lone pairs are specified by the argument ⟨subslist⟩.

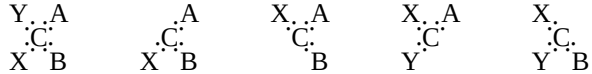
```
\LewistetrahedralB{⟨subslist⟩}
```

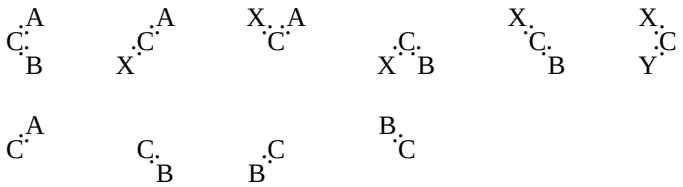
The numbering of the four atoms with lone pairs is shown as follows:

The argument ⟨subslist⟩ is in accord with the general syntax described in Subsection 3.2.1, where the inner argument ⟨locNo⟩ is selected from 0 to 4 as shown above and the inner argument ⟨bdmodifier⟩ is selected from none (Lewis single bond), D (Lewis double bond), T (Lewis triple bond), and N (normal single bond).

The following examples show the applicability of the command `\LewistetrahedralB`.

```
\LewistetrahedralB{0==C;1==A;2==B;3==X;4==Y} \qquad\qquad
\LewistetrahedralB{0==C;1==A;2==B;3==X} \qquad\qquad
\LewistetrahedralB{0==C;1==A;2==B;4==X} \qquad\qquad
\LewistetrahedralB{0==C;1==A;3==Y;4==X} \qquad\qquad
\LewistetrahedralB{0==C;2==B;3==Y;4==X} \\[15pt]
\LewistetrahedralB{0==C;1==A;2==B} \qquad\qquad
\LewistetrahedralB{0==C;1==A;3==X} \qquad\qquad
\LewistetrahedralB{0==C;1==A;4==X} \qquad\qquad
\LewistetrahedralB{0==C;2==B;3==X} \qquad\qquad
\LewistetrahedralB{0==C;2==B;4==X} \qquad\qquad
\LewistetrahedralB{0==C;3==Y;4==X} \\[15pt]
\LewistetrahedralB{0==C;1==A} \qquad\qquad
\LewistetrahedralB{0==C;2==B} \qquad\qquad
\LewistetrahedralB{0==C;3==B} \qquad\qquad
\LewistetrahedralB{0==C;4==B}
```



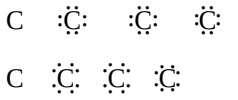


In some cases, \LewistetrahedralB is incapable of accepting a substituent derived from such a command as \lonepairB. To avoid troubles of this type, a rather dirty technique using \setbox may be effective, as shown in the following example.

```
\begingroup
\fboxrule=0pt\fboxsep=1pt
\setbox0=\hbox{\lonepairB[234]{\fbox{\kern0.6pt F}}}
\setbox1=\hbox{\lonepairB[134]{\fbox{\kern0.6pt F}}}
\setbox2=\hbox{\lonepairA[123]{\kern0.6pt F\kern0.6pt}}
\setbox3=\hbox{\LewistetrahedralA{0==B;2==\box2}}
\LewistetrahedralB{0==\box3;3==\raise1pt\box0\kern-1pt;4==\lower2pt\box1\kern-1pt}
\endgroup
```

The following examples show the difference between \LewistetrahedralA and \lonepairA as well as the difference between \LewistetrahedralB and \lonepairB.

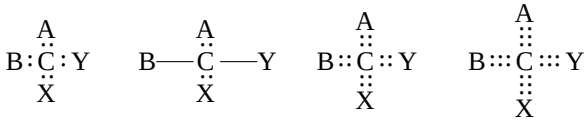
```
\LewistetrahedralA{0==C;1=={};2=={};3=={};4=={}}␣\quad
\LewistetrahedralA{0==C;1==\null;2==\null;3==\null;4==\null}␣\quad
\LewistetrahedralA{0==C;1=={␣};2=={␣};3=={␣};4=={␣}}␣\quad
\lonepairA[1234]{C}␣\\[10pt]
\LewistetrahedralB{0==C;1=={};2=={};3=={};4=={}}␣\quad
\LewistetrahedralB{0==C;1==\null;2==\null;3==\null;4==\null}␣\quad
\LewistetrahedralB{0==C;1=={␣};2=={␣};3=={␣};4=={␣}}␣\quad
\lonepairB[1234]{C}
```



23.3.3 Nested Tetrahedral Lewis Structures

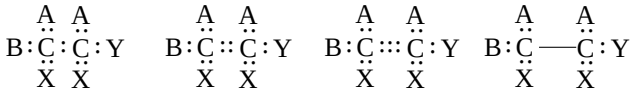
Because the command \LewistetrahedralA is incapable of drawing nested structures, another approach should be taken to to avoid such drawback. For this purpose, the lewisstruc package of the XeLaTeX system supports the command \LewisTetrahedralA, which has been defined in an alternative methodology based on the \tetrahedral command of the aliphat package of the XeLaTeX system. This means that the argument of \LewisTetrahedralA is capable of accommodating a so-called (yl)-function which is widely adopted in the XeLaTeX system. In addition, the argument of \LewisTetrahedralA supports an additional function, which gives us a tool of drawing two pairs of electrons for representing a double bond (D), three pairs of electrons for representing a triple bond (T), and a straight line for representing a single bond.

```
\LewisTetrahedralA{0==C;1==A;2==B;3==X;4==Y}
\LewisTetrahedralA{0==C;1==A;2N==B;3==X;4N==Y}
\LewisTetrahedralA{0==C;1D==A;2D==B;3D==X;4D==Y}
\LewisTetrahedralA{0==C;1T==A;2T==B;3T==X;4T==Y}
```



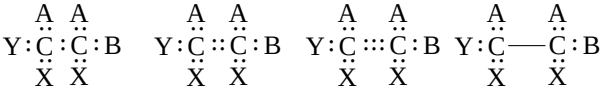
By declaring `2==(yl)` in an inner `\LewisTetrahedralA`, a substituent is produced so as to be attached to the 4-position of an outer `\LewisTetrahedralA`. Thereby, the two tetrahedral Lewis structures are linked to each other as follows:

```
\LewisTetrahedralA{0==C;1==A;2==B;3==X;%
4==\LewisTetrahedralA{2==(yl);0==C;1==A;3==X;4==Y}}
\LewisTetrahedralA{0==C;1==A;2==B;3==X;%
4D==\LewisTetrahedralA{2==(yl);0==C;1==A;3==X;4==Y}}
\LewisTetrahedralA{0==C;1==A;2==B;3==X;%
4T==\LewisTetrahedralA{2==(yl);0==C;1==A;3==X;4==Y}}
\LewisTetrahedralA{0==C;1==A;2==B;3==X;%
4N==\LewisTetrahedralA{2==(yl);0==C;1==A;3==X;4==Y}}
```



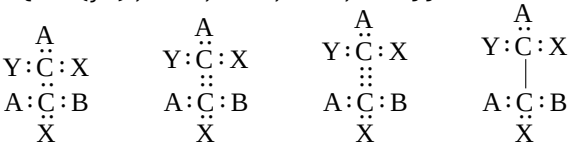
By declaring `4==(yl)` in an inner `\LewisTetrahedralA`, another substituent is produced so as to be attached to the 2-position of an outer `\LewisTetrahedralA`. Thereby, the two tetrahedral Lewis structures are linked to each other as follows:

```
\LewisTetrahedralA{0==C;1==A;4==B;3==X;%
2==\LewisTetrahedralA{4==(yl);0==C;1==A;3==X;2==Y}}
\LewisTetrahedralA{0==C;1==A;4==B;3==X;%
2D==\LewisTetrahedralA{4==(yl);0==C;1==A;3==X;2==Y}}
\LewisTetrahedralA{0==C;1==A;4==B;3==X;%
2T==\LewisTetrahedralA{4==(yl);0==C;1==A;3==X;2==Y}}
\LewisTetrahedralA{0==C;1==A;4==B;3==X;%
2N==\LewisTetrahedralA{4==(yl);0==C;1==A;3==X;2==Y}}
```



Lewis structures of vertical linkage can be drawn in a similar way.

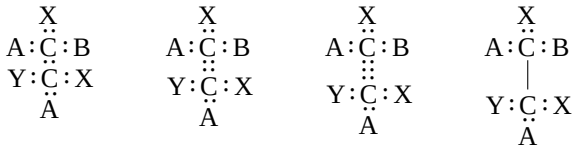
```
\LewisTetrahedralA{0==C;2==A;4==B;3==X;%
1==\LewisTetrahedralA{3==(yl);0==C;1==A;4==X;2==Y}}
\LewisTetrahedralA{0==C;2==A;4==B;3==X;%
1D==\LewisTetrahedralA{3==(yl);0==C;1==A;4==X;2==Y}}
\LewisTetrahedralA{0==C;2==A;4==B;3==X;%
1T==\LewisTetrahedralA{3==(yl);0==C;1==A;4==X;2==Y}}
\LewisTetrahedralA{0==C;2==A;4==B;3==X;%
1N==\LewisTetrahedralA{3==(yl);0==C;1==A;4==X;2==Y}}
```



Another set of Lewis structures of vertical linkage can be drawn in a similar way.

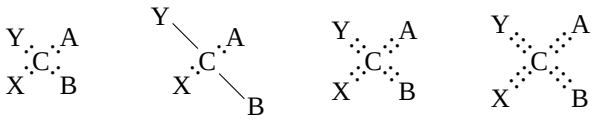
```
\LewisTetrahedralA{0==C;2==A;4==B;1==X;%
3==\LewisTetrahedralA{1==(yl);0==C;3==A;4==X;2==Y}}
\LewisTetrahedralA{0==C;2==A;4==B;1==X;%
3D==\LewisTetrahedralA{1==(yl);0==C;3==A;4==X;2==Y}}
```

```
\LewisTetrahedralA{0==C;2==A;4==B;1==X;%
3T==\LewisTetrahedralA{1==(yl);0==C;3==A;4==X;2==Y}}
\LewisTetrahedralA{0==C;2==A;4==B;1==X;%
3N==\LewisTetrahedralA{1==(yl);0==C;3==A;4==X;2==Y}}
```



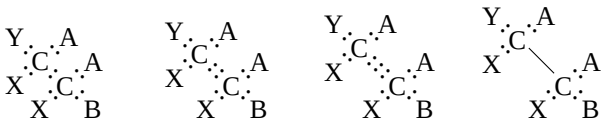
Because the command `\Lewistetrahedral B` is incapable of drawing nested structures, another approach should be taken to to avoid such drawback. For this purpose, the lewisstruc package of the XeLaTeX system supports the command `\LewisTetrahedralB`, which has been defined in an alternative methodology based on the `\squareplanar` command (renamed from `\square`) of the aliphat package of the XeLaTeX system. This means that the argument of `\LewisTetrahedralB` is capable of accommodating a so-called (yl)-function which is widely adopted in the XeLaTeX system. In addition, the argument of `\LewisTetrahedralB` supports an additional function, which gives us a tool of drawing two pairs of electrons for representing a double bond (`D`), three pairs of electrons for representing a triple bond (`T`), and a straight line for representing a single bond.

```
\LewisTetrahedralB{0==C;1==A;2==B;3==X;4==Y}
\LewisTetrahedralB{0==C;1==A;2N==B;3==X;4N==Y}
\LewisTetrahedralB{0==C;1D==A;2D==B;3D==X;4D==Y}
\LewisTetrahedralB{0==C;1T==A;2T==B;3T==X;4T==Y}
```



By declaring `2==(yl)` in an inner `\LewisTetrahedralB`, a substituent is produced so as to be attached to the 4-position of an outer `\LewisTetrahedralB`. Thereby, the two tetrahedral Lewis structures are linked to each other as follows:

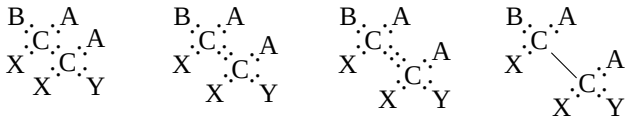
```
\LewisTetrahedralB{0==C;1==A;2==B;3==X;%
4==\LewisTetrahedralB{2==(yl);0==C;1==A;3==X;4==Y}}
\LewisTetrahedralB{0==C;1==A;2==B;3==X;%
4D==\LewisTetrahedralB{2==(yl);0==C;1==A;3==X;4==Y}}
\LewisTetrahedralB{0==C;1==A;2==B;3==X;%
4T==\LewisTetrahedralB{2==(yl);0==C;1==A;3==X;4==Y}}
\LewisTetrahedralB{0==C;1==A;2==B;3==X;%
4N==\LewisTetrahedralB{2==(yl);0==C;1==A;3==X;4==Y}}
```



By declaring `4==(yl)` in an inner `\LewisTetrahedralB`, another substituent is produced so as to be attached to the 2-position of an outer `\LewisTetrahedralB`. Thereby, the two tetrahedral Lewis structures are linked to each other as follows:

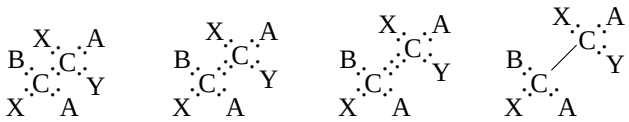
```
\LewisTetrahedralB{0==C;1==A;4==B;3==X;%
2==\LewisTetrahedralB{4==(yl);0==C;1==A;3==X;2==Y}}
\LewisTetrahedralB{0==C;1==A;4==B;3==X;%
2D==\LewisTetrahedralB{4==(yl);0==C;1==A;3==X;2==Y}}
\LewisTetrahedralB{0==C;1==A;4==B;3==X;%
2T==\LewisTetrahedralB{4==(yl);0==C;1==A;3==X;2==Y}}
```

```
\LewisTetrahedralB{0==C;1==A;4==B;3==X;%
2N==\LewisTetrahedralB{4==(yl);0==C;1==A;3==X;2==Y}}
```



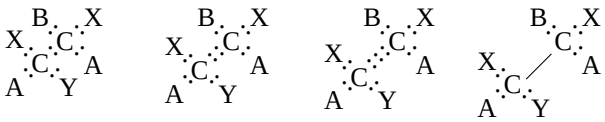
Lewis structures of northeast linkage can be drawn in a similar way.

```
\LewisTetrahedralB{0==C;2==A;4==B;3==X;%
1==\LewisTetrahedralB{3==(yl);0==C;1==A;4==X;2==Y}}
\LewisTetrahedralB{0==C;2==A;4==B;3==X;%
1D==\LewisTetrahedralB{3==(yl);0==C;1==A;4==X;2==Y}}
\LewisTetrahedralB{0==C;2==A;4==B;3==X;%
1T==\LewisTetrahedralB{3==(yl);0==C;1==A;4==X;2==Y}}
\LewisTetrahedralB{0==C;2==A;4==B;3==X;%
1N==\LewisTetrahedralB{3==(yl);0==C;1==A;4==X;2==Y}}
```



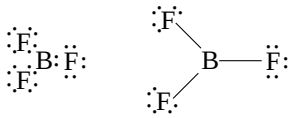
Another set of Lewis structures of southwest linkage can be drawn in a similar way.

```
\LewisTetrahedralB{0==C;2==A;4==B;1==X;%
3==\LewisTetrahedralB{1==(yl);0==C;3==A;4==X;2==Y}}
\LewisTetrahedralB{0==C;2==A;4==B;1==X;%
3D==\LewisTetrahedralB{1==(yl);0==C;3==A;4==X;2==Y}}
\LewisTetrahedralB{0==C;2==A;4==B;1==X;%
3T==\LewisTetrahedralB{1==(yl);0==C;3==A;4==X;2==Y}}
\LewisTetrahedralB{0==C;2==A;4==B;1==X;%
3N==\LewisTetrahedralB{1==(yl);0==C;3==A;4==X;2==Y}}
```



A rather dirty technique is necessary to draw a Lewis structure of boron trifluoride.

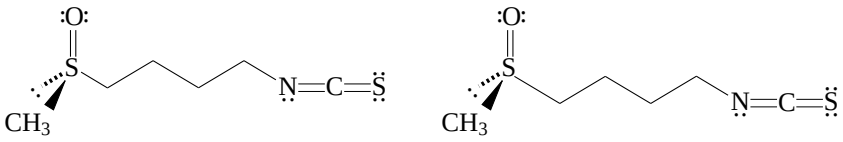
```
\begingroup
\fboxrule=0pt\fboxsep=1pt
\LewisTetrahedralB{%
0==B\LewisSbond\raisebox{-1.3pt}{\lonepairA[123]{\fbox{\kern0.6pt F}}};%
3==\raisebox{1.6pt}{\lonepairB[234]{\fbox{\kern0.6pt F}}}\kern-2pt;%
4==\raisebox{-1.9pt}{\lonepairB[134]{\fbox{\kern0.6pt F}}}\kern-2pt}
%%
\LewisTetrahedralB{%
0==B\sbond\raisebox{-1.3pt}{\lonepairA[123]{\fbox{\kern0.6pt F}}};%
3N==\raisebox{1.6pt}{\lonepairB[234]{\fbox{\kern0.6pt F}}}\kern-2pt;%
4N==\raisebox{-1.9pt}{\lonepairB[134]{\fbox{\kern0.6pt F}}}\kern-2pt}
\endgroup
```



23.4 Additional Examples for Compounds with Lone Pairs

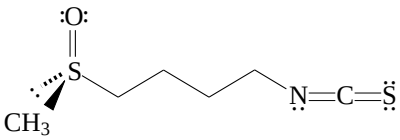
Example 23.8. 1-Isothiocyanato-(4*S*)-(methylsulfonyl)butane (an anti-cancer agent contained in broccoli) has the following structure:

```
\begin{XyMcompd}(1300,450)(100,100){}{}
\dtetrahedralS{0==S;1D==\lonepairA[24]{O};4B==CH$_{3}$;3A==\lonepairB[1]{\null};%
2==\tetramethylene{}{1==(yl);4W==\lonepairA[3]{N}\dbond C\dbond\lonepairA[13]{S}}}
\end{XyMcompd}
\qquad
\begin{XyMcompd}(1400,450)(100,100){}{}
\dtetrahedralS{0==S;1D==\lonepairA[24]{O};4B==CH$_{3}$;3A==\lonepairB[1]{\null};%
0==\phantom{S}%
\pentamethylenei{}{1==(yl);5W==\lonepairA[3]{N}\dbond C\dbond\lonepairA[13]{S}}}
\end{XyMcompd}
```



The latter structure has a more plausible length of an S—C bond. An alternative code can typeset the same compound:

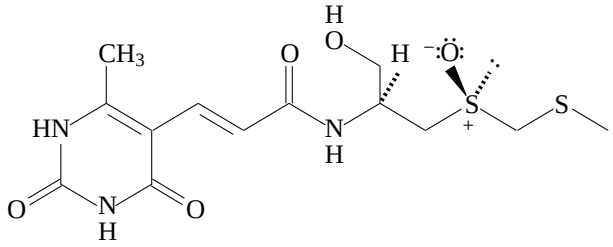
```
\begin{XyMcompd}(1400,450)(100,100){}{}
\dtetrahedralS{0==%
\pentamethylenei{1==S}{1==(yl);%
5W==\lonepairA[3]{N}\dbond C\dbond\lonepairA[13]{S}};%
1D==\lonepairA[24]{O};4B==CH$_{3}$;3A==\lonepairB[1]{\null}}
\end{XyMcompd}
```



□

Example 23.9. The S═O bond of a sulfoxide can be regarded as being delocalized to give S^{+}——O^{-}. For example, the sulfoxide part of sparsomycin is drawn by means of the following code:

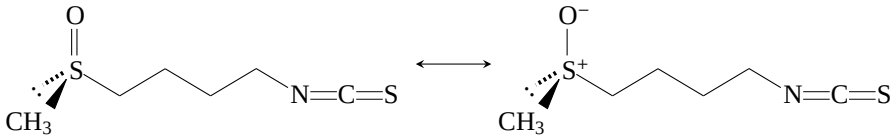
```
\begin{XyMcompd}(2100,800)(100,200){}{}
\sixheterov[a]{4==\downnobond{N}{H};6==\llap{H}{N};
2s==\nonamethylene[b]{5==\downnobond{N}{H};8==\downnobond{S}{$^{+}$};%
9s==\trimethylene{2==S}{1==(yl)}}
{1==(yl);4D==O;6SA==H;6==\dimethylenei{1==\upnobond{O}{H}}{2==(yl)};%
8SB==\llap{$^{-\:}$}\lonepairA[124]{O};8SA==\kern4pt\nelonepair}}%
{1==CH$_{3}$;3D==O;5D==O}
\end{XyMcompd}
```



□

Example 23.10. It should be noted that the organochemical convention allows us to omit lone pairs if unnecessary. Thus, the nitrogen atoms and the oxygen atoms (except the oxygen of the sulfoxide moiety) in the above structural formula of sparsomycin have no information on lone pairs. As a further example, the formula of 1-isothiocyanato-(4*S*)-(methylsulfonyl)butane is allowed to be represented by an abbreviated form, where the lone pairs except that of the sulfur atom (necessary to show the (4*S*)-configuration) are omitted as follows.

```
\begin{XyMcompd}(1400,450)(100,100){}{}
\dtetrahedralS{0==%
\pentamethylenei{1==S}{1==(yl);5W==N\dbond C\dbond S};%
1D==O;4B==CH$_{3}$;3A==\lonepairB[1]{\null}}
\end{XyMcompd}
\reactlrarrow{0pt}{1cm}{}{}
\begin{XyMcompd}(1400,450)(100,100){}{}
\dtetrahedralS{0==%
\pentamethylenei{1==S\rlap{$^{+}$}}{1==(yl);5W==N\dbond C\dbond S};%
1==O$^{-}$;4B==CH$_{3}$;3A==\lonepairB[1]{\null}}
\end{XyMcompd}
```



The right canonical formula shows that unnecessary lone pairs can be omitted even for canonical formulas with formal charges. □

Part VI

Techniques for Combining Structures

Chapter 24

LaTeX Picture Environment for Combining Structures

24.1 General Remarks

24.1.1 Coordinates of the Picture Environment

The macros described in the other chapters of this manual can be combined to construct a more complicated structural formula. This treatment is based on the fact that two or more picture environments of LaTeX can be nested, recognizing each inner picture environment as a LaTeX picture box.

A picture environment of LaTeX is set up with the following statement:

```
\begin{picture}(Lx, Ly)(Sx, Sy),
⋮
\end{picture}
```

This command produces an $L_x \times L_y$ area for drawing a structural formula, where the origin (0, 0) can be shifted by giving differences (S_x, S_y).

The `\put(`P_x, P_y`)` command places an inner picture box (*e.g.*, a fragment created by a macro of the present paper) so that the reference point of the inner picture is located on the (P_x, P_y) point of the outer picture environment.

24.1.2 Reference Points and Inner Origins

A XeLaTeX command is based on an inner picture environment, which has an original point for drawing a structure and a set of sifted values. Suppose the definition of the macro contains an inner picture environment represented by

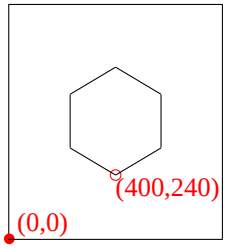
```
\begin{picture}(ℓx, ℓy)(sx, sy).
```

The point (s_x, s_y) of the inner environment becomes the (0,0) point of the structure generated by the XeLaTeX command. This point is called the reference point (or control point) of the XeLaTeX command in the present manual. On the other hand, the origin of the inner environment becomes the $(-s_x, -s_y)$ point of the generated structure. It is called the inner origin of the XeLaTeX command.

For example, the macro `\cyclohexanev` is defined on the basis of an inner picture environment:

```
\begin{picture}(800, 880)(-400, -240).
```

Thereby, the command `\cyclohexanev` generates a skeleton,



in which the symbol ○ represents the inner origin and the symbol ● represents a reference point. The area (domain) of the resulting skeleton is surrounded in a 800 × 880 frame box. As a result, the inner origin is referred to as the (400, 200) point of the resulting macro; and the inner (−400, −240) point is regarded as the new origin (0, 0), which is the reference point (control point) of the macro.

Each macro is characterized by the reference point and the inner origin, which are shown in a framed box beside the specification of the macro. The reference point and the inner origin of each macro are revealed by declaring `\origpttrue` in the preamble of a manuscript. Then, they are printed with the symbols ○ and ●; and the values of them appear on the display. For example, the above cyclohexane structure is typeset by the following statement:

```
{\origpttrue
\begin{center}
\cyclohexanev{}
\end{center}}
```

or by an equivalent statement:

```
\begin{xymspec}
\cyclohexanev{}
\end{xymspec}
```

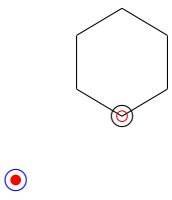
For the reference point and the inner origin of `\cyclohexanev`, see also Section 7.2.

24.1.3 Setting Coordinates

The command `\put` typesets an object, which may be a character string, a structure generated with a macro, or others. When a XeLaTeX command is written as an argument of the command `\put` in an outer picture environment, a structure due to the XeLaTeX command is typeset so that the reference point of the macro is placed on the point designated by the `\put` command. For example,

```
{\origpttrue
\begin{picture}(1000,700)(0,0)
\put(0,0){\cyclohexanev{}}
\put(0,0){\bluex{\circle{80}}}
\put(400,240){\circle{80}}
\end{picture}
}
```

produces



The reference point with ● is encircled by an outer circle representing the origin of the outer picture environment. The inner origin represented with an open circle is encircled by an outer circle centered at the (400, 240) point of the outer environment, resulting in a double circle.

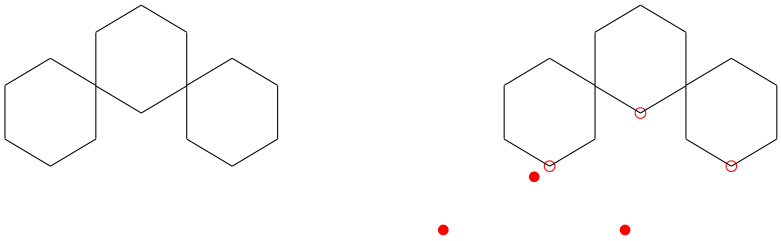
Because we adopt a bond length equal to 200 and a bond slope of (5, 3) or (3, 5), such values as 200, 171, and 103 (and any combinations of these values) appear frequently in typesetting combined structures. Note

that 171 is approximately equal to $200 \times (5/\sqrt{34})$ and 103 is approximately equal to $200 \times (3/\sqrt{34})$, where we have $\sqrt{3^2 + 5^2} = \sqrt{34}$ for both the slopes (5, 3) and (3, 5).

Example 24.1. For example, a spiro compound can be typeset by the statement:

```
\begin{picture}(1200,900)(0,0)
\put(0,0){\cyclohexanev{}}
\put(342,200){\cyclohexanev{}}
\put(684,0){\cyclohexanev{}}
\end{picture}
```

The resulting spiro structure is found as follows:



where the right-hand structure is to show the reference points and the inner origins of the fragments used. In this case, the shifted values (−400, −240) of each fragment are equal to those of another fragment, since each fragment is generated by the same macro. Hence, the argument coordinates of the `\put` can be calculated without considering such shifted values. Thus, the value 342 is equal to 171×2, and 684 is equal to 171×4. □

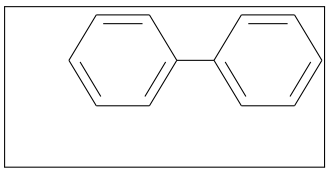
24.2 Combination of Macros Through a Bond

Since each of the macros described in the other chapters of the present manual is based on a picture environment, one of the simplest ways of combining structures is to place individual structures into an outer picture environment. Such combination of macros increases the variety of structural diagrams.

In order to illustrate the method of calculating coordinates, we take the drawing of biphenyl as the first example:

```
\begin{picture}(1200,600)(0,0)
\put(0,0){\bzdrh{4==}}
\put(546,0){\bzdrh{}}
\end{picture}
```

This statement produces the following structure:



which is surrounded by a 1200 × 600 frame generated by the `\fbox` command with the setting of `\fboxsep=0pt`. The first argument of each `\put` command represents the coordinates of the point on which the structure is printed.

The inner origin of the macro `\bzdrh` is the leftmost position of the benzene ring. The structure typeset by the command `\put(0,0){\bzdrh{4==}}` has a rightmost terminal point at (546, 0) with respect to the inner picture environment.[a] The value 546 is calculated by 406 + 140, where 406 is the length of the horizontal hexagon (= 103 + 200 + 103) and 140 is the bond length produced by the argument `{4==}`.

The command `\put(546,0){\bzdrh{}}` prints another benzene ring so that the inner origin of this benzene is placed on the terminal position of the former benzene ring. Note again that the argument coordinates

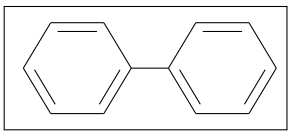
[a] The absolute coordinates with respect to the outer picture environment is (546 + 400, 0 + 240) in this case.

of \put can be calculated without considering such shifted values, (400, 240), since each of the fragments is generated by the same XyMTeX command \bzdrh.

To estimate the correct area (domain) of biphenyl, the following code with declaring \fbox is input

```
\fbox
{%
\begin{picture}(1000,400)(200,200)
\put(0,0){\bzdrh{4==}}
\put(546,0){\bzdrh{}}
\end{picture}%
}
```

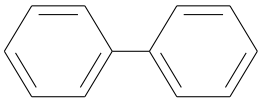
where the area (1000, 400) and the shift values (200,200) are determined in a trial-and-error fashion. Thereby we obtain



If a structural ID number is necessary, the commands \compd and \label are declared after the command \fbox is commented out, i.e.,

```
\begin{tabular}{c}
%\fbox
{%
\begin{picture}(1000,400)(200,200)
\put(0,0){\bzdrh{4==}}
\put(546,0){\bzdrh{}}
\end{picture}%
}
\\
\compd\label{cpd:biphenyl}
\\
\end{tabular}
```

where the tabular environment is used to align the structural diagram and the ID number vertically. Thereby, we obtain



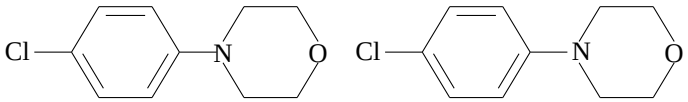
24-1

The compound ID number can be referred to by using \cref command. Thus, the reference description such as \cref{cpd:biphenyl} typesets the ID **24-1**.

Example 24.2. Let us draw 1-chloro-4-morphorinobenzene by means of two different ways.

```
\begin{picture}(1200,600)(0,0)
\put(0,0){\bzdrh{1==Cl;4==}}
\put(546,0){\sixheteroh{1==N;4==O}{}}
\end{picture}
\qquad
\begin{picture}(1200,600)(0,0)
\put(0,0){\bzdrh{1==Cl;4==N}}
\put(566,0){\sixheteroh{1==\null;4==O}{}}
\end{picture}
```

These statements produce essentially the same structure:



24-2 **24-3**

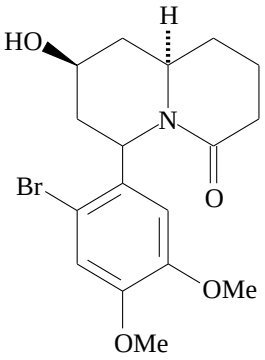
It should be noted that `{4==}` in ⟨subslist⟩ produces a bond without a substituent at the 4-position of the benzene ring, while `1==\null` in ⟨atomlist⟩ creates a vacancy to accomodate the nitrogen atom. In other words, the nitrogen atom of the first formula is regarded as a ring nitrogen of the morphorine ring, while the nitrogen of the second formula is considered to be a substituent of the benzene ring. □

The following example **24-4** illustrates a more complicated structure with a vertical bond linking two fragment structures.

Example 24.3. Thus, the statement:

```
\begin{picture}(1000,1350)(-50,-550)
\put(0,0){\decaheterov{4a==N}{4D==O;7B==HO;{{10}A}==H}}
\put(0,-546){\bzdrv{1==;3==OMe;4==OMe;6==Br}}
\end{picture}
```

prints the following diagram:



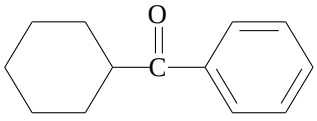
24-4

The first argument of each `\put` command represents the coordinates of the point on which the structure is printed. The value −546 is calculated by 140 (bond length) + 406 (the height of the hexagon = 103 + 200 + 103), because the inner origin of the structure printed by `\decaheterov` is position 5 (the left carbon atom adjacent to the nitrogen atom) and that of the latter structure is position 4 (the bottom carbon attached by the methoxy group). □

Example 24.4. The following example **24-5** illustrates a combined structure in which two cyclic substructures are linked through an aliphatic unit

```
\begin{picture}(1200,450)(200,200)
\put(0,0){\cyclohexaneh{4==}}
\put(754,0){\bzdrh{1==}}
\put(520,100){\tetrahedral{0==C;1D==O}}
\end{picture}
```

This statement produces



24-5

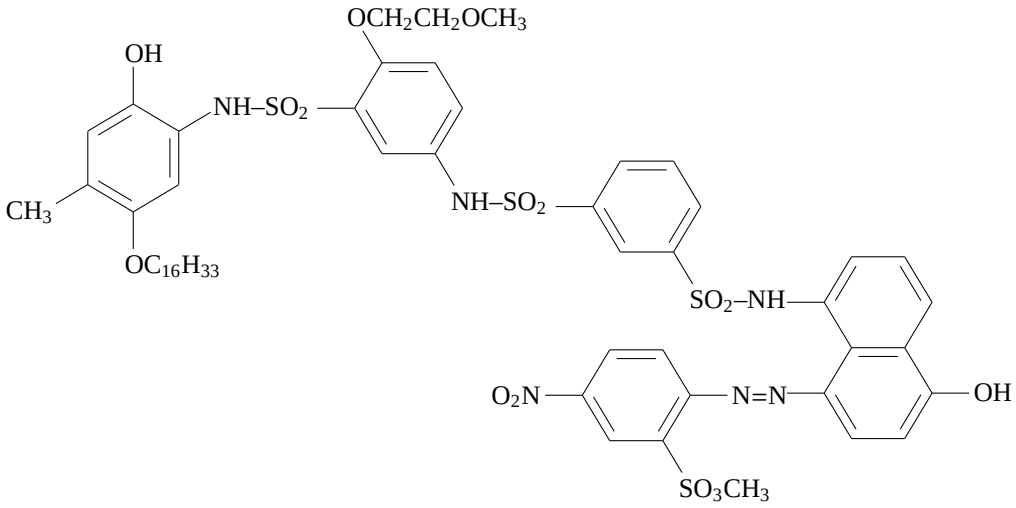
The calculation of the values for `\tetrahedral` is slightly complicated, since its inner origin is different from those of the other commands. The right terminal position due to the `\cyclohexaneh` is the point (546, 0), the x-coordinate of which is equal to the length of a benzene ring (406) plus a bond length (140).

The left terminal position due to the \bzdrh is the point (614, 0), because 754 − 140 = 614. Then, the aliphatic unit (\tetrahedral) should be placed at the average position of *x*-coordinate (546+614)/2 = 580. Since the inner origin of the the \cyclohexaneh is (400, 240) and that of the \tetrahedral is (300, 300), the *x*-coordinate is calculated to be 580 − (300 − 240) = 520 while the *y*-coordinate is calculated to be 400 − 300 = 100. □

Example 24.5. We have reported an article on dye releasers for instant color photography, in which a variety of structural formulas have been typeset by means of original utilities of the LaTeX picture environment [1]. The present XeTeX provides us with a more versatile tool of drawing such complex molecules. Thus, the formula of a cyan dye releaser **24-6** for instant color photography is typeset by the statement:

```
\begin{picture}(3800,1900)(-50,-850)
\put(0,0){\bzdrv{1==OH;2==NH--SO$_{2}$;4==OC$_{16}$H$_{33}$;5==CH$_{3}$}}
\put(993,230){\bzdrh{1==;2==OCH$_{2}$CH$_{2}$OCH$_{3}$;%
5==NH--SO$_{2}$}}
\put(1890,-140){\bzdrh{1==;5==SO$_{2}$--NH}}
\put(2600,-900){\naphdrh{1==;5==OH;8==}}
\put(1850,-850){\bzdrh{1==O$_{2}$N;5==SO$_{3}$CH$_{3}$;4==N=N}}
\end{picture}
```

These commands produce the following structure:



24-6 □

24.3 Ring Fusion in the LaTeX Picture Environment

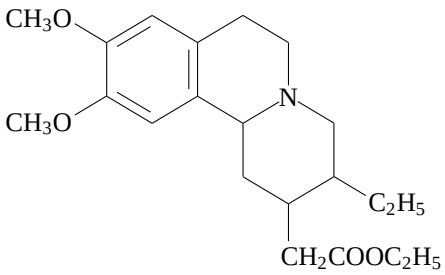
As described in Section 3.1, XeTeX commands for general use (\ComGen) has an optional argument ⟨delbdlist⟩ for deleting skeletal bonds. Hence, each command listed in Table 3.1 can be used as a building block for ring fusion after deletion of appropriate skeletal bonds.[b]

Example 24.6. To illustrate the features of ring fusion in the LaTeX picture environment, let us re-examine the structure **4-21**, which has been drawn alternatively by using \sixfusev according to the addition technique (Section 4.4). Thus, the code based on the LaTeX picture environment:

```
\begin{picture}(1700,1000)(-200,-300)
\put(0,0){\decaheterov[fhk]{3==N}{6==CH$_3$O;7==CH$_3$O}}
\put(513,-303){\sixheterov{1==\null}%
{3==C$_2$H$_5$;4==CH$_2$COOC$_2$H$_5$}[f]}
\end{picture}%
```

[b] The old commands \sixunitv and \fiveunitv are replaced by \sixheterov and \fiveheterov, because the skeletal-bond deletion due to ⟨delbdlist⟩ is available in the latter commands (as \ComGen).

produces the following structural diagram:

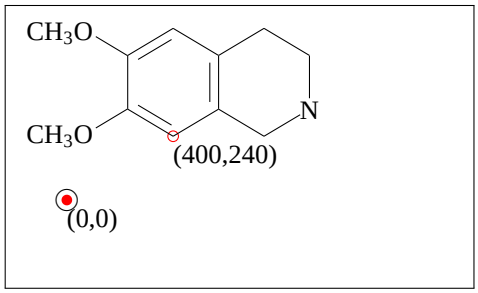


24-7 (= **4-21′**)

which is equivalent to **4-21**.

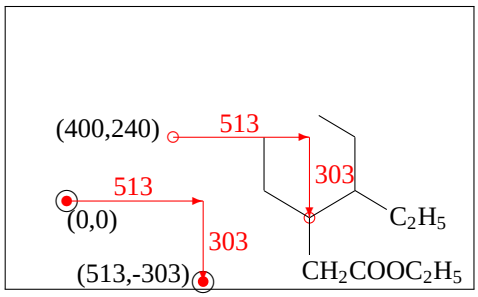
In order to examine the details of the combination for drawing **24-7**, let us typeset the structure with the first command:

```
\decaheterov[fhk]{3==N}{6==CH$_3$O;7==CH$_3$O}
```



and separately the structure with the second command:

```
\sixheterov{1==\null}%
{3==C$_2$H$_5$;4==CH$_2$COOC$_2$H$_5$}[f]
```



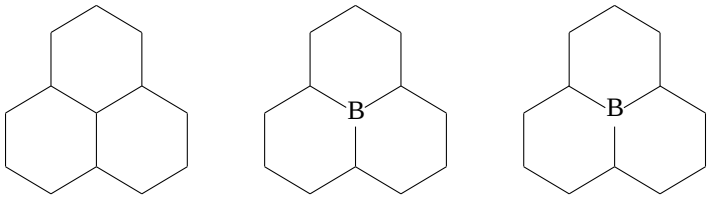
It should be noted that argument ⟨atomlist⟩ in the `\sixheterov` macro contains the assignment '`1==\null`' which assures the vacant bridgehead position. This vacancy is occupied by the bridgehead nitrogen printed by the `\decaheterov` macro. The coordinate $(513, -303)$ is calculated by the bond lengths at issue, i.e., $171 + 171 + 171 = 513$ for the *x*-direction and $200 + 103 = 303$ for the *y*-direction. □

Example 24.7. The following examples illustrate combinations of `decaheterov` and `\sixheterov` to produce a borane and the related carbocycle.

```
\begin{picture}(750,800)(200,200)
\put(0,0){\decaheterov{}{}}
\put(171,303){\sixheterov{}{}[cd]}
\end{picture}
\qquad
\begin{picture}(750,800)(200,200)
\put(0,0){\decaheterov{8a==B}{}}
\put(171,303){\sixheterov{}{}[cd]}
\end{picture}
```

```
\qquad
\begin{picture}(750,800)(200,200)
\put(0,0){\sixheterov{2==\null}{}[a]}
\put(342,0){\sixheterov{}{}[ef]}
\put(171,303){\sixheterovi{1==B}{}}
\end{picture}
```

These statements produce the following structures.



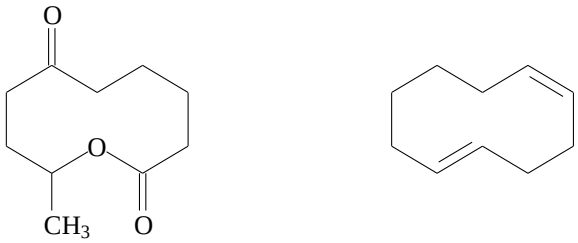
The second and third examples above show alternative ways to depict the carborane. Note that the argument `{2==\null}` in the third example is necessary to print the desired structures. □

For illustrating the wide applicability of the technique using XeLaTeX commands as building-blocks, we show several examples for the combination of two or more building blocks.

Example 24.8. The following two exmaples involve a combination of two `\sixheterov` commands.

```
\begin{picture}(1200,900)(0,0)
\put(0,0){\sixheterov{3==O}{1D==O;4==CH$_{3}$}[b]}
\put(342,0){\sixheterov{5==\null}{4D==O}[e]}
\end{picture}
\qquad
\begin{picture}(1200,900)(0,0)
\put(0,0){\sixheterov[c]{}{}[b]}
\put(342,0){\sixheterov[a]{}{}[e]}
\end{picture}
```

These statements provide

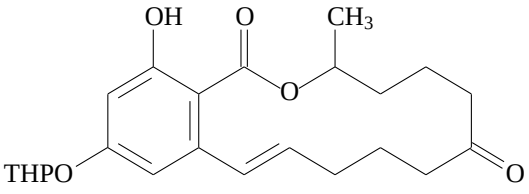


□

Example 24.9. The following example involves a combination of three `\sixheterov` commands and one `\bzdrv` command.

```
\begin{picture}(1900,700)(-150,200)
\put(0,0){\bzdrv[r]{1==OH;5==THPO}}
\put(342,0){\sixheterov[c]{2==O}{1D==O}[be]}
\put(684,0){\sixheterov{6==\null}{1==CH$_{3}$}[be]}
\put(1026,0){\sixheterov{}{3D==O}[e]}
\end{picture}
```

This statement provides

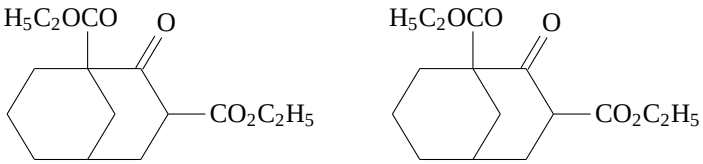


This type of drawing is akin to the addition technique with skeletal bond deletion, which is an effective method to depict large rings. □

Example 24.10. A bicyclo[3.3.1]nonane is typeset by this technique.

```
\begin{picture}(1200,600)(200,200)
\put(0,0){\cyclohexaneh{3Sa==\lmoiety{H$_{5}$C$_{2}$OC\rlap{O}}}}
\put(200,0){\sixheteroh{}{3D==O;4==CO$_{2}$C$_{2}$H$_{5}$}[af]}
\end{picture}
\qquad
\begin{picture}(1200,600)(200,200)
\put(0,0){\cyclohexaneh{3Sa==\lmoiety{H$_{5}$C$_{2}$OC\rlap{O}}}}
\put(200,0){\fiveheteroh{}{2D==O;1==CO$_{2}$C$_{2}$H$_{5}$}[c]}
\end{picture}
```

These statements provide equivalent results as follows:

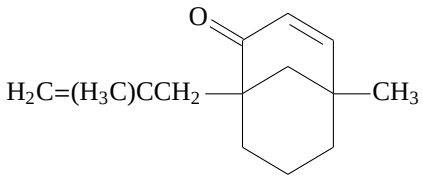


□

Example 24.11. A vertical form of bicyclo[3.3.1]nonane is also typeset by this technique.

```
\begin{picture}(1550,700)(-700,200)
\put(0,0){\cyclohexanev{6Sa==\lmoiety{H$_{2}$C=(H$_{3}$C)CCH$_{2}$};
2Sa==CH$_{3}$}}
\put(0,200){\sixheterov[a]{}{6D==O}[cd]}
\end{picture}
```

This statement provides

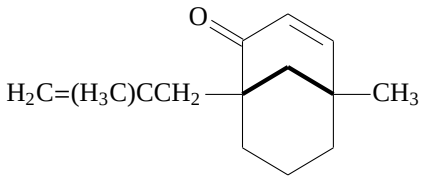


□

Example 24.12. If you want to draw the one-carbon bridge of the bicyclononane in a thick line, you can declare `({aB}{fB})` in the ⟨skelbdlist⟩ of one of the `\sixheterov` commands.

```
\begin{picture}(1550,700)(-700,200)
\put(0,0){\sixheterov({aB}{fB})%
{}{6Sa==\lmoiety{H$_{2}$C=(H$_{3}$C)CCH$_{2}$};2Sa==CH$_{3}$}}
\put(0,200){\sixheterov[a]{}{6D==O}[cd]}
\end{picture}
\end{picture}
```

This statement provides

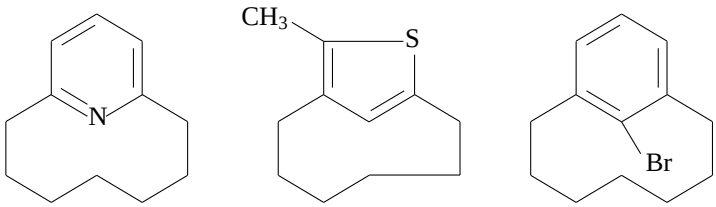


□

Example 24.13 (7). (2,6)-Pyridinophane [2] and 8-methyl[6](2,4)thiophenophane [3] are other examples typeset by this technique. In a similar way, 13-bromo-(2,6)metacyclophane [4] can be printed easily.

```
\begin{picture}(700,800)(200,200)
\put(0,0){\sixheterov{}{}[ab]}
\put(342,0){\sixheterov{}{}[ef]}
\put(171,303){\pyridinevi{}}
\end{picture}
\qquad
\begin{picture}(750,800)(150,200)
\put(0,0){\sixheterov{}{}[ab]}
\put(342,0){\fiveheterovi{}{}[de]}
\put(171,303){\fiveheterov[ad]{3==S}{4==CH$_{3}$}}
\end{picture}
\qquad
\begin{picture}(700,800)(200,200)
\put(0,0){\sixheterov{}{}[ab]}
\put(342,0){\sixheterov{}{}[ef]}
\put(171,303){\bzdrv{4Sa==\kern.5em\raise1ex\hbox{Br}}}
\end{picture}
```

These statements provide



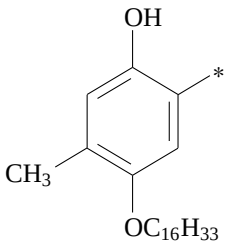
□

24.4 Large Substituents

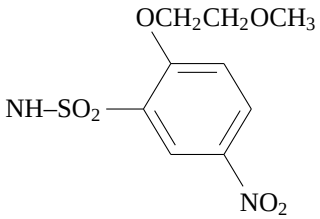
24.4.1 Direct Declaration in the ⟨subslist⟩

In all of the preceding sections, any substituents described in ⟨subslist⟩ are rather simple ones, which at most vary from an atom of one- or two-character to a group of several characters. How about such a complex substituent as produced by a macro?

Example 24.14. Let us consider the substitution of



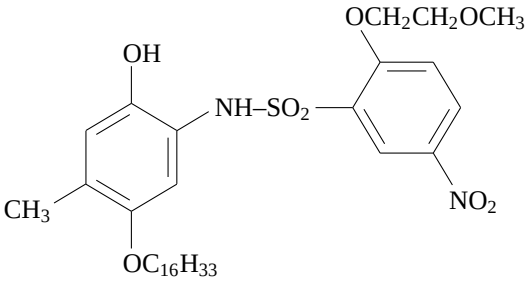
at the 2-position (∗)with the substituent represented by



This task can be accomplished in the light of the technique introduced in Section 24.2. Thus, the statement

```
\begin{picture}(2000,1000)(-100,0)
\put(0,0){\bzdrv{1==OH;2==;4==OC$_{16}$H$_{33}$;5==CH$_{3}$}}
\put(993,230){\bzdrh{1==NH--SO$_{2}$;%
2==OCH$_{2}$CH$_{2}$OCH$_{3}$;5==NO$_{2}$}}
\end{picture}
```

provides



24-8

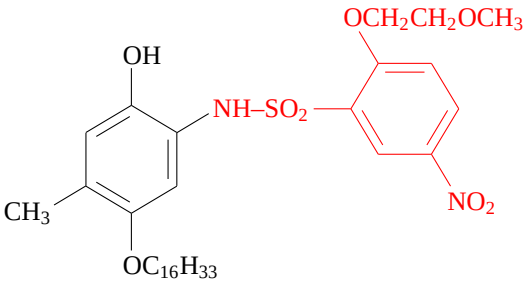
This methodology implies that both of the parts are regarded as fragments to be combined together. The compound **24-8** is an intermediate for synthesizing dye releasers used in instant color photography [5, Chapter 19]. □

On the other hand, useful techniques of another type are available, where either one is regarded as a substituent of the other.

Example 24.15. One of the most direct methods is the adjustment which applies `\kern` (for horizontal adjustment) and `\lower` (or `\raise` for vertical adjustment) to `\hbox` containing the substituent, as colored in red in the following code:

```
\bzdrv{1==OH;%
2==\kern28.5pt\lower37pt\hbox{\bzdrh{1==NH--SO$_{2}$;%
2==OCH$_{2}$CH$_{2}$OCH$_{3}$;5==NO$_{2}$}};%
4==OC$_{16}$H$_{33}$;5==CH$_{3}$}
```

This code produces



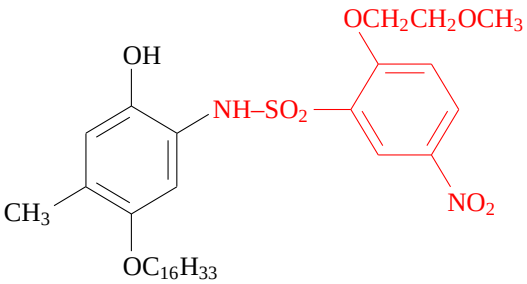
24-9

The reference point of the inner picture environment due to `\bzdrh` is shifted by 28.5pt (horizontal direction) and −37pt (vertical direction) into the rightmost point of the $NH–SO_2$ group. Note that the outer picture environment is unnecessary in this technique. □

Example 24.16. In place of the adjustment due to `\kern28.5pt\lower37pt`, we are able to use `\put(285,-370)`, which is one of the commands for the LaTeX picture environment. Note that the unit length of the XeTeX system is decided to be `\unitlengthe=0.1pt`. Thus, the code:

```
\bzdrv{1==OH;%
2==\put(285,-370){\bzdrh{1==NH--SO$_{2}$;%
2==OCH$_{2}$CH$_{2}$OCH$_{3}$;5==NO$_{2}$}};%
4==OC$_{16}$H$_{33}$;5==CH$_{3}$}
```

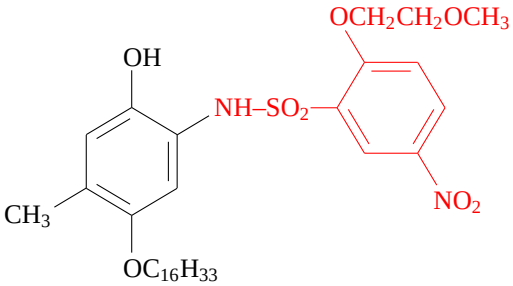
produces the following structure:



24-10 □

Example 24.17. The methods described in Examples 24.15 and 24.16 can be replaced by the combination of `\ryl` and a (yl)-function.

```
\bzdrv{1==OH;%
2==\ryl(5==NH--SO$_{2}$){4==%
\bzdrh{1==(yl);2==OCH$_{2}$CH$_{2}$OCH$_{3}$;5==NO$_{2}$}};%
4==OC$_{16}$H$_{33}$;5==CH$_{3}$}
```



24-11

This method is regarded as an automatic version of the methods described in Examples 24.15 and 24.16. The merit of this method is no explicit declaration of such adjustment values as `\kern28.5pt\lower37pt` (Example 24.15) and `\put(285,-370)` (Example 24.16). □

24.4.2 Use of the `\setbox` Command

A succinct code is available, if you use the TeX command `\setbox` and the related commands.

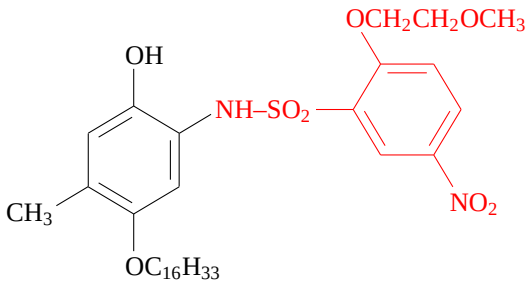
Example 24.18. First, a new box named `\CompBoxa` is created by using the TeX command `\newbox`. Then, a structure regarded as a substituent is constructed in a `\hbox` and stored in the box `\CompBoxa` by means of the command `\setbox` as follows:

```
\newbox\CompBoxa
\setbox\CompBoxa=\hbox{%
 \begin{picture}(0,0)(-285,370)%
%  \put(-285,370){\circle{50}}%change reference point
  \put(0,0){\bzdrh{1==NH--SO$_{2}$;2==OCH$_{2}$CH$_{2}$OCH$_{3}$;%
   5==NO$_{2}$}}%
 \end{picture}}%
```

The inner picture environment has the width of 0pt and the height of 0pt, where the reference point is shifted into the $(-285, 370)$ point which is the rightmost point of the NH–SO_2 group. This reference point is regarded as the $(0, 0)$ point of the substituent stored in `\CompBoxa`. Then, the substituent stored in the box `\CompBoxa` is written in ⟨subslist⟩ of the command `\bzdrv`, i.e.,

```
\bzdrv{1==OH;%
2==\box\CompBoxa;%      %(should be read as 2==\copy\CompBoxa; for multiple use)
4==OC$_{16}$H$_{33}$;5==CH$_{3}$}
```

This statement produces



It should be noted that the token `2==\box\CompBoxa` creates such a complex fragment that makes the code more readable in comparison with a directly assigned code to an argument list. This technique is also useful to avoid the overcrowding of substituents, since the reference point of the substituent can be changed appropriately.

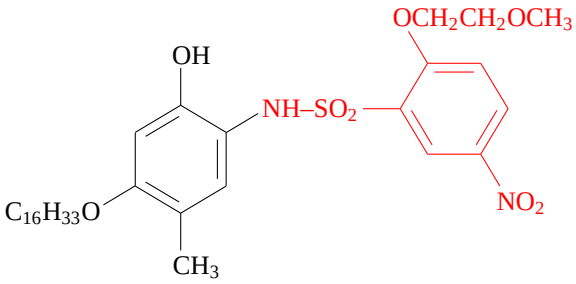
When you multiple times use the stored substituent, you should use the command `\copy` instead of `\box`:

```
\bzdrv{1==OH;2==\copy\CompBoxa;4==OC$_{16}$H$_{33}$;5==CH$_{3}$}
```

Then, you are able to use the stored substituent in another context.

```
\newbox\CompBoxb
\setbox\CompBoxb=\hbox{%
\bzdrv{1==OH;%
2==\copy\CompBoxa;%
5==C$_{16}$H$_{33}$O;4==CH$_{3}$}}%
\mbox{\box\CompBoxb}
```

This statement provides another derivative having the same substituent.



□

24.4.3 Definition of Tentative Macros

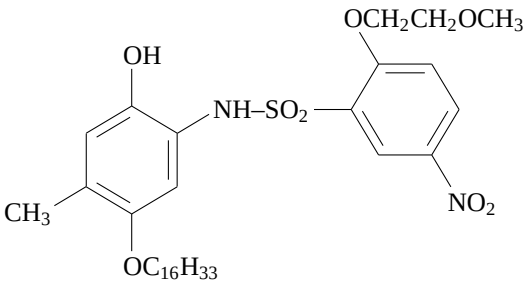
An alternative way of treating a large substituent is to use the definition of a tentative macro such as `\phsulphonyl`:

```
\def\phsulphonyl#1{%
 \begin{picture}(0,0)(-285,370)%
%  \put(-285,370){\circle{50}}%change reference point
   \put(0,0){\bzdrh{1==NH--SO$_{2}$;2==OCH$_{2}$CH$_{2}$OCH$_{3}$;%
    5==#1}}%
 \end{picture}}%
```

which has an argument to select a phenyl substituent. Then, the tentative macro can be used in the ⟨subslist⟩ of a mother structure command.

Example 24.19. For example, the compound described above can be typeset as follows:

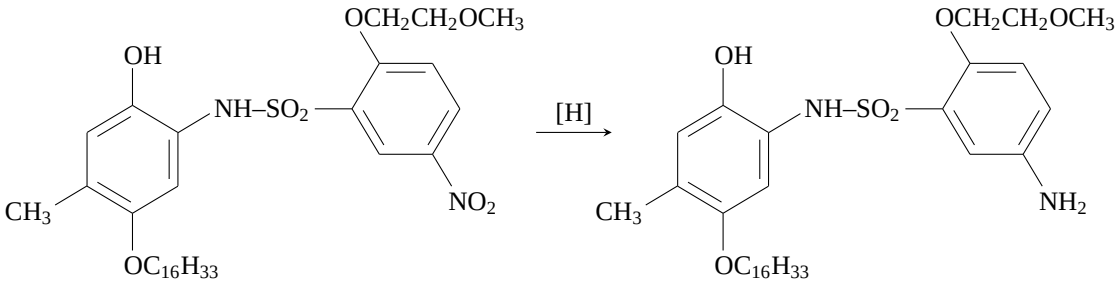
```
\bzdrv{1==OH;2=={\phsulphonyl{NO$_{2}$}};%
 4==OC$_{16}$H$_{33}$;5==CH$_{3}$}
```



□

Example 24.20. Because the substituent printed by `\phsulphonyl` is regarded to have no width and no height, the size of the resulting formula should be reset to have an appropriate width and height for further use. The following example of drawing a synthetic root to an intermediate of dye releasers [5, page 470] shows a resetting method to make a box of an appropriate size by means of a picture environment.

```
\begin{trivlist}\item[]
\begin{picture}(2000,1000)(-100,0)
\put(0,0){\bzdrv{1==OH;2=={\phsulphonyl{NO$_{2}$}};%
 4==OC$_{16}$H$_{33}$;5==CH$_{3}$}}
\end{picture}
\reactrarrow{50pt}{1cm}{[H]}{\strut}
\begin{picture}(2000,1000)(0,0)
\put(0,0){\bzdrv{1==OH;2=={\phsulphonyl{NH$_{2}$}};%
 4==OC$_{16}$H$_{33}$;5==CH$_{3}$}}
\end{picture}
\end{trivlist}
```



□

24.4.4 Nested Substituents

Examples 24.19 and 24.20 imply that a structure constructed by the present technique can be further nested to be a substituent of another macro.

Example 24.21. The following example illustrates multiple nesting for drawing the same dye releaser as **24-6** [5, page 473] , which has been depicted in Section 24.2.

1. (Formula A stored in the box `\CompBoxa`) First, the formula of 2-methanesulfonyl-4-nitro-phenyl-1-azo group (A) is constructed in the box `\CompBoxa` by means of following statement:

   ```
   \setbox\CompBoxa=\hbox{%formula A
    \begin{picture}(0,0)(996,370)%
   %  \put(996,370){\circle{50}}%
     \put(0,0){\bzdrh{1==O$_{2}$N;5==SO$_{3}$CH$_{3}$;4==N=N}}%
    \end{picture}}%
   ```

   Note that the value (996,370) results in the shift of the reference point into the rightmost terminal of the azo group, which is a linking point in the next step. The benzene ring generated by the command `\bzdrh` is designated by the symbol A in the resulting structure **24-12**.

2. (Formula B stored in the box `\CompBoxb`) The formula A stored in a box `\CompBoxa` (defined above) is placed at the 8-position of a naphthalene ring. The resulting formula B is, in turn, stored into `\CompBoxb` (defined above).

```
\setbox\CompBoxb=\hbox{%formula B
 \begin{picture}(0,0)(-100,712)%
%  \put(-100,712){\circle{50}}%
  \put(0,0){\naphdrh{1==SO$_{2}$NH;5==OH;8==\copy\CompBoxa}}%
 \end{picture}%
 }%
```

The value $(-100, 712)$ shifts the reference point into the leftmost terminal of the sulfonamido group at the 1-position of the naphthalene ring. The naphthalene ring generated by the command \naphdrh is designated by the symbol B in the resulting structure **24-12**.

3. (Formula C stored in the box \CompBoxc) The formula B as a sulfamoyl group is placed at the meta position of a benzene ring to produce formula C. Note that the box \CompBoxc is newly defined by using \newbox.

```
\newbox\CompBoxc
\setbox\CompBoxc=\hbox{%formula C
 \begin{picture}(0,0)(-285,370)%
%  \put(-285,370){\circle{50}}%
  \put(0,0){\bzdrh{1==NH--SO$_{2}$;5==\copy\CompBoxb}}%
 \end{picture}%
}%
```

The benzene ring generated by the command \bzdrh is designated by the symbol C in the resulting structure **24-12**.

4. (Formula D stored in the box \CompBoxd)
The resulting formula C is further placed in another benzene ring to generate the formula (D) of a complex substituent. Note that the box \CompBoxd is newly defined by using \newbox.

```
\newbox\CompBoxd
\setbox\CompBoxd=\hbox{%formula D
 \begin{picture}(0,0)(-285,370)%
%  \put(-285,370){\circle{50}}%
  \put(0,0){\bzdrh{1==NH--SO$_{2}$;2==OCH$_{2}$CH$_{2}$OCH$_{3}$;%
   5==\copy\CompBoxc}}%
 \end{picture}%
}%
```

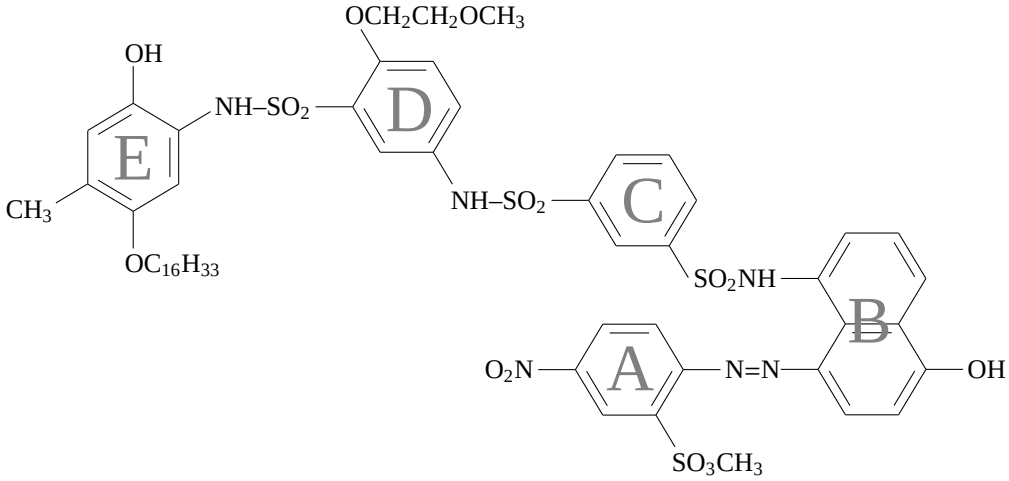
The benzene ring generated by the command \bzdrh is designated by the symbol D in the resulting structure **24-12**.

5. (Formula E stored in the box \CompBoxe) Finally, the substituent D is placed at the ortho position to a hydroxyl group on a benzene ring. Note that the box \CompBoxe is newly defined by using \newbox.

```
\newbox\CompBoxe
\setbox\CompBoxe=\hbox{%formula E
\bzdrv{1==OH;2==\box5;4==OC$_{16}$H$_{33}$;5==CH$_{3}$}}%
\mbox{\box\CompBoxe}
```

The benzene ring generated by the command \bzdrv is designated by the symbol E in the resulting structure **24-12**.

The formula E stored in \CompBoxe is printed by means of the command \box\CompBoxe, giving the following structure.



24-12

One of the merits of the present methodology is that we can use relative coordinates in each step of combining two structures. Hence, the calculation of coordinates is simpler than that based on the method of the preceding chapter. □

Example 24.22. The structural formula **24-13** of adonitoxin can be written in a similar way, where two complex substituents stored in the boxes `\CompBoxa` and `\CompBoxb` are placed on a steroid skeleton. The resulting structure is stored in the box `\CompBoxc`, which is used to print out **24-13**.

1. The box `\CompBoxa` stores a top substituent of lactone type:

```
\setbox\CompBoxa=\hbox{%
 \begin{picture}(0,0)(369,257)%
%  \put(369,257){\circle{50}}%
  \put(0,0){\fiveheterov[e]{3==O}{4D==O}}
 \end{picture}}%
```

2. The box `\CompBoxa` stores a bottom substituent of pyranose type:

```
\setbox\CompBoxb=\hbox{%
 \begin{picture}(0,0)(772,530)%
%  \put(772,530){\circle{50}}%
  \put(0,0){\pyranosew{1Sb==O;1Sa==H;2Sb==H;2Sa==OH;3Sb==H;3Sa==OH;%
  4Sb==HO;4Sa==H;5Sb==H;5Sa==CH$_{3}$}}%
 \end{picture}}%
```

3. The box `\CompBoxc` stores the structure of adonitoxin:

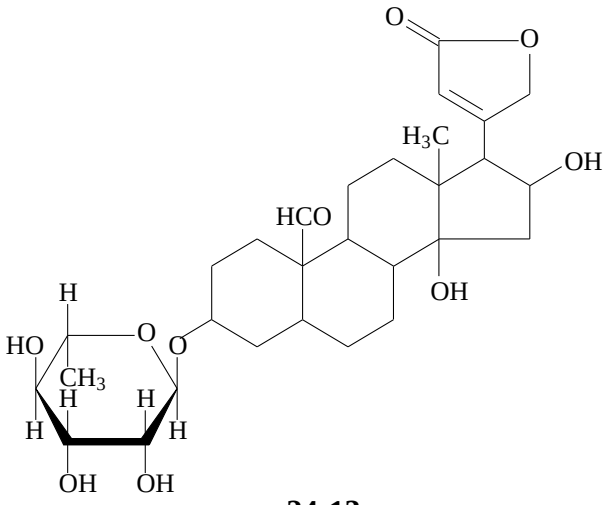
```
\setbox\CompBoxc=\hbox{%
   \steroid{{{10}}==\lmoiety{HCO\kern-.7em};{{14}}==OH;%
   {{13}}==\lmoiety{H$_{3}$C};%
   {{16}}==OH;{{17}}==\copy\CompBoxa;3==\copy\CompBoxb}}%
```

   where the substituents stored in the boxes `\CompBoxa` and `\CompBoxb` are placed on a steroid skeleton.

4. The resulting structure is output by the following code.

```
\begin{center}
\begin{picture}(2500,1800)(-600,-300)
\put(0,0){\mbox{\box\CompBoxc}}
\end{picture}
\end{center}
```

This set of commands produces the structure **24-13** to be drawn:



24-13

□

It is worthwhile to point out that the boxes `\CompBoxa` and `\CompBoxb` in Example 24.22 can be replaced by the methodology based on (yl)-functions.

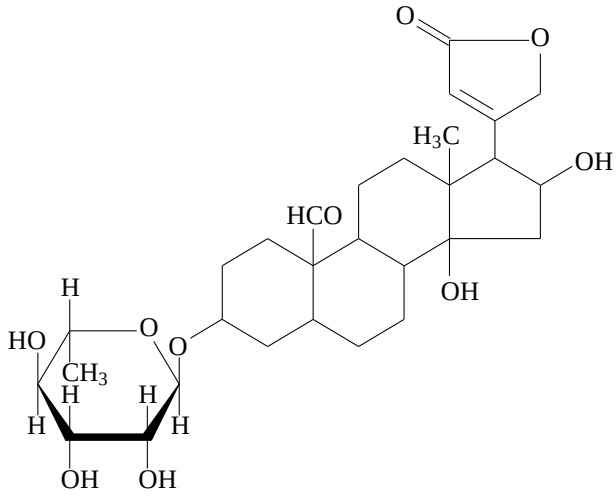
Example 24.23. The boxes `\CompBoxa` and `\CompBoxb` correspond to following expressions based on (yl)-functions, which do not contain such coordinate values as (369, 257) and (772, 530).

```
\CompBoxa → \fiveheterov[e]{3==O}{1==(yl);4D==O}
\CompBoxb →
        \lyl(3==O){8==\pyranosew{1==(yl);1Sa==H;2Sb==H;2Sa==OH;3Sb==H;3Sa==OH;%
        4Sb==HO;4Sa==H;5Sb==H;5Sa==CH$_{3}$}}
```

These expressions are declared in place of `\CompBoxa` and `\CompBoxb` as follows:

```
\steroid{{{10}}==\lmoiety{HCO\kern-.7em};{{14}}==OH;%
{{13}}==\lmoiety{H$_{3}$C};{{16}}==OH;%
{{17}}==\fiveheterov[e]{3==O}{1==(yl);4D==O};%for \CompBoxa
3==\lyl(3==O){8==\pyranosew{1==(yl);1Sa==H;2Sb==H;2Sa==OH;3Sb==H;3Sa==OH;%
4Sb==HO;4Sa==H;5Sb==H;5Sa==CH$_{3}$}}}%for \CompBoxb
```

Thereby, we obtain the formula **24-14**, which is equivalent to **24-13**.



24-14

□

As found by comparing Example 24.22 with Example 24.23, the methodology of Example 24.23 can be regarded as an automatic version of the methodology of Example 24.22. The merit of (yl)-functions (Example 24.23) is no explicit declaration of coordinate values. See also Example 24.17.

References

[1] S. Fujita, K. Koyama, and S. Ono, *Rev. Heteroatom Chem.*, **7**, 229–267 (1992).

[2] S. Fujita and H. Nozaki, *Bull. Chem. Soc. Jpn.*, **44**, 2827–2833 (1971).

[3] S. Fujita, T. Kawaguti, and H. Nozaki, *Tetrahedron Lett.*, 1119–1120 (1971).

[4] S. Fujita, S. Hirano, and H. Nozaki, *Tetrahedron Lett.*, 403–404 (1972).

[5] S. Fujita, "Organic Chemistry of Photography," Springer-Verlag, Berlin-Heidelberg (2004).

(yl)-Functions and the Substitution Technique

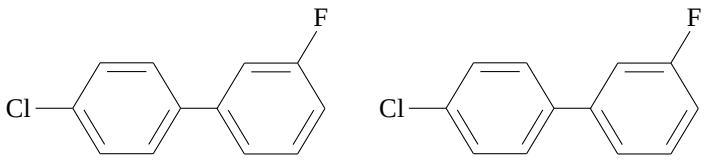
The substitution technique and (yl)-functions have been briefly discussed in Section 2.4. The present chapter is devoted to a detailed discussion on the topics, covering basic ideas to illustrative applications.

25.1 Nested Substituents

Section 24.2 (Chapter 14 of the XƎMTEX book [1]) and Section 24.4 (Chapter 15 of [1]) have described several techniques to draw complicated formulas. Among them, the nested-substituent method (cf. **24-9** and **24-10**) is most promising, because it requires no outer picture environment (cf. **24-8**). For example, the codes

```
\bzdrh{1==Cl;4==\kern-26pt\lower37pt\hbox to0pt{\bzdrh{3==F}\hss}} \hskip50pt
\bzdrh{1==Cl;4==\put(-260,-370){\bzdrh{3==F}}}
```

give combined structures:



which are equivalent to each other. Although these codes show the connectivity between the two phenyl groups, the following disadvantages remain:

1. The code contains no data indicating that the connection site is the meta-position concerning the fluorine atom.
2. In the first code, the commands `\kern` (for horizontal adjustment) and `\lower` (for vertical adjustment) are necessary to adjust the substitution site.
3. In the second code, the command `\put` of the LATEX picture environment is necessary to adjust the substitution site, where the values in a pair of parentheses are determined as the multiples of `\unitlength` (= 0.1pt).

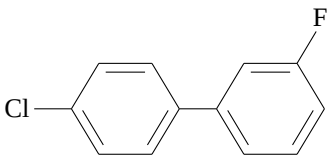
As clarified by the above examples, the main target of XƎMTEX Version 2.00 is to extend the nested-substituent method so that it provides a function of indicating full connectivity data as well as a function of automatic adjustment without using such commands as `\kern` and `\lower`.

25.2 (yl)-Functions

The XyMTEX system (version 2.00 and later) supports (yl)-functions for the purpose of improving the nested-substituent method, which is now called *the substitution technique*. Thereby, any structure drawn by a XyMTEX command (except a few special commands) can be converted into the corresponding substituent by adding the code `(yl)` with a locant number to the ⟨substlist⟩ of the XyMTEX command. The resulting code for the substituent can be added to the ⟨substlist⟩ of any other command for drawing a mother skeleton, where the final code contains the full connectivity data of the combined structure. For example, the code

```
\bzdrh{1==Cl;4==\bzdrh{1==(yl);3==F}}
```

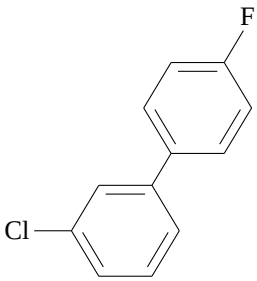
typesets the following structure,



Thus, fluorobenzene produced by the command `\bzdrh{3==F}` is converted into a substituent, i.e. 3-fluorophenyl, by adding the code `(yl)`, as shown in the code, `\bzdrh{1==(yl);3==F}`. Then, the resulting code is added to the ⟨substlist⟩ of another command `\bzdrh`.

The connectivity at the meta-position is represented by the statement `1==(yl)` of the inner code `\bzdrh{1==(yl);3==F}`. Note that the inner code `\bzdrh{1==(yl);3==F}` produces a substituent with no height and no width and that the reference point of the substituent is shifted to the point no. 1 by the (yl)-statement in order to link to the mother structure (the phenyl group produced by the code `\bzdrh{1==Cl;4=={...}}`).

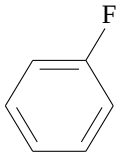
The shift of a reference point becomes clear when we examine a formula,



generated by the code,

```
\bzdrh{1==Cl;3==\bzdrh{6==(yl);3==F}}
```

The original structure of the substituent with no (yl)-function is found to be



as generated by the code

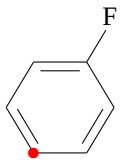
```
\begin{picture}(700,800)(0,0)
\put(0,0){\bzdrh{3==F}}
\put(0,0){\redx{\circle*{40}}}
```

```
\end{picture}
```

where the red solid circle is the reference point. The picture shown above indicates that the reference point is different from any vertices of the benzene ring. On the other hand, the code with a (yl)-function,

```
\begin{picture}(700,800)(0,-200)
\put(0,0){\bzdrh{6==(yl);3==F}}
\put(0,0){\redx{\circle*{40}}}
\end{picture}
```

typesets the following structure,

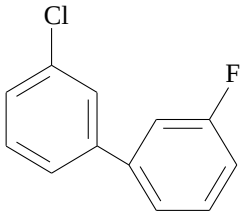


The picture shown above indicates that the reference point is shifted to the position no. 6 of the benzene ring.

The code `\bzdrh{1==(yl);3==F}` producing the substituent can be used in the argument of any structure-drawing command of XyMTEX. The following example is the one in which it is placed in the argument of a command `\bzdrv`. Thus, the code

```
\bzdrv{1==Cl;3==\bzdrh{1==(yl);3==F}}
```

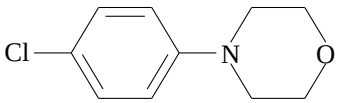
typesets the following structure,



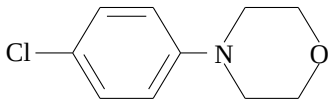
Example 25.1. The structural formula of 1-chloro-4-morphorinobenzene can be drawn in two different ways. The codes,

```
\bzdrh{1==Cl;4==\sixheteroh{1==N;4==O}{1==(yl)}}
\sixheteroh{1==N;4==O}{1==\bzdrh{1==Cl;4==(yl)}}
```

produce the following formulas:



25-1



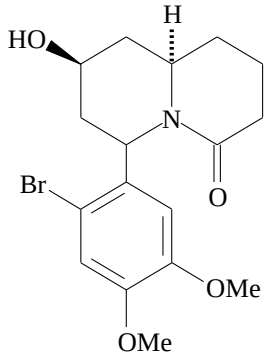
25-2

In the former code, the morphorino group is regarded as a substituent, as the name "1-chloro-4-morphorinobenzene" indicates. On the other hand, the chlorophenyl group is considered to be a substituent in the latter code so as to correspond to the name "N-(4-chlorophenyl)morphorine". See **24-2** and **24-3** for more direct procedures of drawing based on the LaTeX picture environment. □

Example 25.2. Let us redraw the structure **24-4** by using a (yl)-function. Thus, the (yl)-function is quite versatile, as indicated by the code,

```
\decaheterov{4a==N}{4D==O;7B==HO;{{10}A}==H;%
5==\bzdrv{3==OMe;4==OMe;6==Br;1==(yl)}}
```

producing the following structure:

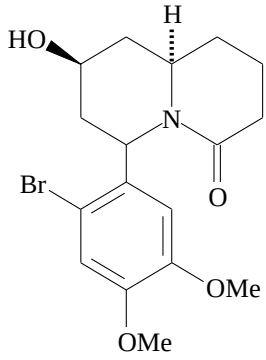


25-3

where the substituted phenyl group is regarded as a substituent. An opposite view can be realized by the code

```
\bzdrv{3==OMe;4==OMe;6==Br;%
1==\decaheterov[]{4a==N}{4D==O;7B==HO;{{10}A}==H;5==(yl)}}
```

which typesets the same structure:



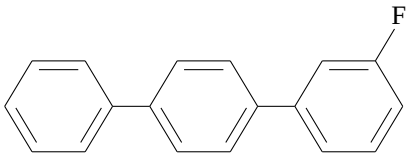
25-4

where the moiety drawn by the command `\decaheterov` is regarded as a substituent. □

Example 25.3. Two or more substituents generated by the (yl)-function can be introduced into a ⟨subslist⟩. For example,

```
\bzdrh{1==\bzdrh{4==(yl)};4==\bzdrh{1==(yl);3==F}}
```

typesets the following structure,



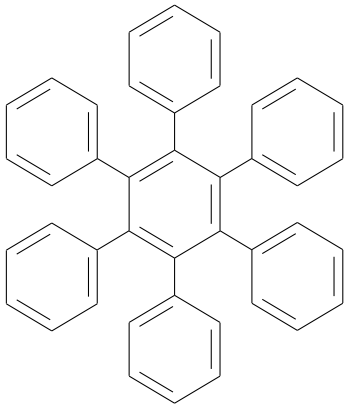
25-5

□

Example 25.4. The structural formula of hexaphenylbenzene can be drawn by this technique. Thus the code,

```
\bzdrv{1==\bzdrv{4==(yl)};%
2==\bzdrv{5==(yl)};3==\bzdrv{6==(yl)};%
4==\bzdrv{1==(yl)};5==\bzdrv{2==(yl)};%
6==\bzdrv{3==(yl)}}
```

generates the following formula:

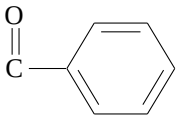


25-6

□

25.3 Nested (yl)-Functions

Two or more (yl)-functions can be nested. For example, a structure



depicted by the code,

```
\tetrahedral{0==C;1D==O;4==\bzdrh{1==(yl)}}
```

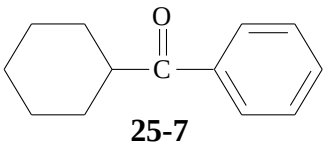
can be converted into a substituent by adding another (yl)-function, as shown in the following code:

```
\tetrahedral{2==(yl);0==C;1D==O;4==\bzdrh{1==(yl)}}
```

Then this substituent is nested in the ⟨subslist⟩ of the command `\cyclohexaneh` to give a code,

```
\cyclohexaneh{4==%
\tetrahedral{2==(yl);0==C;1D==O;4==\bzdrh{1==(yl)}}}
```

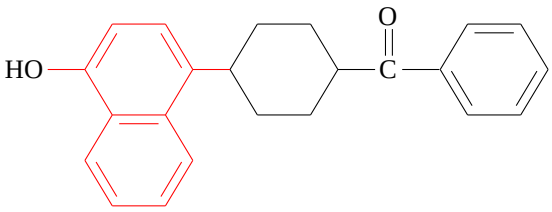
Thereby we have the structural formula of benzoylcyclohexane:



25-7

Compare this structure **25-7** with the structure **24-5**, which has been drawn by the LaTeX picture environment.

Example 25.5. The resulting structure **25-7** can be further converted into a substituent by adding a further (yl)-function. The following example shows that the substituent is linked to the 4-position of a naphthol ring:



25-8

which is typeset by the triply nested code:

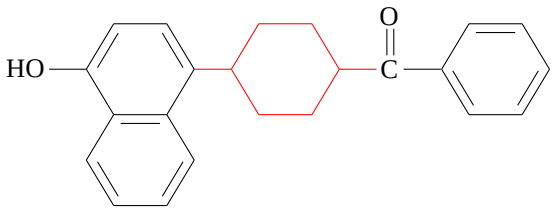
```
\naphdrh{1==HO;4==%
\cyclohexaneh{1==(yl);4==%
\tetrahedral{2==(yl);0==C;1D==O;4==\bzdrh{1==(yl)}}}}
```

Note that the naphthol ring (colored in red) generated by `\naphdrh` is selected as a parent structure for drawing **25-8**.

The same structural formula can be drawn by regarding the 1-naphthol-4-yl group and the benzoyl group as substituents, as shown in the following code:

```
\cyclohexaneh{%
1==\naphdrh{1==HO;4==(yl)};%
4==\tetrahedral{2==(yl);0==C;1D==O;4==\bzdrh{1==(yl)}}}
```

Accordingly, we have



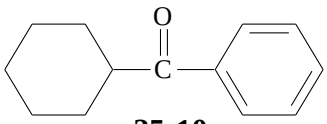
25-9

Note that the cyclohexane ring (colored in red) generated by `\cyclohexaneh` is selected as a parent structure for drawing **25-9**. □

Example 25.6. The structure of benzoylcyclohexane can also be drawn by considering the `\tetrahedral` moiety as a mother skeleton, as shown in the code:

```
\tetrahedral{0==C;1D==O;4==\bzdrh{1==(yl)};2==\cyclohexaneh{4==(yl)}}
```

Thereby, we have the formula,



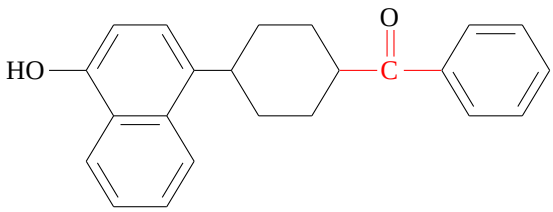
25-10

which shows that two or more substituents produced by the (yl)-function can be written in a ⟨subslist⟩. This treatment corresponds to the alternative name of benzoylcyclohexane, i.e., cyclohexyl phenyl ketone, since the codes `\cyclohexaneh{4==(yl)}` and `\bzdrh{1==(yl)}` represent a cyclohexyl and a phenyl group, respectively. □

Example 25.7. Because a single (yl)-function is permitted to each command, the structure **25-10** drawn by `\cyclohexaneh` with a (yl)-function cannot contain a further (yl)-function, so that it cannot be used as a substituent concerning the cyclohexane ring. However, the ⟨subslist⟩ of the command `\cyclohexaneh` is capable of accommodating the substituent `\naphdrh{1==HO;4==(yl)}` to give

```
\tetrahedral{0==C;1D==O;4==\bzdrh{1==(yl)};%
2==\cyclohexaneh{4==(yl);1==\naphdrh{1==HO;4==(yl)}}}
```

which typesets **25-11** as equivalent to the formula **25-9**:



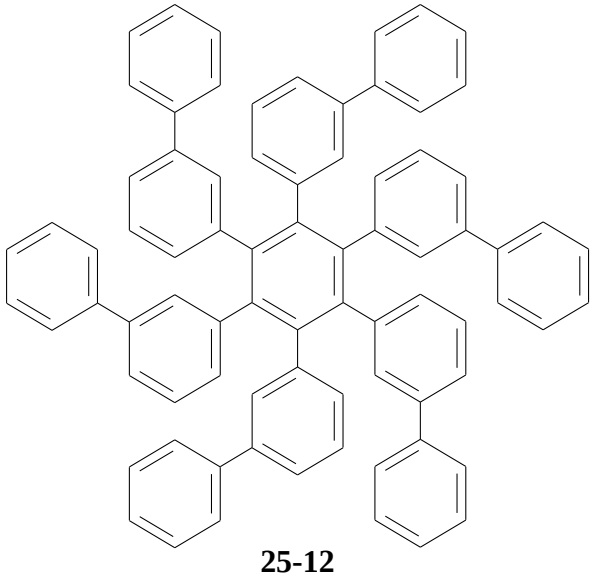
25-11

Note that the carbonyl skeleton (colored in red) generated by `\tetrahedral` is selected as a parent structure for drawing **25-11**. □

Example 25.8. Let us examine multiple nesting using (yl)-functions. The following code with nested (yl)-functions:

```
\bzdrv{%
1==\bzdrv{4==(yl);2==\bzdrv{5==(yl)}};%
2==\bzdrv{5==(yl);3==\bzdrv{6==(yl)}};%
3==\bzdrv{6==(yl);4==\bzdrv{1==(yl)}};%
4==\bzdrv{1==(yl);5==\bzdrv{2==(yl)}};%
5==\bzdrv{2==(yl);6==\bzdrv{3==(yl)}};%
6==\bzdrv{3==(yl);1==\bzdrv{4==(yl)}}}
```

gives a more complicated structure:



25-12

The central benzene ring is a parent structure for drawing the structure **25-12**. Note that each branch (biphenyl unit) is drawn by nested (yl)-functions having a common constitution except locant numbers. □

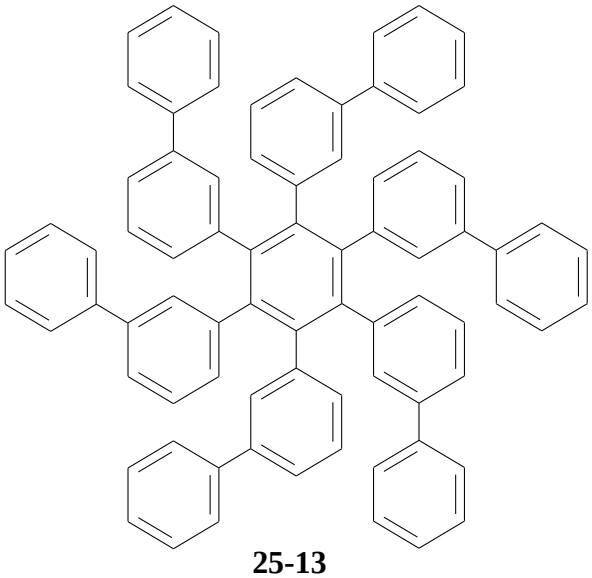
Example 25.9. To simplify the coding of Example 25.8, we define a macro drawing such a biphenyl unit as follows:

```
\def\biph#1#2#3{\bzdrv{#1==(yl);#2==\bzdrv{#3==(yl)}}}
```

in which three locant numbers can be independently specified by the three arguments. Then, this macro is used in the ⟨subslist⟩ of `\bzdrv` to give the code,

```
\bzdrv{%
1==\biph{4}{2}{5};%
2==\biph{5}{3}{6};%
3==\biph{6}{4}{1};%
4==\biph{1}{5}{2};%
5==\biph{2}{6}{3};%
6==\biph{3}{1}{4}}
```

where a set of three locant numbers is declared to depict each biphenyl unit. Thereby, we obtain **25-13**, which is equivalent to **25-12**:



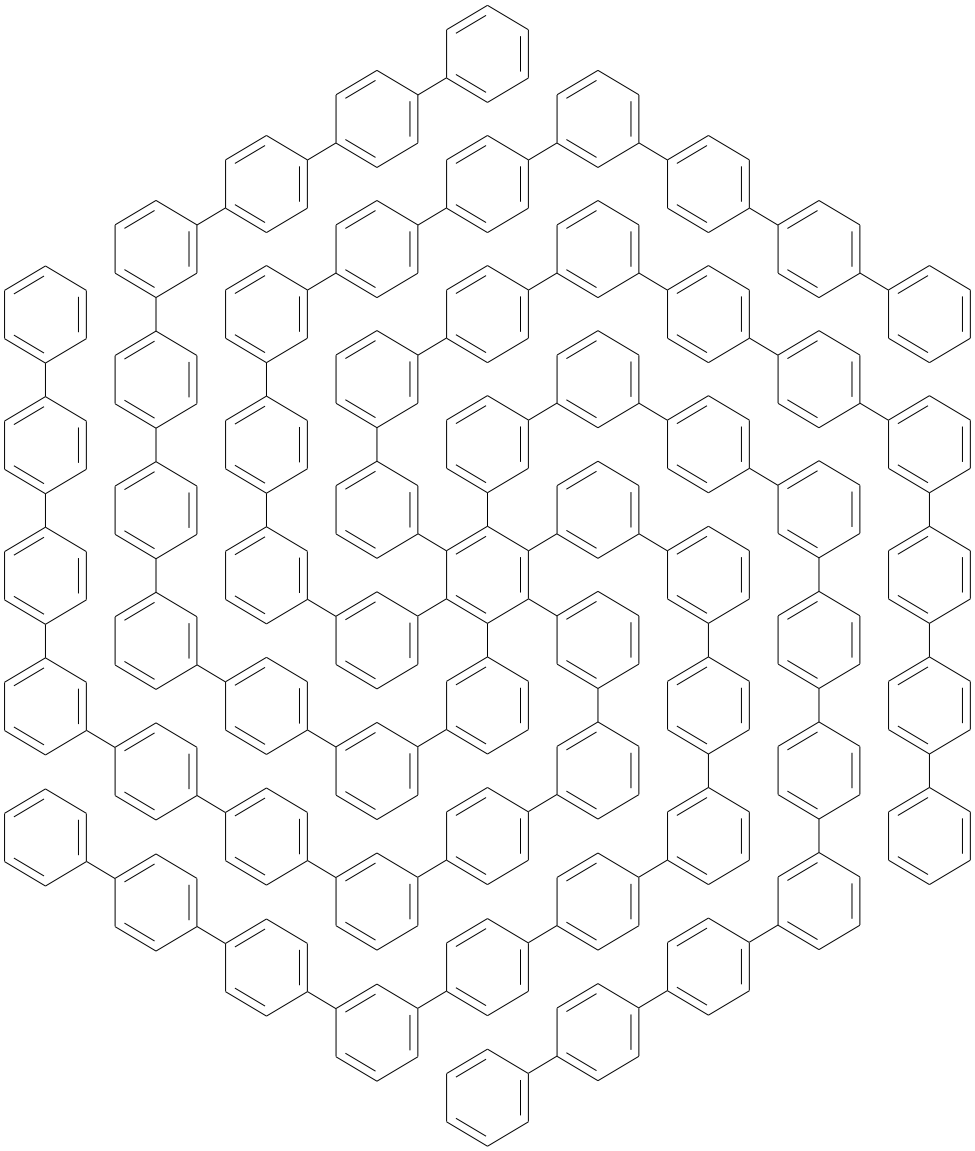
25-13 □

Example 25.10. A more complex nested code,

```
\bzdrv{%
1==\bzdrv{4==(yl);2==\bzdrv{5==(yl);3==\bzdrv{6==(yl);%
3==\bzdrv{6==(yl);4==\bzdrv{1==(yl);4==\bzdrv{1==(yl);%
4==\bzdrv{1==(yl);5==\bzdrv{2==(yl);5==\bzdrv{2==(yl);%
5==\bzdrv{2==(yl)}}}}}}}}}};%
2==\bzdrv{5==(yl);3==\bzdrv{6==(yl);4==\bzdrv{1==(yl);%
4==\bzdrv{1==(yl);5==\bzdrv{2==(yl);5==\bzdrv{2==(yl);%
5==\bzdrv{2==(yl);6==\bzdrv{3==(yl);6==\bzdrv{3==(yl);%
6==\bzdrv{3==(yl)}}}}}}}}}};%
3==\bzdrv{6==(yl);4==\bzdrv{1==(yl);5==\bzdrv{2==(yl);%
5==\bzdrv{2==(yl);6==\bzdrv{3==(yl);6==\bzdrv{3==(yl);%
6==\bzdrv{3==(yl);1==\bzdrv{4==(yl);1==\bzdrv{4==(yl);%
1==\bzdrv{4==(yl)}}}}}}}}}};%
4==\bzdrv{1==(yl);5==\bzdrv{2==(yl);6==\bzdrv{3==(yl);%
6==\bzdrv{3==(yl);1==\bzdrv{4==(yl);1==\bzdrv{4==(yl);%
1==\bzdrv{4==(yl);2==\bzdrv{5==(yl);2==\bzdrv{5==(yl);%
2==\bzdrv{5==(yl)}}}}}}}}}};%
5==\bzdrv{2==(yl);6==\bzdrv{3==(yl);1==\bzdrv{4==(yl);%
1==\bzdrv{4==(yl);2==\bzdrv{5==(yl);2==\bzdrv{5==(yl);%
2==\bzdrv{5==(yl);3==\bzdrv{6==(yl);3==\bzdrv{6==(yl);%
3==\bzdrv{6==(yl)}}}}}}}}}};%
6==\bzdrv{3==(yl);1==\bzdrv{4==(yl);2==\bzdrv{5==(yl);%
2==\bzdrv{5==(yl);3==\bzdrv{6==(yl);3==\bzdrv{6==(yl);%
3==\bzdrv{6==(yl);4==\bzdrv{1==(yl);4==\bzdrv{1==(yl);%
4==\bzdrv{1==(yl)}}}}}}}}}%
}
```

produces the formula **25-14** shown in Fig. 25.1.[a] □

[a]The drawing of **25-14** takes a long time under a usual personal-computer environment. If your computer environment has an insufficient capacity, the code should be independent processed to give an eps file, which is included into a text by using `\includegraphics`.



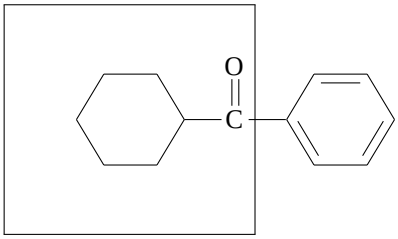
25-14

Figure 25.1. Linking phenylenes drawn by multiple nesting of (yl)-functions.

25.4 Remarks

25.4.1 Domains of Structures Drawn by XMTEX Commands

Substituents produced by the (yl)-function have no dimensions. For example, benzoylcyclohexane **25-7**:



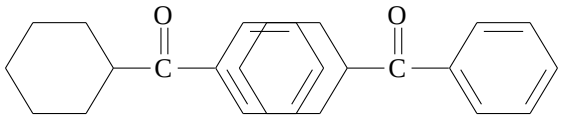
which is produced by the code

```
\fbox{%
\cyclohexaneh{4==%
\tetrahedral{2==(yl);0==C;1D==O;4==\bzdrh{1==(yl)}}}%
}
```

has a drawing domain around the cyclohexane mother skeleton, as surrounded by a frame. Because the benzoyl moiety occupies no area, it may be superimposed on other diagrams so as to require some space adjustments. For example, the above code duplicated without any space adjustment,

```
\cyclohexaneh{4==%
\tetrahedral{2==(yl);0==C;1D==O;4==\bzdrh{1==(yl)}}}
\cyclohexaneh{4==%
\tetrahedral{2==(yl);0==C;1D==O;4==\bzdrh{1==(yl)}}}%
```

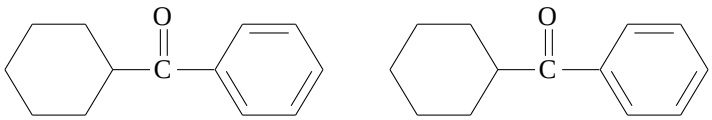
gives an insufficient result:



This superposition can be avoided by a horizontal spacing. Thus the code

```
\cyclohexaneh{4==%
\tetrahedral{2==(yl);0==C;1D==O;4==\bzdrh{1==(yl)}}}
\hskip2cm
\cyclohexaneh{4==%
\tetrahedral{2==(yl);0==C;1D==O;4==\bzdrh{1==(yl)}}}%
```

typesets improved formulas:



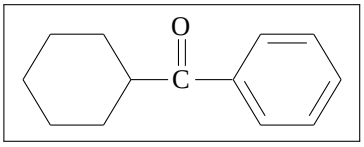
25.4.2 Systematic Specification of Domains

If a more thorough adjustment is required, two environments supported by the XMTEX system. are used to specify the domains of structures drawn by XMTEX commands.

1. (LaTeX `picture` Environment) A formula is placed in a LaTeX `picture` environment as follows.

```
\begin{picture}(1250,450)(200,200)
\cyclohexaneh{4==%
\tetrahedral{2==(yl);0==C;1D==O;4==\bzdrh{1==(yl)}}}
\end{picture}
```

This code produces

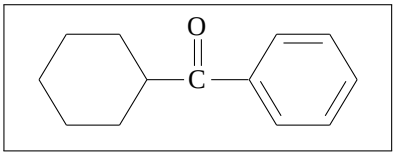


where a frame is added by means of a `\fbox` command.

2. (XyMTeX `XyMcompd` Environment) A formula is placed in a XyMTeX `XyMcompd` environment as follows.

```
\begin{XyMcompd}(1250,450)(200,200){}{}
\cyclohexaneh{4==%
\tetrahedral{2==(yl);0==C;1D==O;4==\bzdrh{1==(yl)}}}
\end{XyMcompd}
```

This code produces



where a frame is added by means of a `\fbox` command.

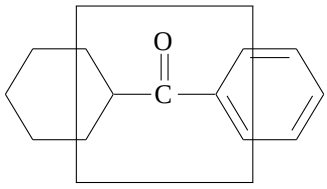
To determine the size of the domain (1250, 450) and the shifted position (200, 200), the command `\fbox` is used in a trial-and-error fashion and it is commented out after the determination of the coordinate values.

The following example illustrates the process of trial-and-error determination of the size of the domain and the shifted position.

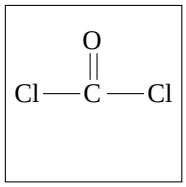
Example 25.11. A drawing domain around a formula depends upon a mother skeleton selected. For example, the formula **25-10** of benzoylcyclohexane at the top of this section has a drawing domain shown by the frame, since a `\cyclohexaneh` is selected as a mother skeleton. On the other hand, the alternative formula of benzoylcyclohexane depicted by the code,

```
\tetrahedral{0==C;1D==O;4==\bzdrh{1==(yl)};2==\cyclohexaneh[]{4==(yl)}}
```

has a drawing domain due to the `\tetrahedral` skeleton. Thus, the code gives the following output:



where the frame indicates such a drawing domain, when an `\fbox` command is used around the command `\tetrahedral`. The domain shown by the frame (due to `\fbox`) is equal to any domain based on the simple use of the `\tetrahedral` command (without using a (yl)-function). For example, compare the above frame with the one appearing in the formula,



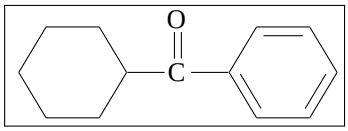
depicted by the code,

```
\fbox{\tetrahedral{0==C;1D==O;4==Cl;2==Cl}}
```

To adjust the drawing domain due to the `\tetrahedral` skeleton, the formula should be placed in a LaTeX picture environment as follows:

```
{\fboxsep=0pt
\fbox{%
\begin{picture}(1250,450)(-350,100)
\tetrahedral{0==C;1D==O;4==\bzdrh{1==(yl)};2==\cyclohexaneh[]{4==(yl)}}
\end{picture}
}}
```

where the sifted value $(-350, 100)$ is determined in a trial-and-error fashion. This code produces



where the frame indicates the net drawing domain (due to the setting of `\fboxsep=0pt`), which is adjusted by using the LaTeX picture environment.

References

[1] S. Fujita, "XMTEX—Typesetting Chemical Structural Formulas," Addison-Wesley Japan, Tokyo (1997).

Chapter 26

Linking Units Coupled with (yl)-Functions

The commands `\ryl` and `\lyl` described in this chapter are added to the chemstr package. The `\divalenth` command is added to the aliphat package. These packages are parts of the XƎMTEX system.

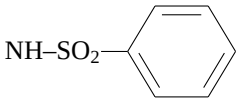
26.1 \ryl command

.

The (yl)-function provides us with a tool to generate a substituent that is linked *directly* to a substitution site of a mother skeleton. There are, however, many cases in which a substituent is linked to a substitution site by an intervening unit (e.g., O, SO_2 and NH). The command `\ryl` is used to generate a right-hand substituent with a linking unit. For example, the code

```
\ryl(5==NH--SO$_{2}$){4==\bzdrh{1==(yl)}}
```

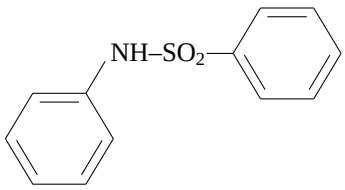
produces a benzenesulfonamido substituent,



The resulting unit is added to the ⟨subslist⟩ of a command for drawing a skeletal command. For example, the code

```
\bzdrh{3==\ryl(5==NH--SO$_{2}$){4==\bzdrh{1==(yl)}}}
```

generates the following formula:

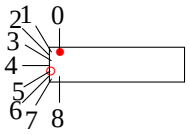


The `\ryl` command takes two arguments.

`\ryl{⟨link⟩}{⟨ylgroup⟩}`

The first argument ⟨link⟩ in the parentheses indicates an intervening unit with an integer showing the slope of a left incidental bond. For example, the number 5 of the code `5==NH--SO$_{2}$` shown above represents that the left terminal is to be linked through $(-5,-3)$ bond, though the linking bond is not typeset by the `\ryl` command only. The slopes of the linking bonds are designated by integers between 0 and 8:

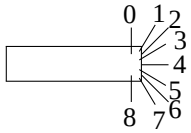
0	$(0,1)$	1	$(-3,5)$	2	$(-1,1)$
3	$(-5,3)$	4	$(-1,0)$	5	$(-5,-3)$
6	$(-1,-1)$	7	$(-3,-5)$	8	$(0,-1)$



Note that, for example, the control point for the number 5 of the code `5==NH--SO$_{2}$` is the end point shown by a red open circle, while the control point for the number 0 of the code `0==NH--SO$_{2}$` is the end point shown by a red solid circle. The linking unit `NH--SO$_{2}$` is designated by a frame.

The second argument ⟨ylgroup⟩ of `\ryl` is a substituent produced by a (yl)-function, where a number before a delimiter (==) indicates the slope of a right incidental bond. For example, the number 4 of the code `4==\bzdrh{1==(yl)}` shown above represents that the right terminal is to be linked through $(1,0)$ bond to the benzene ring generated by the `\bzdrh` command. The slopes of the linking bonds are designated by integers between 0 and 8:

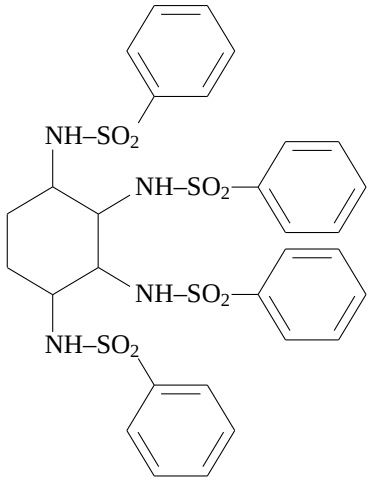
0	$(0,1)$	1	$(3,5)$	2	$(1,1)$
3	$(5,3)$	4	$(1,0)$	5	$(5,-3)$
6	$(1,-1)$	7	$(3,-5)$	8	$(0,-1)$



To illustrate linking bonds with various slopes, the code

```
\cyclohexanev{%
1==\ryl(8==NH--SO$_{2}$){1==\bzdrh{6==(yl)}};%
2==\ryl(5==NH--SO$_{2}$){4==\bzdrh{1==(yl)}};%
3==\ryl(3==NH--SO$_{2}$){4==\bzdrh{1==(yl)}};%
4==\ryl(0==NH--SO$_{2}$){7==\bzdrh{2==(yl)}}}
```

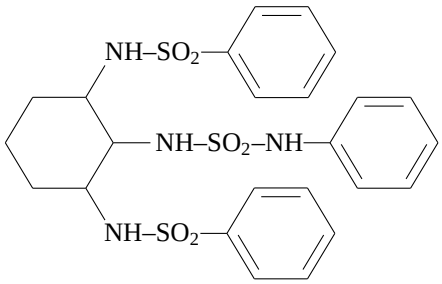
is written to give



Another example is drawn by the code

```
\cyclohexaneh{%
3==\ryl(7==NH--SO$_{2}$){4==\bzdrh{1==(yl)}};%
5==\ryl(1==NH--SO$_{2}$){4==\bzdrh{1==(yl)}};%
4==\ryl(4==NH--SO$_{2}$--NH){4==\bzdrh{1==(yl)}}}
```

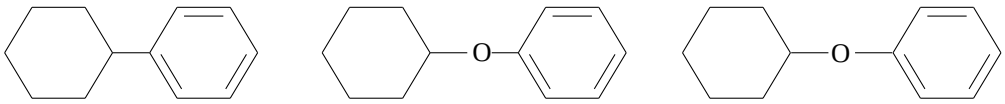
giving



The first argument in the parentheses of the command `\ryl` contains a string of letters after an intermediate delimiter ==, where a left linking site is shifted according to the length of the letter string. The above formula shows such an example as having NH–SO_2–NH.

The following examples compare the (yl)-function with the `\ryl` command.

```
\cyclohexaneh{4==\bzdrh{1==(yl)}}
\cyclohexaneh{4==\ryl(4==O){4==\bzdrh{1==(yl)}}}
\tetrahedral{0==O;2==\cyclohexaneh{4==(yl)};4==\bzdrh{1==(yl)}}
```

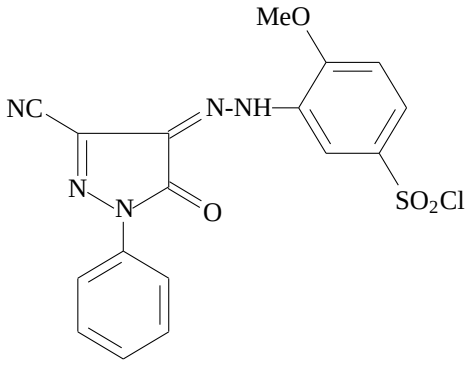


The first example corresponds to the IUPAC name *pheylcyclohexane*, while the second one corresponds to the IUPAC name *phenoxylcyclohexane*. The last example corresponds to the IUPAC name *phenyl cyclohexyl ether*, where the command `\tetrahedral` is used to draw the central unit –O– as a parent structure.

Example 26.1. The compound **21** on page 299 of the XyMTEXbook [1] can be alternatively drawn by using the `\ryl` command, as shown in the code:

```
\fiveheterov[d]{1==N;5==N}{4==NC;1==\bzdrv{1==(yl)};2D==O;%
3D==\ryl(5==N-NH){4==\bzdrh{1==(yl);2==\lmoiety{MeO};5==SO$_{2}$Cl}}}
```

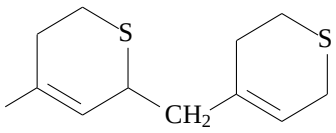
which typesets the following formula:



26-1 (= **21** of [1])

□

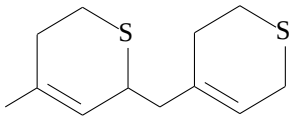
Example 26.2. The first argument of the `\ryl` is optional; i.e., it can be omitted. Such an omitted case is useful to draw a methylene as a vertex (a joint of two edges). For example, a methylene is represented as a character string "CH_2", as shown in the formula,



This formula is generated by the code,

```
\sixheterov[d]{2==S}{5==\null;%
3==\ryl(3==CH$_{2}$){3==\sixheterov[d]{2==S}{5==(yl)}}}
```

where the `\ryl` command takes an optional argument in parentheses to draw CH_2 explicitly. Such a methylene can alternatively be represented as a simple vertex, as shown in the formula,



This formula is generated by the code,

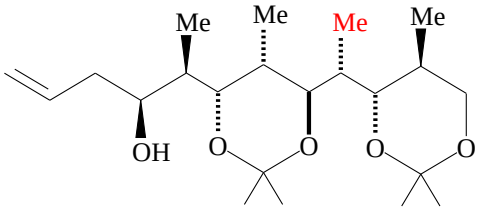
```
\sixheterov[d]{2==S}{5==\null;%
3==\ryl{3==\sixheterov[d]{2==S}{5==(yl)}}}
```

where the `\ryl` command takes no optional argument. □

Example 26.3. The second argument of the `\ryl` command can accommodate substituents other than a substituent generated by the (yl)-function. For example, the inner code `\ryl{0A==Me;...}` in the code,

```
\begin{XyMcompd}(1650,800)(-500,100){}{}
\sixheterov({bB}{eA}){3==O;5==O}{1A==Me;4Sa==\null;4Sb==\null;%
6==\pentamethylenei[a]{}{4B==OH;5B==Me;5==(yl)};%
2==\ryl{0A==\redx{Me};5==\sixheterov({eA}){3==O;5==O}{6==(yl);1B==Me;%
4Sa==\null;4Sb==\null}}}
\end{XyMcompd}
```

represents a methyl group (colored in red) on a vertex due to the command `\ryl`. Thereby, we have



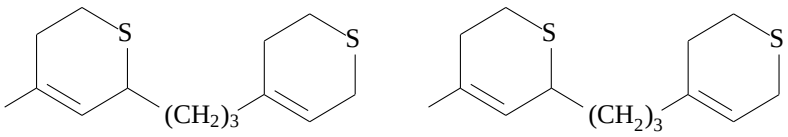
□

Example 26.4. If the linking unit contains a pair of parentheses, it should be surrounded by a pair of braces in order to differentiate them from the parentheses for designating the optional argument. For example, the character string `(CH$_{2}$)$_{3}$` should be input in the form of `{(CH$_{2}$)$_{3}$}` or `\ChemForm{(CH_{2})_{3}}`:

```
\begin{XyMcompd}(1250,500)(150,200){}{}
\sixheterov[d]{2==S}{5==\null;%
3==\ryl(3=={(CH$_{2}$)$_{3}$}){3==\sixheterov[d]{2==S}{5==(yl)}}}
\end{XyMcompd}
\qquad
```

```
\begin{XyMcompd}(1250,500)(150,200){}{}
\sixheterov[d]{2==S}{5==\null;%
3==\ryl(3==\ChemForm{(CH_{2})_{3}}){3==\sixheterov[d]{2==S}{5==(yl)}}}
\end{XyMcompd}
```

These codes provide the following structures:



□

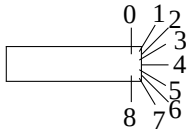
26.2 \lyl command

The command `\lyl` is the left-hand counterpart of the command `\ryl`.

```
\lyl{⟨link⟩}{⟨ylgroup⟩}
```

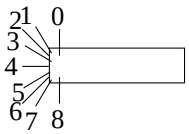
The slopes of the linking bonds concerning the right terminal (⟨link⟩) are designated by integers between 0 and 8:

0	(0, 1)	1	(3, 5)	2	(1, 1)
3	(5, 3)	4	(1, 0)	5	(5, −3)
6	(1, −1)	7	(3, −5)	8	(0, −1)



The slopes of the linking bonds concerning the left terminal (⟨ylgroup⟩) are designated by integers between 0 and 8:

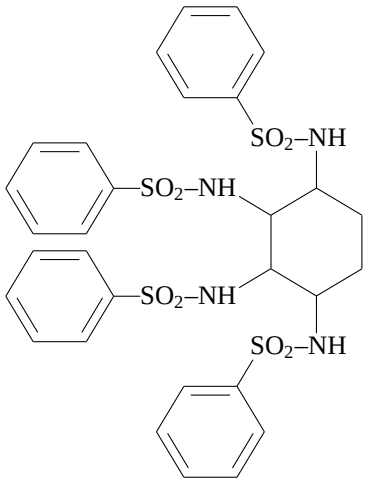
0	(0, 1)	1	(−3, 5)	2	(−1, 1)
3	(−5, 3)	4	(−1, 0)	5	(−5, −3)
6	(−1, −1)	7	(−3, −5)	8	(0, −1)



To illustrate linking bonds with various slopes, the code

```
\cyclohexanev{%
1==\lyl(8==SO$_{2}$--N\rlap{H}){1==\bzdrh{5==(yl)}};%
6==\lyl(5==SO$_{2}$--NH){4==\bzdrh{4==(yl)}};%
5==\lyl(3==SO$_{2}$--NH){4==\bzdrh{4==(yl)}};%
4==\lyl(0==SO$_{2}$--N\rlap{H}){7==\bzdrh{3==(yl)}}}
```

is written to give

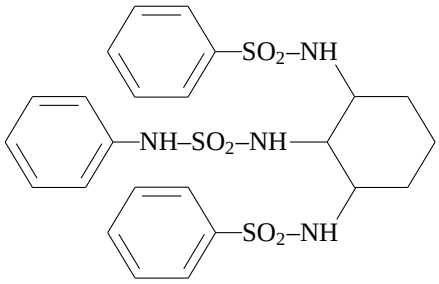


Note that the declaration of `\llap{H}` in `SO$_{2}$--N\rlap{H}` aims at drawing a unit NH which has an N atom as a linking point, where the atom H of the unit NH appears as a size-less atom.

Another example is drawn by the code

```
\cyclohexaneh{%
2==\lyl(7==SO$_{2}$--NH){4==\bzdrh{4==(yl)}};%
6==\lyl(1==SO$_{2}$--NH){4==\bzdrh{4==(yl)}};%
1==\lyl(4==NH--SO$_{2}$--NH){4==\bzdrh{4==(yl)}}}
```

giving

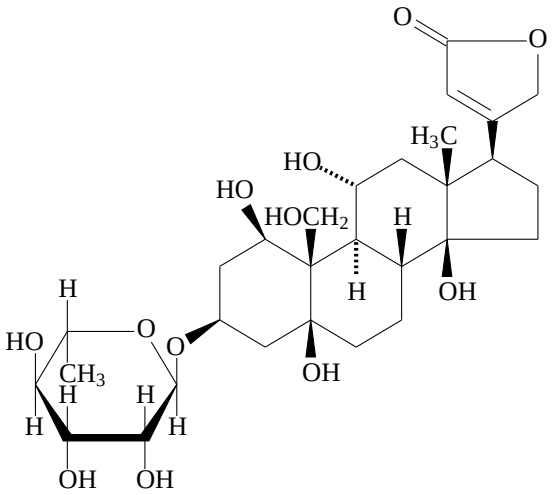


The first argument in the parentheses of the command `\lyl` contains a string of letters after an intermediate delimiter ==, where a left linking site is shifted according to the length of the letter string. The above formula shows such an example as having NH–SO_2–NH.

Example 26.5. The structural formula **26-2** of *g*-strophanthin (ouabain) as a poisonous cardiac glycoside is drawn by the code:

```
\begin{XyMcompd}(2000,1850)(-550,-300){}{}
\steroid{1SB==\lmoiety{HO};5B==OH;8B==H;9A==H;{11}A==HO;%
{10}B==\llap{HO}CH$_{2}$;{14}B==OH;%
{13}B==\lmoiety{H$_{3}$C};%
{17}B==\fiveheterov[e]{3==O}{4D==O;1==(yl)};%
3B==\lyl(3==O){8==%
\pyranosew{1==(yl);1Sa==H;2Sb==H;2Sa==OH;3Sb==H;3Sa==OH;4Sb==HO;%
4Sa==H;5Sb==H;5Sa==CH$_{3}$}}}
\end{XyMcompd}
```

This code typesets the following structural formula:



26-2

See the structure of adonitoxin (**24-13** and **24-14**) in Chapter 24 (cf. Chapter 15 of the XeTeXbook [1]). □

26.3 Nested \ryl and \lyl commands

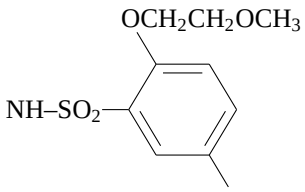
Two or more `\ryl` and `\lyl` commands can be nested.

Example 26.6. Let us illustrate nesting processes by drawing a cyan dye releaser [2, page 474], which has once been depicted in different ways (**24-6** and **24-12** in Chapter 24, cf. Chapters 14 and 15 of the XeTeXbook [1]).

1. First, the code

   ```
   \ryl(4==NH--SO$_{2}$){4==\bzdrh{1==(yl);2==OCH$_{2}$CH$_{2}$OCH$_{3}$;%
   5==\null}}
   ```

   generates a substituent:

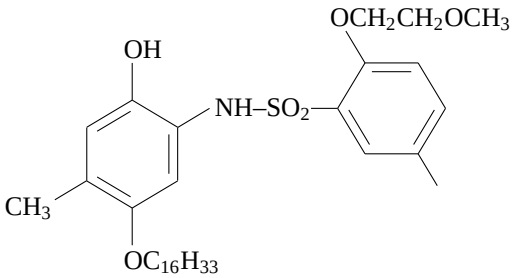
   

   in which the command `\null` is used to show a further substitution site.

2. The resulting substituent is nested in the ⟨subslist⟩ of another `\bzdrv` command as shown in the code:

   ```
   \bzdrv{1==OH;5==CH$_{3}$;4==OC$_{16}$H$_{33}$;%
   2==\ryl(4==NH--SO$_{2}$){4==\bzdrh{1==(yl);2==OCH$_{2}$CH$_{2}$OCH$_{3}$;%
   5==\null}}}
   ```

   Thereby we have

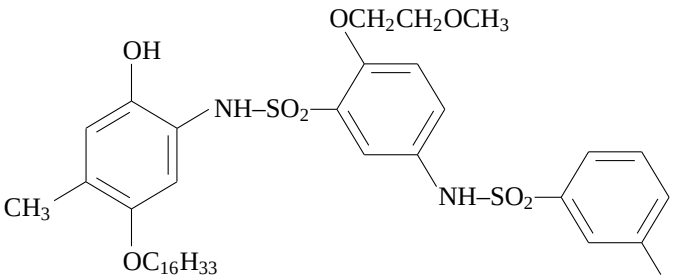
3. The inner code `5==\null` is replaced by a further code of substitution:

```
5==\ryl(2==NH--SO$_{2}$){4==\bzdrh{1==(yl);5==\null}}%
```

to give a code,

```
\bzdrv{1==OH;5==CH$_{3}$;4==OC$_{16}$H$_{33}$;%
2==\ryl(4==NH--SO$_{2}$){4==\bzdrh{1==(yl);2==OCH$_{2}$CH$_{2}$OCH$_{3}$;%
5==\ryl(2==NH--SO$_{2}$){4==\bzdrh{1==(yl);5==\null}}%
}}}
```

This code generates the following structure (**26-3**):

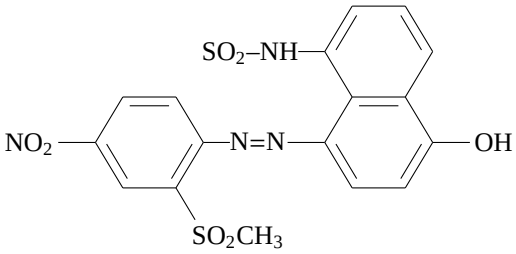


26-3

4. Another substituent is typeset by the code,

```
\ryl(2==SO$_{2}$--NH){4==\naphdrh{1==(yl);5==OH;%
8==\lyl(4==N=N){4==\bzdrh{4==(yl);1==NO$_{2}$;5==SO$_{2}$CH$_{3}$}}}}
```

Then, we have a substituent (**26-4**):

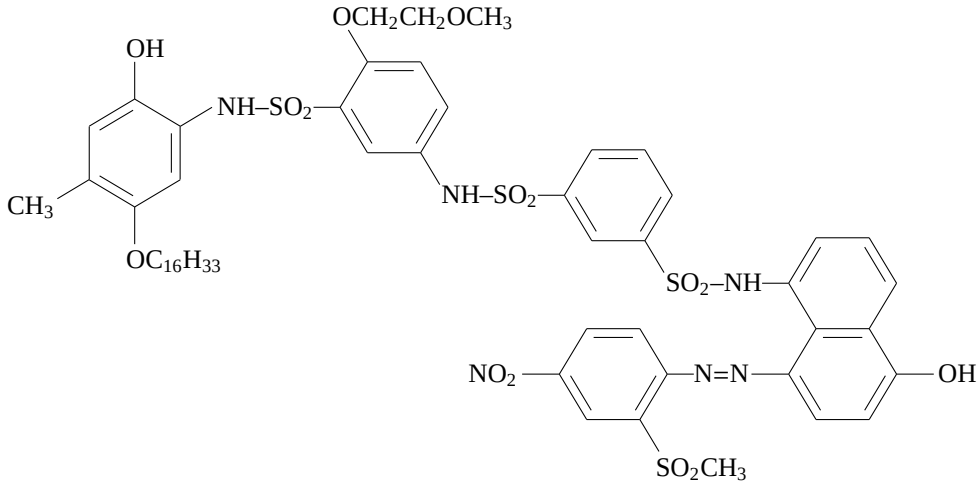


26-4

5. Finally, the inner code `5==\null` for **26-3** is replaced by the code for **26-4** in order to combine **26-3** with **26-4**. Then we obtain a code represented by

```
\bzdrv{1==OH;5==CH$_{3}$;4==OC$_{16}$H$_{33}$;%
2==\ryl(4==NH--SO$_{2}$){4==\bzdrh{1==(yl);2==OCH$_{2}$CH$_{2}$OCH$_{3}$;%
5==\ryl(2==NH--SO$_{2}$){4==\bzdrh{1==(yl);%
5==\ryl(2==SO$_{2}$--NH){4==\naphdrh{1==(yl);5==OH;%
8==\lyl(4==N=N){4==\bzdrh{4==(yl);1==NO$_{2}$;5==SO$_{2}$CH$_{3}$}}}}}}}}}
```

Thereby, we have a target formula:



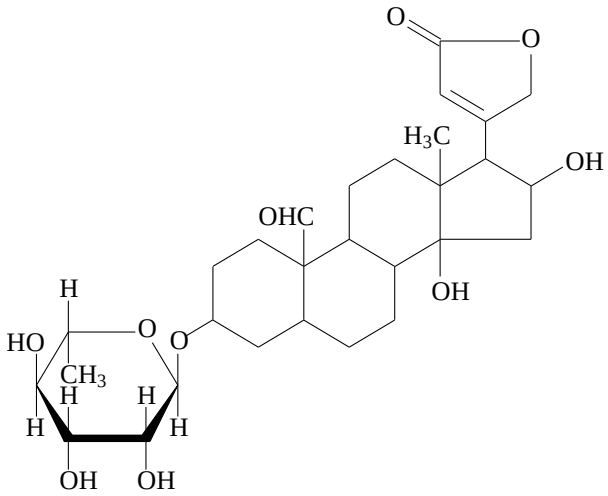
26-5 (= **24-6** = **24-12**)

□

Example 26.7. The structural formula of adonitoxin, which has been drawn by considering the steroid nucleus to be a mother skeleton in Section 24.4 (**24-13** in Example 24.22 and **24-14** in Example 24.23), can be alternatively drawn by nesting a (yl)-function and a `\ryl` command. In this case, the pyranose ring is regarded as a mother skeleton. Thus, the code

```
\pyranosew{1Sa==H;2Sb==H;2Sa==OH;3Sb==H;3Sa==OH;4Sb==HO;%
4Sa==H;5Sb==H;5Sa==CH$_{3}$;%
1Sb==\ryl(8==O){3==%
\steroid{3==(yl);{{10}}==\lmoiety{OHC};{{14}}==OH;%
{{13}}==\lmoiety{H$_{3}$C};{{16}}==OH;%
{{17}}==\fiveheterov[e]{3==O}{4D==O;1==(yl)}}}}
```

typesets the following formula:



26-6 (cf. **24-13** = **24-14**)

See also Example 26.5. □

26.4 Divalent Skeletons

26.4.1 \divalenth Command

The command `\divalenth` generates a divalent skeleton with variable length.

```
\divalenth{⟨divalskel⟩}{⟨subslist⟩}
```

The divalent skeleton is given by a string of alphabets in the ⟨divalskel⟩ argument. The locant number in the ⟨divalskel⟩ argument is fixed to be zero. The argument ⟨subslist⟩ specifies two substituents as a list of substitutions, where the locant numbers 1 and 2 are effective. For example, the code

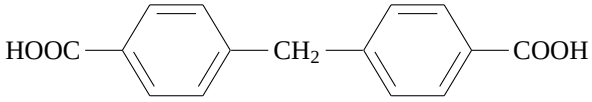
```
\divalenth{0==NHCONH}{1==CH$_{3}$;2==CH$_{3}$}
```

generates a linear formula:

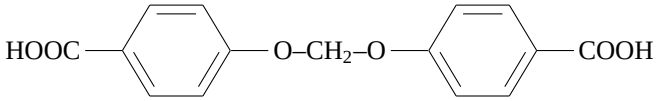
4,4′-Methylenedibenzoic acid can be drawn in the same line. The code

```
\divalenth{0==CH$_{2}$}{1==\bzdrh{4==(yl);1==HOOC};2==\bzdrh{1==(yl);4==COOH}}
```

generates



In place of the CH_2 unit described in the preceding example, we introduce the O–CH_2–O unit so as to give 4,4′-methylenedioxydibenzoic acid. The structural formula can be drawn to be

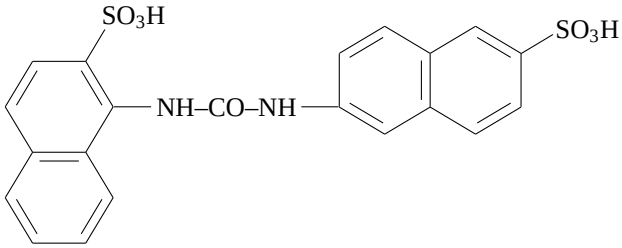


by means of the code:

```
\divalenth{0==O--CH$_{2}$--O}%
{1==\bzdrh{4==(yl);1==HOOC};2==\bzdrh{1==(yl);4==COOH}}
```

Note that the starting point of the moiety generated by the code `2==\bzdrh{1==(yl);4==COOH}` is automatically shifted so as to accommodate the O–CH_2–O skeleton.

Example 26.8. An additional example of the use of the `\divalenth` command is the drawing of 1,6′-ureylenedi-2-naphthalenesulfonic acid



by means of the code

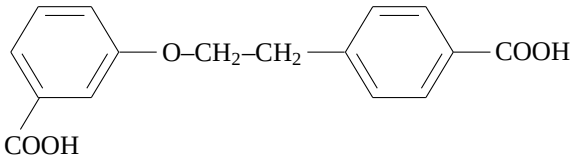
```
\divalenth{0==NH--CO--NH}%
{1==\naphdrh{4==(yl);3==SO$_{3}$H};2==\naphdrv{6==(yl);2==SO$_{3}$H}}
```

□

Example 26.9. As a further example, *p*-[2-(*m*-carboxyphenoxy)ethyl]benzoic acid is drawn by the code

```
\divalenth{0==O--CH$_{2}$--CH$_{2}$}%
{1==\bzdrh{4==(yl);6==COOH};2==\bzdrh{1==(yl);4==COOH}}
```

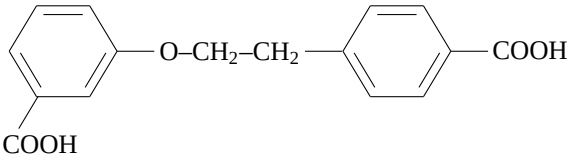
which generates a formula:



The same structure can be depicted by applying the (yl)-function to the `\divalenth` command. The code

```
\bzdrh{6==COOH;4==%
\divalenth{0==O--CH$_{2}$--CH$_{2}$}{1==(yl);2==\bzdrh{1==(yl);4==COOH}}}
```

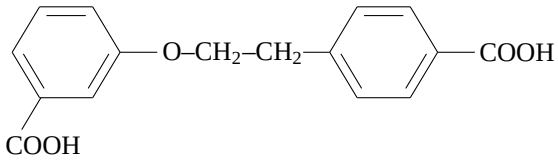
generates the same formula:



This type of usage gives an equivalent function of the command `\ryl` or `\lyl`. Compare this with an example using the `\ryl` command:

```
\bzdrh{6==COOH;4==%
\ryl(4==O--CH$_{2}$--CH$_{2}$){4==\bzdrh{1==(yl);4==COOH}}}
```

This code gives the same formula:



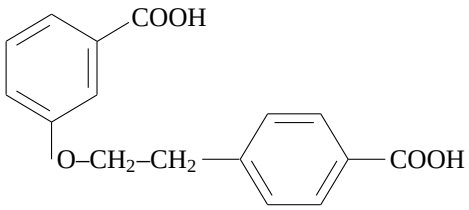
□

Remarks

The use of `\divalenth` with a (yl)-function has no means of adjusting the left-hand point of linking. For example, the code,

```
\bzdrv{2==COOH;4==%
\divalenth{0==O--CH$_{2}$--CH$_{2}$}{1==(yl);2==\bzdrh{1==(yl);4==COOH}}}
```

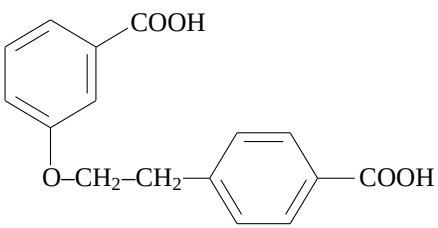
give an insufficient formula:



where the left-hand point of linking should be shifted to a more appropriate direction. On the other hand, the `\ryl` (or `\lyl`) command can correctly specify the left-hand point of linking. Thus the code,

```
\bzdrv{2==COOH;4==%
\ryl(0==O--CH$_{2}$--CH$_{2}$){4==\bzdrh{1==(yl);4==COOH}}}
```

typesets a formula:

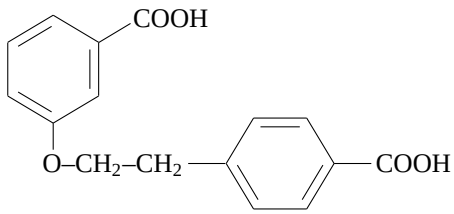


where the code `0==O--CH$_{2}$--CH$_{2}$` specifies the left-hand terminal of the unit O–CH_2–CH_2 is linked at the upper point of the oxygen atom.

The skeleton `O--CH$_{2}$--CH$_{2}$` can be drawn as a central unit of the command `\tetrahedral`. The following code:

```
\tetrahedral{0==O--CH$_{2}$--CH$_{2}$;%
1==\bzdrv{2==COOH;4==(yl)};%
4==\bzdrh{1==(yl);4==COOH}}
```

typesets an equivalent structure:



26.4.2 \BiFunc Command

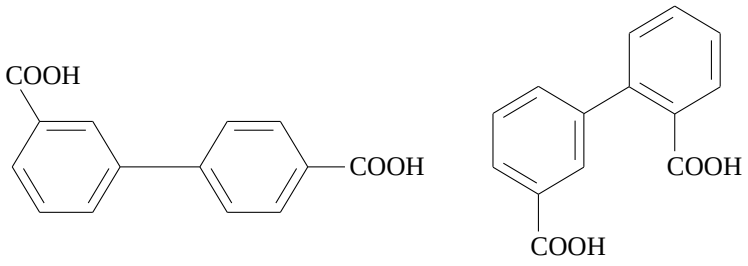
The command `\BiFunc` generates a dumbbell skeleton with a given length.

```
\BiFunc(⟨slope⟩){⟨length⟩}{⟨moietyA⟩}{⟨moietyB⟩}
```

The argument ⟨slope⟩ is given in a similar way to the `\line` command of the LaTeX picture environment, e.g., `(1,0)` and `(2,3)`. The argument ⟨length⟩ specifies the length of the dumbbell skeleton. The argument ⟨moietyA⟩ represents the left-hand substituent (moiety A), while the argument ⟨moietyB⟩ represents the right-hand substituent (moiety B). Thus, the command `\BiFunc` supports the function for linking moiety A and moiety B through a bond with a given slope and a given length. For example, the codes

```
\BiFunc(1,0){300}{\bzdrh{2==COOH;4==(yl)}}{\bzdrh{1==(yl);4==COOH}}
\BiFunc(5,3){171}{\bzdrv{4==COOH;2==(yl)}}{\bzdrv{5==(yl);4==COOH}}
```

generate the following structures:



References

[1] S. Fujita, “XMTEX—Typesetting Chemical Structural Formulas,” Addison-Wesley Japan, Tokyo (1997).

[2] S. Fujita, “Organic Chemistry of Photography,” Springer-Verlag, Berlin-Heidelberg (2004).

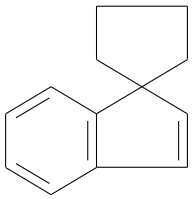
Chapter 27

The Replacement Technique for Drawing Spiro Rings and Related Techniques

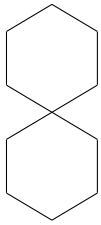
Spiro ring systems based on the replacement technique have been briefly discussed in Section 2.6. The present section is devoted to more detailed discussions on the IUPAC nomenclature of spiro ring systems, the skeletal replacement ('a') nomenclature (cf. Subsection 2.3.2), and the replacement technique.

27.1 General Conventions for Spiro-Ring Attachment

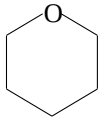
There are several ways for naming spiro compounds in the light of the IUPAC nomenclature [1,2]. Rule A-41.4 [1] or Rule SP-4.1 [2] allows us to use such a name as spiro[cyclopentane-1,1′-indene] for representing the following structure:



The same structure is named indene-1-spiro-1′-cyclohexane in terms of Rule A-42.1. Spiro[5.5]undecane, the name due to Rule A-41.1 and A-41.2 [1] or Rule SP-1.2 [2], is alternatively referred to as cyclohexanespirocyclohexane in terms of Rule A-42.1 [1]:



where the 'cyclohexanespiro' shows the replacement of a carbon atom in a cyclohexane by another cyclohexane ring. These rules essentially take the same methodology as the IUPAC replacement nomenclature, e.g., oxacyclohexane (more formally, oxane or tetrahydropyran) for the formula



generated by the code,

```
\sixheterov{1==O}{}
```

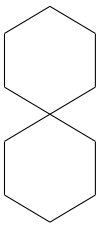
where the prefix ‘oxa’ shows the replacement of a carbon atom with an oxygen atom. Obviously, the prefix ‘cyclohexanespiro’ of the name ‘cyclohexanespirocyclohexane’ is akin to the prefix ‘oxa’ of the name ‘oxacyclohexane’ or ‘oxane’ from the viewpoint of the construction of names. Since the unit due to the latter prefix is designated by the `1==O` involved in the ⟨atomlist⟩, the former prefix can be treated in the same way. Hence, spiro compounds are drawn according to the replacement technique:

1. XƎMTEX regards a spiro ring as a unit for the IUPAC replacement nomenclature, which is generated from an appropriate structure by (yl)-function.
2. the code of the unit due to the (yl)-function is added to the ⟨atomlist⟩ of a parent skeleton.

Spiro[5.5]undecane is regarded as ‘cyclohexana’-cyclohexane (more formally, ‘cyclohexanespiro’-cyclohexane), as found in the code,

```
\sixheterov{1s==\sixheterov{}{4==(yl)}}{}
```

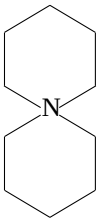
where the code `\sixheterov{}{4==(yl)}` produced by the (yl)-function corresponds to the suffix ‘cyclohexana’ and is written in the ⟨atomlist⟩ of the outer `sixheterov` command. Thereby, we can obtain



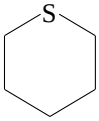
Note that the atom modifier ‘s’ in the code `1s==\sixheterov{}{4==(yl)}` represents no hetero-atom at the spiro position. When a hetero-atom is present at the spiro position, an atom modifier ‘h’ is used in place of ‘s’. For example, the code

```
\sixheterov{1h==\sixheterov{4==N}{4==(yl)}}{}
```

typesets the following formula:



It should be noted that the absence of such atom modifiers represents a usual replacement by a hetero atom, as found in the formula of oxane shown above or in the one of thiacyclohexane (tetrahydrothiane):



generated by the code,

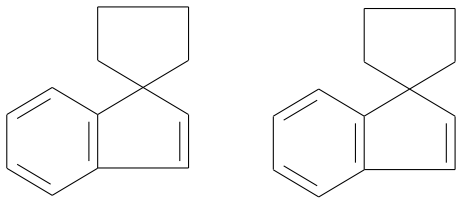
```
\sixheterov{1==S}{}
```

27.2 Illustrative Examples of Drawing Spiro Rings

27.2.1 Mono-Spiro Derivatives

XƎMTEX commands with ⟨subslist⟩ are capable of generating substituents by declaring a (yl)-function. The resulting substituents are used to depict spiro rings by the process described in the preceding section.

Example 27.1. Spiro[cyclopentane-1,1′-indene] described above can be drawn in two ways:

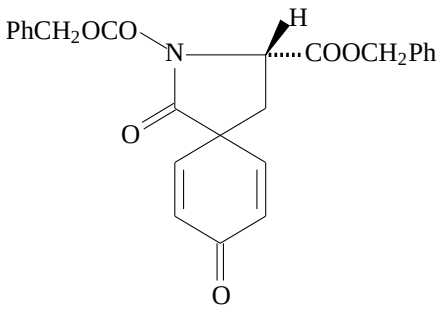


where we use two different codes:

```
\nonaheterovi[begj]{1s==\fiveheterov{}{1==(yl)}}{}
\fiveheterov{1s==\nonaheterovi[begj]{}{1==(yl)}}{}
```

which correspond to ‘cyclohexane-1-spiro-1′-indene’ and ‘indene-1-spiro-1′-cyclohexane’ (formal), respectively. □

Example 27.2. The structure **27-1** of a spiro dienone:



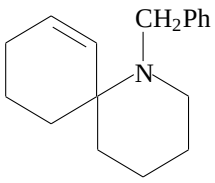
27-1

can be drawn by writing a code,

```
\sixheterov[be]{%
1s==\fiveheterov{4==N}{1==(yl);3SB==H;3SA==COOCH$_{2}$Ph;%
4==PhCH$_{2}$OCO;5D==O}}{4D==O}
```

See **3-69** and **3-85** for more elaborate expressions of stereochemistry. □

Example 27.3. 1-Azaspiro[5.5]undecene, which is the skeleton of histrionicotoxin (Tetrahedron Lett., 1981, **22**, 2247),



can be drawn by the code,

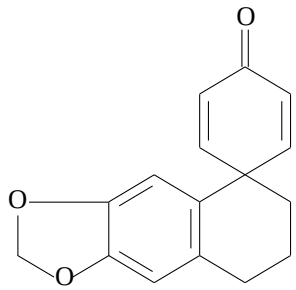
```
\sixheterov{1==N;6s==\cyclohexanev[a]{3==(yl)}}{1==CH$_{2}$Ph}
```

□

Example 27.4. The following example shows a case to which both ring fusion (due to the addition technique) and spiro attachment (due to the replacement technique) are applied. The code,

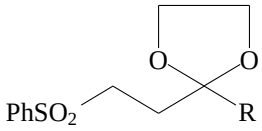
```
\decaheterov[fhk%
{g\fivefusev{1==O;4==O}{}{b}}%
]{1s==\cyclohexanev[be]{1D==O;4==(yl)}}{}
```

gives the following formula:



□

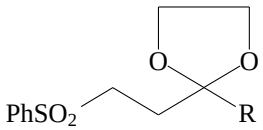
Example 27.5. A 1,3-dioxolane derivative



can be drawn by the code due to the replacement technique:

```
\fiveheterov{2==O;5==O;1s==\trimethylenei{}{3==(yl);1W==PhSO$_{2}$;3W==R}}{}
```

where the command `\fiveheterov` is used to draw a parent skeleton. On the other hand, the following structure is drawn alternatively,

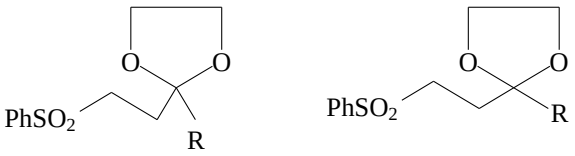


where the command `\trimethylenei` is used to draw a parent skeleton as found in the following code:

```
\trimethylenei{3s==\fiveheterov{2==O;5==O}{1==(yl)}}{1W==PhSO$_{2}$;3W==R}
```

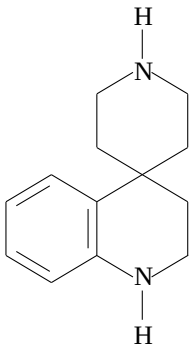
The same compound is also drawn by the substitution technique, as found in the following two codes:

```
\fiveheterov{2==O;5==O}{1Sb==\dimethylenei{}{2==(yl);1W==PhSO$_{2}$};1Sa==R}
\fiveheterov{2==O;5==O}{1G==\dimethylenei{}{2==(yl);1W==PhSO$_{2}$};1F==R}
```



□

Example 27.6. The structure **27-2** of 1,2,3,4-tetrahydroquinoline-4-spiro-4′-piperidine,



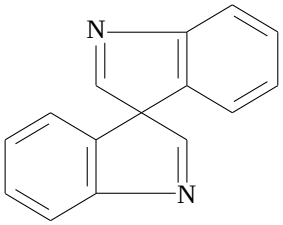
27-2

can be drawn by writing a code,

```
\decaheterovi[fhk]{1==N;4s==\sixheterov{1==N}{4==(yl);1==H}}{1==H}
```

□

Example 27.7. 3,3′-Spirobi[3*H*-indole],



is typeset by the code,

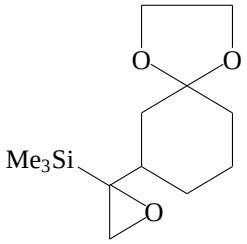
```
\nonaheterovi[begj]{3==N;%
1s==\fiveheterov[bd{b\sixfusev[ac]{}{}{e}}]{4==N}{1==(yl)}}{}
```

□

Example 27.8. The code,

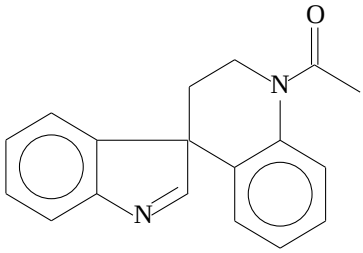
```
\sixheterov[]{1s==\fiveheterov{2==O;5==O}{1==(yl)}}{%
5==\threeheteroh{1==O}{3Sb==Me$_{3}$Si;3==(yl)}}
```

typesets the following structure:



□

Example 27.9. A spiro intermediate during spiro annelation (T. S. T. Wang, *Tetrahedron Lett.*, 1975, 1637),

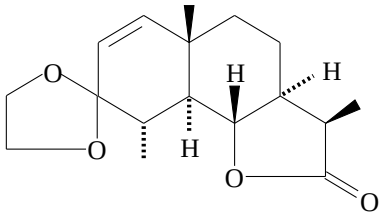


can be drawn by the code,

```
\nonaheterov[aA]{1==N;%
3s==\decaheterovb[B]{8==N}{5==(yl);8==\dimethylenei{}{1D==O;1==(yl)}}}{}
```

□

Example 27.10. A lactone intermediate containing a protected ketone (A. Grieco and M. Nishizawa, *Chem. Commun.*, 1976, 582),



is drawn by the code,

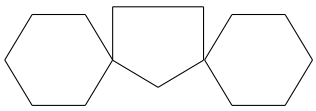
```
\decaheterov[h{c\fivefusevi{4==O}{1GA==H;5GB==H;2B==;3D==O}{E}}]{%
6s==\fiveheterovi{1==O;3==O}{2==(yl)}}{5A==;{10}B==;9A==H}
```

which adopts the addition technique for ring fusion and the replacement technique for spiro ring fusion. □

27.2.2 Multi-Spiro Derivatives

Multi-spiro derivatives are drawn by nesting spiro function.

Example 27.11. For example, cyclohexanespirocyclopentane-3′-spirocyclohexane (Rule A-42.4 [1]),

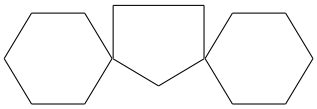


is typeset by the code,

```
\sixheteroh{4s==\fiveheterov{%
2s==\sixheteroh{}{1==(yl)}}{5==(yl)}}{}
```

When `\fiveheterov` is a mother skeleton, such a nested command is unnecessary:

```
\fiveheterov{2s==\sixheteroh{}{1==(yl)};%
5s==\sixheteroh{}{4==(yl)}}{}
```



□

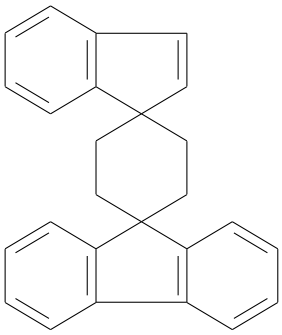
27.2.3 Nested Spiro Compounds

Multi-spiro compounds can be drawn by nested application of the replacement technique (so-called “atom replacement”), where a spiro ring is successively designated in the atom list (⟨atomlist⟩) argument of a mother skeleton.

Example 27.12. The name (Rule A-42.4 [1]), fluorene-9-spiro-1′-cyclohexane-4′-spiro-1′-indene, corresponds to the code,

```
\nonaheterovi[begj{b\sixfusev[ac]{}{}{E}}]{%
1s==\sixheterov{1s==\nonaheterov[begj]{}{1==(yl)}}{4==(yl)}}{}
```

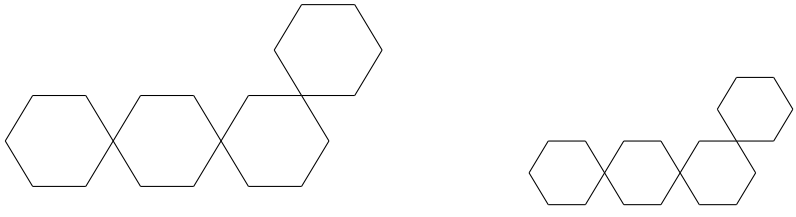
which gives



where the single usage of the addition technique (for ring fusion) and the nested usage of the replacement technique (for spiro ring fusion) are involved. □

Example 27.13. The following example shows a multi-nested drawing of a spiro-compound. The formula appearing in the right-hand side is drawn under declaring `\changeunitlength{0.07pt}`

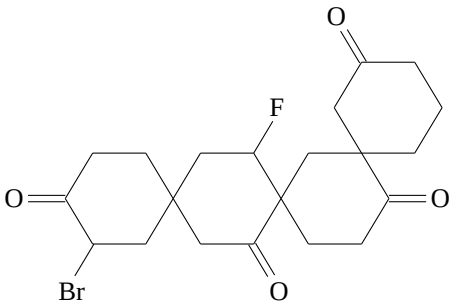
```
\sixheteroh{4s==\sixheteroh{4s==\sixheteroh{%
3s==\sixheteroh{}{6==(yl)}}{1==(yl)}}{1==(yl)}}{}
```

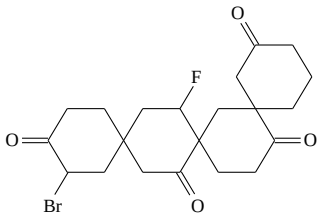


□

Example 27.14. Each component of the formula can take substituents, which are designated by using the corresponding substitution list (⟨substlist⟩).

```
\sixheteroh{4s==\sixheteroh{%
4s==\sixheteroh{3s==\sixheteroh{}{6==(yl);2D==O}}{1==(yl);4D==O}}%
{1==(yl);5D==O;3==F}}{1D==O;6==Br}
```

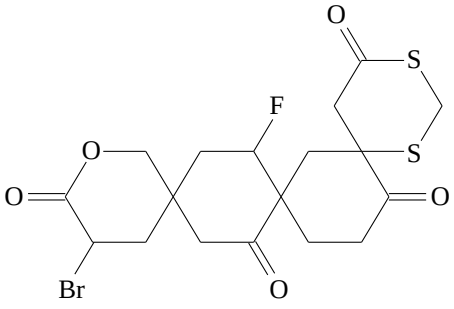


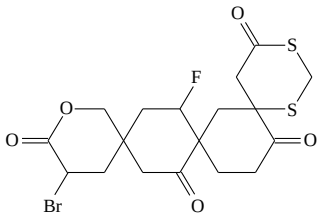


□

Example 27.15. Hetero atoms can be placed on the vertices of each component, where they are designated by using the atom list (⟨atomlist⟩).

```
\sixheteroh{2==O;4s==\sixheteroh{%
4s==\sixheteroh{3s==\sixheteroh{3==S;5==S}{6==(yl);2D==O}}{1==(yl);4D==O}}%
{1==(yl);5D==O;3==F}}{1D==O;6==Br}
```





□

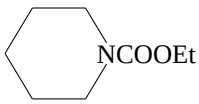
27.3 Atom Replacement

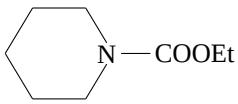
27.3.1 Substituents with Hetero Terminals

The ⟨atomlist⟩ of each command is capable of accommodating a group if a sufficient space is available. For example, compare two codes,

```
\sixheteroh{4==NCOOEt}{}
\sixheteroh{4==N}{4==COOEt}
```

generating formulas equivalent chemically to each other:



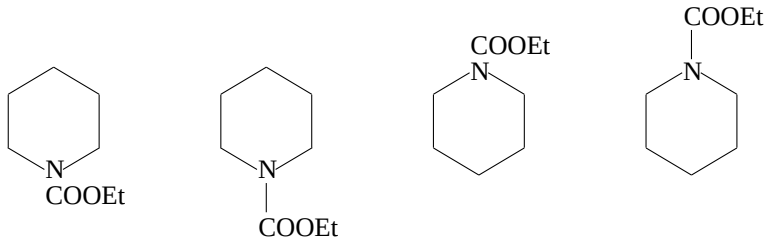


Note that the former example uses an ⟨atomlist⟩ and the latter uses a ⟨substlist⟩ for describing substituents.

Even when no such space is available, the use of a command, \upnobond or \downnobond, give a solution (see XMTEXbook [3, pages 259–260]):

```
\upnobond{⟨atom⟩}{⟨subst⟩}
\downnobond{⟨atom⟩}{⟨subst⟩}
```

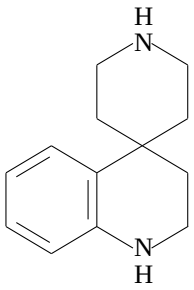
where an atomic component is divided into an atom (⟨atom⟩) and a substituent (⟨subst⟩) . Compare the following formulas,



which are generated by the codes,

```
\sixheterov{4==\downnobond{N}{COOEt}}{}
\sixheterov{4==N}{4==COOEt}
\sixheterov{1==\upnobond{N}{COOEt}}{}
\sixheterov{1==N}{1==COOEt}
```

Example 27.16. The bonds N—H appearing in **27-2** are frequently omitted as found in the following structure:



27-3

This structure can be drawn by writing a code,

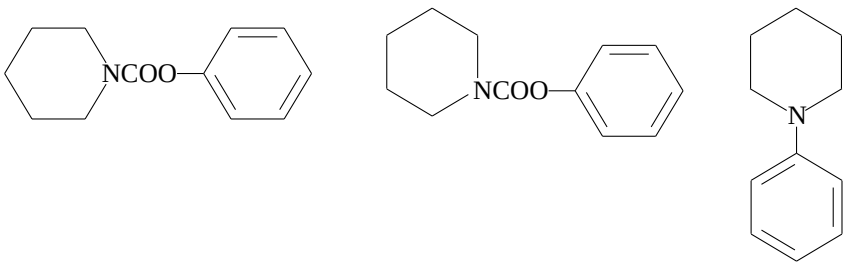
```
\decaheterovi[fhk]{1==\downnobond{N}{H};%
4s==\sixheterov{1==\upnobond{N}{H}}{4==(yl)}}{}
```

where the commands \upnobond and \downnobond are used. □

These examples show that an atomic component (e.g., NCOOEt) can be regarded as a component for atom replacement using an ⟨atomlist⟩. This methodology can be applied to a case in which such a substituent is generated by the (yl)-function or by such a linking command as \ryl or \lyl.

Example 27.17. The following example shows the use the \ryl command in the ⟨atomlist⟩ of \sixheteroh.

```
\sixheteroh{4h==\ryl(4==NCOO){4==\bzdrh{1==(yl)}}}{}
\hskip2cm
\sixheterov{3h==\ryl(4==NCOO){4==\bzdrh{1==(yl)}}}{}
\hskip2cm
\sixheterov{4h==\ryl(0==N){8==\bzdrv{1==(yl)}}}{}
```

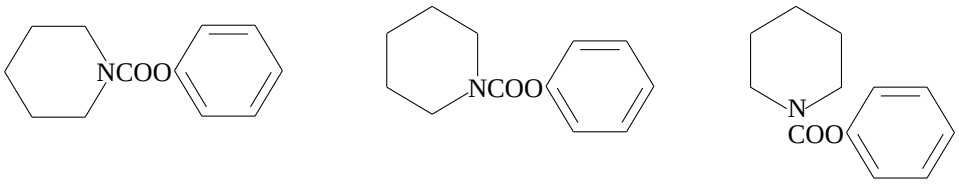


A bond between a COO unit and a phenyl group is frequently omitted. For this purpose, we use command \ayl defined as

```
\makeatletter
\def\ayl{\@ifnextchar({\@ayl@}{\@ayl@(10,40)}}
\def\@ayl@(#1,#2)#3{%
\begingroup\yl@xdiff=0 \yl@ydiff=0%
\kern#1\unitlength\raise#2\unitlength\hbox to0pt{#3\hss}%
\endgroup}
\makeatother
```

Thereby, we have the following examples.

```
\sixheteroh{4==NCOO\ayl{\bzdrh{1==(yl)}}}{}
\hskip2cm
\sixheterov{3==NCOO\ayl{\bzdrh{1==(yl)}}}{}
\hskip2cm
\sixheterov{4==\downnobond{N}{COO\ayl{\bzdrh{1==(yl)}}}}{}
```




```
\tetramethylene[a]{3==\downnobond{N}{COO\ayl{\bzdrh{1==(yl)}}}}{}
\hskip2cm
\tetramethylene[a]{3==N}{3==COO\ayl{\bzdrh{1==(yl)}}}
```

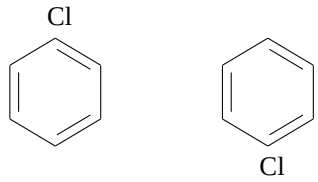

```
\hexamethylene[a]{3==\downnobond{N}{COO\ayl(5,-3){\bzdrh{2==(yl)}}}}{}
\hskip2cm
\hexamethylene[a]{3==N}{3==COO\ayl(5,-3){\bzdrh{2==(yl)}}}
```

□

27.3.2 Substituents with Carbon Terminals

The commands \upnobond and \downnobond can be used to draw substituents with carbon terminals. For example, chlorobenzene with no linking (C)—Cl bond is drawn by the following codes:

```
\sixheterov[ace]{1==\upnobond{}{Cl};1s==}{}
\sixheterov[ace]{4==\downnobond{}{Cl};4s==}{}
```

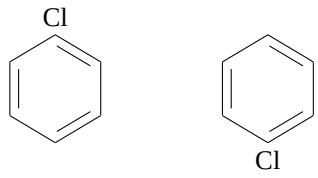


although this technique is rather dirty.

A more direct method uses the commands \put and \makebox of the LaTeX picture environment. For example, the codes:

```
\sixheterov[ace]{1s==\put(0,30){\makebox(0,0)[b]{Cl}}}{}
\sixheterov[ace]{4s==\put(0,-30){\makebox(0,0)[t]{Cl}}}{}
```

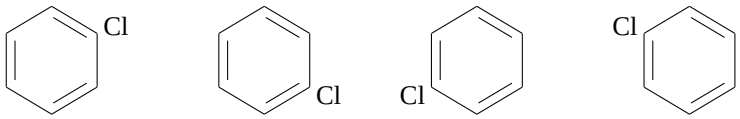
produce the following structures:



This technique is applicable to draw other structures in which a chlorine atom is substituted at a different position. Thus, the codes:

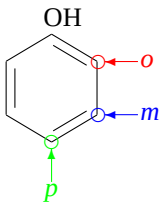
```
\sixheterov[ace]{2s==\put(20,30){\makebox(0,0)[l]{Cl}}}{}
\sixheterov[ace]{3s==\put(20,-30){\makebox(0,0)[l]{Cl}}}{}
\sixheterov[ace]{5s==\put(-20,-30){\makebox(0,0)[r]{Cl}}}{}
\sixheterov[ace]{6s==\put(-20,30){\makebox(0,0)[r]{Cl}}}{}
```

produce the following structures:



Example 27.18. This technique is applicable to draw a structure with several comments other than substituents. For example, additional commands for the LaTeX picture environment, e.g., \circle and \vector, are used to denote *o*-, *m*-, and *p*-positions:

```
\sixheterov[ace]{%
1s==\put(-30,30){\makebox(0,0)[bl]{OH}};%
2s==\put(0,0){\redx{\circle{50}}};%
2s==\put(150,0){\redx{\vector(-1,0){125}}};%
2s==\put(160,0){\makebox(0,0)[l]{\redx{\textit{o}}}};%
3s==\put(0,0){\redx{\circle{50}}};%
3s==\put(150,0){\redx{\vector(-1,0){125}}};%
3s==\put(160,0){\makebox(0,0)[l]{\redx{\textit{m}}}};%
4s==\put(0,0){\redx{\circle{50}}};%
4s==\put(0,-150){\redx{\vector(0,1){125}}};%
4s==\put(0,-160){\makebox(0,0)[t]{\redx{\textit{p}}}}}{}
```



□

27.3.3 Drawing Additional Skeletal Bonds

The command \PutBondLine can be used to draw an additional skeletal bond according to the replacement technique. The syntax of this command is shown as follows:

```
\PutBondLine(⟨start⟩)(⟨endpint⟩){⟨thickness⟩}
\PutDashedBond(⟨start⟩)(⟨endpint⟩){⟨thickness⟩}
```

where the arguments ⟨start⟩ and ⟨endpoint⟩ represent the coordinates of a starting point and an endpoint for drawing a skeletal bond, while the argument ⟨thickness⟩ represents the thickness of the skeletal bond. Note that the *x*- and *y*-values of each coordinate are given as multiple values of \unitlength (= 0.1pt). The command \PutDashedBond is a dotted-line version of the \PutBondLine.

According to the replacement technique, these commands are declared in the ⟨atomlist⟩ of such a parent command as \sixheterov:

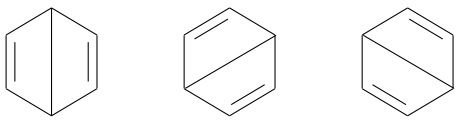
```
\sixheterov{3s==\PutBondLine(0,0)(-342,0){0.4pt}}{}
\sixheterov{1s==\PutBondLine(0,0)(171,-303){0.4pt}}{}
\sixheterov{3s==\PutDashedBond(0,0)(-342,0){2pt}}{}
\sixheterov{1s==\PutDashedBond(0,0)(171,-303){2pt}}{}
```

These codes provide the following structures:

Example 27.19. Similarly, different structures of the Dewar benzene can be drawn by using the command \PutBondLine according to the replacement technique:

```
\sixheterov[be]{1s==\PutBondLine(0,0)(0,-406){0.4pt}}{}
\sixheterov[cf]{2s==\PutBondLine(0,0)(-342,-200){0.4pt}}{}
\sixheterov[ad]{3s==\PutBondLine(0,0)(-342,200){0.4pt}}{}
```

These codes provide the following structures:



□

The XeLaTeX system supports a set of commands \WedgeAsSubst and \HashWedgeAsSubst to draw wedges and hashed wedges as skeletal bonds:

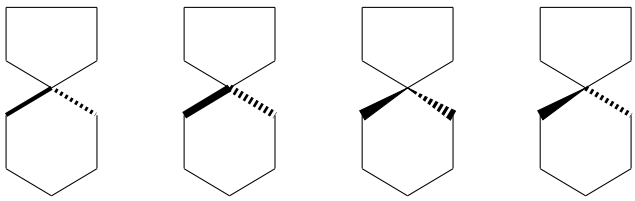
```
\WedgeAsSubst(⟨start⟩)(⟨slope⟩){⟨length⟩}
\HashWedgeAsSubst(⟨start⟩)(⟨slope⟩){⟨length⟩}
```

where the argument ⟨start⟩ represents the coordinate of a starting point, the argument ⟨slope⟩ represents the slope of a wedge or hashed wedge, and the argument ⟨length⟩ represents a bond length.

According to the replacement technique, these commands are declared in the ⟨atomlist⟩ of a mother skeleton, as found in the following codes:

```
\fiveheterov{1s==\sixheterov({aA}{fB}){}{1==(yl)}}{}
%
\fiveheterov{1s==\sixheterov{%
1s==\PutBondLine(0,0)(-171,-103){2.8pt};%
1s==\PutDashedBond(0,0)(171,-103){2.8pt};%
}{1==(yl)}[af]}{}
%
\fiveheterov{1s==\sixheterov{%
1s==\WedgeAsSubst(0,0)(-5,-3){171};%
1s==\HashWedgeAsSubst(0,0)(5,-3){171};%
}{1==(yl)}[af]}{}
%
\fiveheterov{1s==\sixheterov{%
1s==\WedgeAsSubst(0,0)(-5,-3){171};%
1s==\PutDashedBond(0,0)(171,-103){2pt};%
}{1==(yl)}[af]}{}
```

These codes generate the following structures:



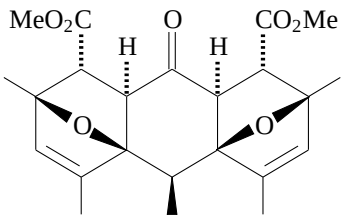
Note that the original skeletal bonds at `a` and `f` in each six-membered ring are deleted by declaring `[af]` as the last optional argument ⟨delbdlist⟩.

The X$\mathrm{\ddot{a}}$MTEX system supports another set of commands `\WedgeAsSubstX` and `\HashWedgeAsSubstX` to draw wedges and hashed wedges as skeletal bonds:

```
\WedgeAsSubstX(⟨start⟩)(⟨endpint⟩)[⟨thickness⟩]
\HashWedgeAsSubstX(⟨start⟩)(⟨endpint⟩)[⟨thickness⟩]
```

where the arguments ⟨start⟩ and ⟨endpoint⟩ represent the coordinates of a starting point and an endpoint for drawing a skeletal bond, while the optional argument ⟨thickness⟩ represents the thickness of the skeletal bond. Note that the *x*- and *y*-values of each coordinate are given as multiple values of `\unitlength` (= 0.1pt).

Example 27.20. These commands can be applied to draw bonds for constructing bridges, as found in a *meso* compound:



the stereoselective hydroboration of which has been reported [4, page 144]. This structure is drawn by the following code:

```
\decaheterov[f%
{b\sixfusev[c]{%
```

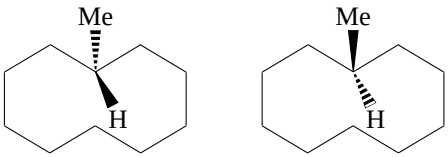
```
5s==\WedgeAsSubstX(0,0)(130,78);%
2s==\put(-205,-140){O};%
2s==\WedgeAsSubstX(0,0)(-130,-78)%
}{1A==CO$_{2}$Me;2==\null;4==\null}{E}}%
]{9s==\WedgeAsSubstX(-35,35)(-165,103);%
7s==\put(145,-140){O};%
7s==\WedgeAsSubstX(0,0)(130,-78)%
}{1D==O;2FA==H;4B==\null;5==\null;7==\null;%
8A==\lmoiety{MeO$_{2}$C};{10}A==H}
```

Note that the bridgehead position (the 9-position) due to `\decaheterov` does not fully support the replacement technique, so that the code `\WedgeAsSubstX(-35,35)(-165,103)` is declared in place of a simpler code `\WedgeAsSubstX(0,0)(-130,65)` to adjust the starting point. □

Example 27.21. These commands can be also applied to draw bonds for substituents, as found in the following codes:

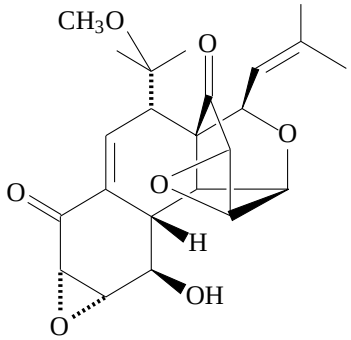
```
\decaheterov{%
{10}s==\put(-35,200){\makebox(0,0)[b]{Me}};%
{10}s==\put(50,-120){\makebox(0,0)[t]{H}};%
{10}s==\HashWedgeAsSubstX(-35,25)(-35,180);%
{10}s==\WedgeAsSubstX(-35,25)(30,-100);%
{10}s==\PutBondLine(-35,25)(136,128){0.4pt};%
{10}s==\PutBondLine(-35,25)(-206,128){0.4pt}%
}{}[ijk]
%
\decaheterov{%
{10}s==\put(-35,200){\makebox(0,0)[b]{Me}};%
{10}s==\put(50,-120){\makebox(0,0)[t]{H}};%
{10}s==\HashWedgeAsSubstX(-35,25)(30,-100);%
{10}s==\WedgeAsSubstX(-35,25)(-35,180);%
{10}s==\PutBondLine(-35,25)(136,128){0.4pt};%
{10}s==\PutBondLine(-35,25)(-206,128){0.4pt}%
}{}[ijk]
```

These codes generate the following structures:



Because the bridgehead position due to `\decaheterov` does not fully support the replacement technique, it is necessary to adjust the starting point and the endpoint decided by `\WedgeAsSubstX` etc., e.g., `\WedgeAsSubstX(-35,25)(30,-100)` in place of `\WedgeAsSubstX(0,0)(60,125)`. □

Example 27.22. More than six years after its publication, the controversial report on hexacyclinol has been retracted [5], as commented in C&EN [6]. The correct structural formula **27-4** of hexacyclinol is now established [7,8]:



27-4

This structure is drawn by the following code:

```
\decaheterovt[j%
{c\fivefusevi{2==O;%
1s==\WedgeAsSubstX(0,0)(50,150)[4];%
1s==\put(50,150){\trimethylene[a]{}{1==(yl);2==\null}};%
3s==\whitex{\PutBondLine(-220,-100)(-220,150){2.8pt}};%clip
3s==\whitex{\PutBondLine(-220,-100)(-440,0){2.8pt}};%clip
3s==\whitex{\PutBondLine(-220,150)(-440,50){2.8pt}};%clip
3s==\WedgeAsSubstX(0,0)(-220,-100);%
3s==\PutBondLine(-220,-100)(-220,150){0.4pt};%
3s==\PutBondLine(-220,-100)(-440,0){0.4pt};%
3s==\PutBondLine(-220,150)(-440,50){0.4pt};%
3s==\put(-450,20){\makebox(0,0)[r]{O}};%
5s==\whitex{\PutBondLine(50,150)(130,-50){2.8pt}};%clip
5s==\WedgeAsSubstX(0,0)(50,150)[4];%
5s==\PutBondLine(50,150)(130,-50){0.4pt};%
5s==\put(50,150){\tetrahedral{3==(yl);1D==O}}{}{D}}%
{g\threefuseh({aA}{bA}){2==O}{}{C}}%
]{}{8D==O;5B==OH;9B==H;2A==\utetrahedralS{1==(yl);2==\null;4==\null;3==CH$_{3}$O}}
```

In this code, wedged skeletal bonds are drawn by using the `\WedgeAsSubstX` command according to the replacement technique. To clip a background skeletal bond, a foreground bond is doubly drawn by `\PutBondLine`, first in white (thickness 2.8pt) and afterward in black (thickness 0.4pt). □

References

[1] IUPAC, “Nomenclature of Organic Chemistry, Sections A, B, C, D, E, F and H,” Pergamon Press (1979).

[2] IUPAC Commission on Nomenclature of Organic Chemistry (III.1), *Pure Appl. Chem.*, **71**, 531–558 (1999).

[3] S. Fujita, “XMTEX—Typesetting Chemical Structural Formulas,” Addison-Wesley Japan, Tokyo (1997).

[4] R. S. Ward, “Selectivity in Organic Synthesis,” John Wiley & Sons, Chichester (1999).

[5] J. J. La Clair, *Angew. Chem. Intern. Ed.*, **57**, 11661 (2012).

[6] B. Halford, *Chem & Eng. News*, **90 (Issue 47, Nov. 1912)**, 10 (2012), Correction: Chem & Eng. News, 90, Issue 49, Dec. 3 (2012), page 4.

[7] J. A. Parco Jr., S. Su, X. Lei, S. Bardhan, and S. D. Rychnovsky, *Angew. Chem. Intern. Ed.*, **45**, 5790–5792 (2006).

[8] G. Saielli and A. Bagno, *Org. Lett.*, **11**, 1409–1412 (2009).

The Addition Technique for Ring Fusion and Related Techniques

The full syntax of the commands for ring fusion (represented collectively by `\ComFuse`) has been discussed briefly in Subsection 2.5.2 (page 25) and detailedly in Chapter 4. Many illustrative examples of the addition technique, which is based on the commands for ring fusion (`\ComFuse`), have been also shown in Chapter 4. The present chapter is devoted to a supplementary description of the addition technique for ring fusion from a practical viewpoint.

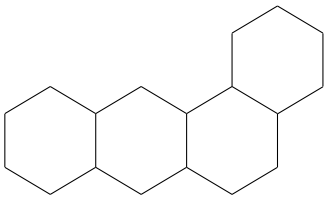
28.1 Ring Fusion on Carbocyclic Compounds

28.1.1 Designation of Fused Bonds

A unit to be fused is written in the ⟨bondlist⟩ of a command with a bond specifier (a lowercase or uppercase alphabet). For example, the code

```
\hanthracenev[{A\sixfusev{}{}{d}}]{}
```

gives a perhydroanthracene with a fused six-membered ring at the bond ‘`a`’ of the perhydroanthracene nucleus:



28-1

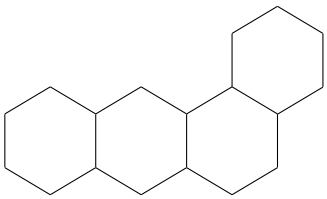
The letter ‘`A`’ of the code `{A\sixfusev{}{}{d}}` is a bond specifier that represents the older terminal of the bond ‘`a`’ of the perhydroanthracene nucleus (For the designation of the bonds of perhydroanthracene, see Subsection 11.1.2. cf. Chapter 5 of the XyMTEXbook [1]).[a] Note that the younger terminal of the bond ‘`a`’ is designated by the letter ‘`a`’. On the other hand, the code `\sixfusev{}{}{d}` of `{A\sixfusev{}{}{d}}` in the ⟨bondlist⟩ represents the fused six-membered ring with the bond ‘`d`’ omitted. The letter ‘`d`’ indicates that the fusing point of the unit is the younger terminal of the omitted bond ‘`d`’. If the the fusing point of the unit is the other (older) terminal, the corresponding uppercase letter ‘`D`’ should be used.

[a] The word ‘older’ or ‘younger’ is concerned with the order of numbering of vertices. For a six-membered ring, the numbering 1—2—3—4—5—6—1 shows that the terminal 1 of the bond ‘`a`’ (1—2) is younger, while the terminal 2 of the bond ‘`a`’ is older. It should be noted that the terminal 6 of the bond ‘`f`’ (6—1) is younger, while the terminal 1 of the bond ‘`f`’ is older.

Accordingly, the same formula can be drawn by the code exchanging uppercase and lowercase letters,

```
\hanthracenev[{a\sixfusev{}{}{D}}]{}
```

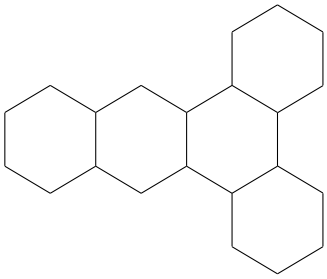
Thereby, we have



Two or more rings can be fused. For example, the code

```
\hanthracenev[{A\sixfusev{}{}{d}}{C\sixfusev{}{}{f}}]{}
```

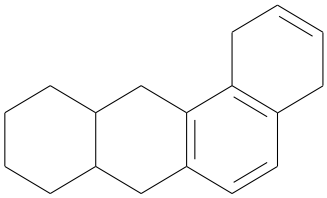
generates a formula with two fused rings at the bonds ‘a’ and ‘c’ of a perhydroanthracene nucleus.



The ⟨bondlist⟩ can accommodates usual bond specifiers without a fusing unit in order to designate inner double bonds. For example, the code

```
\hanthracenev[aco{A\sixfusev[a]{}{}{d}}]{}
```

gives a hydroanthracene that has inner double bonds as well as a fused six-membered ring:



Note that the command `\sixfusev` can take an optional argument to designate inner double bonds, as shown by the code `\sixfusev[a]{}{}{d}`.

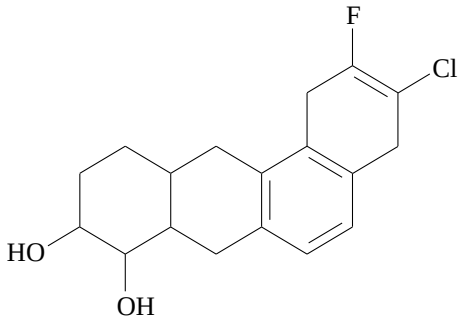
28.1.2 Additional Information on Substituents

In order to specify substituents in addition, we can use the ⟨subslist⟩ of the command `\hanthracenev` as well as the one of the command `\sixfusev`.

Example 28.1. For example, the code

```
\hanthracenev[aco{A\sixfusev[a]{}{1==F;2==Cl}{d}}]{5==OH;6==HO}
```

gives a hydroanthracene having additional substituents:

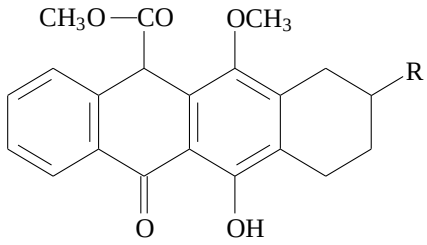


□

Example 28.2. The compound **13** on of the XƎMTEXbook [1, Chapter IV-4 on page 294] can alternatively be drawn by applying the present technique. Thus, the code

```
\hanthracenev[achjop{b\sixfusev{}{2==R}{E}}]{%
1==OCH$_{3}$;4==OH;{10}D==O;%
9==\lyl(8==C\rlap{O}){4==CH$_{3}$O}}
```

gives the following formula:



28-2

□

28.2 Ring Fusion on Heterocyclic Compounds

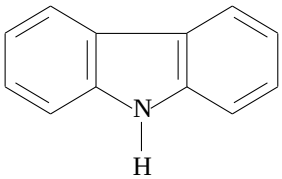
28.2.1 Designation of Fused Bonds

The methodology of ring fusion for heterocyclic compounds is the same as described for carbocyclic compounds. Thus, a unit to be fused is written in the ⟨bondlist⟩ of a command with a bond specifier (a lowercase or uppercase alphabet).

Example 28.3. For example, the code

```
\nonaheterov[begj{b\sixfusev[ac]{}{}{e}}]{1==N}{1==H}
```

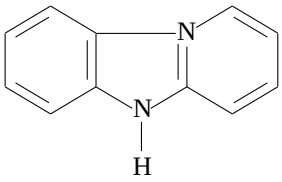
gives the structural formula **28-3** of carbazole:



28-3

which is depicted by attaching a six-membered ring (`\sixfusev[ac]{}{}{e}`) to the bond 'b' of an indole nucleus. □

Example 28.4. Let us consider the replacement of a carbon atom with a nitrogen atom at one of the fused positions in the above compound, as shown by the following formula:



28-4

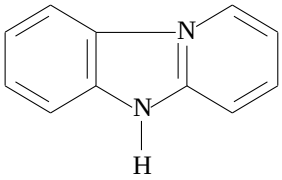
This formula is obtained by writing the code:

```
\nonaheterov[begj{b\sixfusev[ac]{6==\null}{}{e}}]{1==N;3==N}{1==H}
```

where the code `6==\null` in the ⟨atomlist⟩ of `\sixfusev` (for the fused six-membered ring) and the code `3==N` in the ⟨atomlist⟩ of `\nonaheterov` produces the nitrogen atom at the fused position. The specification of the nitrogen atom is also available by exchanging `\null` and `N`. Thus the code

```
\nonaheterov[begj{b\sixfusev[ac]{6==N}{}{e}}]{1==N;3==\null}{1==H}
```

gives the same structural formula:

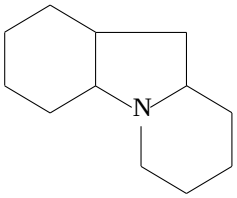


□

Example 28.5. The ring fusion at the bond ‘a’ of perhydroindole is represented by the code

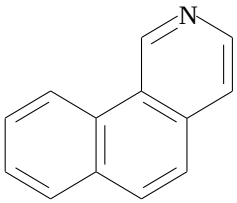
```
\nonaheterov[{a\sixfusev{6==\null}{}{f}}]{1==N}{}
```

which gives a heterocycle:



□

Example 28.6. Benz[*h*]isoquinoline,



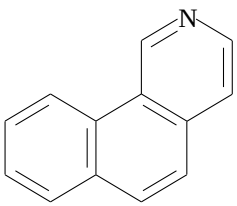
can be typeset by the code,

```
\decaheterovt[acfhk{h\sixfusev[df]{}{}{B}}]{2==N}{}
```

in which the bond specifier ‘h’ corresponds to the *h* of the IUPAC name. Note that the IUPAC name regards the structure as an isoquinoline (drawn by `\decaheterovt`) fused by a benzo moiety. The same structure can be drawn by the alternative code:

```
\decaheterov[acfhk{a\sixfusev[bf]{1==N}{}{D}}]{}{}
```

which regards the structure as a naphthalene nucleus (drawn by `\decaheterov`) with a fused heterocycle. Thereby, we have



□

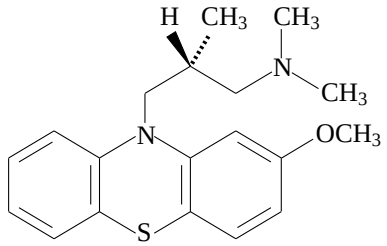
28.2.2 Additional Information on Substituents

The ⟨subslist⟩ of a command for a parent skeleton or of a command for ring fusion can be used in order to specify additional substituents.

Example 28.7. For example, the phenothiazine moiety **28-5** of levomepromazine maleate (hirnamin®) is drawn by the following code:

```
\decaheterov[bfhk%
{b\sixfusev[ac]{}{2==OCH$_{3}$}{E}}%
]{1==N;4==S}{1==%
\tetramethylene{4==N}{1==(yl);4==CH$_{3}$;4W==CH$_{3}$;2SB==H;2SA==CH$_{3}$}}
```

Thereby, we obtain



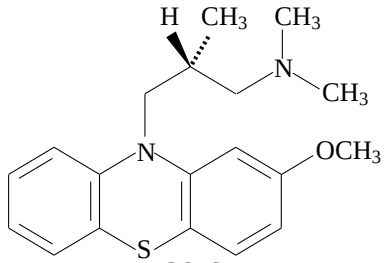
28-5

Note that the side chain of **28-5** is depicted by the substitution technique. As a result, its vertical bond attached to the skeletal nitrogen atom is a bond for linking a substituent (140\unitlength from the center of the skeletal nitrogen), so that it is shorter than a skeletal bond (200\unitlength). □

Example 28.8. To elongate the vertical bond in the side chain of **28-5**, the vertical bond is regarded as a skeletal bond of a hypothetical six-membered ring, which is drawn by another fusing unit \sixfusev.

```
\decaheterov[bfhk%
{b\sixfusev[ac]{}{2==OCH$_{3}$}{E}}%fusing unit
{a\sixfusev{2s==\dimethylene{2==N}{1==(yl);2==CH$_{3}$;2W==CH$_{3}$};%
5==\null}{1SB==H;1SA==CH$_{3}$}{D}[bc]}%another fusing unit
]{1==N;4==S}{}
```

This code generates an equivalent structure with an elongated vertical bond:



28-6

□

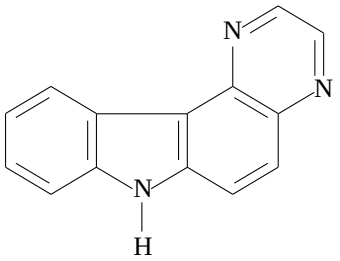
28.3 Nested Ring Fusion

According to the addition technique, the \sixfusev command for ring fusion is capable of accommodating another \sixfusev command in a nested fashion.

Example 28.9. By this technique, the carbazole structure **28-3** can take a further fused ring so as to produce the structural formula of 7*H*-pyrazino[2,3-*c*]carbaozole. Thus, the code,

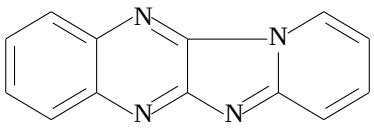
```
\nonaheterov[begj{b\sixfusev[ac%
{a\sixfusev[bf]{6==N;3==N}{}{D}}%
]{}{}{e}}]{1==N}{1==H}
```

gives the structural formula of the fused heterocycle:



which is depicted by attaching a six-membered ring (`\sixfusev[ac]{}{}{e}`) to the bond 'b' of an indole nucleus. □

Example 28.10. The structural formula of pyrido[1′,2′:1,2]imidazo[4,5-*b*]quinoxaline,



28-7

is generated by the code,

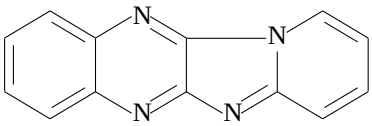
```
\nonaheterov[adh%
{b\sixfusev[ac]{6==\null}{}{e}}%
{f\sixfusev[ace]{}{}{b}}]{1==N;3==N;4==N;7==N}{}
```

Because this code is intended to contain no nested ring fusion, the order of structure construction is different from that of the IUPAC name.

The IUPAC name of **28-7**, i.e., pyrido[1′,2′:1,2]imidazo[4,5-*b*]quinoxaline, corresponds to a quinoxaline with a fused five-membered ring (an imidazo moiety) which is in turn fused by a six-membered ring (a pyrido moiety). The order of constructing the IUPAC name is realized in the code with nested ring fusion,

```
\decaheterov[acegi%
{b\fivefusev[a{b\sixfusev[ac]{6==\null}{}{e}}]{1==N;3==N}{}{d}}]
{1==N;4==N}{}
```

which produces the same structure,



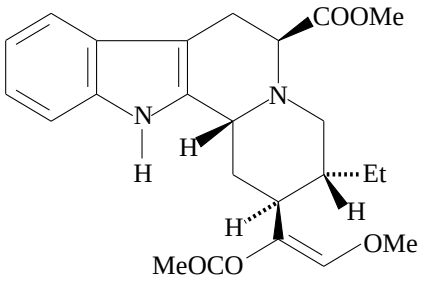
28-8 (= **28-7**)

Note that the indicators '1′,2′' and '1,2'of the locant [1′,2′:1,2] in the IUPAC name correspond respectively to the bond specifiers , 'E' and 'b', appeared in the code, `{b\sixfusev[ac]{6==\null}{}{E}}`. On the other hand, the indicators, '4,5' and '*b*' of of the locant [4,5-*b*] are respectively associated with the specifiers, 'd' and 'b', appeared in the code, `{b\fivefusev[...]{1==N;3==N}{}{d}}`. □

Example 28.11. An alkaloid with a coryanthes skeleton (R. T. Brown and C. L. Chapple, *Chem. Commun.*, 1973, 887) can be typeset by the code with nested fusion,

```
\nonaheterov[begj{b\sixfusev[%
{c\sixfusev{1==\null}{3SB==H;3SA==Et;4GA==H;%
4B==\dimethylenei[a]{}{1==(yl);2W==OMe;1W==MeOCO}}{F}}]%
{3==N}{4GB==H;2B==COOMe}{e}}]{1==N}{1==H}
```

where a six-five ring drawn by the command `\nonaheterov` is regarded as a mother skeleton. Thus, we obtain



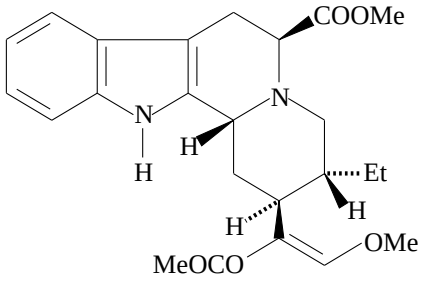
28-9

For the command `\dimethylenei`, see Chapter 21. □

Example 28.12. When a six-six ring drawn by the command `\decaheterovb` is regarded as a mother skeleton, as shown in the code with another nested ring fusion,

```
\decaheterovb[f{f\fivefusev[d{d\sixfusev[df]{}{}{b}}]%
{1==N}{1==H}{b}}]{8a==N}{9B==H;2SA==Et;2SB==H;8B==COOMe;3GA==H;%
3B==\dimethylenei[a]{}{1==(yl);2W==OMe;1W==MeOCO}}
```

we find another way of drawing the same structural formula,



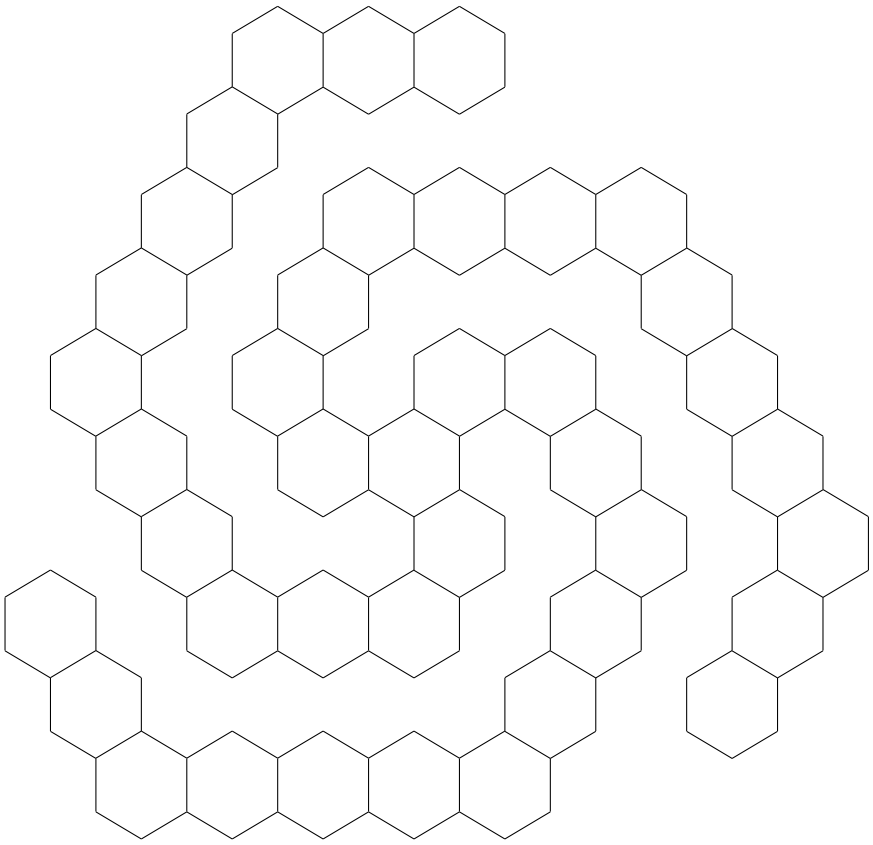
28-10 (= **28-9**)

□

Example 28.13. The following example shows a code with complicated nested structure:

```
\cyclohexanev[%
{a\sixfusev[{b\sixfusev[{c\sixfusev[{c\sixfusev[%
{d\sixfusev[{d\sixfusev[{d\sixfusev[%
{e\sixfusev[{e\sixfusev[{e\sixfusev[{e\sixfusev[%
{f\sixfusev[{f\sixfusev[]{}{}{C}}]{}{}{C}}%
]{}{}{B}}]{}{}{B}}]{}{}{B}}]{}{}{B}}%
]{}{}{A}}]{}{}{A}}]{}{}{A}}]{}{}{F}}%
]{}{}{F}}]{}{}{E}}]{}{}{D}}%
{c\sixfusev[{d\sixfusev[{e\sixfusev[{e\sixfusev[%
{f\sixfusev[{f\sixfusev[{f\sixfusev[%
{a\sixfusev[{a\sixfusev[{a\sixfusev[{a\sixfusev[%
{b\sixfusev[{b\sixfusev[]{}{}{E}}]{}{}{E}}%
]{}{}{D}}]{}{}{D}}]{}{}{D}}]{}{}{D}}%
]{}{}{C}}]{}{}{C}}]{}{}{C}}]{}{}{B}}%
]{}{}{B}}]{}{}{A}}]{}{}{F}}%
{e\sixfusev[{f\sixfusev[{a\sixfusev[{a\sixfusev[%
{b\sixfusev[{b\sixfusev[{b\sixfusev[%
{c\sixfusev[{c\sixfusev[{c\sixfusev[{c\sixfusev[%
{d\sixfusev[{d\sixfusev[]{}{}{A}}]{}{}{A}}%
]{}{}{F}}]{}{}{F}}]{}{}{F}}]{}{}{F}}%
]{}{}{E}}]{}{}{E}}]{}{}{E}}]{}{}{D}}%
]{}{}{D}}]{}{}{C}}]{}{}{B}}%
]{}
```

This code generates a multiply fused formula **28-11** (Fig. 28.1). □



28-11

Figure 28.1. Nested addition technique for drawing a spiral fusion of benzene rings.

28.4 Additional Bonds by the Replacement or Addition Technique

28.4.1 Endocyclic Triple Bonds for Drawing Benzyne and Related Structures

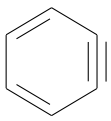
A bond of the slope `(#3,#4)` and of length `#5`, where its terminal is located at the position separated by `(#1,#2)` from a given starting position, can be added by using a newly-defined command:

```
\makeatletter
\def\addbond(#1,#2)(#3,#4)#5{\Put@Line(#1,#2)(#3,#4){#5}}
\makeatother
```

For example, an additional endocyclic bond of benzyne can be drawn by writing the following code:

```
\sixheterov[bdf]{2s==\addbond(30,-25)(0,-1){150}}{}
```

which produces the structure of benzyne as follows:

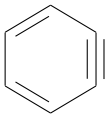


It should be noted that the additional bond is drawn as an endocyclic atom, which is designated in the atom list (`2s==\addbond...`) according to the replacement technique.

Another code:

```
\sixheterov[bdf{b{\addbond(30,-25)(0,-1){150}}}]{}{}
```

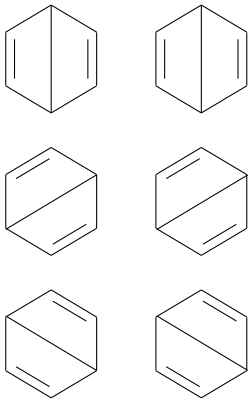
where the additional bond is designated in the bond list ({b{\addbond(30,-25)(0,-1){150}}}) according to the addition technique, produces an equivalent structure with an endocyclic triple bond:



Example 28.14. Dewar benzenes can be drawn by using the \addbond command according to the addition or replacement technique. The codes:

```
\sixheterov[be{a{\addbond(0,0)(0,-1){406}}}]{}{}
\sixheterov[be]{1s==\addbond(0,0)(0,-1){406}}{} \par
\sixheterov[cf{b{\addbond(0,0)(-5,-3){342}}}]{}{}
\sixheterov[cf]{2s==\addbond(0,0)(-5,-3){342}}{} \par
\sixheterov[ad{c{\addbond(0,0)(-5,3){342}}}]{}{}
\sixheterov[ad]{3s==\addbond(0,0)(-5,3){342}}{}
```

produce the following structures:



For an alternative way of the replacement technique for drawing the Dewar benzene, see Subsection 27.3.3. □

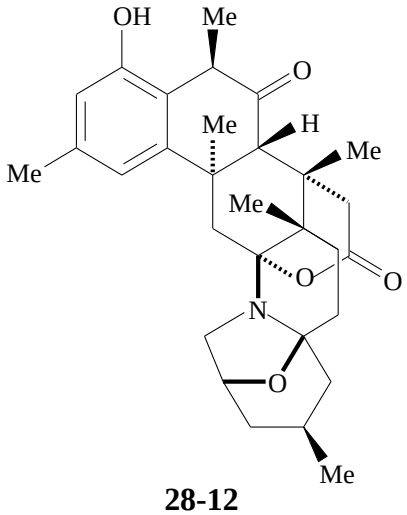
28.4.2 \PutBondLine Command for Drawing Additional Bonds

A more flexible command \PutBondLine can be used to draw an additional skeletal bond according to the addition technique along with the replacement technique (cf. Subsection 27.3.3). The syntax of this command has been already described in Subsection 27.3.3.

Example 28.15. The structure **28-12** of zoanthenol as one of zoanthamine alkaloids [2] is drawn by the code:

```
\decaheterov[egi%
{c\sixfusev[%
{b\sixfusev({aA}{dA}){4==O}{1GB==Me;3D==O}{F}[e]}%
{c{\white \PutBondLine(130,-80)(130,-326){2.8pt}}}%
{c\PutBondLine(0,0)(130,-80){0.4pt}}%
{c\PutBondLine(0,0)(130,-80){0.4pt}}%
{c\PutBondLine(130,-80)(130,-326){0.4pt}}%
{c\PutBondLine(0,-406)(130,-326){0.4pt}}%
{c\sixfusev({eB})[%
{d\fivefuseh({dB}{eB})[%
{d\PutBondLine(0,0)(-70,171){0.4pt}}%
{d\PutBondLine(-70,171)(80,260){0.4pt}}%
]{5==O}{}{a}[bc]}%
{d\sixfuseh{}{5B==Me}{B}[a]}%
]{5==N}{1FB==Me}{F}[abc]}%
]{}{1GB==H;6GA==Me}{F}%
}]{}{1B==Me;2D==O;6==Me;8==OH}
```

This code produces the following structure:



28-12

Note that the code `{c{\white \PutBondLine(130,-80)(130,-326){2.8pt}}}` is declared to draw a white line, which cuts a background bond to show the overlapping of two bonds. □

Example 28.16. Let us draw the structure **28-13** of dynemicin A, which is known as an anti-cancer enediyne drug. First, we define a command for drawing a linear component composed of a wedged single bond — a triple bond— a single bond.

```
\def\sBtsbond#1#2#3{%
\rotatebox{#1}{%
\begin{picture}(0,0)(0,0)
\WedgeAsSubst(0,0)(0,1){#2}%
\put(0,#2){%
\whitex{\PutBondLine(0,5)(0,200){5pt}}%
\PutBondLine(-15,5)(-15,200){0.4pt}%
\PutBondLine(0,5)(0,200){0.4pt}%
\PutBondLine(15,5)(15,200){0.4pt}
\put(0,205){%
\PutBondLine(0,5)(0,#3){0.4pt}%
}}%
\end{picture}}}
```

where the first argument represents the rotation angle, the second represents the length of the wedged single bond, the third represents the length of the single bond. Two examples are shown as follows:

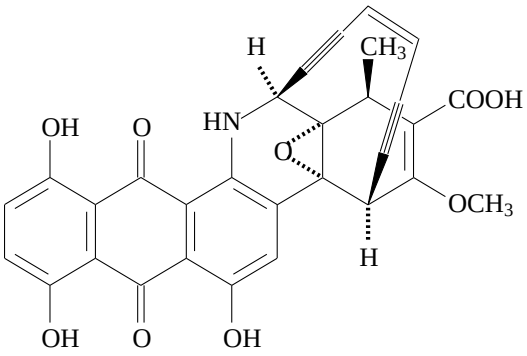
`\sBtsbond{0}{200}{200}` `\sBtsbond{30}{200}{200}`

Then, the main skeleton of **28-13** is drawn by the addition technique in terms of the scheme, 666 ← 6 ← 6 ← 3. The enediyne part is drawn by using the newly-defined command `\sBtsbond` along with the command `\PutBondLine`.

```
\begin{XyMcompd}(1900,1350)(250,0){cpd:dynemicinA}{}
\hanthracenev[achjop%
{a\sixfusev[%
{b\sixfusev[b%
{e\threefusehi({aA}{cA}){1==O}{}{b}}%
```

```
]{4s==\sBtsbond{-17}{200}{250}%
}{1B==CH$_{3}$;2==COOH;3==OCH$_{3}$;4A==H}{E}}%
]{6==HN;1s==\sBtsbond{-45}{140}{140};%
1s==\PutBondLine(342,342)(530,220){0.4pt};%
1s==\PutBondLine(342,310)(510,200){0.4pt}%
}{1Sd==H}{D}}%
]{4==OH;5==OH;8==OH;9D==O;{10}D==O}
\end{XyMcompd}
```

This code generates the following structure:



28-13

□

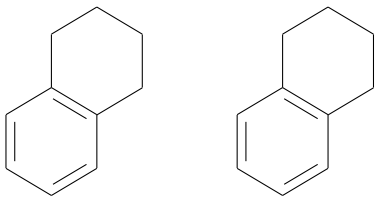
28.5 Remarks

28.5.1 Special ⟨bondlist⟩ Arguments

It should be noted that the ⟨bondlist⟩ argument of such commands as `\bzdrv`, `\naphdrv`, and `\anthracenev` cannot be used for the addition technique for ring fusion. In place of such specific commands, the ⟨bondlist⟩ argument of the corresponding general command, e.g. `\cyclohexanev` or `\sixheterov` corresponding to `\bzdrv`, should be used for the purpose of ring fusion. For example, a fused benzene ring should be drawn by using the `\cyclohexanev` or `\sixheterov` command, as shown in the codes:

```
\cyclohexanev[ace{a\sixfusev{}{}{D}}]{}
\sixheterov[ace{a\sixfusev{}{}{D}}]{}{}
```

These codes generate the following formulas:

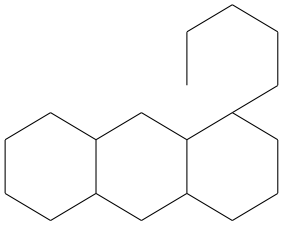


28.5.2 XyMTEX Warning

An incorrect result due to a wrong specification of a fused bond is notified by a XyMTEX warning. For example, the code,

```
\hanthracenev[{a\sixfusev{}{}{d}}]{}
```

gives a formula of wrong fusion:



According to this wrong situation, a XyMTeX warning[b] appears in a display or in a log file, e.g.,

```
XyMTeX Warning: Mismatched fusion at bond ‘a, i, or other’
on input line 1904
```

There are two ways to correct the wrong fusion and, as a result, to avoid such a XyMTeX warning. First, the code

```
\hanthracenev[{A\sixfusev{}{}{d}}]{}
```

in which the acceptor bond specifier ‘a’ is changed into ‘A’, gives a correct result, as found in the top example **28-1** of this chapter. Alternatively, the donor bond specifier ‘d’ can be changed into ‘D’. Thus, the code,

```
\hanthracenev[{a\sixfusev{}{}{D}}]{}
```

also typesets the same structure as **28-1** with correct fusion.

References

[1] S. Fujita, “XyMTeX—Typesetting Chemical Structural Formulas,” Addison-Wesley Japan, Tokyo (1997).

[2] F. Yoshimura, K. Tanino, and M. Miyashita, *Yuki Gosei Kagaku Kyokai-Shi*, **71**, 124–135 (2013).

[b] This warning does not always inform a correct situation.

Part VII

Advanced Techniques for Drawing Structures

Stereochemistry

The XeLaTeX system supports three combinations of stereochemical bonds, i.e., wedged bonds/hashed dash bonds, wedged bonds/hashed wedged bonds, and bold dash bonds/hashed dash bonds, which can be switched under the PDF-compatible and PostScript-compatible modes.

29.1 Stereochemical Expressions of Bonds

29.1.1 Wedged Bonds and Hashed Dash Bonds

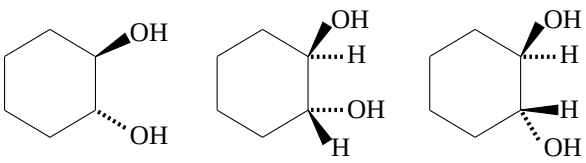
According to "Basic Terminology of Stereochemistry" of IUPAC Recommendations 1996 [1], a bond from an atom in the plane of drawing to an atom above the plane (i.e., so-called β-bond) is shown with a bold wedge, which starts from the atom in the plain at the narrow end of the wedge; and a bond below the plane (i.e., so-called α-bond) is shown with a hashed bold dash (short parallel lines or unwedged hashed bond). Hence, the combination of wedges and hashed dashes is selected as a default setting for XeLaTeX version 4.02 and later. Thus, the following declaration is loaded first to begin with a default condition:

```
\wedgehasheddash
```

Under this default setting, for example, the the following codes:

```
\cyclohexanev{2B==OH;3A==OH}
\cyclohexanev{2SA==H;2SB==OH;3SA==OH;3SB==H}
\cyclohexanev{2SA==H;2SB==OH;3Sd==OH;3Su==H}
```

generate formulas represented by:



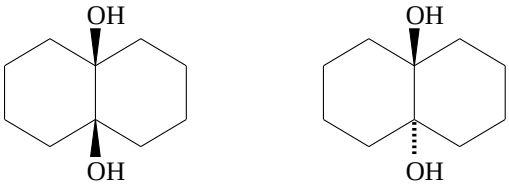
Stereochemical information is specified by bond modifiers for ⟨subslist⟩, which are collected in Table 3.2, e.g., `2B`, `2SA`, `3Sd`. The bond modifier `A` (or `u`) denotes an α-bond (or under the plane of a page), so that it outputs a hashed bold dash (short parallel lines or unwedged hashed bond) under a default condition of

the XyMTEX system. On the other hand, the bond modifier `B` (or `u`) denotes a β-bond (or over the plane of a page), so that it output a bold wedge under a default condition of the XyMTEX system. For locant numbering for such six-membered rings as `\cyclohexanev`, see Chapters 7 and 14.

Example 29.1. Codes for drawing *cis*- and *trans*-decalinediol:

```
\decaheterov{}{9B==OH;{10}B==OH}
\decaheterov{}{9A==OH;{10}B==OH}
```

generate the following formulas:

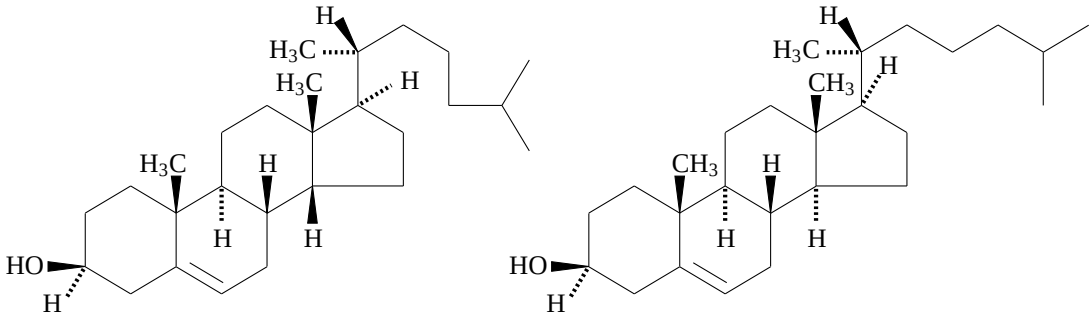


For locant numbering for such fused six-to-six-membered rings as `\dedaheterov`, see Chapters 9 and 16. □

Example 29.2. Cholesterol (Cholest-5-en-3β-ol) can be drawn by the following codes:

```
\begin{center}
\begin{XyMcompd}(1850,1150)(0,200){}{}
\steroidchain[e]{3Su==HO;3Sd==H;8B==H;9A==H;{{10}B}==\lmoiety{H$_{3}$C};%
{{13}B}==\lmoiety{H$_{3}$C};{{14}B}==H;{{17}GA}==H;%
{{20}SA}==\lmoiety{H$_{3}$C};{{20}SB}==H}
\end{XyMcompd}
\hskip-10pt
\begin{XyMcompd}(2050,1150)(0,200){}{}
\cholestane[e]{3Su==HO;3Sd==H}
\end{XyMcompd}
\end{center}
```

where the latter code is based on a shortcut command for drawing cholestane derivatives with an alternatively folded side chain. Thereby, we can obtain the following diagrams:

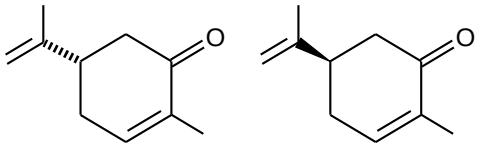


For locant numbering for steroid derivatives, see Chapter 13. For shortcut commands for steroids, see Table 13.7 and so on. □

Example 29.3. If thicker hashed dashes are required, the declaration `\def\thickLineWidth{3pt}` changes the default thickness (1.6pt) of a hashed dash into 3pt, as shown in the following example:

```
\begin{center}
\def\thinLineWidth{0.8pt}
\def\thickLineWidth{3pt}
\let\substfont=\sffamily
\begin{tabular}{cc}
\begin{XyMcompd}(700,500)(0,250){}{}
\cyclohexanev[c]{2D==O;3==\null;%
```

```
6A==\dimethylene[A]{1==\null}{2==(yl);2==\null}}
\end{XyMcompd}
&
\begin{XyMcompd}(700,500)(0,250){}{}
\cyclohexanev[c]{2D==O;3==\null;%
6B==\dimethylene[A]{1==\null}{2==(yl);2==\null}}
\end{XyMcompd}
\\
\noalign{\vskip5pt}
\compd\label{cpd:carvoneS} & \compd\label{cpd:carvoner} \\
(\textit{S})-carbone & (\textit{R})-carbone \\
odor: caraway & odor: spearmint \\
\end{tabular}
\end{center}
```



29-1
(*S*)-carbone
odor: caraway

29-2
(*R*)-carbone
odor: spearmint

□

29.1.2 Wedged Bonds and Hashed Wedged Bonds

The use of a wedge of parallel lines (a hashed wedged bond) is not recommended by "Basic Terminology of Stereochemistry" of IUPAC Recommendations 1996 [1]. However, the combination of wedged bonds and hashed wedged bonds is frequently used and now recognized as a recommended standard [2]. By declaring the switching command:

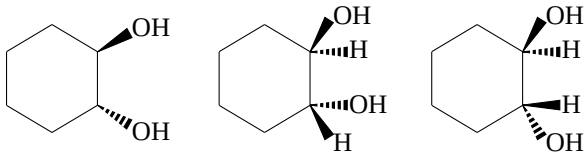
```
\wedgehashedwedge
```

you are able to draw structural formulas by using the combination of wedged bonds and hashed wedged bonds.

For example, the the following codes:

```
\wedgehashedwedge
\cyclohexanev{2B==OH;3A==OH}
\cyclohexanev{2SA==H;2SB==OH;3SA==OH;3SB==H}
\cyclohexanev{2SA==H;2SB==OH;3Sd==OH;3Su==H}
```

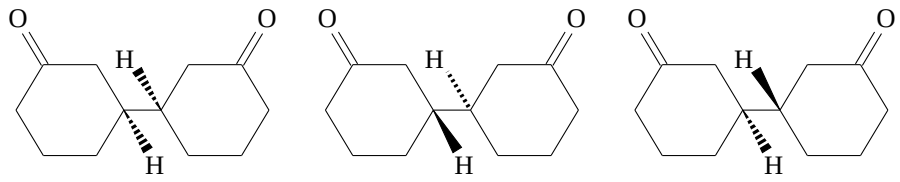
generate formulas represented by:



As found by the inspection of the three formulas depicted above, the β- and α-bonds are drawn by the combination of wedged bonds and hashed wedged bonds after the declaration of `\wedgehashedwedge`. Thus, a single declaration of `\wedgehashedwedge` at the top (the preamble) of a document file is sufficient if the combination of wedged bonds and hashed wedged bonds is used throughout the document.

Example 29.4. If the switch \wedgehasheddash is declared, the drawing mode is returned to the default mode, as shown in the following examples:

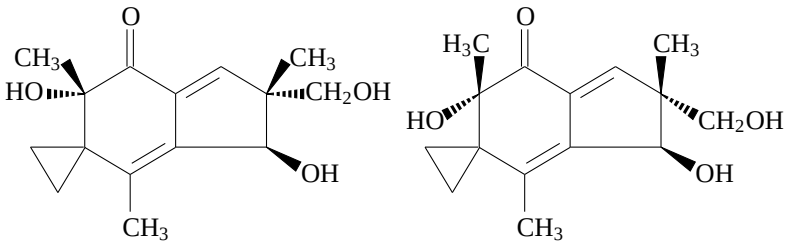
```
\wedgehashedwedge
\cyclohexaneh{2D==O;4GA==H;4==\cyclohexaneh{1==(yl);3D==O;1GA==H}}\hskip1cm
\wedgehasheddash%return to the default mode
\cyclohexaneh{2D==O;4GB==H;4==\cyclohexaneh{1==(yl);3D==O;1GA==H}}\hskip1cm
\wedgehashedwedge
\cyclohexaneh{2D==O;4GA==H;4==\cyclohexaneh{1==(yl);3D==O;1GB==H}}
```



□

Example 29.5. Illudin S, an anti-tumor antibiotic substance, is drawn in two ways in which the directions of wedges are altered:

```
\wedgehashedwedge
\nonaheterovi[di]{5s==\cyclopropanev{2==(yl)}}%
{2SB==CH$_{3}$;2SA==CH$_{2}$OH;3B==OH;4==CH$_{3}$;%
6SB==CH$_{3}$;6SA==HO;7D==O} \hskip1cm
\nonaheterovi[di]{5s==\cyclopropanev{2==(yl)}}%
{2FB==CH$_{3}$;2GA==CH$_{2}$OH;3B==OH;4==CH$_{3}$;%
6GB==\lmoiety{H$_{3}$C};6FA==HO;7D==O}
```

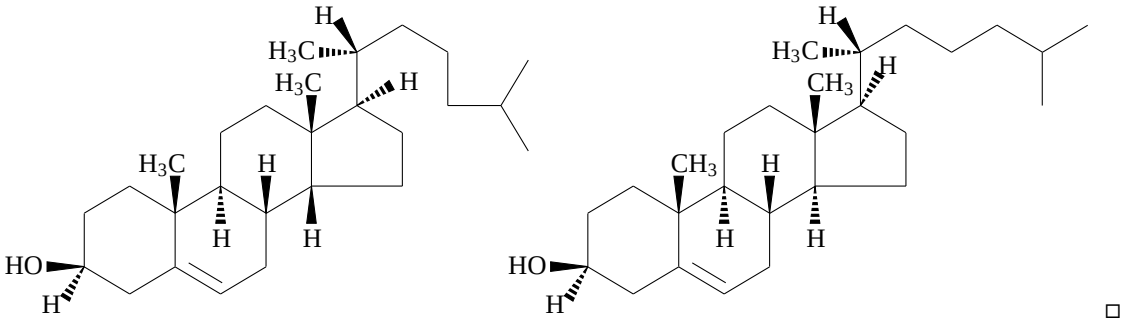


□

Example 29.6. The structural formula of cholesterol (cholest-5-en-3β-ol) drawn above is rewritten under the declaration of \wedgehashedwedge, as shown in the codes:

```
\begin{center}
\wedgehashedwedge
\begin{XyMcompd}(1850,1150)(0,200){}{}
\steroidchain[e]{3Su==HO;3Sd==H;8B==H;9A==H;{{10}B}==\lmoiety{H$_{3}$C};%
{{13}B}==\lmoiety{H$_{3}$C};{{14}B}==H;{{17}GA}==H;%
{{20}SA}==\lmoiety{H$_{3}$C};{{20}SB}==H}
\end{XyMcompd}
\hskip-10pt
\begin{XyMcompd}(2050,1150)(0,200){}{}
\cholestane[e]{3Su==HO;3Sd==H}
\end{XyMcompd}
\end{center}
```

Note that the difference between the present codes and the previous ones is only the addition of one line of the declaration \wedgehashedwedge. Thereby, we can obtain the following diagrams:



29.1.3 Bold Dash Bonds and Hashed Dash Bonds

A bold dash bond may be used instead of a bold wedged bond according to IUPAC Recommendations 1996 [1]. This type of expressions is not recommended now by the revised IUPAC Recommendations 2006, "Graphical Representation of Stereochemical Configuration" [2]. However, this type of expressions should be supported, because there are occasional cases in which old documents with this type of expressions are referred to as they are. By declaring the switching command:

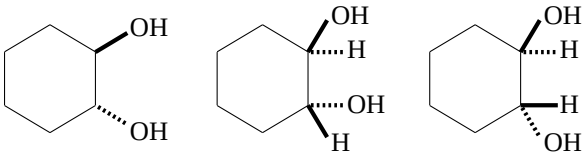
```
\dashhasheddash,
```

you are able to draw structural formulas by using the combination of bold dash bonds and hashed dash bonds.

Under the setting of `\dashhasheddash`, for example, the the following codes:

```
\dashhasheddash
\cyclohexanev{2B==OH;3A==OH}
\cyclohexanev{2SA==H;2SB==OH;3SA==OH;3SB==H}
\cyclohexanev{2SA==H;2SB==OH;3Sd==OH;3Su==H}
```

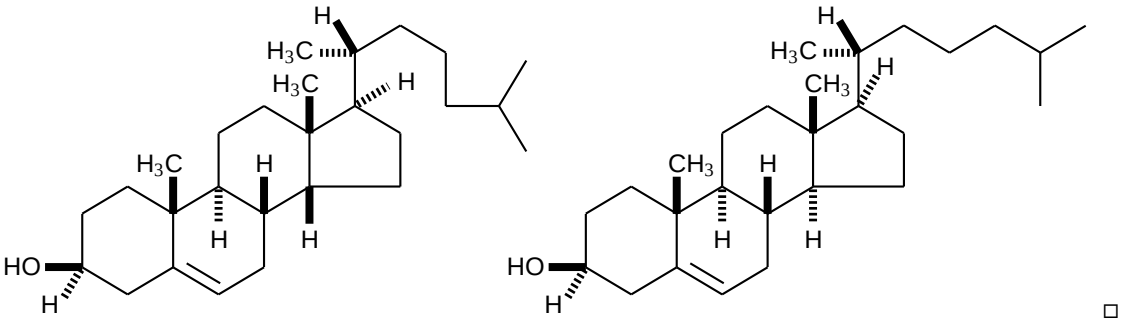
generate formulas represented by:



Example 29.7. To exemplify dash/hashed dash, cholesterol (Cholest-5-en-3β-ol) drawn above is rewritten under the declaration `\dashhasheddash`, as shown in the codes:

```
\begin{center}
\dashhasheddash
\def\thinLineWidth{0.8pt}%for bonds with configurations
\def\thickLineWidth{3pt}%for usual bonds
\let\substfont=\sffamily
\begin{XyMcompd}(1850,1150)(0,200){}{}
\steroidchain[e]{3Su==HO;3Sd==H;8B==H;9A==H;{{10}B}==\lmoiety{H$_{3}$C};%
{{13}B}==\lmoiety{H$_{3}$C};{{14}B}==H;{{17}GA}==H;%
{{20}SA}==\lmoiety{H$_{3}$C};{{20}SB}==H}
\end{XyMcompd}
\hskip-10pt
\begin{XyMcompd}(2050,1150)(0,200){}{}
\cholestane[e]{3Su==HO;3Sd==H}
\end{XyMcompd}
\end{center}
```

Note that an essential difference between the present codes and the previous ones is the addition of one line of the declaration `\dashhasheddash`, although bonds are changed to be thicker than defaults. Thereby, we can obtain the following diagrams:



□

29.2 PDF-Compatible Mode and PostScript-Compatible Mode vs. TEX/LATEX-Compatible Mode

Three profiles of the PDF-compatible mode (or the PostScript compatible mode), which have been discussed in the preceding section, are summarized in Fig. 29.1. For the purpose of comparison, Fig. 29.1 also contains structural formulas drawn by the TEX/LATEX-compatible mode, which does not support the three profiles at issue.

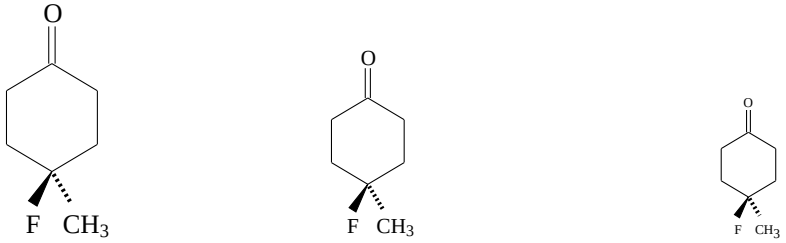
Fig. 29.1 is obtained by the following codes:

```
\begin{center}
\begin{tabular}{ccc}
\hline
\noalign{\vskip5pt}
\multicolumn{3}{c}{\bf %
PDF-compatible mode and PostScript-compatible mode} \\
default (0.1pt) &
\verb/\changeunitlength{0.08pt}/ &
\verb/\changeunitlength{0.06pt}/ \\[5pt]
\hline
\noalign{\vskip5pt}
\multicolumn{3}{l}{%
\texttt{$\backslash$wedgehasheddash}: default (wedge and hashed dash)} \\[5pt]
\cyclohexanev{1D==O;4SA==CH$_{3}$;4SB==F} &
\changeunitlength{0.08pt}
\cyclohexanev{1D==O;4SA==CH$_{3}$;4SB==F} &
\changeunitlength{0.06pt}
\cyclohexanev{1D==O;4SA==CH$_{3}$;4SB==F} \\
\noalign{\vskip10pt}
\multicolumn{3}{l}{%
\texttt{$\backslash$wedgehashedwedge}: (wedge and hashed wedge)} \\[5pt]
\wedgehashedwedge
\cyclohexanev{1D==O;4SA==CH$_{3}$;4SB==F} &
\wedgehashedwedge
\changeunitlength{0.08pt}
\cyclohexanev{1D==O;4SA==CH$_{3}$;4SB==F} &
\wedgehashedwedge
\changeunitlength{0.06pt}
\cyclohexanev{1D==O;4SA==CH$_{3}$;4SB==F} \\
\noalign{\vskip10pt}
\multicolumn{3}{l}{%
\texttt{$\backslash$dashhasheddash}: (dash and hashed dash)} \\[5pt]
```

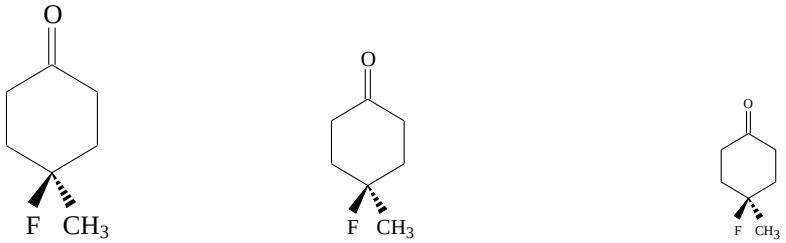
PDF-compatible mode and PostScript-compatible mode

default (0.1pt) `\changeunitlength{0.08pt}` `\changeunitlength{0.06pt}`

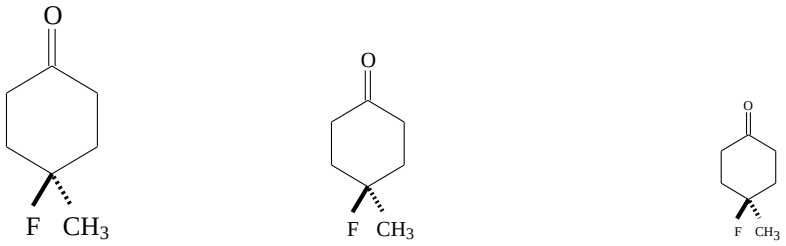
`\wedgehasheddash`: default (wedge and hashed dash)



`\wedgehashedwedge`: (wedge and hashed wedge)



`\dashhasheddash`: (dash and hashed dash)



TEX/LATEX-compatible mode

default (0.1pt) `\changeunitlength{0.08pt}` `\changeunitlength{0.06pt}`

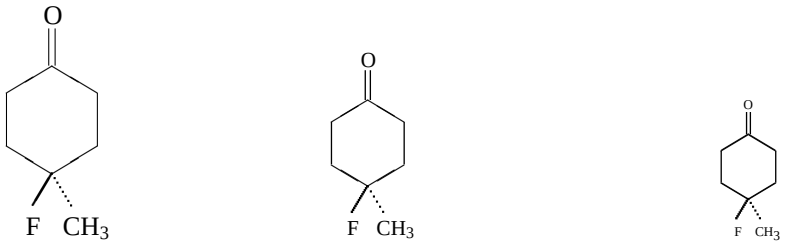


Figure 29.1. PDF-compatible mode and PostScript-compatible mode vs. TEX/LATEX-compatible mode. Three profiles of representing configurations are available in the PDF-compatible mode (or the PostScript compatible mode), while they are not supported by the TEX/LATEX-compatible mode.

```
\dashhasheddash
\cyclohexanev{1D==O;4SA==CH$_{3}$;4SB==F} &
\dashhasheddash
\changeunitlength{0.08pt}
\cyclohexanev{1D==O;4SA==CH$_{3}$;4SB==F} &
\dashhasheddash
\changeunitlength{0.06pt}
```

```
\cyclohexanev{1D==O;4SA==CH$_{3}$;4SB==F}  \\
\noalign{\vskip10pt}
\hline
\hline
\noalign{\vskip5pt}
\multicolumn{3}{c}{\bf %
\TeX/\LaTeX-compatible mode} \\
default (0.1pt) &
\verb/\changeunitlength{0.08pt}/ &
\verb/\changeunitlength{0.06pt}/ \\[5pt]
\hline
\noalign{\vskip5pt}
\reducedsizepicture
\cyclohexanev{1D==O;4SA==CH$_{3}$;4SB==F} &
\reducedsizepicture
\changeunitlength{0.08pt}
\cyclohexanev{1D==O;4SA==CH$_{3}$;4SB==F} &
\reducedsizepicture
\changeunitlength{0.06pt}
\cyclohexanev{1D==O;4SA==CH$_{3}$;4SB==F} \\
\noalign{\vskip10pt}
\hline
\end{tabular}
\end{center}
```

By means of the sizeredc package which is automatically loaded in the X$\mathfrak{Y}$MTEX package, the original LATEX picture environment can be used by a switching declaration `\reducedsizepicture` in order to reduce the sizes of formulas, as shown in the bottom of Fig. 29.1.

29.3 Tetrahedral and Related Configurations

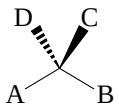
29.3.1 Tetrahedral Configurations Depicted with Four Explicit Bonds

The depiction of tetrahedral configurations has been discussed in Chapter 20. The `\htetrahedralS` command is suitable to draw a preferred diagram with two plain bonds, one solid wedged bonds, and one hashed wedged bond, which is in accord with the IUPAC Recommendations 2006 [2, ST-1.1.1]. Note that three atoms A—(Central Carbon)—B are postulated to be coplanar in the above diagrams.

Thus, the code

```
\wedgehashedwedge
\htetrahedralS{1==A;2==B;3B==C;4A==D}
```

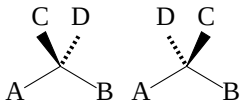
generates a following diagram:



Such preferred diagrams can alternatively drawn by using `\trimethylene`. Thus, the codes:

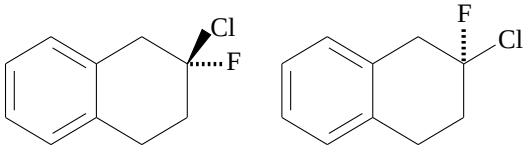
```
\trimethylene{1==A;3==B}{2SB==C;2SA==D}
\trimethylene{1==A;3==B}{2Su==C;2Sd==D}
```

generate the following diagrams:



Example 29.8. The diagram **29-3**, which is based on the depiction style of [2, ST-1.1.1], is preferred to the diagram **29-4**, which is based on the depiction style of [2, ST-1.1.2]. Note that the right six-membered ring and the chlorine atom are presumed to be coplanar in the latter diagram **29-4**, which is acceptable according to [2, ST-1.1.2] because the chlorine atom is regarded to be rather smaller than the six-membered ring.

```
\begin{tabular}{cc}
\begin{XyMcompd}(800,500)(250,250){}{}
\decalinev[egi]{2SB==Cl;2SA==F}
\end{XyMcompd}
&
\begin{XyMcompd}(800,500)(250,250){}{}
\decalinev[egi]{2==Cl;2FA==F}
\end{XyMcompd}
\\
\compd\label{cpd:decalineClFa} & \compd\label{cpd:decalineClFb} \\
\textit{Preferred} & \textit{Acceptable}
\end{tabular}
```

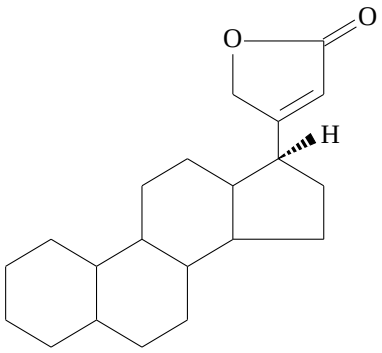


29-3 *Preferred* **29-4** *Acceptable*

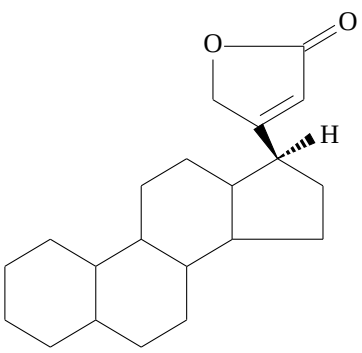
It should be noted that a six-membered ring is tentatively presumed to be planar when graphical representations (wedged bonds and hashed bonds) of stereochemical configurations are considered [2]. Graphical representations based on this convention are sufficient to imply the true three-dimensional molecular architecture. □

Example 29.9. The diagram **29-5**, which is based on the depiction style of [2, ST-1.1.2], is preferred to the diagram **29-6**, which is based on the depiction style of [2, ST-1.1.1]. Note that the steroid ring and the lactone ring are presumed to be coplanar in the former diagram **29-5**, which is adopted to be preferred according to [2, ST-1.1.2] because the steroid ring and the lactone ring are regarded to construct a skeleton to be considered totally.

```
\wedgehashedwedge
\begin{tabular}{cc}
\begin{XyMcompd}(1300,1300)(250,250){}{}
\steroid{{{17}}==\fiveheterov[a]{4==O}{1==(yl);3D==O};{17}GA==H}
\end{XyMcompd}
&
\begin{XyMcompd}(1300,1300)(250,250){}{}
\steroid{{17}SB==\fiveheterov[a]{4==O}{1==(yl);3D==O};{17}GA==H}
\end{XyMcompd}
\\
\compd\label{cpd:steroidfiveA} & \compd\label{cpd:steroidfiveB} \\
\textit{Preferred} & \textit{Acceptable}
\end{tabular}
```



29-5
Preferred

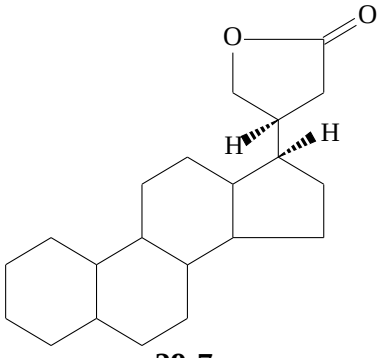


29-6
Acceptable

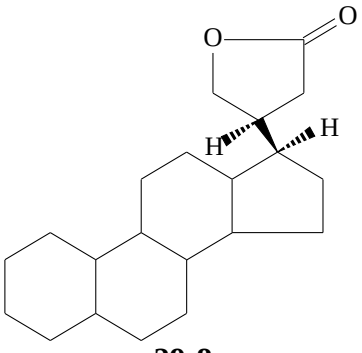
The coplanarity of a steroid ring and a lactone ring does not reflect an actual three-dimensional structure. It is a convention for assigning graphical representations (wedged bonds and hashed bonds) of stereochemical configurations [2]. □

Example 29.10. According to the IUPAC Recommendations 2006 [2, ST-0.5], stereobonds between stereocenters should be avoided at all costs. It follows that **29-8** is not acceptable because the bond linking the steroid skeleton and the lactone ring is such a stereobond between stereocenters.

```
\wedgehashedwedge
\begin{tabular}{cc}
\begin{XyMcompd}(1300,1300)(250,250){}{}
\steroid{{{17}}==\fiveheterov{4==O}{1==(yl);3D==O;1GA==H};{17}GA==H}
\end{XyMcompd}
&
\begin{XyMcompd}(1300,1300)(250,250){}{}
\steroid{{17}SB==\fiveheterov{4==O}{1==(yl);3D==O;1GA==H};{17}GA==H}
\end{XyMcompd}
\\
\compd\label{cpd:steroidfiveC} & \compd\label{cpd:steroidfiveD} \\
\textit{Preferred} & \textit{Not acceptable}
\end{tabular}
```



29-7
Preferred



29-8
Not acceptable

□

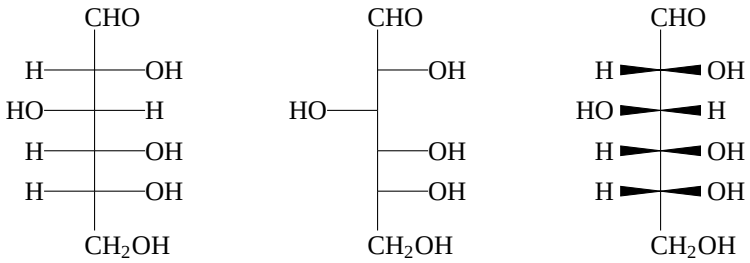
29.3.2 Fischer Projections

Preferred diagrams and acceptable diagrams of Fischer projections are discussed in the IUPAC Recommendations 2006 [2, ST-1.8].

Example 29.11. To draw a Fischer projection by the XƎMTEX system, a necessary number of the commands `\tetrahedral` is nested vertically, where the substitution technique based on (yl)-functions is applied to each `\tetrahedral` command, where such codes as `1==\tetrahedral{3==(yl);2==H;4==OH;%` appear repeatedly.

```
\begin{center}
\begin{tabular}{c}
\begin{XyMcompd}(600,1000)(0,50){}{}
\tetrahedral{2==H;3==CH$_{2}$OH;4==OH;%
1==\tetrahedral{3==(yl);2==H;4==OH;%
1==\tetrahedral{3==(yl);2==HO;4==H;%
1==\tetrahedral{3==(yl);2==H;4==OH;1==CHO%
}}}}
\end{XyMcompd}
\\
\compd\label{cpd:FischerproA} \\
\textit{Preferred}
\end{tabular}
\qquad
\begin{tabular}{c}
\begin{XyMcompd}(600,1000)(0,50){}{}
\tetrahedral{3==CH$_{2}$OH;4==OH;%
1==\tetrahedral{3==(yl);4==OH;%
1==\tetrahedral{3==(yl);2==HO;%
1==\tetrahedral{3==(yl);4==OH;1==CHO%
}}}}
\end{XyMcompd}
\\
\compd\label{cpd:FischerproB} \\
\textit{Acceptable}
\end{tabular}
\qquad
\begin{tabular}{c}
\begin{XyMcompd}(600,1000)(0,50){}{}
\tetrahedral{2B==H~;3==CH$_{2}$OH;4B==~OH;%
1==\tetrahedral{3==(yl);2B==H~;4B==~OH;
1==\tetrahedral{3==(yl);2B==HO~;4B==~H;
1==\tetrahedral{3==(yl);2B==H~;4B==~OH;1==CHO%
}<,100,,100>}<,100,,100>}<,100,,100>}<,100,,100>
\end{XyMcompd}
\\
\compd\label{cpd:FischerproC} \\
\textit{Acceptable}
\end{tabular}
\end{center}
```

Note that the last code uses optional arguments to adjust the lengths of wedged bonds. These codes produce the following Fischer projections:



29-9 *Preferred* **29-10** *Acceptable* **29-11** *Acceptable*

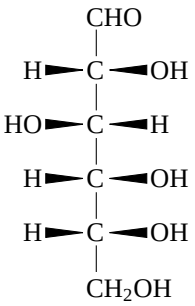
□

Example 29.12. Non-Fischer diagrams with explicitly-printed central carbon atoms are possible because they can readily be interpreted to the same rule used for interpreting wedged and hashed bonds, as found in the

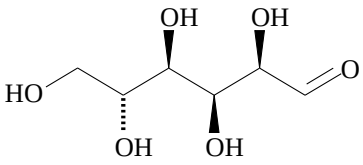
first code for drawing **29-12**. The second code for drawing **29-13** uses the command `\heptamethylenei` for drawing a zigzag polymethylene. This type of representations is preferred for general usage [2, ST-1.8].

```
\begin{tabular}{c}
\begin{XyMcompd}(600,1150)(0,50){}{}
\tetrahedral{0==C;2B==H;3==CH$_{2}$OH;4B==OH;%
1==\tetrahedral{0==C;3==(yl);2B==H;4B==OH;
1==\tetrahedral{0==C;3==(yl);2B==HO;4B==H;
1==\tetrahedral{0==C;3==(yl);2B==H;4B==OH;1==CHO}}}}
\end{XyMcompd} \\
\compd\label{cpd:nonFischerA}
\end{tabular}
\begin{tabular}{c}
\begin{XyMcompd}(1250,550)(-50,-50){}{}
\heptamethylenei[f]{7==O}{1W==HO;2A==OH;3B==OH;4B==OH;5B==OH}
\end{XyMcompd} \\
\compd\label{cpd:nonFischerB} \\
\end{tabular}
```

These codes produce the following non-Fischer projections:



29-12



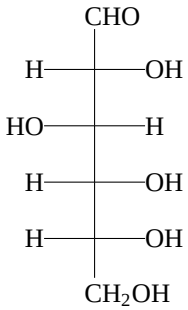
29-13

□

Example 29.13. If you consider that the default length of a vertical C—C bond in **29-9** is too short, the optional argument `<,,,>` can be used to elongate such vertical C—C bonds. For example, the code:

```
\begin{tabular}{c}
\begin{XyMcompd}(600,1150)(0,50){}{}
\tetrahedral{2==H;3==CH$_{2}$OH;4==OH;%
1==\tetrahedral{3==(yl);2==H;4==OH;1==\tetrahedral{3==(yl);2==HO;4==H;
1==\tetrahedral{3==(yl);2==H;4==OH;1==CHO}}<160,,,>}<160,,,>}<160,,,>
\end{XyMcompd} \\
\compd\label{cpd:FischerproD} \\
\end{tabular}
```

generates the following diagram with elongated C—C bonds.



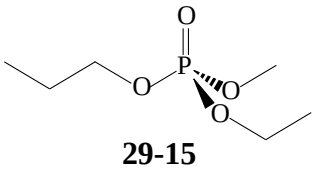
29-14

Compare between **29-9** and **29-14** under paying attention to the lengths of their C—C bonds. See also the code for drawing **29-11**, which shows another embodiment of changing bond lengths. □

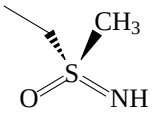
29.3.3 Tetrahedral Stereocenters Including Higher-Order Bonds

Tetrahedral heteroatomic stereocenters, which are indicated by the appropriate placement of bold and/or hashed wedged bonds [2, ST-1.5], can be drawn by using commands described in Chapter 20 as well as Chapter 19. Such heteroatomic stereocenters frequently include higher-order bonds. For example, preferred diagrams of chiral phosphates and sulfoximides are drawn by using `\DtetrahedralS` and `\htetrahedralS`. Acceptable diagrams can also be drawn by using `\tetrahedral`, where bond modifiers such as '`B`' (for α-configurations) and '`A`' (for β-configurations) specify the configuration of tetrahedral heteroatomic stereocenters.

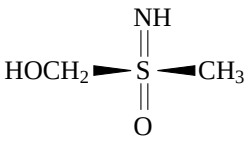
```
\wedgehashedwedge
\begin{tabular}{c}
\begin{XyMcompd}(1100,500)(-350,50){}{}
\DtetrahedralS{0==P;1D==O;2==\tetramethylenei{4==O}{4==(yl)};%
3A==\dimethylene{1==O}{1==(yl)};4B==\put(0,-50){\trimethylenei{1==O}{1==(yl)}}}
\end{XyMcompd}
\\
\compd\label{cpd:phosphate} \\
\textit{Preferred}
\end{tabular}
\begin{tabular}{c}
\begin{XyMcompd}(400,400)(100,150){}{}
\htetrahedralS{0==S;1D==O;2D==NH;3B==CH$_{3}$;%
4A==\dimethylenei{}{2==(yl)}}
\end{XyMcompd}
\\
\compd\label{cpd:sulfoximideA} \\
\textit{Preferred}
\end{tabular}
\begin{tabular}{c}
\begin{XyMcompd}(750,500)(-150,50){}{}
\tetrahedral{0==S;1D==NH;3D==O;4B==CH$_{3}$;2B==HOCH$_{2}$}
\end{XyMcompd}
\\
\compd\label{cpd:sulfoximideB} \\
\textit{Acceptable}
\end{tabular}
```



29-15
Preferred



29-16
Preferred



29-17
Acceptable

29.3.4 Allenes

To draw allenes in accordance with the IUPAC Recommendations 2006 [2, ST-1.6], a command named `\allenestero` is defined as follows:

```
\def\allenestero#1#2#3#4{%
\begin{XyMcompd}(850,500)(150,70){}{}
\Ltrigonal{0==C;2==#1;3==#2;1D==C;%
0==\PutBondLine(280,15)(420,15){0.4pt};%
0==\PutBondLine(280,45)(420,45){0.4pt};%
0==\put(470,0){C};%
0==\WedgeAsSubst(510,30)(5,-3){140};%
0==\HashWedgeAsSubst(510,30)(5,3){140};%
```

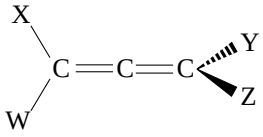
```
0==\put(710,100){#3};%
0==\put(710,-104){#4}%
}
\end{XyMcompd}}
```

In this definition, the left half portion is based on the command \Ltrigonal (cf. Section 19.3), while the right half portion is constructed by a set of low-level commands such as \PutBondLine. Note that the command \put of the LaTeX picture environment can be used in the arguments of \Ltrigonal, because the XyMTeX system is based on the LaTeX picture environment.

In terms of the definition, all four substituents are explicitly depicted to show the configuration of allenes. For example, the code:

```
\allenestero{X}{W}{Y}{Z}
```

generates a preferred diagram:



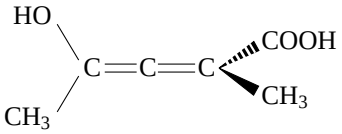
The code for drawing the left half portion (based on the command \Ltrigonal) can be replaced by codes based on such lower-level commands as \PutBondLine and \put. Thus, a command named \AlleneStero is defined as follows:

```
\def\AlleneStero#1#2#3#4{%
\begin{XyMcompd}(850,500)(-150,-200){}{}
\put(-120,195){\llap{#1}}%
\put(-120,-185){\llap{#2}}%
\PutBondLine(-18,60)(-99,195){0.4pt}%
\PutBondLine(-18,0)(-99,-135){0.4pt}%
\put(0,0){C}%
\PutBondLine(80,15)(200,15){0.4pt}%
\PutBondLine(80,45)(200,45){0.4pt}%
\put(210,0){C}%
\PutBondLine(280,15)(420,15){0.4pt}%
\PutBondLine(280,45)(420,45){0.4pt}%
\put(430,0){C}%
\WedgeAsSubst(510,30)(5,-3){140}%
\HashWedgeAsSubst(510,30)(5,3){140}%
\put(670,100){\rlap{#3}}%
\put(670,-104){\rlap{#4}}%
\end{XyMcompd}}
```

Thereby, the code:

```
\AlleneStero{HO}{CH$_{3}$}{COOH}{CH$_{3}$}
```

generates a preferred diagram:



29.4 Skeletal Bonds Drawn by the Replacement Technique

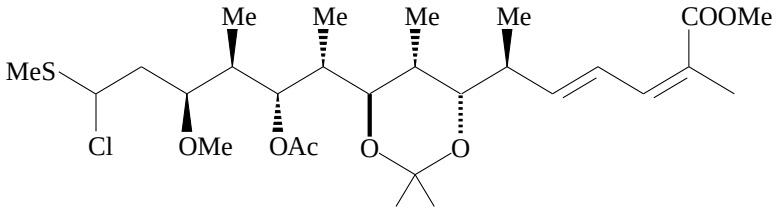
29.4.1 Skeletal Bond Exceptions

Skeletal bonds in a ring system can be drawn in a bold line or a dotted line by using the skeletal list ⟨skelbdlist⟩ as an optional argument (cf. Section 3.1 and Subsection 3.3.2). However, they are not drawn in wedged forms even in the present version of the XyMTEX system.[a]

Example 29.14. For example, the code:

```
\wedgehashedwedge
\sixheterov({bA}{eB}){3==O;5==O;6s==\heptamethylene{}
{1W==MeS;1==Cl;3B==OMe;4B==Me;5A==OAc;6A==Me;7==(yl)};%
2s==\heptamethylene[ce]{}{1==(yl);2B==Me;6==COOMe}}
{1A==Me;4Sa==\null;4Sb==\null}
```

draws the following formula:



29-18

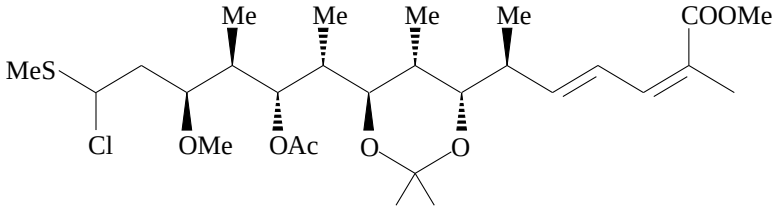
where skeletal bonds are expressed as bold dashes or hashed dashes even if the switching command `\wedgehashedwedge` is declared. □

In the above drawing, the structure **29-18** has been regarded as a derivative of 1,3-dioxane, which is drawn by the command `\sixheterov`. On the other hand, the structure **29-18** can be alternatively regarded as a cyclic acetal of a tetrahydroxypentadecane, where two hydroxyl groups with α- and β-configurations are incorporated in the six-membered cyclic acetal of acetone. From this point of view, the C—O bonds as skeletal bonds are desired to be changed into wedges. For this purpose, you should rely on a rather dirty technique.

Example 29.15. For example, the code:

```
\wedgehashedwedge
\begin{XyMcompd}(2800,800)(-1100,150){}{}
\sixheterov{3==O;5==O;6s==\heptamethylene{}
{1W==MeS;1==Cl;3B==OMe;4B==Me;5A==OAc;6A==Me;7==(yl);7B==\null};%
2s==\heptamethylene[ce]{}{1==(yl);2B==Me;6==COOMe;1A==\null}}
{1A==Me;4Sa==\null;4Sb==\null}[be]
\end{XyMcompd}
```

contains `7B==\null` in `\heptamethylene` (for drawing the left side chain) as well as `1A==\null` in another `\heptamethylene` (fro drawing the right side chain). This code generate the following formula:



29-19

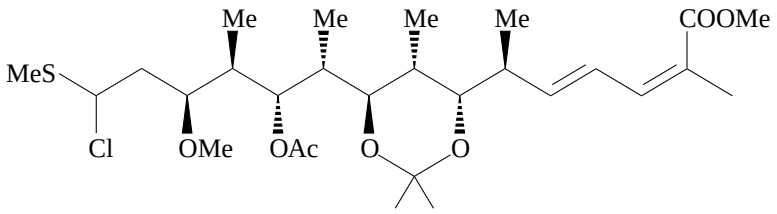
[a] This is because it is impossible to decide unambiguously whether either one endpoint of a ring bond is the starting point or the endpoint of a wedge.

The optional argument [be] in the end of this code is the ⟨delbdlist⟩ of the \sixheterov command; and the omitted bonds are replaced by a wedge (due to 7B==\null in the first \heptamethylene command) and by a hashed wedge (due to 1A==\null in the second \heptamethylene command). □

Example 29.16. If the structure of a tetrahydroxypentadecane skeleton is emphasized, it can be drawn by the combination of \decamethylene and \hexamenthylenei (10 + 6 − 1 = 15) according to the replacement technique (colored in red). Then, a 1,3-dioxane ring is constructed by the replacement technique, where \sixheterov is used under deletion of skeletal bonds a, b, e, and f (colored in blue), as found in the code:

```
\wedgehashedwedge
\begin{XyMcompd}(2800,800)(-100,-250){}{}
\decamethylene{%
{10}s==\hexamethylenei[bd]{}{1==(yl);5==COOMe};
8s==\sixheterov{3==\null;5==\null}{1==(yl);4Sa==\null;4Sb==\null}[abef]
}{1W==MeS;1==Cl;3B==OMe;4B==Me;5A==OAc;6A==Me;7B==O;8A==Me;9A==O;{10}B==Me}
\end{XyMcompd}
```

This code generates an almost equivalent structure:



29-20 □

29.4.2 Commands for the Replacement Technique

As shown in the preceding section, the optional argument ⟨skelbdlist⟩ supports bold dash bonds and hashed dash bonds to represent α- and β-bonds for stereochemistry. Such bonds can be changed into wedges and hashed wedges by means of a rather dirty technique. This technique is refined into a more systematic one by applying the commands defined in Subsection 27.3.3. Their formats of syntax are again summarized as follows:

\PutBondLine(⟨start⟩)(⟨endpint⟩){⟨thickness⟩}	(straight-lined bonds)
\PutDashedBond(⟨start⟩)(⟨endpint⟩){⟨thickness⟩}	(dashed bonds)
\WedgeAsSubst(⟨start⟩)(⟨slope⟩){⟨length⟩}	(wedge bonds)
\HashWedgeAsSubst(⟨start⟩)(⟨slope⟩){⟨length⟩}	(hashed wedge bonds)

For their arguments, see Subsection 27.3.3. To apply these commands to stereochemical documentation, several examples and the effects of ⟨thickness⟩ are shown below:

\PutBondLine(0,0)(200,0){0.4pt}		\PutBondLine(0,0)(200,0){2pt}	
\PutDashedBond(0,0)(200,0){1.6pt}		\PutDashedBond(0,0)(200,0){3pt}	
\WedgeAsSubst(0,0)(1,0){200}		\HashWedgeAsSubst(0,0)(1,0){200}	

Example 29.17. The following examples show the comparison of a default expression with a modified expression due to \WedgeAsSubst and \HashWedgeAsSubst. Thus the codes:

```
\wedgehashedwedge
\sixheteroh({bA}{eB}){3==O;5==O}{1A==Me;2==\null;6==\null;4Sa==\null;4Sb==\null}
\hskip2cm
\sixheteroh{3==O;5==O;2s==\HashWedgeAsSubst(0,0)(1,0){160};%
6s==\WedgeAsSubst(0,0)(1,0){160}}%
{1A==Me;2==\null;6==\null;4Sa==\null;4Sb==\null}[be]
```

generate the following structural formulas:

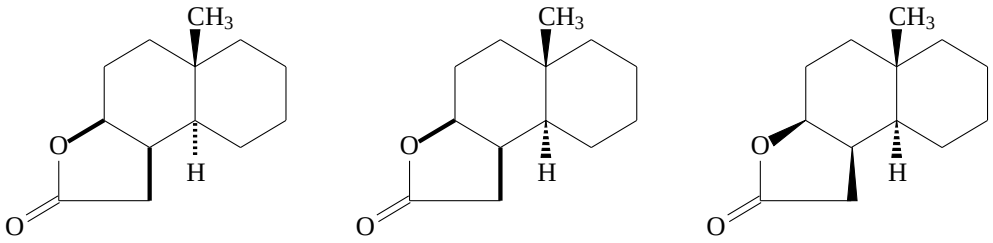
The left formula shows a default expression of skeletal bonds, which is unchanged even if such a switch as `\wedgehashedwedge` is declared. The right formula shows the change of such skeletal bonds by using the macros `\WedgeAsSubst` and `\HashWedgeAsSubst`. It should be noted that these macros are described in the ⟨atomlist⟩ according to the replacement technique (the atom-replacement methodology) for spiro substituents and that superposed skeletal bonds are omitted by the ⟨delbdlist⟩ at the end of the second code (`[be]`). □

Example 29.18. The following examples show three modes of bold skeletal bonds:

```
\begin{tabular}{lll}
default & \verb/\wedgehashedwedge/ & customized \\
\decaheterov[%
{f\fivefusevi({bB}{eB}){5==O}{4D==O}{A}}]{}{9A==H;{{10}B}==CH$_{3}$} &
\wedgehashedwedge
\decaheterov[%
{f\fivefusevi({bB}{eB}){5==O}{4D==O}{A}}]{}{9A==H;{{10}B}==CH$_{3}$} &
\wedgehashedwedge
\decaheterov[%
{f\fivefusevi{5==O;2s==\WedgeAsSubst(0,0)(0,-1){200};%
1s==\WedgeAsSubst(0,0)(-5,-3){130}}{4D==O}{A}[be]}]{}{9A==H;{{10}B}==CH$_{3}$}
\\
\end{tabular}
```

These codes generate structural formulas having various combinations, i.e., default (wedged bonds, hashed dash bonds, and dash skeletal bonds), the `\wedgehashedwedge` mode (wedged bonds, hashed wedged bonds, and dash skeletal bonds), and a customized mode (wedged bonds, hashed wedged bonds, and wedged skeletal bonds):

default `\wedgehashedwedge` customized

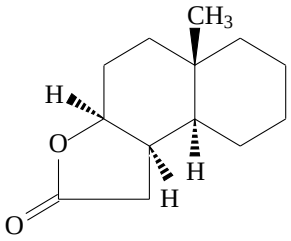


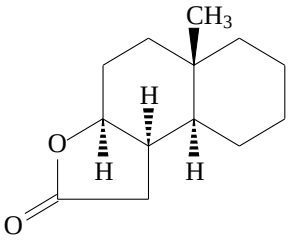
These expressions stress the decaline ring system (6-6) as a template of synthesis so that the five-membered lactone is regarded as a tentative substituent. □

Example 29.19. If one changes his/her viewpoint, the same molecule may be alternative drawn as follows:

```
\decaheterov[%
{f\fivefusevi{5==O}{4D==O}{A}}]{}{9A==H;5SA==H;6GA==H;{{10}B}==CH$_{3}$}
\hskip2cm
\decaheterov[%
{f\fivefusevi{5==O}{4D==O;2FA==H}{A}}]{}{9A==H;6FA==H;{{10}B}==CH$_{3}$}
```

These codes generate such expressions that the tricyclic ring system (6-6-5) is taken into predominant consideration:





□

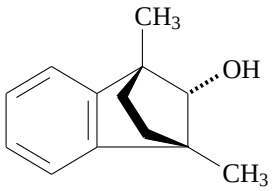
The commands `\WedgeAsSubstX` and `\HashWedgeAsSubstX` correspond to `\WedgeAsSubst` and `\HashWedgeAsSubst`, where the (x, y)-coordinates of the starting and ending points are given to ⟨start⟩ and ⟨endpint⟩ in addition to the optional argument ⟨thickness⟩ (default 10).

`\WedgeAsSubstX(`⟨start⟩`)(`⟨endpint⟩`)[`⟨thickness⟩`]`	(wedge bonds)
`\HashWedgeAsSubstX(`⟨start⟩`)(`⟨endpint⟩`)[`⟨thickness⟩`]`	(hashed wedge bonds)

For their arguments, see Subsection 27.3.3. The effects of ⟨thickness⟩ are shown below:

`\WedgeAsSubstX(0,0)(200,0)`		`\HashWedgeAsSubstX(0,0)(200,0)`
`\WedgeAsSubstX(0,0)(200,0)[10]`		`\HashWedgeAsSubstX(0,0)(200,0)[10]`
`\WedgeAsSubstX(0,0)(200,0)[20]`		`\HashWedgeAsSubstX(0,0)(200,0)[20]` 

Example 29.20. When a bridged ring system has additional substituents at bridge atoms, those substituents are connected to atom that have plain bonds within the ring [2, ST-1.3.3]. This rule is exemplified by the following structure:



29-21

which is drawn by the code:

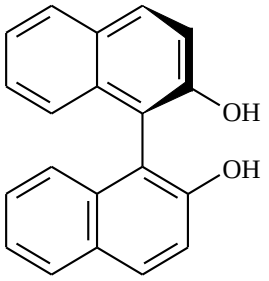
```
\begin{XyMcompd}(850,700)(280,200){cpd:bridgering}{}
\nonaheterovi[egj]{%
1s==\WedgeAsSubstX(0,0)(-80,-120);%
1s==\PutBondLine(-80,-107)(18,-260){3.5pt};%
3s==\WedgeAsSubstX(0,0)(-160,50)
}{2A==OH;1==CH$_{3}$;3==CH$_{3}$}
\end{XyMcompd}
```

Note that each methyl at the bridge atom is linked with a straight single (plain) bond, which shows that the methyl substituent is contained in the page. □

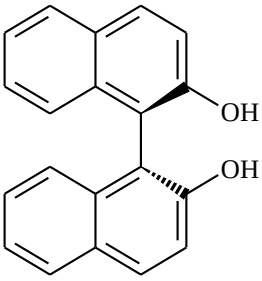
29.4.3 Hindered Biaryls and Related Compounds

Although hindered rotation of biaryls has been expressed variously, a plausible convention is described in the IUPAC recommendation [2, ST-1.7].

Example 29.21. Hindered biaryls are represented by such formulas as **29-22** (preferred) and **29-23** (acceptable) to emphasize hindered rotation [2, ST-1.7].



29-22
Preferred



29-23
Acceptable

These formulas (**29-22** and **29-23**) are drawn by the following codes:

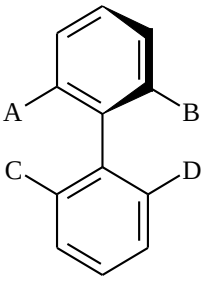
```
\begin{center}
\def\thinLineWidth{0.8pt}
\begin{tabular}{c}
\begin{XyMcompd}(850,1050)(-480,-400){}{}
\BiFunc(0,1){200}
{\naphdrv{1==(yl);2==OH}}
{\decaheterov[bdfhj]{%
1s==\WedgeAsSubst(0,0)(5,-3){171};%
3s==\PutBondLine(0,-20)(0,220){3pt};%
4s==\WedgeAsSubst(0,0)(5,3){171}%
}{4==(yl);3==OH}[abc]}
\end{XyMcompd}
\\
\noalign{\vskip5pt}
\compd\label{cpd:binaphA} \\
\textit{Preferred} \\
\end{tabular}
\qquad
\begin{tabular}{c}
\begin{XyMcompd}(850,1050)(-480,-400){}{}
\BiFunc(0,1){200}
{\decaheterov[bdfhj]{%
1s==\HashWedgeAsSubst(0,0)(5,-3){171}%
}{1==(yl);2==OH}[a]}
{\decaheterov[bdfhj]{%
4s==\WedgeAsSubst(0,0)(5,3){171}%
}{4==(yl);3==OH}[c]}
\end{XyMcompd}
\\
\noalign{\vskip5pt}
\compd\label{cpd:binaphB} \\
\textit{Acceptable} \\
\end{tabular}
\end{center}
```

In the above codes, two naphthyl moieties (`\naphdrv` or `\decaheterov`) are linked by using the command `\BiFunc`. See Subsection 26.4.2 for the syntax of the command `\BiFunc`, which generates a dumbbell skeleton with a given length. The wedged bonds and boldfaced bonds in the naphthalene rings are drawn by the replacement technique, where `\WedgeAsSubst` and `\PutBondLine` are declared in the ⟨atomlist⟩ of the command `\decaheterov`. □

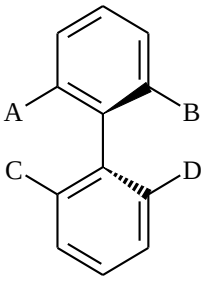
Example 29.22. The commands `\naphdrv` and `\decaheterov` in the above codes for drawing **29-22** and **29-23** are replaced by the commands `\benzenev` and `\sixheterov`. Thereby, the following codes are obtained after a few modifications for attaching substituents:

```
\begin{center}
\def\thinLineWidth{0.8pt}
\begin{tabular}{c}
\begin{XyMcompd}(850,1050)(-480,-400){}{}
\BiFunc(0,1){200}
{\benzenev{1==(yl);2==D;6==C}}
{\sixheterov[bdf]{%
1s==\WedgeAsSubst(0,0)(5,-3){171};%
3s==\PutBondLine(0,-20)(0,220){3pt};%
4s==\WedgeAsSubst(0,0)(5,3){171}%
}{4==(yl);3==B;5==A}[abc]}
\end{XyMcompd}
\\
\noalign{\vskip5pt}
\compd\label{cpd:biphenylA} \\
\textit{Preferred} \\
\end{tabular}
\qquad
\begin{tabular}{c}
\begin{XyMcompd}(850,1050)(-480,-400){}{}
\BiFunc(0,1){200}
{\sixheterov[bdf]{%
1s==\HashWedgeAsSubst(0,0)(5,-3){171}%
}{1==(yl);2==D;6==C}[a]}
{\sixheterov[bdf]{%
4s==\WedgeAsSubst(0,0)(5,3){171}%
}{4==(yl);3==B;5==A}[c]}
\end{XyMcompd}
\\
\noalign{\vskip5pt}
\compd\label{cpd:biphenylB} \\
\textit{Acceptable} \\
\end{tabular}
\end{center}
```

These codes generates biphenyl derivatives **29-24** and **29-25**, the hindered rotation of which is represented by wedged and related bonds.



29-24
Preferred



29-25
Acceptable

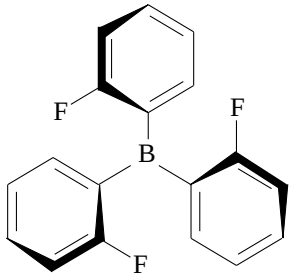
□

Example 29.23. The hindered rotation of molecular propellers is represented in a similar way to biphenyl derivatives [2, ST-5.4]. The following code is based on the substitution technique, where three commands `\sixheterov` are declared in the ⟨subslist⟩ of `\Dtrigonal`. Wedged and related bonds for representing hindered rotation are also drawn by the replacement technique using `\WedgeAsSubst` and `\PutBondLine` in the ⟨atomlist⟩ of `\sixheterov`.

```
\begin{XyMcompd}(980,1000)(-200,-150){}{}
\Dtrigonal{0==B;%
```

```
1==\sixheterov[ace]{%
1s==\WedgeAsSubst(0,0)(-5,-3){171};%
5s==\PutBondLine(0,-20)(0,220){3pt};%
4s==\WedgeAsSubst(0,0)(-5,3){171}%
}{4==(yl);5==F}[def];%
2==\sixheterov[ace]{%
6s==\WedgeAsSubst(0,0)(5,3){180};%
1s==\PutBondLine(-10,10)(181,-113){3pt};%
3s==\WedgeAsSubst(0,0)(0,1){200}%
}{6==(yl);1==F}[abf];%
3==\sixheterov[ace]{%
5s==\WedgeAsSubst(0,0)(5,-3){180};%
4s==\PutBondLine(-10,-10)(181,103){3pt};%
2s==\WedgeAsSubst(0,0)(0,-1){210}%
}{2==(yl);3==F}[bcd]}
\end{XyMcompd}
```

This code generates the following structure:



□

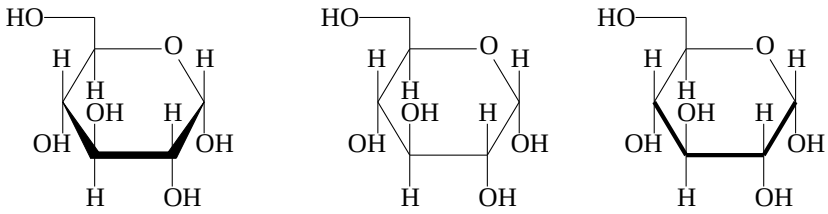
29.4.4 Haworth Diagrams of Furanoses and Pyranoses

Wedged skeletal bonds for Haworth diagrams of furanoses and pyranoses have been already discussed in Subsection 18.3.1. Preferred and acceptable graphical representations of Haworth projections are discussed in the IUPAC Recommendations 2006 [2, ST-1.9].

Example 29.24. The following example shows three representations of pyranoses: a preferred diagram (**29-26**) and an acceptable one (**29-27**) in addition to a conventional diagram (**29-28**). Under the default loading, the XyMTEX system supports the command `\pyranosew` for drawing **29-26** as well as the command `\pyranose` for drawing **29-28**.

```
\begin{center}
\begin{tabular}{ccc}
\begin{XyMcompd}(800,800)(50,0){}{}
\pyranosew{1Sa==OH;1Sb==H;2Sa==OH;2Sb==H;3Sa==H;3Sb==OH;4Sa==OH;4Sb==H;5Sa==H;%
5Sb==\tetrahedral{3==(yl);2==HO}}
\end{XyMcompd}
&
\def\thickLineWidth{0.4pt}
\def\thinLineWidth{0.4pt}
\begin{XyMcompd}(800,800)(50,0){}{}
\pyranose{1Sa==OH;1Sb==H;2Sa==OH;2Sb==H;3Sa==H;3Sb==OH;4Sa==OH;4Sb==H;5Sa==H;%
5Sb==\tetrahedral{3==(yl);2==HO}}
\end{XyMcompd}
&
\begin{XyMcompd}(800,800)(50,0){}{}
\pyranose{1Sa==OH;1Sb==H;2Sa==OH;2Sb==H;3Sa==H;3Sb==OH;4Sa==OH;4Sb==H;5Sa==H;%
5Sb==\tetrahedral{3==(yl);2==HO}}
\end{XyMcompd}
\\
```

```
\compd\label{cpd:HaworthpyA} & \compd\label{cpd:HaworthpyB} &
\compd\label{cpd:HaworthpyC} \\
\textit{Preferred} (\XyMTeX{} default) &
\textit{Acceptable} & (\XyMTeX{} default) \\
\end{tabular}
\end{center}
```

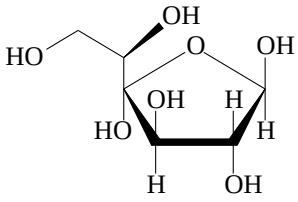


29-26 *Preferred* (XyMTeX default) **29-27** *Acceptable* **29-28** (XyMTeX default)

□

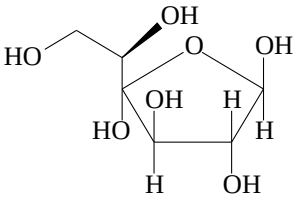
Example 29.25. On the same line as the Haworth diagrams of pyranoses, the following example shows three representations of furanoses: a preferred diagram (**29-29**) and an acceptable one (**29-30**) in addition to a conventional diagram (**29-31**). Under the default loading (the PDF-compatible mode and the PostScript-compatible mode), the XyMTeX system supports the command `\furanosew` for drawing **29-26** as well as the command `\furanose` for drawing **29-28**.

```
\begin{center}
\begin{tabular}{ccc}
\begin{XyMcompd}(900,750)(-100,0){}{}
\furanosew{1Sb==OH;1Sa==H;2Sa==OH;2Sb==H;3Sa==H;3Sb==OH;4Sa==HO;%
4Sb==\dimethylenei{%
2s==\WedgeAsSubstX(0,0)(140,120);%
2s==\put(145,125){OH}}{2==(yl);1W==HO}}
\end{XyMcompd}
&
\def\thickLineWidth{0.4pt}
\def\thinLineWidth{0.4pt}
\begin{XyMcompd}(900,750)(-100,0){}{}
\furanose{1Sb==OH;1Sa==H;2Sa==OH;2Sb==H;3Sa==H;3Sb==OH;4Sa==HO;%
4Sb==\dimethylenei{%
2s==\WedgeAsSubstX(0,0)(140,120);%
2s==\put(145,125){OH}}{2==(yl);1W==HO}}
\end{XyMcompd}
&
\begin{XyMcompd}(900,750)(-100,0){}{}
\furanose{1Sb==OH;1Sa==H;2Sa==OH;2Sb==H;3Sa==H;3Sb==OH;4Sa==HO;%
4Sb==\dimethylenei{%
2s==\WedgeAsSubstX(0,0)(140,120);%
2s==\put(145,125){OH}}{2==(yl);1W==HO}}
\end{XyMcompd}
\\
\compd\label{cpd:HaworthfurA} & \compd\label{cpd:HaworthfurB} &
\compd\label{cpd:HaworthfurC} \\
\textit{Preferred} (\XyMTeX{} default) &
\textit{Acceptable} & (\XyMTeX{} default) \\
\end{tabular}
\end{center}
```



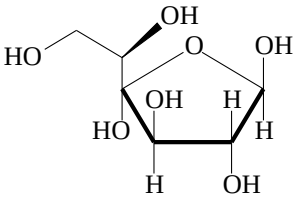
29-29

Preferred (X$\mathfrak{Z}$MTEX default)



29-30

Acceptable



29-31

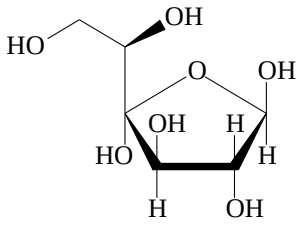
(X$\mathfrak{Z}$MTEX default)

□

Example 29.26. If the 4*β*-bond of **29-29** is desired to be elongated, the replacement technique using `\PutBondLine` is applied to the ⟨atomlist⟩ of `\fivesugarh`, which is used in place of `\furanosew`. For the application of `\fivesugarh`, see Subsection 18.3.1. Thus, the code:

```
\begin{XyMcompd}(950,800)(-150,0){}{}
\fivesugarh{5==O;1s==\WedgeAsSubst(0,0)(-3,-5){120};%
4s==\WedgeAsSubst(0,0)(3,-5){120};%
3s==\PutBondLine(-17,0)(307,0){2.8pt};%
4s==\PutBondLine(0,0)(0,250){0.4pt};%elongated
4s==\put(0,250){\dimethylenei{%
2s==\WedgeAsSubstX(0,0)(140,84);%
2s==\put(150,84){OH}}{2==(yl);1W==HO}}%
}{1Sb==OH;1Sa==H;2Sa==OH;2Sb==H;3Sa==H;3Sb==OH;4Sa==HO}[abc]
\end{XyMcompd}
```

generates the following diagram:



□

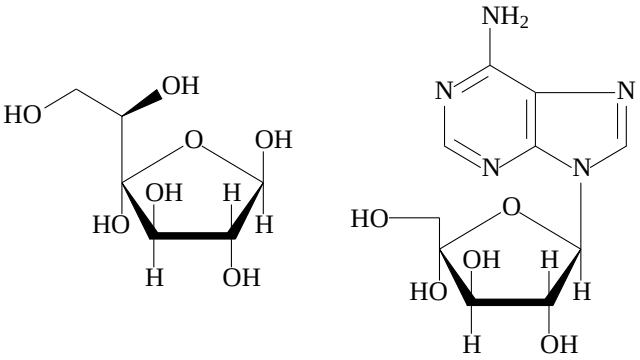
Example 29.27. If the command `\fivesugarh` is frequently used to draw diagrams with wedged skeletal bonds, it is convenient to define `\fivesugarhw` as follows:

```
\makeatletter
\def\fivesugarhw{\@ifnextchar[{\@fivesugarhw}{\@fivesugarhw[]}}
\def\@fivesugarhw[#1]#2#3{%
\fivesugarh[#1]{5==O;1s==\WedgeAsSubst(0,0)(-3,-5){120};%
4s==\WedgeAsSubst(0,0)(3,-5){120};%
3s==\PutBondLine(-17,0)(307,0){2.8pt};#2}{#3}[abc]}
\makeatother
```

Thereby, required codes become slightly simpler as follows:

```
\begin{XyMcompd}(950,800)(-150,0){}{}
\fivesugarhw{%
4s==\PutBondLine(0,0)(0,250){0.4pt};%
4s==\put(0,250){\dimethylenei{%
2s==\WedgeAsSubstX(0,0)(140,84);%
2s==\put(150,84){OH}}{2==(yl);1W==HO}}%
}{1Sb==OH;1Sa==H;2Sa==OH;2Sb==H;3Sa==H;3Sb==OH;4Sa==HO}
\end{XyMcompd}
\qquad
\begin{XyMcompd}(950,1300)(-50,0){}{}
\fivesugarhw{%
1s==\PutBondLine(0,0)(0,250){0.4pt};%
```

```
1s==\put(0,250){\nonaheterov[begj]{1==N;3==N;5==N;7==N}{1==(yl);4==NH$_{2}$}}%
}{1Sa==H;2Sa==OH;2Sb==H;3Sa==H;3Sb==OH;4Sa==HO;
4Sb==\tetrahedral{3==(yl);2==HO}}%
\end{XyMcompd}
```



□

Example 29.28. In a similar way, it is convenient to define `\sixsugarhw` to draw diagrams with wedged skeletal bonds:

```
\makeatletter
\def\sixsugarhw{\@ifnextchar[{\@sixsugarhw}{\@sixsugarhw[]}}
\def\@sixsugarhw[#1]#2#3{%
\sixsugarh[#1]{6==O;1s==\WedgeAsSubst(0,0)(-3,-5){120};%
4s==\WedgeAsSubst(0,0)(3,-5){120};%
3s==\PutBondLine(-17,0)(307,0){2.8pt};#2}{#3}[abc]}
\makeatother
```

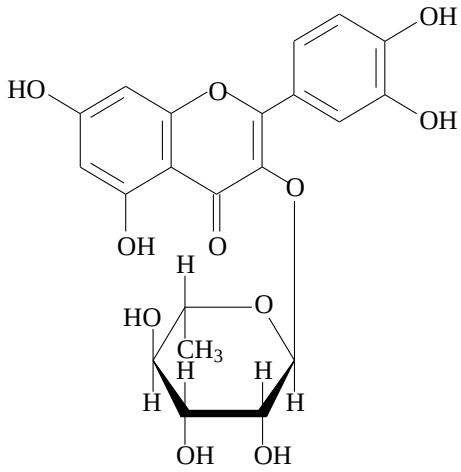
Thereby, the structure **29-32** of quercitrin, which is a flavonoid glycoside, is drawn by the replacement technique using the ⟨atomlist⟩ of the above-defined command `\sixsugarhw`. Similarly the structure **29-33** of plantagoside, which is also a flavonoid glycoside, is drawn by the replacement technique using the ⟨atomlist⟩ of `\sixsugarhw`.

```
\begin{center}
\begin{tabular}{c}
\begin{XyMcompd}(1600,1750)(-280,0){}{}
\sixsugarhw{%
1s==\PutBondLine(0,0)(0,600){0.4pt};%
1s==\put(0,600){\lyl(8==O){3==\decaheterov[bfhk]{1==O}{3==(yl);4D==O;5==OH;7==HO;%
2==\benzenev{5==(yl);2==OH;3==OH}}}}%
}{1Sa==H;2Sa==OH;2Sb==H;3Sa==OH;3Sb==H;4Sa==H;4Sb==HO;5Sa==CH$_{3}$;5Sb==H}%
\end{XyMcompd}
\\
\compd\label{cpd:quercitrin} \\
quercitrin \\
\end{tabular}
\quad
\wedgehashedwedge
\begin{tabular}{c}
\begin{XyMcompd}(1600,1700)(-730,0){}{}
\sixsugarhw{%
1s==\PutBondLine(0,0)(0,600){0.4pt};%
1s==\put(0,600){\lyl(8==O){3==\sixheterov[bdf]{%
5s==\put(-120,-72){\decaheterov[fhk]{1==O}{2==(yl);2A==\null;4D==O;5==OH;7==HO}}
}{3==(yl);1==OH;2==OH}}}%
}{1Sa==H;2Sa==OH;2Sb==H;3Sa==H;3Sb==OH;4Sa==HO;4Sb==H;%
5Sb==\llap{HO}CH$_{2}$;5Sa==H}%
\end{XyMcompd}
\\
```

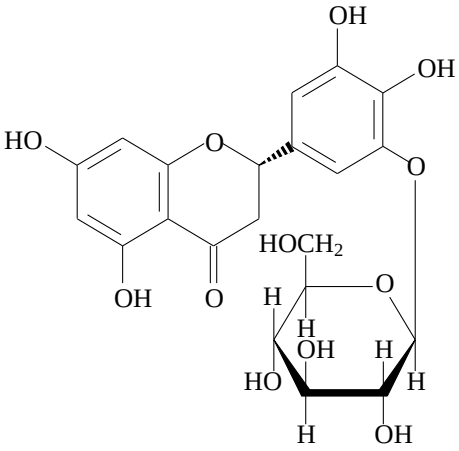
```
\compd\label{cpd:plantagoside} \\
plantagoside \\
\end{tabular}
\end{center}
```

The construction of **29-32** can be schematically represented by 6 → 6-6 → [\lyl (O)] → pyranose, where a red arrow represents the substitution technique, while a blue arrow represents the replacement technique. On the other hand, the construction of **29-33** can be schematically represented by 6-6 → 6 → [\lyl (O)] → pyranose, where all of the steps are based on the replacement technique.

In the first code for drawing **29-32**, the input `1s==\PutBondLine(0,0)(0,600){0.4pt}` draws an elongated vertical bond at the 1-position of the pyranose ring. The input `1s==\put(0,600){\lyl(8==O)-{3==...` indicates the attachment of the flavonoid ring through the oxygen atom, which is placed by using `\lyl` command. Note that the coordinate `(0,600)` is common to assign the joint position. These features hold true in the second code for drawing **29-33**.



29-32
quercitrin



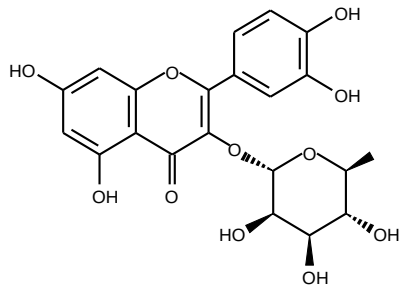
29-33
plantagoside

□

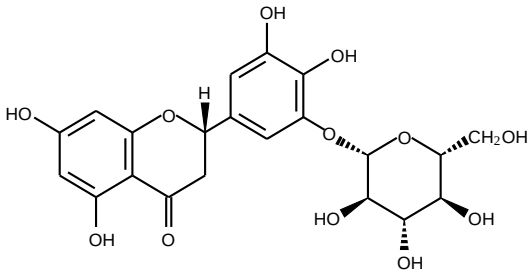
Example 29.29. An alternative to Haworth projections is Mills depictions, where the ring system is drawn according to standard conventions for depicting structural diagrams within a plane [2, ST-1.10]. The Haworth projections in quercitrin (**29-32**) and plantagoside (**29-33**) are changed into Mills depictions so as to generate alternatives **29-34** and **29-35**. To show the feasibility of the XyMTEX adjustment, the unit length, the bond thickness, and the size and family of the substituent font are changed, as found in the following codes for drawing the structures **29-34** and **29-35**.

```
\changeunitlength{0.08pt}
\def\thinLineWidth{0.8pt}
\let\substfont=\sffamily
\let\substfontsize=\scriptsize
\wedgehashedwedge
\begin{tabular}{c}
%\fbox
%{%
\begin{XyMcompd}(1800,1400)(-1000,0){}{}
\sixheterov{1==O}{%
6A==\lyl(5==O){3==\decaheterov[bfhk]{1==O}{3==(yl);4D==O;5==OH;7==HO;%
2==\benzenev{5==(yl);2==OH;3==OH}}}; %
2B==\null;3A==OH;4B==OH;5B==HO}
\end{XyMcompd}
%}
\\
\compd\label{cpd:quercitrinX} \\
quercitrin \\
\end{tabular}
```

```
\begin{tabular}{c}
%\fbox
%{%
\begin{XyMcompd}(2400,1300)(-1450,0){}{}
\sixheterov{1==O}{%
6A==\lyl(5==O){3==\sixheterov[bdf]{}{3==(yl);1==OH;2==OH;
5==\decaheterov[fhk]{1==O}{2==(yl);2FB==H;4D==O;5==OH;7==HO}}};%
2A==CH$_{2}$OH;3B==OH;4A==OH;5B==HO}
\end{XyMcompd}
%}
\\
\compd\label{cpd:plantagosideX} \\
plantagoside \\
\end{tabular}
```



29-34
quercitrin



29-35
plantagoside

□

Compare between **29-33** and **29-35**. The diagram **29-35** is based on the depiction style of [2, ST-1.1.2], where the flavonoid structure (a six-membered ring and a six-to-six fused ring) is presumed to be coplanar. Thus, the linking bond between the six-membered ring and the six-to-six fused ring is drawn as a plain bond, so that the configuration at the 2-position of the six-to-six fused ring is represented by the explicit depiction of the β-hydrogen with a solid wedged bond.

29.4.5 Helicenes

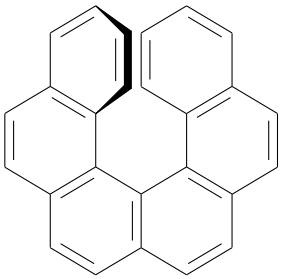
The helical or screw-shaped structure of helicenes is indicated by a pair of solid wedged bonds on one end of the helix [2, ST-5.2].

Example 29.30. To draw such non-planarity in the drawing system of XyMTEX, the addition technique for drawing fused rings is multiply applied to the command `\decaheterov`, as found in the following code:

```
\begin{tabular}{c}
\begin{XyMcompd}(1000,1050)(50,250){}{}
\decaheterov[acfhk%
%right-hand helix
{a\sixfusev[bf%
{f\sixfusev[ae]{}{}{C}}%
]{}{}{D}}%
%left-hand helix
{h\sixfusev[ae%
{a\sixfusev[f]{%
1s==\WedgeAsSubstX(0,0)(122,-103);%
3s==\PutBondLine(-54,-10)(-54,210){3pt};%
3s==\PutBondLine(-100,20)(-100,180){0.4pt};%
4s==\WedgeAsSubstX(0,0)(122,103)%
```

```
}{}{D}[abc]}%
]{}{}{C}}%
]{}{}
\end{XyMcompd}
\\
\compd\label{cpd:helicene} \\
\end{tabular}
```

This code generates the following helicene:



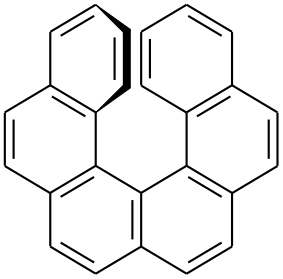
29-36

The right-hand helix is drawn by the doubly-nested application of the addition technique. On the other hand, three bonds of the terminal ring of the left-hand helix are deleted by its optional argument `[abc]` of `\sixfusev`. Then, they are replaced by wedged and related bonds (`\WedgeAsSubstX` and `\PutBondLine` colored in red) by applying the replacement technique in the ⟨atomlist⟩ of `\sixfusev` for drawing the terminal ring. □

Example 29.31. The structure of helicene can be alternatively drawn by applying the addition technique. The three bonds in the terminal ring of the left-hand helix are drawn by declaring `\WedgeAsSubstX` and `\PutBondLine` (colored in red) in the ⟨bondlist⟩ of `\sixfusev`. Thus, the code:

```
\def\thinLineWidth{0.8pt}
\begin{tabular}{c}
\begin{XyMcompd}(1000,1050)(50,250){}{}
\decaheterov[acfhk%
%right-hand helix
{a\sixfusev[bf%
{f\sixfusev[ae]{}{}{C}}%
]{}{}{D}}%
%left-hand helix
{h\sixfusev[ae%
{a\sixfusev[f%
{a\WedgeAsSubstX(0,0)(122,-103)}%
{c\PutBondLine(-54,-10)(-54,210){3pt}}%
{c\PutBondLine(-100,20)(-100,180){0.8pt}}%
{d\WedgeAsSubstX(0,0)(122,103)}%
]{}{}{D}[abc]}%
]{}{}{C}}%
]{}{}
\end{XyMcompd}
\\
\compd\label{cpd:heliceneX} \\
\end{tabular}
```

generates the following structure:



29-37

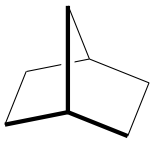
Note that the control points of the bonds ‘a’, ‘c’, and ‘d’ for the addition technique (using the ⟨bondlinst⟩) are located at the locant numbers ‘1’, ‘3’, and ‘4’ for the replacement technique (using the ⟨atomlist⟩). In the above drawing, the bond thickness in **29-37** is changed by declaring `\def\thinLineWidth{0.8pt}`. □

29.5 Front-to-Back Ordering of Crossing Bonds

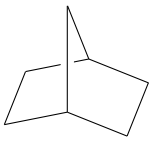
29.5.1 Restrictions on Perspective Drawings

According to the IUPAC Recommendations 2006 [2, ST-3.1], the use of perspective drawings should be limited to *ring systems* and should usually be further limited to *bridged ring systems*. As a guide to the viewer, the front-to-back ordering of crossing bonds in such perspective drawings of ring systems is recommended to be depicted with a small discontinuity in the back-most bond.

The command `\bornane` for drawing a norbornane skeleton (bicyclo[2.2.2]heptane) generates the diagram **29-38** under the default condition of the XyMTEX system, where such a small discontinuity is embodied in addition to boldfaced front bonds. If you obey the IUPAC Recommendations 2006 [2, ST-3.1] strictly, the command `\frontthicktothintrue` should be declared, so that the diagram **29-39** is obtained as an IUPAC preferred embodiment. Note that the the default condition of the XyMTEX system is operated under the global declaration of `\frontthicktothinfalse`.



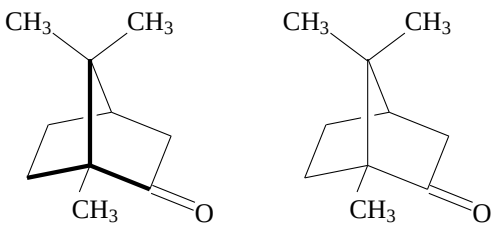
29-38
`\borane{}{}`
XyMTEX default



29-39
`\frontthicktothintrue \borane{}{}`
Preferred [2, ST-3.1]

Example 29.32. The structure of camphor (1,7,7-trimethylbicyclo[2.2.1]heptan-2-one) is drawn in two fashions, i.e., a XyMTEX-default diagram (left) and an IUPAC-preferred diagram (right), by inputing the following codes:

```
\begin{XyMcompd}(700,800)(150,100){}{}
\bornane{7Sa==CH$_{3}$;7Sb==CH$_{3}$;4==CH$_{3}$;3D==O}
\end{XyMcompd}
\qquad
\begin{XyMcompd}(700,800)(150,100){}{}
\frontthicktothintrue
\bornane{7Sa==CH$_{3}$;7Sb==CH$_{3}$;4==CH$_{3}$;3D==O}
\end{XyMcompd}
```



□

Because the command \bornane does not support the argument ⟨atomlist⟩, a skeletal atom cannot be introduced to such a bornane derivative as (+)-(*1R,4S*)-camphanoyl chloride. Moreover, the replacement technique is not applicable, because the argument ⟨bondlist⟩ of the command \bornane does not support the replacement technique.

For the purpose of introducing a skeletal atom, the command \SetTwoAtoms is used to put an atom after the truncation of a vertex. Compare the following two outputs:

—O— vs. —O—

which are generated by the codes:

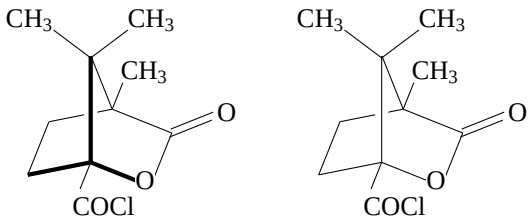
```
\begin{picture}(300,100)(0,0)
\put(0,30){\redx{\line(1,0){300}}}
\put(100,0){O}
\end{picture}
vs.\
\begin{picture}(300,100)(0,0)
\put(0,30){\redx{\line(1,0){300}}}
\put(100,0){\SetTwoAtoms{O}}
\end{picture}
```

Note that the latter code suppresses the output of the red line in the central portion of the letter 'O'.

Example 29.33. The input \put(642,220){\makebox(0,0){\SetTwoAtoms{O}}} (colored in red) for drawing (+)-(*1R,4S*)-camphanoyl chloride contains \makebox(0,0) which prints out the letter 'O' with no dimension (no size) at the location (642,220) of the vertex at issue.

```
\begin{XyMcompd}(750,800)(150,100){}{}
\put(0,0){\bornane{7Sa==CH$_{3}$;7Sb==CH$_{3}$;1==CH$_{3}$;2D==O;4==COCl}}
\put(642,220){\makebox(0,0){\SetTwoAtoms{O}}}
\end{XyMcompd}
\qquad
\begin{XyMcompd}(750,800)(150,100){}{}
\frontthicktothintrue
\put(0,0){\bornane{7Sa==CH$_{3}$;7Sb==CH$_{3}$;1==CH$_{3}$;2D==O;4==COCl}}
\put(642,220){\makebox(0,0){\SetTwoAtoms{O}}}
\end{XyMcompd}
```

These codes generate the following diagrams:



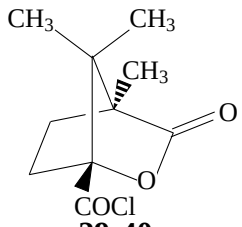
The left diagram is a XyMTEX-default printing, while the right diagram is a preferred embodiment according to the IUPAC Recommendations 2006 [2, ST-3.1]. Note that the command \put can be used in the XyMcompd environment of the XyMTEX system, just as it can be used in the LaTeX picture environment. □

Configuration in perspective drawings is discussed in the IUPAC Recommendations 2006 [2, ST-3.2], which points out that a well-drawn projection can be interpreted as implying the absolute configuration specified by the original three-dimensional structure. This means that wedged or hashed wedged bonds are unnecessary in such a well-drawn projection.

Example 29.34. Contrary to this principle, the IUPAC Recommendations 2006 indicates that a wedge or hashed wedge at a bridgehead position is regarded as being acceptable, as found in the following example. Thus the code:

```
\wedgehashedwedge
\begin{XyMcompd}(750,800)(150,100){}{}
\frontthicktothintrue
\put(0,0){\bornane{7Sa==CH$_{3}$;7Sb==CH$_{3}$;1A==CH$_{3}$;2D==O;4B==COCl}}
\put(642,220){\makebox(0,0){\SetTwoAtoms{O}}}
\end{XyMcompd}
```

generates an IUPAC-acceptable diagram with a wedge and a hashed wedge at the bridgehead positions:



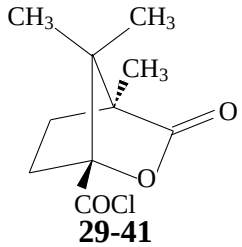
29-40

□

Example 29.35. The wedge and the hashed wedge in the diagram **29-40** are desirable to be thinner than the default setting, although this target may be an optional thing. This target requires a rather dirty technique, as found in the code:

```
\begin{XyMcompd}(750,800)(150,100){}{}
\frontthicktothintrue
\put(0,0){\bornane{7Sa==CH$_{3}$;7Sb==CH$_{3}$;1==CH$_{3}$;2D==O;4==COCl}}
\put(642,220){\makebox(0,0){\SetTwoAtoms{O}}}%                          (0)
\put(518,487){\whitex{\PutBondLine(1,2.5)(40,100){0.8pt}}}%             (1)
\put(518,487){\HashWedgeAsSubstX(6,15)(38,95)[6]}%                      (2)
\put(518,487){\WedgeAsSubstX(0,0)(4,10)[1]}%                            (3)
\put(437,287){\whitex{\PutBondLine(-1,-2.5)(-40,-100){0.8pt}}}%         (4)
\put(437,287){\WedgeAsSubstX(0,0)(-40,-100)[6]}%                        (5)
\end{XyMcompd}
```

The above code generates the following IUPAC-acceptable diagram with a thinner wedge and a thinner hashed wedge (compare between **29-40** and **29-41**):



29-41

The blue-colored input lines (1)–(3) aim at drawing a hashed wedge at the bridgehead position linking with a methyl group. Line (1) outputs a white line to erase the bond printed out by declaring `1==CH$_{3}$` in the ⟨subslist⟩ of `\bornane`. Then Line (2) outputs a hashed wedge which is slightly shorter that the original linking bond in order to prevent the undesirable truncation of the bridgehead position. The Line (3) outputs a very short wedge at the nearest portion to the the bridgehead position. The optional argument ⟨thickness⟩ of `\WedgeAsSubstX` or `\HashWedgeAsSubstX` is used to adjust the thickness of a wedge or a hashed wedge (cf. Subsection 29.4.2).

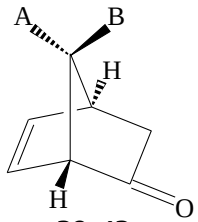
On the other hand, the green-colored input lines (4) and (5) aim at drawing a wedge at the bridgehead position linking with a chlorocarbonyl group. Line (4) outputs a white line to erase the bond printed out by declaring `4==COCl` in the ⟨subslist⟩ of `\bornane`. Then Line (5) outputs a wedge which has the same length as the original linking bond. □

Example 29.36. An alternative code for drawing an IUPAC-acceptable diagram which has a wedge or hashed wedge at a bridgehead position is shown below:

```
\begin{XyMcompd}(750,800)(150,100){cpd:camph-COCl}{}
```

```
\frontthicktothintrue
\put(518,487){\HashWedgeAsSubstX(0,0)(38,95)[6]}
\put(518,487){\putratom{40}{105}{H}}
\put(437,287){\WedgeAsSubstX(0,0)(-40,-100)[6]}
\put(437,287){\putratom{-80}{-180}{H}}
\put(437,680){\HashWedgeAsSubstX(0,0)(-140,105)[6]}
\put(437,680){\putlatom{-140}{115}{A}}
\put(437,680){\WedgeAsSubstX(0,0)(140,105)[6]}
\put(437,680){\putratom{140}{115}{B}}
\put(0,0){\bornane[e]{3D==O}}
\end{XyMcompd}
```

Note that this code contains no declaration of substituents other than a carbonyl group (`3D==0`) in the ⟨subslist⟩ of `\bornane`. The other substituents with a wedge or a hashed wedge are externally declared by using the `XyMcompd` environment. The above code generates the following diagram:

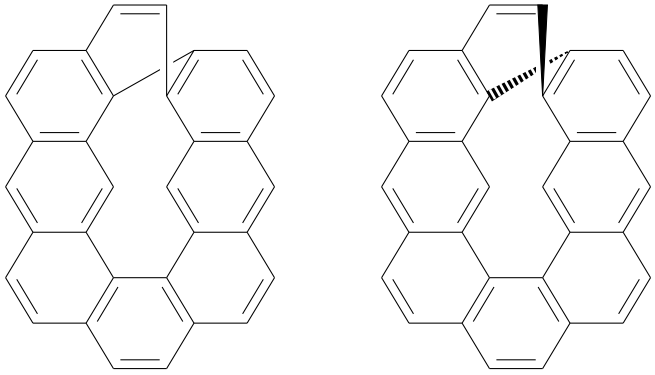


29-42

□

29.5.2 Möbius Bands

According to the IUPAC Recommendations 2006 [2, ST-5.3], the configuration of a Möbius band is simply indicated by the front-to-back ordering of the bonds that cross, as shown in the preferred diagram **29-43**. It is acceptable to further emphasize the non-planarity with a solid wedged bond and a hashed wedged bond at the crossing location, as shown in the acceptable diagram **29-44**.



29-43
Preferred

29-44
Acceptable

Example 29.37. The above diagrams are generated by inputting the following codes, in which the addition technique for constructing a fused ring is multiply used in a nested fashion, as found in the right-hand and the left-hand portions.

```
\begin{tabular}{c}
\begin{XyMcompd}(950,1450)(-30,200){}{}
\sixheteroh[ace%
%right-hand side
{c\sixfuseh[d%
{b\sixfuseh[df%
{b\sixfuseh[ace]{}{}{E}}%
```

```
]{}{}{E}}%
]{}{}{F}}%
%left-hand side
{a\sixfuseh[f%
{b\sixfuseh[df%
{b\sixfuseh[ace%
{d\PutBondLine(0,0)(303,171){0.4pt}}%
{d\whitex{\PutBondLine(200,80)(200,150){5pt}}}%
{c\fivefusehi[b]{}{}{E}[d]}%
]{}{}{E}}%
]{}{}{E}}%
]{}{}{D}}%
]{}{}
\end{XyMcompd}
\\
\compd\label{cpd:moebiusbandA} \\
\textit{Preferred} \\
\end{tabular}
\qquad
\begin{tabular}{c}
\begin{XyMcompd}(950,1450)(-30,200){}{}
\sixheteroh[ace%
{d\HashWedgeAsSubstX(0,1026)(-303,855)}%
%right-hand side
{c\sixfuseh[d%
{b\sixfuseh[df%
{b\sixfuseh[ace]{}{}{E}}%
]{}{}{E}}%
]{}{}{F}}%
%left-hand side
{a\sixfuseh[f%
{b\sixfuseh[df%
{b\sixfuseh[ace%
{d\whitex{\PutBondLine(200,80)(200,150){5pt}}}%
{d\WedgeAsSubstX(200,0)(200,342)}%
{c\fivefusehi[b]{}{}{E}[cd]}%
]{}{}{E}}%
]{}{}{E}}%
]{}{}{D}}%
]{}{}
\end{XyMcompd}
\\
\compd\label{cpd:moebiusbandB} \\
\textit{Acceptable} \\
\end{tabular}
```

The command `\fivefusehi` in the left-hand portion of **29-43** or of **29-44** draws a front five-membered ring, where its vertical bond (a straight-line for **29-43** or a wedge for **29-44**) should be drawn to be front. Note that the front-to-back ordering of the crossing is represented by bond clipping due to a thick white line, which is printed out by inputting `{d\whitex{\PutBondLine(200,80)(200,150){5pt}}}` before the declaration of the command `\fivefusehi`.

29.5.3 Remarks on Depicting the Front-to-Back Ordering of Crossing Bonds

It is worthwhile here to emphasize the technique for showing the front-to-back ordering of the crossing. The color `white` (and related commands) supported by the xcolor package means opaqueness (non-transparency), just as other colors (used as a text) are opaque. For example, the codes `{\Large M\kern-1em{\white W}}`

and `{\Large M\kern-1em{\red W}}` produce M and M, where the back letter M is hidden by the front letter W at each crossing location. This phenomenon is applied to show the front-to-back ordering of the crossing in a structural formula.

```
\begin{center}
\begin{tabular}{c}
\begin{picture}(300,300)(-150,-150)
\PutBondLine(0,-150)(0,150){1pt}%
\whitex{\PutBondLine(-50,0)(50,0){5pt}}%
\PutBondLine(-150,0)(150,0){1pt}%
\end{picture}
\\
white: opaque
\end{tabular}
\qquad
\begin{tabular}{c}
\begin{picture}(300,300)(-150,-150)
\PutBondLine(0,-150)(0,150){1pt}%
\redx{\PutBondLine(-50,0)(50,0){5pt}}%
\PutBondLine(-150,0)(150,0){1pt}%
\end{picture}
\\
red: opaque
\end{tabular}
\end{center}
```

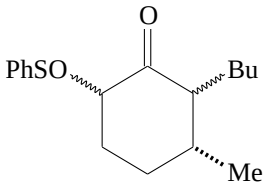
As found in the first code, a vertical bond is first drawn as a back figure. After a thick horizontal white line is drawn, a horizontal line is drawn as a front figure. Thereby, the first code generates the left diagram below. On the other hand, the color of the thick horizontal line is changed from white to red in the second code, which generates the right diagram below.

white: opaque red: opaque

29.6 Wavy Bonds for Unspecified Configurations

29.6.1 Bond Modifiers Added for Wavy Bonds

According to the IUPAC Provisional Recommendations 2004 [3], a wavy line can be used to indicate either that the configuration is unknown but only one form is present, or if explained in the text both isomers are present and will be defined when required. In particular, synthetic intermediates are frequently expressed by structural formulas having wavy bonds, e.g.,



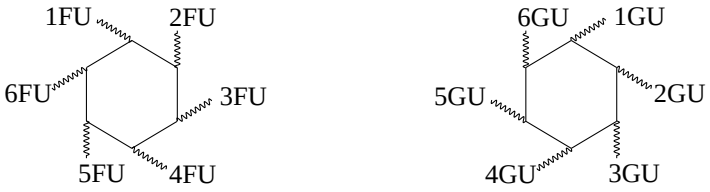
X$\mathrm{\ddot{E}}$TEX Version 4.03 and later supports wavy bonds as additional bond modifiers, i.e., U, SU, SV, FU, and GU, as listed in Table 3.2. The corresponding program codes have been added to chemstr.sty (automatically loaded by the X$\mathrm{\ddot{E}}$TEX system) and other existing package files.

Among the additional bond modifiers (Table 3.2), U, SU, and SV have the following specifications for six-membered rings:

These diagrams are drawn by the following codes:

```
\sixheterov{}{1U==1U;2U==2U;3U==3U;4U==4U;5U==5U;6U==6U}
\hskip3cm
\sixheterov{}{1SU==1SU;2SU==2SU;3SU==3SU;4SU==4SU;5SU==5SU;6SU==6SU;%
1SV==1SV;2SV==2SV;3SV==3SV;4SV==4SV;5SV==5SV;6SV==6SV}
```

The remaining bond modifiers, FU and GU, are intended to draw bridgehead configurations in fused structures:



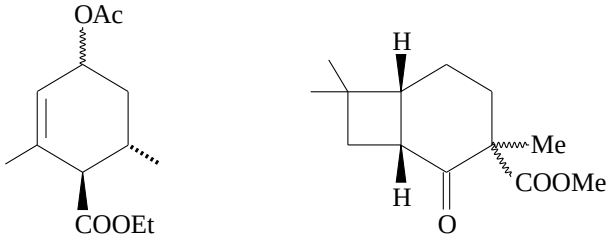
These diagrams are drawn by the following codes:

```
\sixheterov{}{1FU==1FU;2FU==2FU;3FU==3FU;4FU==4FU;5FU==5FU;6FU==6FU}
\hskip3cm
\sixheterov{}{1GU==1GU;2GU==2GU;3GU==3GU;4GU==4GU;5GU==5GU;6GU==6GU}
```

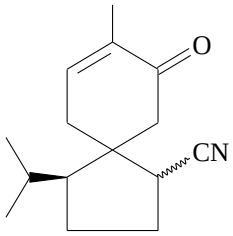
29.6.2 Examples of Wavy Bonds Specified as Bond Modifiers

Wavy Bonds in Carbocycles

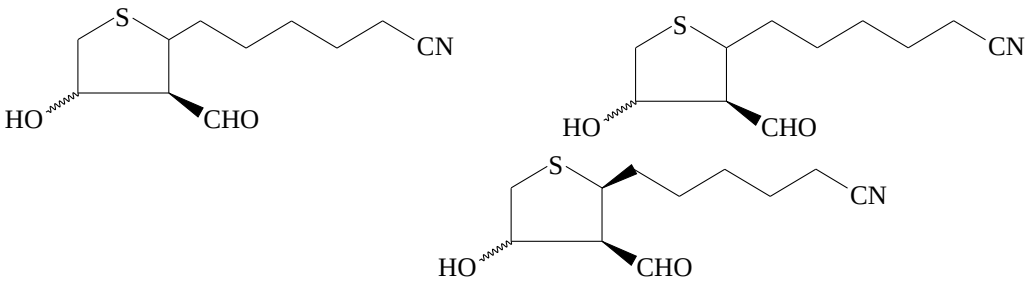
```
\sixheterov[e]{}{1U==OAc;3A==;4B==COOEt;5==}
\hskip2cm
\sixheterov[{e\fourfuse{}{4Sa==;4Sb==}{b}}]{}
{4D==O;3SU==Me;3SV==COOMe;5FB==H;6GB==H}
```



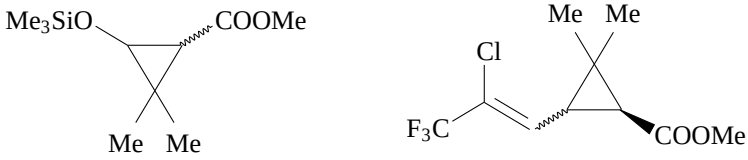

```
\fiveheterovi{1s==\sixheterov[f]{}{4==(yl);2D==O;1==}}%
{2U==CN;5Su==\LtetrahedralS{1==(yl);2==;3==}}
```



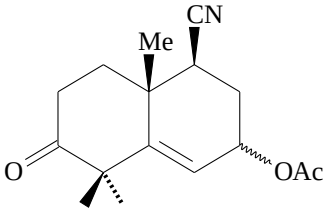

```
\pentamethylenei{}{%
1W==\fiveheterovi{1==S}{2==(yl);3B==CHO;4U==HO};5W==CN}
\hskip3cm
\hexamethylene{1s==\fiveheterovi{1==S}{2==(yl);3B==CHO;4U==HO}}{6W==CN}
\\
\fiveheterovi{1==S}{3B==CHO;4U==HO;2B==\pentamethylenei{}{1==(yl);5W==CN}}
```



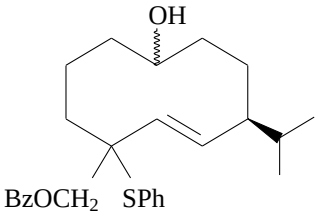

```
\threeheterov{}{1Sa==Me;1Sb==Me;2U==COOMe;3==Me$_{3}$SiO}
\hskip3cm
\threeheterovi{}{1Sa==Me;1Sb==Me;2B==COOMe;%
3U==\dimethylenei[a]{}{2==(yl);1==Cl;1W==F$_{3}$C}}
```




```
\decalinev[d]{1B==CN;3U==OAc;5SA==;5SB==;6D==O;{10}B==Me}
```




```
\decaheterov[d]{}{3B==\UtetrahedralS{2==(yl);1==;4==};%
{10}U==OH;5Sa==SPh;5Sb==BzOCH$_{2}$}[k]
```

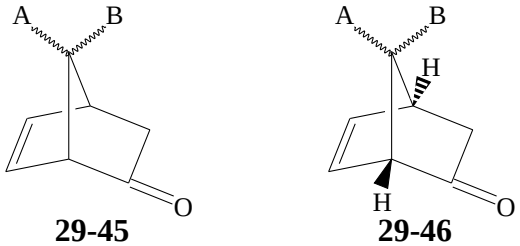


Wavy Bonds in Bicyclic Compounds

According to the IUPAC Recommendations 2006 [2, ST-3.2], unspecified or unknown absolute configuration within a perspective diagram is indicated by using wavy bonds.

Example 29.38. For example, unspecified configuration at the 7-position of a norbornane skeleton is depicted by the code:

```
\begin{tabular}{c}
\begin{XyMcompd}(750,800)(150,100){}{}
\frontthicktothintrue
\bornane[e]{7SU==A;7SV==B;3D==O}
\end{XyMcompd}
\\
\compd\label{cpd:bornaneUa} \\
\textit{Preferred}
\end{tabular}
\qquad
\begin{tabular}{c}
\begin{XyMcompd}(750,800)(150,100){}{}
\frontthicktothintrue\wedgehashedwedge
\bornane[e]{7SU==A;7SV==B;3D==O;1A==H;4B==H}
\end{XyMcompd}
\\
\compd\label{cpd:bornaneUb} \\
\textit{Acceptable}
\end{tabular}
```



29-45 *Preferred* **29-46** *Acceptable*

□

Wavy Bonds in Steroids

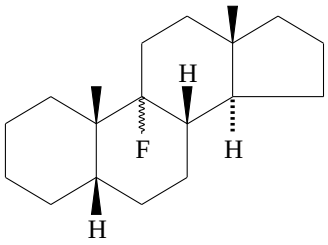
In steroid nomenclature (cf. Chapter 13), atoms C-8 (β), C-9 (α), and C-14 (α) are always assumed to be in standard configuration unless explicitly denoted with a wavy bond or otherwise specified [2, ST-0.4].

Example 29.39. For example, the following codes:

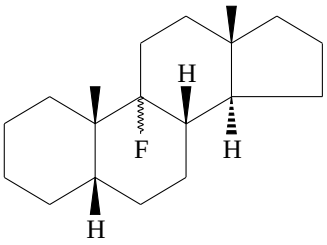
```
\begin{tabular}{c}
\steroid{5B==H;8B==H;9U==F;{10}B==\null;{14}A==H;{13}B==\null} \\
\noalign{\vskip-10pt}
\textit{Acceptable} (\XyMTeX{} default) \\
\end{tabular}
\qquad
```

```
\begin{tabular}{c}
{\wedgehashedwedge
\steroid{5B==H;8B==H;9U==F;{10}B==\null;{14}A==H;{13}B==\null}} \\
\noalign{\vskip-10pt}
\textit{Prerferred} \\
\end{tabular}
```

generate diagrams which have a fluorine atom of unspecified configuration at the 9-position:



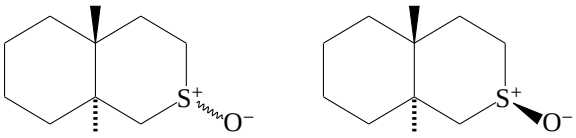
Acceptable (XƎMTEX default)



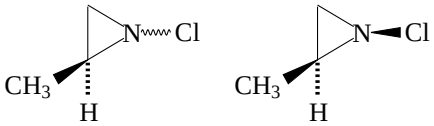
Preferred □

Wavy Bonds in Heterocycles

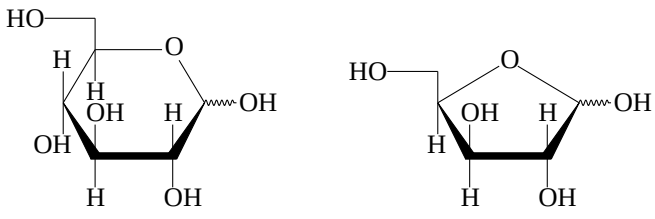
```
\decaheterov{3==S$^{+}$}{9A==;{10}B==;3U==O$^{-}$}
\decaheterov{3==S$^{+}$}{9A==;{10}B==;3B==O$^{-}$}
```




```
\threeheteroh{1==N}{1U==Cl;2SB==CH$_{3}$;2SA==H}
\hskip1cm
\threeheteroh{1==N}{1B==Cl;2SB==CH$_{3}$;2SA==H}
```



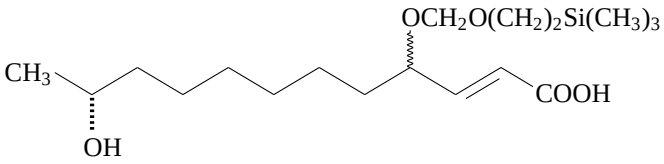

```
\begin{XyMcompd}(900,800)(80,0){}{}
\pyranosew{1U==OH;2Sa==OH;2Sb==H;3Sa==H;3Sb==OH;4Sa==OH;4Sb==H;5Sa==H;%
5Sb==\tetrahedral{3==(yl);2==HO}}
\end{XyMcompd}
\hskip1cm
\begin{XyMcompd}(950,800)(0,0){}{}
\furanosew{1U==OH;2Sa==OH;2Sb==H;3Sa==H;3Sb==OH;4Sa==H;%
4Sb==\tetrahedral{3==(yl);2==HO}}
\end{XyMcompd}
```



Wavy Bonds in Aliphatic Chains

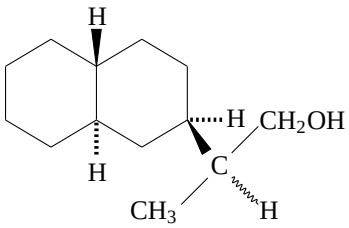
```
\hexamethylene{}{3SA==OH;3SB==CH$_{3}$} \qquad
\hexamethylene{}{3SV==OH;3SU==CH$_{3}$}
```


```
\begin{XyMcompd}(2350,600)(-100,-50){}{}
\decamethylene[i]{}{1W==CH$_{3}$;1A==OH;%
8U==OCH$_{2}$O(CH$_{2}$)$_{2}$Si(CH$_{3}$)$_{3}$;{10}W==COOH}
\end{XyMcompd}
```



Example 29.40. According to the IUPAC Recommendations 2006 [2, ST-0.5], stereobonds between stereocenters should be avoided at all costs. It follows that **29-47** is not acceptable.

```
\begin{XyMcompd}(1200,850)(250,-50){}{}
\decalinev{9A==H;{10}B==H;3SA==H;%
3SB==\squareplanar{4==(yl);0==C;1==CH$_{2}$OH;2U==H;3==CH$_{3}$}}
\end{XyMcompd}
```



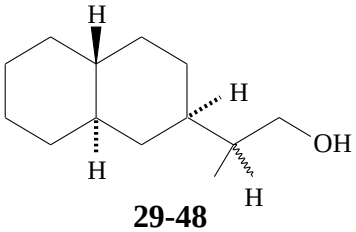
29-47

Not acceptable

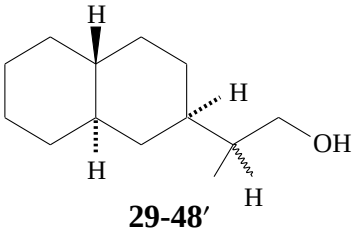
□

Example 29.41. In place of the above code, two codes are shown below to draw **29-48** and **29-48′**, which are preferred according to the IUPAC Recommendations 2006 [2, ST-0.5].

```
\begin{tabular}{cc}
\begin{XyMcompd}(1200,750)(250,50){}{}
\decaheterov{%
3s==\trimethylenei{}{1==(yl);2Sb==\null;2SV==H;3W==OH}%
}{9A==H;{10}B==H;3FA==H}
\end{XyMcompd}
&
\begin{XyMcompd}(1200,750)(250,50){}{}
\decaheterov{%
3s==\PutBondLine(0,0)(171,-103){0.4pt};
3s==\put(171,-103){\dimethylene{}{1==(yl);1Sb==\null;1SV==H;2W==OH}}%
}{9A==H;{10}B==H;3FA==H}
\end{XyMcompd}
\\
\compd\label{cpd:twostereoA} & \large \cref{cpd:twostereoA}$^{\prime}$ \\
\textit{Preferred} & \textit{Preferred} \\
\end{tabular}
```



29-48
Preferred



29-48′
Preferred

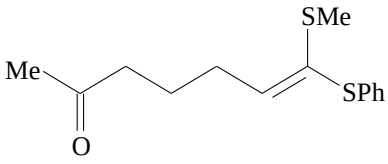
These diagrams presume that a six-to-six fused ring with a branched chain of carbon content 3 is regarded as a coplanar skeleton, where the configurations of two hydrogens are depicted by a hashed bond and a wavy bond. □

Double Bonds of Unspecified Configuration

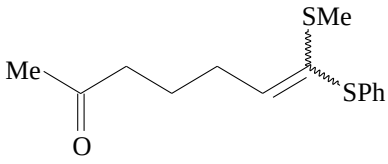
Double bonds of unspecified configuration are depicted according to the IUPAC Recommendations 2006 [2, ST-4.4].

Example 29.42. For example, a preferred diagram **29-50** is drawn by using the bond modifiers '`U`' and '`WU`' at the right terminal position of `\hexamethylene`.

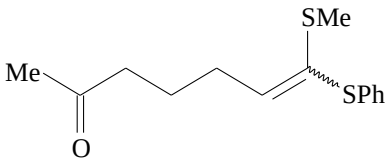
```
\begin{tabular}{cc}
\begin{XyMcompd}(1350,600)(-50,-50){}{}
\hexamethylene[e]{}{1W==Me;1D==O;6==SMe;6W==SPh}
\end{XyMcompd} &
\begin{XyMcompd}(1350,600)(-50,-50){}{}
\hexamethylene[e]{}{1W==Me;1D==O;6U==SMe;6WU==SPh}
\end{XyMcompd} \\
\compd\label{cpd:zigzagolefinA} & \compd\label{cpd:zigzagolefinB} \\
(specified) & \textit{Preferred} \\
\begin{XyMcompd}(1350,600)(-50,-50){}{}
\hexamethylene[e]{}{1W==Me;1D==O;6==SMe;6WU==SPh}
\end{XyMcompd} &
\begin{XyMcompd}(1350,600)(-50,-50){}{}
\hexamethylene[e]{}{1W==Me;1D==O;6U==SMe;6W==SPh}
\end{XyMcompd} \\
\compd\label{cpd:zigzagolefinC} & \compd\label{cpd:zigzagolefinD} \\
\textit{Acceptable}& \textit{Acceptable} \\
\end{tabular}
```



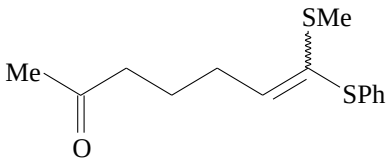
29-49
(specified)



29-50
Preferred



29-51
Acceptable



29-52
Acceptable

□

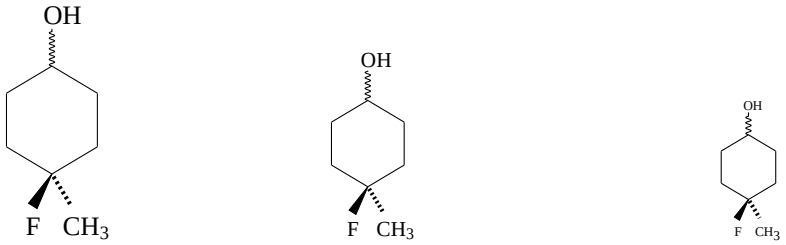
Wavy Bonds for PDF-Compatible Mode and PostScript-Compatible Mode vs. for TEX/LATEX-Compatible Mode

Wavy bonds can be drawn also in the TEX/LATEX-compatible Mode. Three types of diagrams in the PDF-compatible mode (or the PostScript-compatible mode) are summarized in Fig. 29.2, which also contains structural formulas by the TEX/LATEX-compatible mode for comparison (cf. Fig. 29.1).

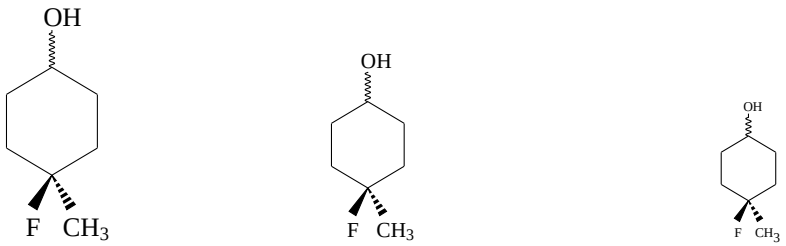
PDF-compatible mode and PostScript-compatible mode

default (0.1pt) `\changeunitlength{0.08pt}` `\changeunitlength{0.06pt}`

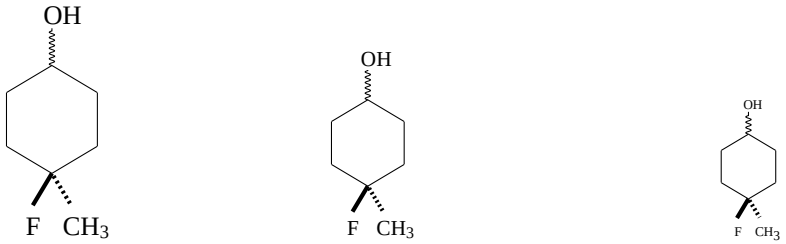
`\wedgehasheddash`: default (wedge and hashed dash)



`\wedgehashedwedge`: (wedge and hashed wedge)



`\dashhasheddash`: (dash and hashed dash)



TEX/LATEX-compatible mode

default (0.1pt) `\changeunitlength{0.08pt}` `\changeunitlength{0.06pt}`

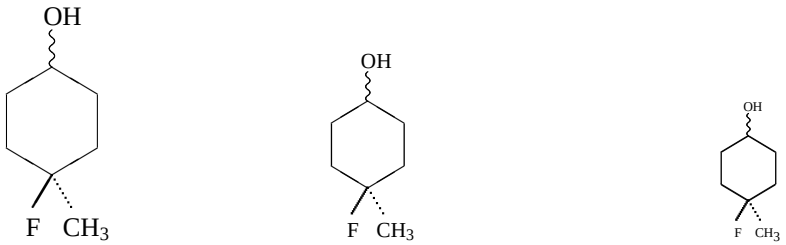


Figure 29.2. Wavy bonds under the PDF-compatible mode (or the PostScript-compatible mode) as well as under the TEX/LATEX-compatible mode. Three profiles of representing configurations are available in the PDF-compatible mode (or the PostScript compatible mode), while they are not supported by the TEX/LATEX-compatible mode.

To obtain Fig. 29.2, all of the inputs:

```
\cyclohexanev{1D==O;4SA==CH$_{3}$;4SB==F}
```

appearing in the code for drawing Fig. 29.1 (on page 470) are changed into

```
\cyclohexanev{1U==OH;4SA==CH$_{3}$;4SB==F}
```

29.6.3 Variable Wavy Bonds

Commands for Drawing Variable Wavy Bonds

The commands `\WavyAsSubst` and `\WavyAsSubstX` are defined to draw variable wavy bonds. The formats of these commands are specified in a similar way to the commands named `\...AsSubst` and `\...AsSubstX`.

```
\WavyAsSubst(⟨start⟩)(⟨slope⟩){⟨length⟩}
\WavyAsSubstX(⟨start⟩)(⟨endpint⟩)
```

For their arguments, see the arguments of the related commands described in Subsection 27.3.3. Typical examples for setting the arguments are shown below:

```
\WavyAsSubst(0,0)(1,0){200}
\WavyAsSubst(0,0)(5,-3){200}
```

```
\WavyAsSubstX(0,0)(200,0)
\WavyAsSubstX(0,0)(200,-120)
```

These commands can be declared in an argument ⟨bondlist⟩ for the addition technique as well as an argument ⟨atomlist⟩ for the replacement technique.

Wavy Skeletal Bonds

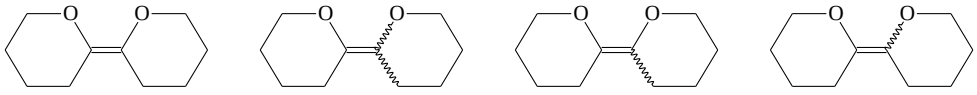
Double bonds of unspecified configuration are represented by using wavy bonds according to the IUPAC Recommendations 2006 [2, ST-4.4].

Example 29.43. The following codes use the command `\WavyAsSubst` to generate wavy skeletal bonds by the replacement technique, where each command `\WavyAsSubst` is declared in the ⟨atomlist⟩ of `\sixheteroh`.

```
\changeunitlength{0.08pt}
\begin{tabular}{cccc}
\begin{XyMcompd}(900,400)(250,220){}{}
\sixheteroh{3==O}{4D==\sixheteroh{2==O}{1==(yl)}}
\end{XyMcompd} &
\begin{XyMcompd}(900,400)(250,220){}{}
\sixheteroh{3==O}{4D==%
\sixheteroh{2==O;
1s==\WavyAsSubst(0,0)(3,-5){103};%
1s==\WavyAsSubst(0,0)(3,5){80}%
}{1==(yl)}[af]}
\end{XyMcompd} &
\begin{XyMcompd}(900,400)(250,220){}{}
\sixheteroh{3==O}{4D==%
\sixheteroh{2==O;
1s==\WavyAsSubst(0,0)(3,-5){103};%
}{1==(yl)}[f]}
\end{XyMcompd} &
\begin{XyMcompd}(900,400)(250,220){}{}
\sixheteroh{3==O}{4D==%
\sixheteroh{2==O;
1s==\WavyAsSubst(0,0)(3,5){80}%
}{1==(yl)}[a]}
```

```
\end{XyMcompd} \\
\compd\label{cpd:six-d-sixA} & \compd\label{cpd:six-d-sixB} &
\compd\label{cpd:six-d-sixC} & \compd\label{cpd:six-d-sixD} \\
(specified) & \textit{Preferred} & \textit{Acceptable}& \textit{Acceptable} \\
\end{tabular}
```

These codes generate the following formulas:

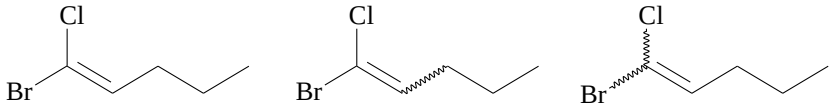


29-53 (specified) **29-54** *Preferred* **29-55** *Acceptable* **29-56** *Acceptable* □

Example 29.44. When a double bonds with unspecified configuration appears in an inner portion of an aliphatic chain, a wavy bond is used to show the unspecified configuration according to the IUPAC Recommendations 2006 [2, ST-4.4].

```
\begin{tabular}{ccc}
\begin{XyMcompd}(850,400)(0,150){}{}
\pentamethylenei[a]{}{1W==Br;1==Cl}
\end{XyMcompd} &
\begin{XyMcompd}(850,400)(0,150){}{}
\pentamethylenei[a%
{b\replaceSKbond(0,0)(5,3){171}{\white}}%
{b\WavyAsSubst(0,0)(5,3){171}}%
]{}{1W==Br;1==Cl}
\end{XyMcompd} &
\begin{XyMcompd}(850,400)(0,150){}{}
\pentamethylenei[a]{%
1s==\WavyAsSubst(0,0)(-5,-3){140};1s==\put(-150,-138){\llap{Br}}%
}{1U==Cl}
\end{XyMcompd} \\
\compd\label{cpd:penteneA} & \compd\label{cpd:penteneB} &
\compd\label{cpd:penteneC} \\
(specified) & \textit{Preferred}& \textit{Acceptable} \\
\end{tabular}
```

In the second code shown above, the command `\replaceSKbond` (defined for coloring skeletal bonds in Subsection 39.1.2) is applied to erase a skeletal bond of an aliphatic chain drawn by `\pentamethylenei`. After a white line is drawn on the bond to be erased, a wavy bond is drawn at the same location as the erased bond. The above codes generate the following diagrams:



29-57 (specified) **29-58** *Preferred* **29-59** *Acceptable* □

References

[1] IUPAC Organic Chemistry Division, *Pure Appl. Chem.*, **68**, 2193–2222 (1996).

[2] J. Brecher and IUPAC Chemical Nomenclature and Structure Representation Division, *Pure Appl. Chem.*, **78**, 1897–1970 (2006).

[3] IUPAC Chemical Nomenclature and Structure Representation Division, *Provisional Recommendations. Nomenclature of Organic Chemistry* (2004).
http://www.iupac.org/reports/provisional/abstract04/favre_310305.html.

Chapter 30

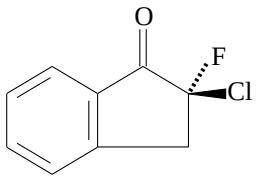
Drawing by Low-Level Commands

30.1 Five-Membered Rings as Regular Pentagons

30.1.1 Drawing Carbocyclic Five-Membered Rings

In the default setting of the XyMTEX system, a five-membered ring is depicted in the form of a home plate. For example, the default setting of the XyMTEX system outputs the structure of an indane derivative in the following form:

```
\begin{XyMcompd}(800,650)(250,250){}{}
\indanevi[egj]{1D==O;2Su==Cl;2Sd==F}
\end{XyMcompd}
```



To output a regular pentagon in place of such a home-plate form, low-level commands such as `\PutBondLine`, `\WedgeAsSubst`, and `\HashWedgeAsSubst` (cf. Subsections 27.3.3 and 29.4.2) are used in the XyMTEX `XyMcompd` environment or the LaTeX `picture` environment.

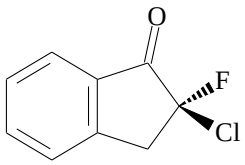
First, a command `\carbonylrotate` is defined to draw a rotatable carbonyl group, which is capable of taking an argument for setting the angle of rotation. The carbonyl oxygen retains its original vertical direction, even if the five-membered skeleton is rotated.

```
\makeatletter
\def\carbonylrotate#1{%
\rotatebox{#1}{\begin{picture}(0,0)(0,0)
\PutBondLine(13,0)(13,140){0.4pt}%
\PutBondLine(-13,0)(-13,140){0.4pt}%
%%%%%%%%%%%%%
%oxygen atom% retaining its original vertical direction
%%%%%%%%%%%%%
\@tempcnta=-#1\relax
\put(0,180){\rotatebox{\the\@tempcnta}{\makebox(0,0){\SetTwoAtomx{O}}}}%
\end{picture}}}
\makeatother
```

Then, skeletal bonds for a five-membered ring are drawn by using \PutBondLine in the LaTeX picture environment. As found in the following code: a carbonyl group is attached to the five-membered ring after rotation; chlorine and fluorine substituents are placed by using \WedgeAsSubst and \HashWedgeAsSubst; and ring fusion is accomplished by using \sixfusev.

```
\begin{XyMcompd}(800,600)(-350,-100){}{}
%skeletal bonds for a five-membered ring
\PutBondLine(0,0)(0,200){0.4pt}%
\PutBondLine(0,200)(190,262){0.4pt}%
\PutBondLine(190,262)(308,100){0.4pt}%
\PutBondLine(308,100)(190,-62){0.4pt}%
\PutBondLine(190,-62)(0,0){0.4pt}%
%carbonyl rotated
\put(190,262){\carbonylrotate{-12}}%
%substituents
\HashWedgeAsSubst(308,100)(5,3){120}%
\put(448,160){\makebox(0,0)[lb]{\SetTwoAtomx{F}}}%
\WedgeAsSubst(308,100)(5,-3){120}%
\put(448,40){\makebox(0,0)[lt]{\SetTwoAtomx{Cl}}}%
%fused six-membered ring
\put(0,0){\sixfusev[bdf]{}{}{B}}%
\end{XyMcompd}
```

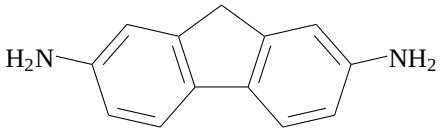
Thereby, we obtain a target diagram with a regular pentagon:



Example 30.1. In order to depict a structural formula of 2,7-diaminofluorene, fusing units should be rotated to be fused at the slanted edges of a regular pentagon. For example, the code:

```
\begin{XyMcompd}(1500,500)(-650,-150){}{}
\PutBondLine(0,0)(200,0){0.4pt}%
\PutBondLine(200,0)(262,190){0.4pt}%
\PutBondLine(262,190)(100,308){0.4pt}%
\PutBondLine(100,308)(-62,190){0.4pt}%
\PutBondLine(-62,190)(0,0){0.4pt}%
\put(0,0){\rotatebox{18}{\sixfusev[bdf]{}{6==%
\rotatebox{-18}{\makebox(0,0)[r]{\llap{H$_{2}$}N}}}{B}}}%
\put(200,0){\rotatebox{-18}{\sixfusev[ace]{}{2==%
\rotatebox{18}{\makebox(0,0)[l]{N\rlap{H$_{2}$}}}}{e}}}%
\end{XyMcompd}
```

generates a structural formula of 2,7-diaminofluorene:

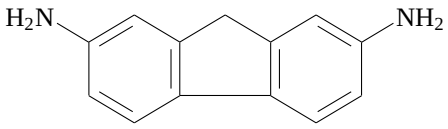


Note that the whole object of the left fusing unit due to \sixfusev is rotated by 18° (= 90° − 72°), while the substituent NH_2 is rotated oppositely by −18°. The right fusing unit is reversely rotated.

Compare this formula with the following one, which is depicted by the addition technique of the XyMTeX system:

```
\begin{XyMcompd}(1550,450)(-400,250){}{}
```

```
\fiveheterovi[%
{d\sixfusev[bdf]{}{6==H$_{2}$N}{B}}%
{b\sixfusev[ace]{}{2==NH$_{2}$}{E}}]{}{}
\end{XyMcompd}
```



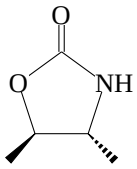
□

30.1.2 Drawing Heterocyclic Five-Membered Rings

A heterocyclic ring is produced by placing an atom on a vertex of a five-membered ring after truncation with a white-colored box (cf. Subsection 29.5.3). This process is accomplished by using the command `\SetTwoAtoms` (no space surrounding an atom) or `\SetTwoAtomx` (a thin space surrounding an atom). For example, the code

```
\begin{XyMcompd}(400,600)(-100,-100){}{}
\PutBondLine(0,0)(200,0){0.4pt}%
\PutBondLine(200,0)(262,190){0.4pt}%
\PutBondLine(262,190)(100,308){0.4pt}%
\PutBondLine(100,308)(-62,190){0.4pt}%
\PutBondLine(-62,190)(0,0){0.4pt}%
\put(262,190){\makebox(0,0){\SetTwoAtoms{N\rlap{H}}}}%
\put(-62,190){\makebox(0,0){\SetTwoAtoms{O}}}%
\PutBondLine(90,308)(90,448){0.4pt}%
\PutBondLine(110,308)(110,448){0.4pt}%
\put(100,448){\makebox(0,0){\SetTwoAtomx{O}}}%
\WedgeAsSubst(0,0)(-1,-1){100}%
\HashWedgeAsSubst(200,0)(1,-1){100}%
\end{XyMcompd}
```

generates the following structural formula:

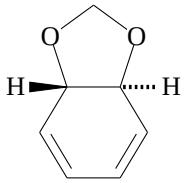


Note that the commands `\SetTwoAtoms` (or `\SetTwoAtomx`) outputs a skeletal atom after the truncation of a vertex. The command `makebox(0,0)` outputs a character string as a dimensionless object.

Fusing units such as `\sixfuseh` (cf. Chapter 4) can be combined in the XyMTEX `XyMcompd` environment or the LaTeX `picture` environment. For example, the code:

```
\begin{XyMcompd}(500,700)(-150,-350){}{}
\PutBondLine(0,0)(200,0){0.4pt}%
\PutBondLine(200,0)(262,190){0.4pt}%
\PutBondLine(262,190)(100,308){0.4pt}%
\PutBondLine(100,308)(-62,190){0.4pt}%
\PutBondLine(-62,190)(0,0){0.4pt}%
\put(262,190){\makebox(0,0){\SetTwoAtoms{O}}}%
\put(-62,190){\makebox(0,0){\SetTwoAtoms{O}}}%
\put(0,0){\sixfuseh[df]{}{2FB==H;3GA==H}{b}}%
\end{XyMcompd}
```

generates a six-to-five fused ring system:



Example 30.2. Let us now draw the structure of indigo. First, a command named `\indigoleft` is defined to depict the left half of the indigo structure:

```
%left half of indigo
\def\indigoleft{%
\begin{picture}(0,0)(308,100)
\PutBondLine(0,0)(0,200){0.4pt}%
\PutBondLine(0,200)(190,262){0.4pt}%
\PutBondLine(190,262)(308,100){0.4pt}%
\PutBondLine(308,100)(190,-62){0.4pt}%
\PutBondLine(190,-62)(0,0){0.4pt}%
\put(190,262){\rotatebox{-18}{%
\PutBondLine(-15,0)(-15,120){0.4pt}%
\PutBondLine(15,0)(15,120){0.4pt}}}%
\put(195,390){O}%
\put(190,-62){\makebox(0,0){\SetTwoAtomx{N}}}%
\put(190,-120){\makebox(0,0)[t]{H}}%
\put(0,0){\sixfusev[bdf]{}{}{B}}%
\end{picture}}
```

where the whole object is shifted so that the rightmost vertex of the original coordinate $(308, 100)$ is regarded as the reference point $(0, 0)$ during the depiction of the indigo structure.

Second, a command named `\indigoright` is defined to depict the right half of the indigo structure:

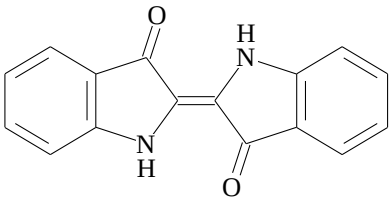
```
%right half of indigo
\def\indigoright{%
\begin{picture}(0,0)(-308,100)%
%\put(0,0){\circle{40}}%
%\put(-308,100){\circle{40}}%
\PutBondLine(0,0)(0,200){0.4pt}%
\PutBondLine(0,200)(-190,262){0.4pt}%
\PutBondLine(-190,262)(-308,100){0.4pt}%
\PutBondLine(-308,100)(-190,-62){0.4pt}%
\PutBondLine(-190,-62)(0,0){0.4pt}%
\put(-190,-62){\rotatebox{-18}{%
\PutBondLine(-15,0)(-15,-120){0.4pt}%
\PutBondLine(15,0)(15,-120){0.4pt}}}%
\put(-280,-260){O}%
\put(-190,262){\makebox(0,0){\SetTwoAtomx{N}}}%
\put(-190,320){\makebox(0,0)[b]{H}}%
\put(0,0){\sixfusev[ace]{}{}{e}}%
\end{picture}}
```

where the reference point is shifted to be located at the leftmost vertex $(-308, 100)$, which is regarded as $(0, 0)$ during the depiction of the indigo structure.

Finally, the two halves are linked through a double bond. The code:

```
\begin{XyMcompd}(1350,750)(-600,-350){cpd:indigoA}{}%
\put(0,0){\indigoleft}%
\put(140,0){\indigoright}%
\PutBondLine(0,-15)(140,-15){0.4pt}%
\PutBondLine(0,15)(140,15){0.4pt}%
\end{XyMcompd}
```

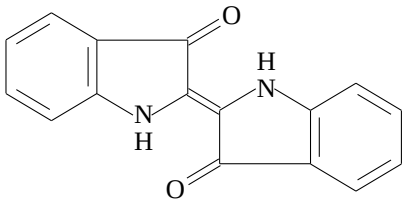
generates the following formula of indigo:



30-1

Compare the formula **30-1** with the following one **30-2**, which is depicted by the successive application of the substitution technique and the addition technique.

```
\begin{XyMcompd}(1400,750)(250,-50){cpd:indigoB}{}%
\nonaheterov[egj]{1==\downnobond{N}{H}}{3D==O;%
2D==\fiveheterovi[%
{b\sixfusev[ace]{}{}{E}}%
]{1==\upnobond{N}{H}}{5==(yl);4D==O}}
\end{XyMcompd}
```



30-2

□

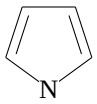
Example 30.3. Let us depict a porphyrin ring system, which is a macrocyclic tetrapyrrolic ring system [1]. First, we define a command named `\pyrrolerotate` to draw a pyrrole ring which is rotatable by a given degree (`#1`) and capable of assigning a double bond at a given edge (`#2`).

```
\makeatletter
\def\pyrrolerotate#1#2{%
\rotatebox{#1}{%
%%%%%%%%%%%%%%%%
%skeletal bond %
%%%%%%%%%%%%%%%%
\begin{picture}(0,0)(100,-308)
\PutBondLine(0,0)(200,0){0.4pt}%
\PutBondLine(200,0)(262,-190){0.4pt}%
\PutBondLine(262,-190)(100,-308){0.4pt}%
\PutBondLine(100,-308)(-62,-190){0.4pt}%
\PutBondLine(-62,-190)(0,0){0.4pt}%
%methyl
%\PutBondLine(262,-190)(380,-250){0.4pt}%
%%%%%%%%%%%%%%%
%double bond %
%%%%%%%%%%%%%%%
\@tfor\member:=#2\do{%
\if\member a\relax
\PutBondLine(223,-177)(100,-265){0.4pt}%\bonda%
\else\if\member b\relax
\PutBondLine(176,-32)(223,-177){0.4pt}%\bondb%
\else\if\member c\relax
\PutBondLine(24,-32)(176,-32){0.4pt}%\bondc%
\else\if\member d\relax
\PutBondLine(24,-32)(-23,-177){0.4pt}%\bondd%
```

```
\else\if\member e\relax
\PutBondLine(-23,-177)(100,-265){0.4pt}%\bonde
\fi\fi\fi\fi\fi%
}%
%%%%%%%%%%%%%%%
%nitrogen atom% retaining its original vertical direction
%%%%%%%%%%%%%%%
\@tempcnta=-#1\relax
\put(100,-308){\rotatebox{\the\@tempcnta}{\makebox(0,0){\SetTwoAtoms{N}}}}%
\end{picture}}}
\makeatother
```

The command \rotatebox is supported by the graphicx package. The processing of the argument #2 is conducted by the command \@tfor (defined in the chemstr package of the X$\mathfrak{M}$TEX system), just as the processing of the ⟨bondlist⟩ of most X$\mathfrak{M}$TEX commands is based on this command.

The skeletal nitrogen retains its original vertical direction, even if the pyrrole skeleton is rotated, as shown in the following outputs. Note that the rotation is conducted around the reference point located at the nitrogen atom of the pyrrole ring.




```
\pyrrolerotate{0}{bd}
```


```
\pyrrolerotate{45}{bd}
```


```
\pyrrolerotate{-45}{bd}
```

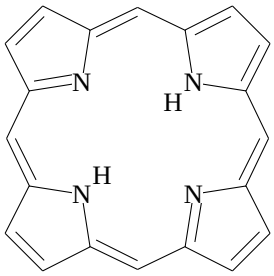
Then, four pyrrole rings generated by using \pyrrolerotate are located at appropriate positions in the LaTeX picture environment, so that a new command \porphineskeleton is defined as follows:

```
\def\porphineskeleton{%
\begin{picture}(1100,1100)(0,0)
%pyrrole rings
\put(-210,210){\pyrrolerotate{45}{ce}}
\put(210,210){\pyrrolerotate{-45}{bd}}
\put(-210,-210){\pyrrolerotate{135}{c}}
\put(210,-210){\pyrrolerotate{-135}{ac}}
%other skeletal bonds
\PutBondLine(181,406)(0,493){0.4pt}%
\PutBondLine(0,493)(-181,406){0.4pt}%
\PutBondLine(181,-406)(0,-493){0.4pt}%
\PutBondLine(0,-493)(-181,-406){0.4pt}%
\PutBondLine(406,181)(493,0){0.4pt}%
\PutBondLine(493,0)(406,-181){0.4pt}%
\PutBondLine(-406,181)(-493,0){0.4pt}%
\PutBondLine(-493,0)(-406,-181){0.4pt}%
%double bond for the other skeletal bonds
\PutBondLine(-382,-156)(-460,0){0.4pt}%
\PutBondLine(382,-156)(460,0){0.4pt}%
\PutBondLine(-156,382)(0,460){0.4pt}%
\PutBondLine(-156,-382)(0,-460){0.4pt}%
\end{picture}}
```

The structure of porphine is depicted by using the command \porphineskeleton. Thus, the code:

```
\begin{XyMcompd}(1100,1100)(-550,-550){}{}
\put(0,0){\porphineskeleton}
\put(210,210){\put(-40,-40){\makebox(0,0)[rt]{H}}}
\put(-210,-210){\put(40,40){\makebox(0,0)[lb]{H}}}
\end{XyMcompd}
```

generates the following structure of porphine:

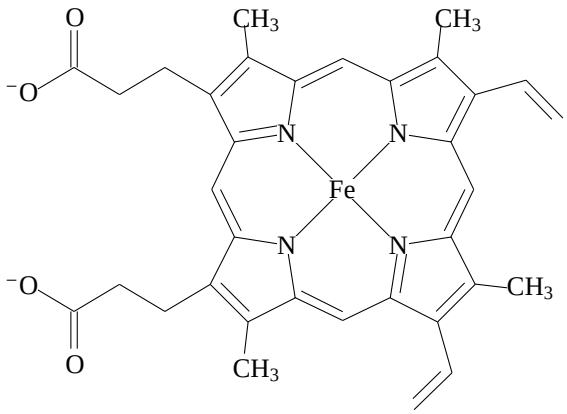


□

Example 30.4. Heme is a derivative of porphine. The structure **30-3** of heme is depicted by the code:

```
\begin{XyMcompd}(2000,1600)(-1200,-850){cpd:heme}{}
%central bonds
\PutBondLine(0,0)(210,210){0.4pt}%\bond NE
\PutBondLine(0,0)(-210,210){0.4pt}%bond NW
\PutBondLine(0,0)(210,-210){0.4pt}%\bond SE%
\PutBondLine(0,0)(-210,-210){0.4pt}%\bond SW%
%skeleton
\put(0,0){\porphineskeleton}
%central Fe atom
\put(0,0){\makebox(0,0){\SetTwoAtomx{Fe}}}%
%side chains
\PutBondLine(356,498)(370,618){0.4pt}
\put(380,638){\makebox(0,0){C\rlap{H$_{3}$}}}
\put(498,356){\rotatebox{-15}{\trimethylene[b]{}{1==(yl)}}}
\PutBondLine(498,-356)(618,-370){0.4pt}
\put(618,-370){\makebox(0,0)[l]{CH$_{3}$}}
\put(356,-498){\rotatebox{-105}{\trimethylene[b]{}{1==(yl)}}}
\PutBondLine(-356,498)(-370,618){0.4pt}
\put(-380,638){\makebox(0,0){C\rlap{H$_{3}$}}}
\put(-498,356){\pentamethylene{1==$^{-}$O}{5==(yl);2D==O}}
\put(-498,-356){\pentamethylenei{1==$^{-}$O}{5==(yl);2D==O}}
\PutBondLine(-356,-498)(-370,-618){0.4pt}
\put(-380,-638){\makebox(0,0)[t]{C\rlap{H$_{3}$}}}
\end{XyMcompd}
```

where the porphine skeleton is depicted by `\porphineskeleton`, the four central bonds are added by `\PutBondLine`, the central Fe atom is added as a front object by using `\SetTwoAtomx`, and the side chains are based on `\trimethylene`, `\pentamethylene` and `\pentamethylene`. The above code generates the following formula:



30-3

□

30.2 Seven-Membered Rings as Regular Heptagons

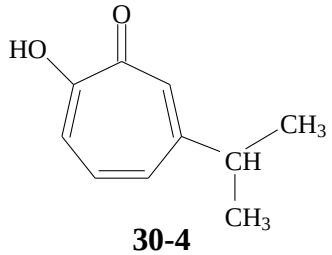
Because seven-membered rings are not supported by the state of the art of he XyMTEX system, they should be depicted by using low-level commands such as \PutBondLine, \WedgeAsSubst, and \HashWedgeAsSubst (cf. Subsections 27.3.3 and 29.4.2).

30.2.1 Drawing Carbocyclic Seven-Membered Rings

Example 30.5. The structure **30-4** of hinokitiol is drawn by inputting the code:

```
\begin{XyMcompd}(1100,800)(-300,-150){cpd:hinokitiol}{}
%skeletal bonds
\PutBondLine(0,0)(200,0){0.4pt}%
\PutBondLine(200,0)(325,157){0.4pt}%
\PutBondLine(325,157)(281,352){0.4pt}%
\PutBondLine(281,352)(100,439){0.4pt}%
\PutBondLine(100,439)(-81,352){0.4pt}%
\PutBondLine(-81,352)(-125,157){0.4pt}%
\PutBondLine(-125,157)(0,0){0.4pt}%
%double bonds
\PutBondLine(13,28)(187,28){0.4pt}%
\PutBondLine(295,153)(256,332){0.4pt}%
\PutBondLine(-95,153)(-56,332){0.4pt}%
%substituents
\PutBondLine(-81,352)(-181,452){0.4pt}%
\put(-181,452){\llap{HO}}%
\PutBondLine(85,439)(85,579){0.4pt}%
\PutBondLine(115,439)(115,579){0.4pt}%
\put(100,584){\makebox(0,0)[b]{O}}%
\PutBondLine(325,157)(470,100){0.4pt}%
\put(460,110){\Utrigonal{3==(yl);0==CH;1==CH$_{3}$;2==CH$_{3}$}}
\end{XyMcompd}
```

where the command \Utrigonal is declared to draw an isopropyl group by using a (yl)-function. Thereby, we obtain the structural diagram **30-4** of hinokitiol:



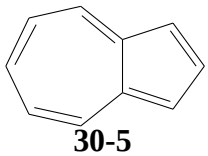
30-4 □

Example 30.6. Azulene has a five-to-seven fused ring, which is isomeric to a naphthalene ring. The following code consists of multiple declaration of \PutBondLine to give skeletal bonds and endocyclic double bonds:

```
\begin{XyMcompd}(650,450)(-400,-100){cpd:azulene}{}
%skeletal bonds for the seven-membered ring
\PutBondLine(0,0)(0,200){0.4pt}%
\PutBondLine(0,200)(-157,325){0.4pt}%
\PutBondLine(-157,325)(-352,281){0.4pt}%
\PutBondLine(-352,281)(-439,100){0.4pt}%
\PutBondLine(-439,100)(-352,-81){0.4pt}%
\PutBondLine(-352,-81)(-157,-125){0.4pt}%
\PutBondLine(-157,-125)(0,0){0.4pt}%
%skeletal bonds for the five-membered ring
```

```
%\PutBondLine(0,0)(0,200){0.4pt}%duplicated
\PutBondLine(0,200)(190,262){0.4pt}%
\PutBondLine(190,262)(308,100){0.4pt}%
\PutBondLine(308,100)(190,-62){0.4pt}%
\PutBondLine(190,-62)(0,0){0.4pt}%
%double bonds for the seven-membered ring
\PutBondLine(-28,187)(-153,290){0.4pt}%
\PutBondLine(-325,256)(-405,105){0.4pt}%
\PutBondLine(-153,-95)(-332,-56){0.4pt}%
%double bonds for the five-membered ring
\PutBondLine(24,18)(180,-33){0.4pt}%
\PutBondLine(277,100)(180,233){0.4pt}%
\end{XyMcompd}
```

This code generates the following formula **30-5** of azulene:



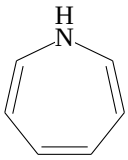
30-5

□

30.2.2 Drawing Heterocyclic Seven-Membered Rings

Example 30.7. For example, the structure **30-6** of azepine is depicted by inputting the following code:

```
\begin{XyMcompd}(400,600)(-100,0){cpd:azepine}{}
%skeletal bonds
\PutBondLine(0,0)(200,0){0.4pt}%
\PutBondLine(200,0)(325,157){0.4pt}%
\PutBondLine(325,157)(281,352){0.4pt}%
\PutBondLine(281,352)(100,439){0.4pt}%
\PutBondLine(100,439)(-81,352){0.4pt}%
\PutBondLine(-81,352)(-125,157){0.4pt}%
\PutBondLine(-125,157)(0,0){0.4pt}%
%double bonds
\PutBondLine(13,28)(187,28){0.4pt}%
\PutBondLine(295,153)(256,332){0.4pt}%
\PutBondLine(-95,153)(-56,332){0.4pt}%
\put(100,439){\makebox(0,0){\SetTwoAtoms{N}}}%
\put(100,489){\makebox(0,0)[b]{H}}%
\end{XyMcompd}
```



30-6

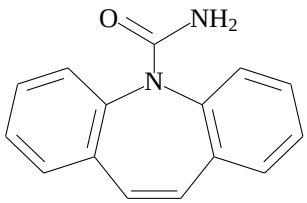
□

Example 30.8. The structure **30-7** of carbamazepine (tegretol®) is depicted by inputing the following code:

```
\begin{XyMcompd}(1050,750)(-450,0){cpd:carbamazepin}{}
%skeletal bonds
\PutBondLine(0,0)(200,0){0.4pt}%
\PutBondLine(200,0)(325,157){0.4pt}%
\PutBondLine(325,157)(281,352){0.4pt}%
\PutBondLine(281,352)(100,439){0.4pt}%
\PutBondLine(100,439)(-81,352){0.4pt}%
```

```
\PutBondLine(-81,352)(-125,157){0.4pt}%
\PutBondLine(-125,157)(0,0){0.4pt}%
%double bonds
\PutBondLine(13,28)(187,28){0.4pt}%
%fused benzenes
\put(281,352){\rotatebox{13}{\sixfusev[ace]{}{}{E}}}
\put(-81,352){\rotatebox{-13}{\sixfusev[bdf]{}{}{b}}}
%substituent
\put(100,579){\trimethylenei[a]{1==O;3==NH$_{2}$}{2==(yl);2==\null}}
%skeletal nitrogen
\put(100,439){\makebox(0,0){\SetTwoAtoms{N}}}%
\end{XyMcompd}
```

where the seven-membered azepine ring is constructed by the command `\PutBondLine`. The benzene rings are fused by using `\sixfusev` after rotation. This code generates the structure of carbamazepin:

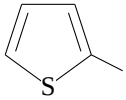


30-7 □

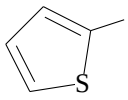
Example 30.9. Let us depict the structural formula **30-8** of olanzapine (zyprexa®), which is approved as an atypical antipsychotic. First, a command for drawing a thiophene ring is defined so that the thiophene ring is rotated clockwise by a degree given by its argument:

```
\def\thiophenrotate#1{%
\rotatebox{#1}{%
\begin{picture}(0,0)(0,0)
\PutBondLine(0,0)(200,0){0.4pt}%
\PutBondLine(200,0)(262,-190){0.4pt}%
\PutBondLine(262,-190)(100,-308){0.4pt}%
\PutBondLine(100,-308)(-62,-190){0.4pt}%
\PutBondLine(-62,-190)(0,0){0.4pt}%
%methyl
\PutBondLine(262,-190)(380,-250){0.4pt}%
%double bond
\PutBondLine(176,-32)(223,-177){0.4pt}%
\PutBondLine(24,-32)(-23,-177){0.4pt}%
%sulfur atom
\put(100,-308){\rotatebox{-#1}{\makebox(0,0){\SetTwoAtoms{S}}}}%
\end{picture}}}
```

Because the reference point is located at the upper-left vertex, the rotation occurs around the reference point. The sulfur atom retains its original direction, as found in the following examples.



`\thiophenrotate{0}`



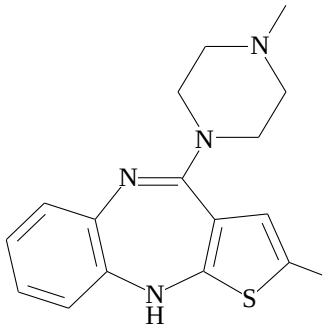
`\thiophenrotate{45}`

Then the thiophene ring along with a benzene ring is fused to a seven-membered ring, as found in the following code:

```
\begin{XyMcompd}(1150,1250)(-450,-550){cpd:olanzapine}{}
%skeletal bonds
\PutBondLine(0,0)(200,0){0.4pt}%
```

```
\PutBondLine(200,0)(325,-157){0.4pt}%
%\PutBondLine(325,-157)(281,-352){0.4pt}%fused edge omitted
\PutBondLine(281,-352)(100,-439){0.4pt}%
\PutBondLine(100,-439)(-81,-352){0.4pt}%
\PutBondLine(-81,-352)(-125,-157){0.4pt}%fused edge retained
\PutBondLine(-125,-157)(0,0){0.4pt}%
%double bonds
\PutBondLine(13,-28)(187,-28){0.4pt}%
%fused benzene
\put(-81,-352){\rotatebox{13}{\sixfusev[bdf]{}{}{B}}}%
%fused thiophene
\put(325,-157){\thiophenrotate{6}}%
%substituent
\put(260,100){\sixheteroh{3==N;6==N}{6==(yl);6==\null;3==\null}}%
%skeletal nitrogen
\put(0,0){\makebox(0,0){\SetTwoAtoms{N}}}%
\put(100,-439){\makebox(0,0){\SetTwoAtoms{N}}}%
\put(100,-485){\makebox(0,0)[t]{H}}%
\end{XyMcompd}
```

where commands for drawing seven-membered skeletal bonds, a double bond, a fused benzene ring (due to `\sixfusev`), a fused thiophene ring (due to `\thiophenrotate`), a substituent, and skeletal nitrogens are declared. Thereby, we are able to depict the structure **30-8** of olanzapine:

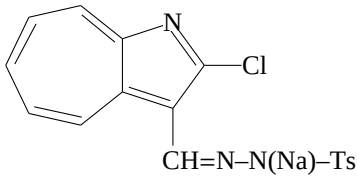


30-8 □

Example 30.10. The structural formula **30-9** of azaazulene is drawn by the following code, which is a modification of the code for drawing **30-5**.

```
\begin{XyMcompd}(1200,650)(-400,-300){cpd:azaazulene}{}
%skeletal bonds for the seven-membered ring
\PutBondLine(0,0)(0,200){0.4pt}%
\PutBondLine(0,200)(-157,325){0.4pt}%
\PutBondLine(-157,325)(-352,281){0.4pt}%
\PutBondLine(-352,281)(-439,100){0.4pt}%
\PutBondLine(-439,100)(-352,-81){0.4pt}%
\PutBondLine(-352,-81)(-157,-125){0.4pt}%
\PutBondLine(-157,-125)(0,0){0.4pt}%
%skeletal bonds for the five-membered ring
%\PutBondLine(0,0)(0,200){0.4pt}%duplicated
\PutBondLine(0,200)(190,262){0.4pt}%
\PutBondLine(190,262)(308,100){0.4pt}%
\PutBondLine(308,100)(190,-62){0.4pt}%
\PutBondLine(190,-62)(0,0){0.4pt}%
%double bonds for the seven-membered ring
\PutBondLine(-28,187)(-153,290){0.4pt}%
\PutBondLine(-325,256)(-405,105){0.4pt}%
\PutBondLine(-153,-95)(-332,-56){0.4pt}%
```

```
%double bonds for the five-membered ring
\PutBondLine(24,18)(180,-33){0.4pt}%
\PutBondLine(277,100)(180,233){0.4pt}%
%skeletal atoms
\put(190,262){\makebox(0,0){\SetTwoAtoms{N}}}%
%substituents
\PutBondLine(308,100)(448,100){0.4pt}%
\put(450,100){\makebox(0,0)[l]{\SetTwoAtoms{Cl}}}%
\PutBondLine(190,-62)(190,-202){0.4pt}%
\put(150,-290){CH=N--N(Na)--Ts}%
\end{XyMcompd}
```



30-9

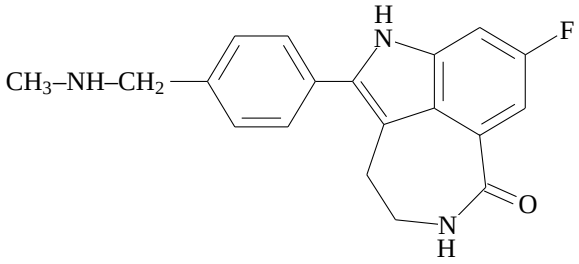
□

Example 30.11. Rucaparib **30-10** is a PARP inhibitor, which is now being investigated as a potential anti-cancer agent [2,3]. The structural formula **30-10** of rucaparib is drawn by the following code:

```
%\fbox
%{%
\begin{XyMcompd}(2050,950)(-1600,-550){cpd:rucaparib}{}%
%skeletal bonds for the five-membered ring
\PutBondLine(0,0)(0,200){0.4pt}%
\PutBondLine(0,200)(-190,262){0.4pt}%
\PutBondLine(-190,262)(-308,100){0.4pt}%
\PutBondLine(-308,100)(-190,-62){0.4pt}%
\PutBondLine(-190,-62)(0,0){0.4pt}%
%double bond
\PutBondLine(-277,100)(-180,-33){0.4pt}%
%skeletal atom
\put(-190,262){\makebox(0,0){\SetTwoAtomx{N}}}%
\put(-190,320){\makebox(0,0)[b]{H}}%
%fused benzene
\put(0,0){\sixfusev[ace]{}{2==F}{e}}%
%fused azepine
\put(-190,-62){\rotatebox{-6}{%
\begin{picture}(0,0)(-81,352)
\PutBondLine(0,0)(200,0){0.4pt}%
\PutBondLine(200,0)(325,157){0.4pt}%
\PutBondLine(325,157)(281,352){0.4pt}%
%\PutBondLine(281,352)(100,439){0.4pt}%deleted for fusion
%\PutBondLine(100,439)(-81,352){0.4pt}%deleted for fusion
\PutBondLine(-81,352)(-125,157){0.4pt}%
\PutBondLine(-125,157)(0,0){0.4pt}%
\put(325,157){\rotatebox{-18}{%exocyclic carbonyl group
\PutBondLine(0,-15)(120,-15){0.4pt}%
\PutBondLine(0,15)(120,15){0.4pt}}}%
\put(490,110){\rotatebox{6}{\makebox(0,0){O}}}%
\put(200,0){\rotatebox{6}{\makebox(0,0){\SetTwoAtomx{N}}}}%
\put(200,-50){\rotatebox{6}{\makebox(0,0)[t]{\SetTwoAtomx{H}}}}%
\end{picture}}}%
%side chain
\PutBondLine(-448,100)(-308,100){0.4pt}%
```

```
\put(-448,100){\sixheteroh[ace]{}{4==(yl);1==CH$_{3}$--NH--CH$_{2}$}}%
\end{XyMcompd}
%}
```

where the outer `picture` environment is used to draw a five-to-six fused ring as a parent skeleton. The skeleton is fused with a seven-membered ring, which is drawn in the inner `picture` environment. The skeleton is further attached by a phenyl substituent. Thereby, we obtain the following diagram:



30-10 □

30.3 Eight-Membered Rings as Regular Octagons

Because eight-membered rings are not supported by the state of the art of he XeLaTeX system, they should be depicted by using low-level commands such as `\PutBondLine`, `\WedgeAsSubst`, and `\HashWedgeAsSubst` (cf. Subsections 27.3.3 and 29.4.2).

30.3.1 Drawing Carbocyclic Eight-Membered Rings

Example 30.12. To draw two diagrams of cyclooctatetraene, a command named `\cyclooctaneskeleton` is first defined to depict a regular octagon as a common skeleton:

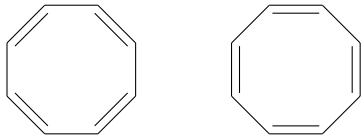
```
\def\cyclooctaneskeleton{%
%skeletal bonds for the eight-membered ring
\PutBondLine(-100,-242)(100,-242){0.4pt}%
\PutBondLine(100,-242)(242,-100){0.4pt}%
\PutBondLine(242,-100)(242,100){0.4pt}%
\PutBondLine(242,100)(100,242){0.4pt}%
\PutBondLine(100,242)(-100,242){0.4pt}%
\PutBondLine(-100,242)(-242,100){0.4pt}%
\PutBondLine(-242,100)(-242,-100){0.4pt}%
\PutBondLine(-242,-100)(-100,-242){0.4pt}}%
```

Then, two sets of double bonds are attached to the common skeleton, respectively, in the `XyMcompd` environments.

```
\begin{XyMcompd}(500,500)(-250,-250){cpd:cyclooctatetraeneA}{}%
%common skeleton for the eight-membered ring
\put(0,0){\cyclooctaneskeleton}
%double bonds
\PutBondLine(88,-212)(212,-88){0.4pt}%
\PutBondLine(88,212)(212,88){0.4pt}%
\PutBondLine(-88,-212)(-212,-88){0.4pt}%
\PutBondLine(-88,212)(-212,88){0.4pt}%
\end{XyMcompd}
\qquad
\begin{XyMcompd}(500,500)(-250,-250){cpd:cyclooctatetraeneB}{}%
%common skeleton for the eight-membered ring
\put(0,0){\cyclooctaneskeleton}
%double bonds
```

```
\PutBondLine(-212,-88)(-212,88){0.4pt}%
\PutBondLine(-88,-212)(88,-212){0.4pt}%
\PutBondLine(212,-88)(212,88){0.4pt}%
\PutBondLine(-88,212)(88,212){0.4pt}%
\end{XyMcompd}
```

Thereby, we obtain **30-11** and **30-12** as equivalent diagrams:



30-11 **30-12** □

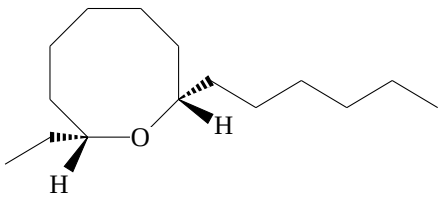
30.3.2 Drawing Heterocyclic Eight-Membered Rings

An oxacyclooctane ring can be produced by placing an atom on a vertex of a eight-membered ring, which is drawn by the command `\cyclooctaneskeleton` defined above. The command `\SetTwoAtomx` is used to place a skeletal atom after truncation of a vertex at issue. For the process of truncation with a white-colored box, see Subsection 29.5.3.

Example 30.13. For example, the structure **30-13** of (+)-*cis*-lauthisan ((*2S,8R*)-8-ethyl-2-hexyl-1-oxacyclooctane) is drawn by the code:

```
\begin{XyMcompd}(1600,750)(-400,-450){cpd:lauthisan}{}%
%common skeleton for the eight-membered ring
\put(0,0){\cyclooctaneskeleton}
%skeletal oxygen atom
\put(100,-242){\makebox(0,0){\SetTwoAtomx{O}}}%
%substituents
\WedgeAsSubst(242,-100)(5,-3){120}%
\put(380,-160){\makebox(0,0)[lt]{\SetTwoAtomx{H}}}%
\HashWedgeAsSubst(242,-100)(5,3){120}%
\put(362,-28){\hexamethylenei{}{1==(yl)}}%
\WedgeAsSubst(-100,-242)(-3,-5){72}%
\put(-172,-380){\makebox(0,0)[rt]{\SetTwoAtomx{H}}}%
\HashWedgeAsSubst(-100,-242)(-1,0){140}%
\put(-240,-242){\dimethylene{}{2==(yl)}}%
\end{XyMcompd}
```

where the side chains are generated by using `\hexamethylenei` and `\dimethylene` after declaration of (yl)-functions. The process of placing each side chain is based on the replacement technique (cf. Section 2.7).



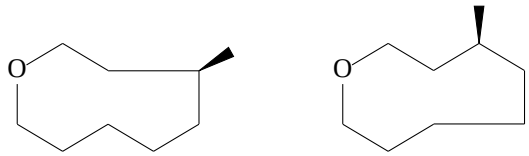
30-13 □

30.4 Nine-Membered Rings

Nine- or larger-membered rings are preferentially drawn as non-convex polygons, in which two or more atoms point inwards relative to the rest of ring. According to the default setting of the XyMTEX, for example, nine-membered rings can be drawn by using `\nonaheterov` or `\nonaheterovi` under declaring an optional argument ⟨delbdlist⟩ `[j]` (cf. Section 3.5.3). Thus the codes:

```
\nonaheterov{}{3B==\null}[j]
\nonaheterovi{}{1B==\null}[j]
```

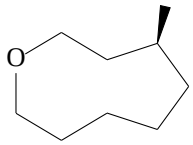
generate the following diagrams:



Example 30.14. The right part stemming from a home-plate form can be reformed into a diagram based on a regular pentagon, which is drawn by using low-level commands `\PutBondLine` and attached by a fusing unit `\sixfusev`. Thus the code:

```
\begin{XyMcompd}(600,550)(-350,-100){cpd:cyclononaneA}{}%
%regular pentagon
%\PutBondLine(0,0)(0,200){0.4pt}%fused edge deleted
\PutBondLine(0,200)(190,262){0.4pt}%
\PutBondLine(190,262)(308,100){0.4pt}%
\PutBondLine(308,100)(190,-62){0.4pt}%
\PutBondLine(190,-62)(0,0){0.4pt}%
%six-membered fusing unit
\put(0,0){\sixfusev{6==O}{}{B}}
%substituent
\WedgeAsSubstX(190,262)(220,400)[4]%
\end{XyMcompd}
```

generates a reformed diagram:



30-14

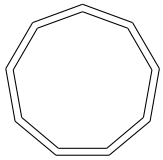
□

Example 30.15. To draw a regular nonagon as a convex polygon with double bonds, the data of respective vertices are calculated as follows:

```
\begin{picture}(600,600)(-300,-300)
%regular nonagon
\PutBondLine(0,293)(-188,224){0.4pt}%
\PutBondLine(-188,224)(-289,51){0.4pt}%
\PutBondLine(-289,51)(-254,-147){0.4pt}%
\PutBondLine(-254,-147)(-100,-275){0.4pt}%
\PutBondLine(-100,-275)(100,-275){0.4pt}%
\PutBondLine(100,-275)(254,-147){0.4pt}%
\PutBondLine(254,-147)(289,51){0.4pt}%
\PutBondLine(289,51)(188,224){0.4pt}%
\PutBondLine(188,224)(0,293){0.4pt}%
%double bonds
\PutBondLine(0,265)(-170,203){0.4pt}%
\PutBondLine(-170,203)(-261,46){0.4pt}%
\PutBondLine(-261,46)(-229,-133){0.4pt}%
\PutBondLine(-229,-133)(-91,-249){0.4pt}%
\PutBondLine(-91,-249)(91,-249){0.4pt}%
\PutBondLine(91,-249)(229,-133){0.4pt}%
\PutBondLine(229,-133)(261,46){0.4pt}%
```

```
\PutBondLine(261,46)(170,203){0.4pt}%
\PutBondLine(170,203)(0,265){0.4pt}%
\end{picture}
```

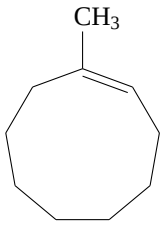
This code generate the following diagram:



□

Example 30.16. By starting from these data, the structure **30-15** of 1-methyl-1-cyclononene is drawn by inputting the following code:

```
\begin{XyMcompd}(600,850)(-300,-300){cpd:MecycloC9}{}%
%regular nonagon
\PutBondLine(0,293)(-188,224){0.4pt}%
\PutBondLine(-188,224)(-289,51){0.4pt}%
\PutBondLine(-289,51)(-254,-147){0.4pt}%
\PutBondLine(-254,-147)(-100,-275){0.4pt}%
\PutBondLine(-100,-275)(100,-275){0.4pt}%
\PutBondLine(100,-275)(254,-147){0.4pt}%
\PutBondLine(254,-147)(289,51){0.4pt}%
\PutBondLine(289,51)(188,224){0.4pt}%
\PutBondLine(188,224)(0,293){0.4pt}%
%double bond
\PutBondLine(170,203)(0,265){0.4pt}%
%substituent
\PutBondLine(0,293)(0,433){0.4pt}%
\put(0,440){\makebox(0,0)[b]{C\rlap{H$_{3}$}}}%
\end{XyMcompd}
```



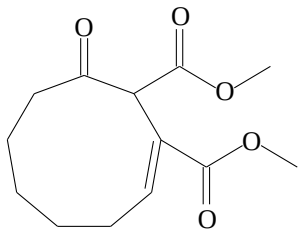
30-15

□

Example 30.17. The structure **30-16** of dimethyl 9-oxo-2-cyclononene-1,2-dicarboxylate is drawn in a similar way, where two methoxycarbonyl groups are generated by the replacement technique applied to `\tetramethylene` and `\tetramethylenei`.

```
\begin{XyMcompd}(1100,900)(-300,-300){cpd:cycloC9COCOOMe}{}%
%regular nonagon
\PutBondLine(0,293)(-188,224){0.4pt}%
\PutBondLine(-188,224)(-289,51){0.4pt}%
\PutBondLine(-289,51)(-254,-147){0.4pt}%
\PutBondLine(-254,-147)(-100,-275){0.4pt}%
\PutBondLine(-100,-275)(100,-275){0.4pt}%
\PutBondLine(100,-275)(254,-147){0.4pt}%
\PutBondLine(254,-147)(289,51){0.4pt}%
\PutBondLine(289,51)(188,224){0.4pt}%
\PutBondLine(188,224)(0,293){0.4pt}%
%double bond
\PutBondLine(261,46)(229,-133){0.4pt}%
```

```
%substituent
\PutBondLine(13,293)(13,433){0.4pt}%
\PutBondLine(-13,293)(-13,433){0.4pt}%
\put(0,440){\makebox(0,0)[b]{O}}%
\put(188,224){\tetramethylene{3==O}{1==(yl);2D==O}}%
\put(289,51){\tetramethylenei{3==O}{1==(yl);2D==O}}%
\end{XyMcompd}
```



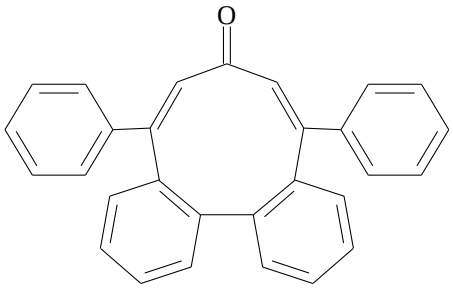
30-16

□

Example 30.18. The structure **30-17** of 5,9-diphenyl-7*H*-dibenzo[*a*,*c*]cyclononen-7-one [4] is drawn by the code:

```
\begin{XyMcompd}(1600,1100)(-820,-550){cpd:diBzcycoC9}{}%
%regular nonagon
\PutBondLine(0,293)(-188,224){0.4pt}\PutBondLine(-188,224)(-289,51){0.4pt}%
\PutBondLine(-289,51)(-254,-147){0.4pt}\PutBondLine(-254,-147)(-100,-275){0.4pt}%
\PutBondLine(-100,-275)(100,-275){0.4pt}\PutBondLine(100,-275)(254,-147){0.4pt}%
\PutBondLine(254,-147)(289,51){0.4pt}\PutBondLine(289,51)(188,224){0.4pt}%
\PutBondLine(188,224)(0,293){0.4pt}%
%double bond
\PutBondLine(170,203)(261,46){0.4pt}\PutBondLine(-170,203)(-261,46){0.4pt}%
%substituent
\PutBondLine(13,293)(13,433){0.4pt}\PutBondLine(-13,293)(-13,433){0.4pt}%
\put(0,440){\makebox(0,0)[b]{O}}%
\PutBondLine(289,51)(429,45){0.4pt}%
\put(429,45){\benzeneh{1==(yl)}}%
\PutBondLine(-289,51)(-429,45){0.4pt}%
\put(-429,45){\benzeneh{4==(yl)}}%
%fused benzenes
\put(100,-275){\rotatebox{-49}{\sixfusev[ace]{}{}{e}}}%
\put(-100,-275){\rotatebox{49}{\sixfusev[bdf]{}{}{B}}}%
\end{XyMcompd}
```

In this code, the phenyl substituents are attached by replacement technique using `\benzeneh` after the declaration of a (yl)-function; and the fused benzene rings are attached by the addition technique using a fusing unit `\sixfusev` after rotation by `\rotatebox` (supported by the graphicx package). This code generates the following diagram:



30-17

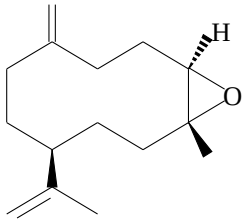
□

30.5 Ten-Membered Rings

Ten-membered rings are preferentially drawn as non-convex polygons. They can be drawn by using `\decaheterov` under declaring an optional argument ⟨delbdlist⟩ `[k]`, as exemplified in Section 3.5.3. A preferred depiction of configurations in a non-convex epoxycyclodecane is described in the IUPAC Recommendations 2006 [5, ST-1.4]. An example structure **30-18** listed in the IUPAC Recommendations can be drawn by the code:

```
\begin{XyMcompd}(900,800)(200,0){cpd:C10epoxideA}{}%
\wedgehashedwedge
\decaheterov[{b\threefuseh{1==O}{}{B}}]%
{}{2Sd==H;3SB==\null;%
5B==\trimethylene[a]{}{2==(yl)};8D==\null}[k]
\end{XyMcompd}
```

This code generates a preferred depiction style:

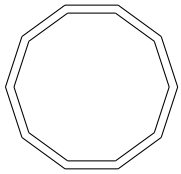


30-18

Example 30.19. To draw a regular decagon as a convex polygon with double bonds, the data of respective vertices are calculated as follows:

```
\begin{picture}(700,700)(-350,-350)
%regular decagon
\PutBondLine(324,0)(262,190){0.4pt}%
\PutBondLine(262,190)(100,308){0.4pt}%
\PutBondLine(100,308)(-100,308){0.4pt}%
\PutBondLine(-100,308)(-262,190){0.4pt}%
\PutBondLine(-262,190)(-324,0){0.4pt}%
\PutBondLine(-324,0)(-262,-190){0.4pt}%
\PutBondLine(-262,-190)(-100,-308){0.4pt}%
\PutBondLine(-100,-308)(100,-308){0.4pt}%
\PutBondLine(100,-308)(262,-190){0.4pt}%
\PutBondLine(262,-190)(324,0){0.4pt}%
%double bonds
\PutBondLine(292,0)(236,172){0.4pt}%
\PutBondLine(236,172)(90,278){0.4pt}%
\PutBondLine(90,278)(-90,278){0.4pt}%
\PutBondLine(-90,278)(-236,172){0.4pt}%
\PutBondLine(-236,172)(-292,0){0.4pt}%
\PutBondLine(-292,0)(-236,-172){0.4pt}%
\PutBondLine(-236,-172)(-90,-278){0.4pt}%
\PutBondLine(-90,-278)(90,-278){0.4pt}%
\PutBondLine(90,-278)(236,-172){0.4pt}%
\PutBondLine(236,-172)(292,0){0.4pt}%
\end{picture}
```

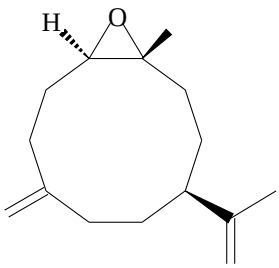
This code generate the following diagram:



□

Example 30.20. Another preferred depiction of configurations in a convex epoxycyclodecane is described in the IUPAC Recommendations 2006 [5, ST-1.4]. An example structure **30-19** listed in the IUPAC Recommendations can be drawn by the code:

```
\begin{XyMcompd}(950,1000)(-400,-450){cpd:C10epoxideB}{}
%regular decagon
\PutBondLine(324,0)(262,190){0.4pt}%
\PutBondLine(262,190)(100,308){0.4pt}%
\PutBondLine(100,308)(-100,308){0.4pt}%
\PutBondLine(-100,308)(-262,190){0.4pt}%
\PutBondLine(-262,190)(-324,0){0.4pt}%
\PutBondLine(-324,0)(-262,-190){0.4pt}%
\PutBondLine(-262,-190)(-100,-308){0.4pt}%
\PutBondLine(-100,-308)(100,-308){0.4pt}%
\PutBondLine(100,-308)(262,-190){0.4pt}%
\PutBondLine(262,-190)(324,0){0.4pt}%
\put(100,308){\threefusevi{1==O}{}{b}}
%epoxy
\WedgeAsSubst(100,308)(1,1){100}%
\HashWedgeAsSubst(-100,308)(-1,1){100}%
\put(-205,408){\makebox(0,0)[rb]{\SetTwoAtomx{H}}}%
%exocyclic double bond
\put(-262,-190){\rotatebox{30}{%
\PutBondLine(0,15)(-171,15){0.4pt}%
\PutBondLine(0,-15)(-171,-15){0.4pt}}}%
%substituent
\WedgeAsSubst(262,-190)(5,-3){171}%
\PutBondLine(433,-293)(604,-190){0.4pt}%
\PutBondLine(418,-293)(418,-464){0.4pt}%
\PutBondLine(448,-293)(448,-464){0.4pt}%
\end{XyMcompd}
```



30-19

Compare between **30-18** and **30-19**, which are both preferred according to the IUPAC Recommendations 2006 [5, ST-1.4]. □

References

[1] G. P. Moss and IUPAC and IUB, Joint Commission of Biochemical Nomenclature, *Pure Appl. Chem.*, **59**, 779–832 (1987).

[2] L. M. Jarvis, *Chem & Eng. News*, **91 (Issue 24, June 17. 2013)**, 13–16 (2013).

[3] L. M. Jarvis, *Chem & Eng. News*, **91 (Issue 25, July 17. 2013)**, 13–16 (2013).

[4] H. L. Ammon and M. Rabinovitz, *Acta Cryst.*, **C39**, 400–403 (1983).

[5] J. Brecher and IUPAC Chemical Nomenclature and Structure Representation Division, *Pure Appl. Chem.*, **78**, 1897–1970 (2006).

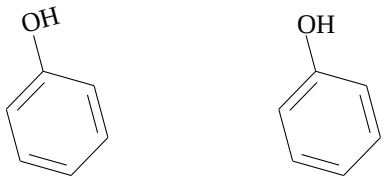
New Commands for Drawing Five-, Seven-, and Eight-Membered Rings

This chapter is devoted to give sample definitions of simplified XƎMTEX commands, i.e., `\FiveCycle` for drawing rotatable five-membered rings, `\SevenCycle` for drawing rotatable seven-membered rings, and `\EightCycle` for drawing rotatable eight-membered rings. They are applied to depict the complex structural formula of ciguatoxin.

31.1 Common Commands for Treating Arguments

Let consider rotations of phenol by using `\rotatebox` of the graphicx package:

```
\rotatebox{15}{\benzenev{1==OH}}
\rotatebox{15}{\benzenev{1==\rotatebox{-15}{OH}}}
```



Under usual conditions, the character string ‘OH’ is also rotated as found in the left output. For the purpose of constructing a fused ring system, the character string ‘OH’ should retain its vertical direction as shown in the right output, where the character string ‘OH’ is inversely rotated as compared with the total rotation of the phenyl skeleton.

To operate this disrotatory treatment, commands named `\PutAtomRotatedRa` (or `\PutAtomRotatedRb`) and `\PutAtomRotatedLa` (or `\PutAtomRotatedLa`) are defined as follows:

```
\makeatletter
%%%%%%%%%%%%%%%%%%%%%%%%%%
%Treatment of Arguments%
%%%%%%%%%%%%%%%%%%%%%%%%%%
\def\SeparatePut#1{%
\def\TempX{}\def\TempY{}\def\TempAtom{}%
\setbox0=\hbox{\def\put(##1,##2)##3{\gdef\TempX{##1}\gdef\TempY{##2}%
\gdef\TempAtom{##3}}#1\relax
\ifx\TempX \empty\relax
\gdef\TempAtom{#1}\fi}}
%%%%%%%%%%%%%%%%%%%%%%%%%%
```

```
% Placing Atoms Rotated%
%%%%%%%%%%%%%%%%%%%%%%%%
\def\HboxMR#1{\hbox to 0.8em{#1\hss}}
\def\HboxML#1{\hbox to 0.8em{\hss#1}}
%left-handed
\def\PutAtomRotatedRa(#1,#2)#3#4{%
\SeparatePut{#4}%
\ifx\TempX \empty\relax
\put(#1,#2){%
\rotatebox{#3}{\makebox(0,0){%
\HboxMR{\SetTwoAtomx{#4}}}}}\else
\put(#1,#2){\put(\TempX,\TempY){%
\rotatebox{#3}{\makebox(0,0){%
\HboxMR{\expandafter\SetTwoAtomx{\TempAtom}}}}}}%
\fi}%
\def\PutAtomRotatedRb(#1,#2)#3#4{%
\put(#1,#2){#4}}%
%right-handed
\def\PutAtomRotatedLa(#1,#2)#3#4{%
\SeparatePut{#4}%
\ifx\TempX \empty\relax
\put(#1,#2){%
\rotatebox{#3}{\makebox(0,0){%
\HboxMR{\SetTwoAtomx{#4}}}}}\else
\put(#1,#2){\put(\TempX,\TempY){%
\rotatebox{#3}{\makebox(0,0){%
\HboxML{\expandafter\SetTwoAtomx{\TempAtom}}}}}}%
\fi}%
\def\PutAtomRotatedLb(#1,#2)#3#4{%
\put(#1,#2){#4}}%
\makeatother
```

The command \PutAtomRotatedRa works well even if the last argument is input in the form of \put(200,200){OH} or simply of OH. For example, the following two codes:

```
\begin{picture}(500,500)(0,0)
\put(0,0){\redx{\circle{40}}}
\put(200,200){\bluex{\circle{40}}}
\rotatebox{15}{%
\PutAtomRotatedRa(0,0){-15}{\put(200,200){OH}}}
\end{picture}
\qquad
\begin{picture}(500,500)(0,0)
\put(0,0){\redx{\circle{40}}}
\put(200,200){\bluex{\circle{40}}}
\rotatebox{15}{%
\PutAtomRotatedRa(200,200){-15}{OH}}
\end{picture}
```

depict equivalent results:

31.2 Command for Drawing Rotatable Five-Membered Rings

In this section, we will define a command named \FiveCycle for drawing rotatable five-membered rings.

31.2.1 Syntax of the Command \FiveCycle

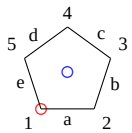
The syntax of the command \FiveCycle is as follows:

```
\FiveCycle(⟨refpoint⟩){⟨rotdegree⟩}[⟨bondlist⟩]{⟨atomlist⟩}[⟨delbdlist⟩]
```

The default coordinates of respective vertices of \FiveCycle are assigned to be

$$1 \text{ — } (0,0); \quad 2 \text{ — } (200,0); \quad 3 \text{ — } (262,190); \quad 4 \text{ — } (100,308); \quad 5 \text{ — } (-62,190);$$

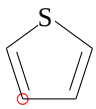
where the locant numbers are shown bellow:



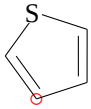
The center of the regular pentagon is located at (100, 138), as marked by a blue circle.

The argument ⟨refpoint⟩ denotes the coordinate of a shifted reference point. The original reference point (0, 0) is located at the 1-position, as shown by a red small circle. The argument ⟨rotdegree⟩ denotes the angle of rotation, the value of which is determined anti-clockwise. The rotation is operated around the shifted reference point. The optional argument ⟨bondlist⟩ is a list of locant alphabets selected from a–e to assign skeletal double bonds, where the syntax is based on the general convention described in Subsection 3.3.1. The argument ⟨atomlist⟩ is a list of skeletal atoms, where the syntax is based on the general convention described in Subsection 3.2.2. The optional argument ⟨delbdlist⟩ is a list of deleted bonds, where the syntax is based on the general convention described in Subsection 3.3.3.

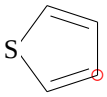
The effect of rotation angles is shown in Fig. 31.1, where the value 18 is calculated by 108 − 90, because the internal angle of a regular pentagon is equal to $180\times3/5 = 108°$. Each reference point (center of rotation) is located at the vertex marked with a red small circle.




```
\FiveCycle(0,0){0}[be]{4==S}
```




```
\FiveCycle(0,0){18}[be]{4==S}
```




```
\FiveCycle(0,0){90}[be]{4==S}
```


```
\FiveCycle(0,0){-18}[be]{4==S}
```

Figure 31.1. Effect of rotation angles by ⟨rotdegree⟩ of \FiveCycle. Each reference point (center of rotation) is located at the vertex marked with a red small circle.

31.2.2 Definition of the Command \FiveCycle

The definition of the command \FiveCycle is based on the conventions of the XeLaTeX system. The source list is shown below. Although complicated treatments by \@ifnextchar are preliminarily conducted to treat optional arguments, the net command of \FiveCycle is \@@FiveCycle with six arguments.

```
\makeatletter
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%Drawing Rotatable Five-Membered Rings%
```

```
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
\def\FiveCycle(#1,#2)#3{\@ifnextchar[{\@FiveCycle(#1,#2){#3}}%
{\@FiveCycle(#1,#2){#3}[]}}%
\def\@FiveCycle(#1,#2)#3[#4]#5{%
\@ifnextchar[{\@@FiveCycle(#1,#2){#3}[#4]{#5}}%
{\@@FiveCycle(#1,#2){#3}[#4]{#5}[]}}
\def\@@FiveCycle(#1,#2)#3[#4]#5[#6]{%
\rotatebox{#3}{%
\begin{picture}(0,0)(#1,#2)%
%%%%%%%%%%%%%%%
%double bonds%
%%%%%%%%%%%%%%%
\@tfor\member:=#4\do{%bondlist
\if\member a\relax
\PutBondLine(24,32)(176,32){\thinLineWidth}%
\else\if\member b\relax
\PutBondLine(176,32)(223,177){\thinLineWidth}%
\else\if\member c\relax
\PutBondLine(223,177)(100,265){\thinLineWidth}%
\else\if\member d\relax
\PutBondLine(100,265)(-23,177){\thinLineWidth}%
\else\if\member e\relax
\PutBondLine(-23,177)(24,32){\thinLineWidth}%
\fi\fi\fi\fi\fi%
}%
%%%%%%%%%%%%%%%%%
%skeletal bonds%
%%%%%%%%%%%%%%%%%
{\resetbdsw%
\@bond@@omit{#6}%
\ifx\@aaa\empty\else
\PutBondLine(0,0)(200,0){\thinLineWidth}\fi%bond a (1--2)
\ifx\@bbb\empty\else
\PutBondLine(200,0)(262,190){\thinLineWidth}\fi%bond b (2--3)
\ifx\@ccc\empty\else
\PutBondLine(262,190)(100,308){\thinLineWidth}\fi%bond c(3--4)
\ifx\@ddd\empty\else
\PutBondLine(100,308)(-62,190){\thinLineWidth}\fi%bond d (4--5)
\ifx\@eee\empty\else
\PutBondLine(-62,190)(0,0){\thinLineWidth}\fi%bond e (5--6)
}%
%%%%%%%%%%%%%%%%%
%skeletal atoms%
%%%%%%%%%%%%%%%%%
{\@tempcnta=-#3\relax
\@forsemicol\member:=#5\do{%
\ifx\member\empty \relax\else%
\expandafter\@m@mb@r\member;\relax%
\expandafter\twoch@r\@membera{}\relax%
\if\@tmpb s\relax
\let\PutAtomRotatedR=\PutAtomRotatedRb
\let\PutAtomRotatedL=\PutAtomRotatedLb
\else
\let\PutAtomRotatedR=\PutAtomRotatedRa
\let\PutAtomRotatedL=\PutAtomRotatedLa
\fi
\ifcase\@tmpa \relax%
```

```
\or%position 1
\PutAtomRotatedL(0,0){\the\@tempcnta}{\@memberb}%
\or%position 2
\PutAtomRotatedR(200,0){\the\@tempcnta}{\@memberb}%
\or%position 3
\PutAtomRotatedR(262,190){\the\@tempcnta}{\@memberb}%
\or%position 4
\PutAtomRotatedR(100,308){\the\@tempcnta}{\@memberb}%
\or%position 5
\PutAtomRotatedL(-62,190){\the\@tempcnta}{\@memberb}%
\fi\fi}%
\end{picture}}%
}
\makeatother
```

In the above source list, the processing of the arguments ⟨refpoint⟩ (`(#1,#2)`) and ⟨rotdegree⟩ (`#3`) are conducted by using the common commands defined in Section 31.1. The processing of the ⟨bondlist⟩ (`#4`) is based on the LaTeX command `\@tfor`, which is a common way to the XeLaTeX system. The processing of the ⟨aromlist⟩ (`#5`) is conducted by using the XeLaTeX command `\@forsemicol`, which is a list-treating command with considering a semicolon as a delimiter. The processing of the optional argument ⟨delbdlist⟩ (`#6`) is based on the XeLaTeX command `\@bond@@omit`, which detects skeletal bonds to be deleted.

As found in the syntax on page 529, the command `\FiveCycle` lacks the argument ⟨subslist⟩ for the sake of simplicity. Hence, a substituent with a bond is attached to the five-membered ring through the ⟨atomlist⟩ by virtue of the atom replacement (an improper application of the replacement technique). For this purpose, new commands are defined: `\carbonylrotate` for drawing a rotatable carbonyl group `\exodoublebond` for drawing a rotatable double bond, and `\exosinglebond` for drawing a rotatable vertical single bond. These bonds are originally drawn in vertical direction, but can be rotated by the angle assigned by their arguments.

```
\makeatletter
%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%rotatable carbonyl group%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%
\def\carbonylrotate#1{%
\@ifnextchar[{\c@rbonylrotate{#1}}{\c@rbonylrotate{#1}[0]}}
\def\c@rbonylrotate#1[#2]{%
\rotatebox{#1}{\begin{picture}(0,0)(0,0)
\PutBondLine(13,0)(13,140){\thinLineWidth}%
\PutBondLine(-13,0)(-13,140){\thinLineWidth}%
%%%%%%%%%%%%%
%oxygen atom% retaining its original vertical direction
%%%%%%%%%%%%%
\@tempcnta=-#1\relax
\put(0,180){\rotatebox{\the\@tempcnta}{\makebox(0,0){%
\hbox to0.8em{\SetTwoAtomx{#2}\hss}}}}%
\end{picture}}}
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%rotatable exocyclic double bond%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
\def\exodoublebond#1{%
\rotatebox{#1}{\begin{picture}(0,0)(0,0)
\PutBondLine(13,0)(13,140){\thinLineWidth}%
\PutBondLine(-13,0)(-13,140){\thinLineWidth}%
\end{picture}}}
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%rotatable exocyclic single bond%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
\def\exosinglebond#1{%
```

```
\rotatebox{#1}{\begin{picture}(0,0)(0,0)
\PutBondLine(0,0)(0,160){\thinLineWidth}%
\end{picture}}}
\makeatother
```

Several examples for using \carbonylrotate are shown below:

```
\carbonylrotate{0}%
\carbonylrotate{-45}%
\carbonylrotate{-90}%
\hskip 3cm
\carbonylrotate{0}[NH]%
\carbonylrotate{-45}[NH]%
\carbonylrotate{-90}[NH]%
\hskip 3cm
\carbonylrotate{0}[S]%
\carbonylrotate{-45}[S]%
\carbonylrotate{-90}[S]%
```

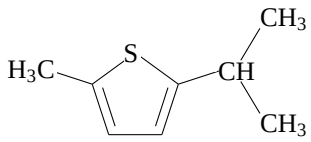
31.2.3 Examples of Using \FiveCycle

Monocyclic Compounds

Example 31.1. The structure **31-1** of 2-isopropyl-5-methylthiophene is drawn by using \FiveCycle as follows:

```
\begin{XyMcompd}(1100,550)(-400,-50){cpd:diAlthiopheneA}{}
\FiveCycle(0,0){0}[be]{%
3s==\exosinglebond{-72};%
3==\put(180,50){\Rtrigonal{1==(yl);0==CH;2==CH$_{3}$;3==CH$_{3}$}};
5s==\exosinglebond{72};%
5==\put(-180,50){\llap{H$_{3}$}C};%
4==S}
\end{XyMcompd}
```

where the bond at 2- or 5-position is drawn by the command \exosinglebond after rotation by −72° or 72°. The above code generates the following structure.



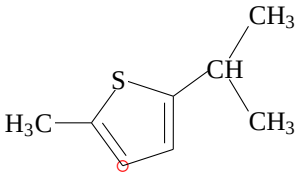
31-1 □

Example 31.2. This structure can be rotated by inputting the ⟨rotangle⟩, where the center of rotation is shown by a red small circle. The codes:

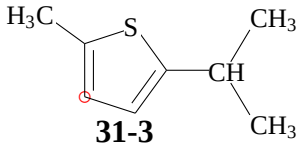
```
\begin{XyMcompd}(1100,550)(-400,-50){cpd:diAlthiopheneB}{}
\put(0,0){\redx{\circle{40}}}
\FiveCycle(0,0){18}[be]{%
3s==\exosinglebond{-72};%
3==\put(180,50){\Rtrigonal{1==(yl);0==CH;2==CH$_{3}$;3==CH$_{3}$}};
5s==\exosinglebond{72};%
5==\put(-180,50){\llap{H$_{3}$}C};%
4==S}
\end{XyMcompd}
```

```
\qquad
\begin{XyMcompd}(1100,550)(-400,-50){cpd:diAlthiopheneC}{}
\put(0,0){\redx{\circle{40}}}
\FiveCycle(0,0){-18}[be]{%
3s==\exosinglebond{-72};%
3==\put(180,50){\Rtrigonal{1==(yl);0==CH;2==CH$_{3}$;3==CH$_{3}$}};
5s==\exosinglebond{72};%
5==\put(-180,50){\llap{H$_{3}$}C};%
4==S}
\end{XyMcompd}
```

generate the following rotated diagrams:



31-2

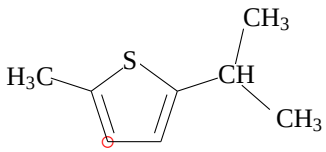


31-3

Each of the substituents retains the vertical direction after rotation. In particular, the two methyl groups of the isopropyl substituent are aligned vertically both in **31-2** and **31-3**, because the isopropyl substituent keeps its direction as a result of the disrotatory motion. □

Example 31.3. In comparison with **31-1**, the following code depicts a slightly different isopropyl substituent.

```
\begin{XyMcompd}(1100,600)(-400,-50){cpd:diAlthiopheneD}{}
\put(0,0){\redx{\circle{40}}}
\FiveCycle(0,0){0}[be]{%
3==\put(180,30){%
\rotatebox{18}{\Rtrigonal{1==(yl);%
2==\rotatebox{-18}{\SetTwoAtomx{CH$_{3}$}};%
3==\rotatebox{-18}{\SetTwoAtomx{CH$_{3}$}};%
0==\rotatebox{-18}{\raisebox{3pt}{\SetTwoAtomx{CH}}}}}};%
3s==\exosinglebond{-72};%
5==\put(-180,50){\llap{H$_{3}$}C};%
5s==\exosinglebond{72};%
4==S}
\end{XyMcompd}
```



31-4

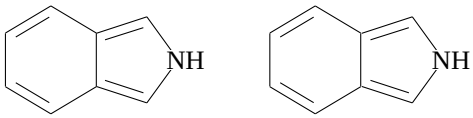
Note that all of the bond angles of the isopropyl substituent are approximately equal to 120°. □

Fused and Spiro Ring Systems

Example 31.4. By using `\FiveCycle`, the structural diagram of isoindole is drawn by the addition technique as well as by the replacement technique. Note that `\FiveCycle` is regarded as producing a fusing unit or a moiety generated by a (yl)-function, as found in the following codes:

```
\begin{XyMcompd}(650,450)(250,250){}{}
\sixheterov[df{B\FiveCycle(0,0){-18}[ad]{3==NH}[e]}]{}{}
\end{XyMcompd}
\qquad
\begin{XyMcompd}(650,450)(250,250){}{}
\sixheterov[df]{3s==\FiveCycle(0,0){-18}[ad]{3==NH}[e]}{}
\end{XyMcompd}
```

where the first code contains `\FiveCycle` in the ⟨bondlist⟩ of the command `\sixheterov` (the addition technique), while the second code contains `\FiveCycle` in the ⟨atomlist⟩ (an improper application of the replacement technique). These codes generate the following diagrams:

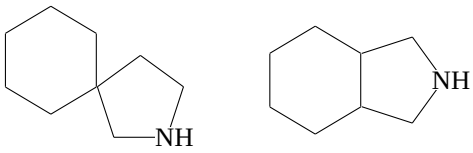


□

Example 31.5. It is worthwhile to give further comments on the improper application of the replacement. The original aim of the replacement technique is to bring about spiro ring fusion shown in the first code below. On the other hand, the present improper application of the replacement technique results in ring fusion after rotation as shown in the second code below.

```
\begin{XyMcompd}(650,500)(250,150){}{}
\sixheterov{3s==\FiveCycle(-62,190){0}{2==NH}}{}
\end{XyMcompd}
\qquad
\begin{XyMcompd}(650,450)(250,250){}{}
\sixheterov{3s==\FiveCycle(-62,190){54}{2==NH}[d]}{}
\end{XyMcompd}
```

These codes generate the following diagrams:

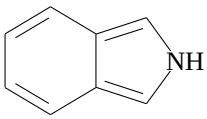


Note that the rotation angle of the latter is calculated by 180 − 18 − 108 = 54°. □

Example 31.6. The above five-to-six fused rings are drawn by the scheme 5 → 6. The inverse scheme 6 → 5 is also effective as found in the code:

```
\begin{XyMcompd}(650,450)(-300,-100){}{}%{cpd:kkk}{}
\FiveCycle(0,0){-18}[ad]{3==NH;1s==\rotatebox{18}{\sixheterov[df]{}{3==(yl)}}}[e]
\end{XyMcompd}
```

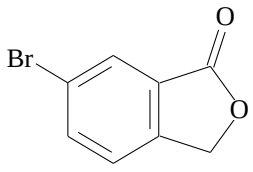
This code generates an equivalent diagram:



□

Example 31.7. As an example of attaching substituents, the structure of 6-bromo-*3H*-isobenzofuran-1-one is drawn by the code:

```
\begin{XyMcompd}(800,600)(50,250){}{}
\sixheterov[bdf]{3s==\FiveCycle(0,0){-18}{3==O;%
4s==\exodoublebond{0};4s==\put(-50,155){\rotatebox{18}{O}}%
}[e]}{6==Br}
\end{XyMcompd}
```



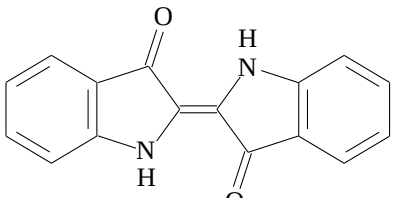
□

Several Natural Products with Five-Membered Rings

Example 31.8. The command `\indigoleft` and `\indigoright` used to draw indigo **30-1** can be replaced by `\FiveCycle`. Thus the code:

```
\begin{XyMcompd}(1400,750)(250,100){cpd:indigoZ}{}%
\sixheterov[bdf]{3s==\FiveCycle(0,0){-18}{%
2==\raisebox{-5pt}{\downnobond{\SetTwoAtomx{N}}{H}};%
4s==\exodoublebond{0};4s==\put(-50,155){\rotatebox{18}{O}};%
3s==\exodoublebond{-72};%
3s==\put(133,43){\FiveCycle(-62,190){36}{%
4==\rotatebox{18}{\SetTwoAtomx{N}};4==\put(30,100){\rotatebox{18}{H}};%
1s==\exodoublebond{144};1s==\put(-150,-180){\rotatebox{-18}{O}};%
2s==\rotatebox{-18}{\sixheterov[ace]{}{5==(yl)}[e]}}}
}[e]}{}
\end{XyMcompd}
```

generates the following formula:



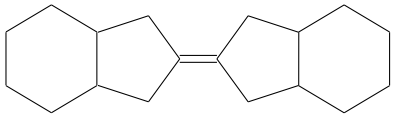
31-5

which is equivalent to **30-1**. □

Example 31.9. The omission of skeletal atoms, substituents, and endocyclic double bonds is helpful to trace the nested construction of the structure **31-5**. Thus the code based on the nested scheme 6 ← 5 (← =) ← 5 ← 6 is written as follows:

```
\begin{XyMcompd}(1400,450)(250,250){}{}
\sixheterov{%                                       %outer 6-membered ring
3s==\FiveCycle(0,0){-18}{%                          %5-membered ring
3s==\exodoublebond{-72};%                           %= exocyclic double bond
3s==\put(133,43){\FiveCycle(-62,190){36}{%          %5-membered ring
2s==\rotatebox{-18}{\sixheterov{}{5==(yl)}[e]}}}%   %6-membered ring
}[e]}{}
\end{XyMcompd}
```

The coordinates $(133, 43)$ are calculated to be $140 \times (190/200) = 133$ and $140 \times (62/200) = 43$, where we postulate $\sin 72^\circ = 190/200$ and $\cos 72^\circ = 62/200$ by referring to the values shown on page 529. This code generates the net skeleton of **31-5** as follows:



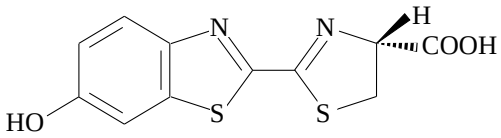
The structure **31-5** can be rebuilt by adding the omitted objects (skeletal atoms, substituents, and endocyclic double bonds) to this net skeleton. □

Example 31.10. The structure **31-6** of firefly luciferin is drawn by the code:

```
\begin{XyMcompd}(1750,500)(0,200){cpd:luciferin}{}%
\sixheterov[bdf]{3s==\FiveCycle(0,0){-18}[c]{%
2==S;4==N;%
3s==\exosinglebond{-72};%
3s==\put(150,50){\FiveCycle(-62,190){36}[d]{%
1==\rotatebox{18}{\SetTwoAtomx{S}};%
```

```
4==\rotatebox{18}{\SetTwoAtomx{N}};%
3s==\HashWedgeAsSubstX(7,-3)(140,-60)[7];%
3s==\put(160,-60){\rotatebox{-18}{\makebox(0,0)[l]{COOH}}};%
3s==\WedgeAsSubstX(0,0)(140,60)[7];%
3s==\put(160,60){\rotatebox{-18}{\makebox(0,0)[l]{H}}}}}%
}[e]}{5==HO}
\end{XyMcompd}
```

which is based on the nested scheme 6 ← 5 (← —) ← 5. This code generates the following diagram:

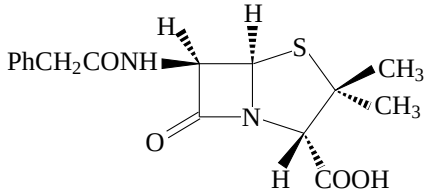


31-6 □

Example 31.11. The five-membered ring of home-plate type in penicillin G (**4-76**) can be changed into a regular pentagon by inputting the code:

```
\begin{XyMcompd}(1500,750)(-300,-50){cpd:X4-penicillinGx}{}
\wedgehashedwedge
\fourhetero{2==\null;
2s==\FiveCycle(0,0){-18}{1==N;4==S;%
3s==\HashWedgeAsSubstX(0,0)(140,-15)[7];%
3s==\put(160,-15){\rotatebox{18}{\makebox(0,0)[l]{CH$_{3}$}}};%
3s==\WedgeAsSubstX(0,0)(110,120);%
3s==\put(130,120){\rotatebox{18}{\makebox(0,0)[l]{CH$_{3}$}}};%
2s==\HashWedgeAsSubstX(0,0)(100,-100);%
2s==\put(80,-120){\rotatebox{18}{\makebox(0,0)[tl]{COOH}}};%
2s==\WedgeAsSubstX(0,0)(-40,-140)[5];%
2s==\put(-40,-160){\rotatebox{18}{\makebox(0,0)[t]{H}}}}[e]%
}{1D==O;4Su==PhCH$_{2}$CONH;4Sd==H;3FA==H}
\end{XyMcompd}
```

where `\FiveCycle` is declared in the ⟨atomlist⟩ of `\fourhetero` according to an improper application of the replacement technique (not the addition technique). This code generates the following diagram **31-7** having a regular pentagon:

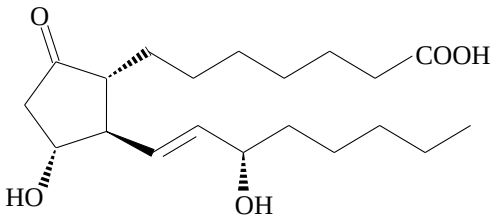


31-7 □

Example 31.12. The structure **31-8** of prostaglandin E1 (PGE1) is drawn by the code:

```
\begin{XyMcompd}(1750,800)(-150,-250){cpd:PGE1}{}
\wedgehashedwedge
\FiveCycle(0,0){18}{%
1s==\HashWedgeAsSubstX(0,0)(-90,-120);%
1s==\put(-90,-130){\rotatebox{-18}{\makebox(0,0)[tr]{HO}}};%
4s==\exodoublebond{0};4s==\put(-50,160){\rotatebox{-18}{O}};%
3s==\HashWedgeAsSubstX(0,0)(180,50);%
3s==\put(180,50){\rotatebox{-18}{\hexamethylenei{}{1==(yl);6W==COOH}}};%
2s==\WedgeAsSubstX(0,0)(140,-130);%
2s==\put(140,-130){\rotatebox{-18}{\octamethylene[a]{}{1==(yl);3A==OH}}}}
\end{XyMcompd}
```

where the four substituents of the cyclopentane ring are placed according to the atom replacement using the ⟨atomlist⟩ of `\FiveCycle`. This code generates the following formula:



31-8 □

31.3 Command for Drawing Rotatable Seven-Membered Rings

In this section, we will define a command named `\SevenCycle` for drawing rotatable seven-membered rings.

31.3.1 Syntax of the Command `\SevenCycle`

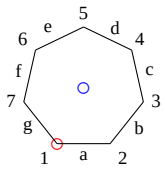
The syntax of the command `\SevenCycle` is as follows:

```
\SevenCycle(⟨refpoint⟩){⟨rotdegree⟩}[⟨bondlist⟩]{⟨atomlist⟩}[⟨delbdlist⟩]
```

The default coordinates of respective vertices of `\SevenCycle` are assigned to be

1 — (0, 0); 2 — (200, 0); 3 — (325, 157); 4 — (281, 352); 5 — (100, 439);
6 — (−81, 352); 7 — (−125, 157)

where the locant numbers are shown bellow:



The center of the regular heptagon is located at (100, 208), as marked by a blue circle.

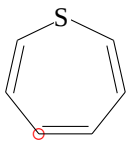
The argument ⟨refpoint⟩ denotes the coordinate of a shifted reference point. The original reference point (0, 0) is located at the 1-position, as shown by a red small circle. The argument ⟨rotdegree⟩ denotes the angle of rotation, the value of which is determined anti-clockwise. The rotation is operated around the shifted reference point. The optional argument ⟨bondlist⟩ is a list of locant alphabets selected from `a`–`g` to assign skeletal double bonds, where the syntax is based on the general convention described in Subsection 3.3.1. The argument ⟨atomlist⟩ is a list of skeletal atoms, where the syntax is based on the general convention described in Subsection 3.2.2. The optional argument ⟨delbdlist⟩ is a list of deleted bonds, where the syntax is based on the general convention described in Subsection 3.3.3.

The effect of rotation angles is shown in Fig. 31.2, where the value 13 is calculated by $90-(128.6\times2-180)$, because the internal angle of a regular pentagon is equal to $180 \times 5/7 = 128.6°$. The angle 26° is calculated to be $(180 - 128.6)/2$. Each reference point (center of rotation) is located at the vertex marked with a red small circle.

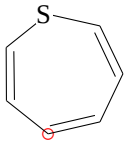
31.3.2 Definition of the Command `\SevenCycle`

The definition of the command `\SevenCycle` is based on the conventions of the XeLaTeX system. The source list is shown below. Although complicated treatments by `\@ifnextchar` are preliminarily conducted to treat optional arguments, the net command of `\SevenCycle` is `\@@SevenCycle` with six arguments.

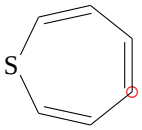
```
\makeatletter
\def\SevenCycle(#1,#2)#3{\@ifnextchar[{\@SevenCycle(#1,#2){#3}}%
```



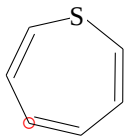
\SevenCycle(0,0){0}[acf]{5==S}



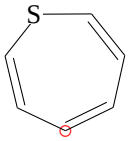
\SevenCycle(0,0){13}[acf]{5==S}



\SevenCycle(0,0){90}[acf]{5==S}



\SevenCycle(0,0){-13}[acf]{5==S}



\SevenCycle(0,0){26}[acf]{5==S}

Figure 31.2. Effect of rotation angles by ⟨rotdegree⟩ of \SevenCycle. Each reference point (center of rotation) is located at the vertex marked with a red small circle.

```
{\@SevenCycle(#1,#2){#3}[]}%
\def\@SevenCycle(#1,#2)#3[#4]#5{%
\@ifnextchar[{\@@SevenCycle(#1,#2){#3}[#4]{#5}}%
{\@@SevenCycle(#1,#2){#3}[#4]{#5}[]}}
\def\@@SevenCycle(#1,#2)#3[#4]#5[#6]{%
\rotatebox{#3}{%
\begin{picture}(0,0)(#1,#2)%
%%%%%%%%%%%%%%%
%double bonds%
%%%%%%%%%%%%%%%
\@tfor\member:=#4\do{%bondlist
\if\member a\relax
\PutBondLine(13,28)(187,28){\thinLineWidth}%
\else\if\member b\relax
\PutBondLine(187,28)(295,153){\thinLineWidth}%
\else\if\member c\relax
\PutBondLine(295,153)(256,332){\thinLineWidth}%
\else\if\member d\relax
\PutBondLine(256,332)(100,409){\thinLineWidth}%
\else\if\member e\relax
\PutBondLine(100,409)(-56,332){\thinLineWidth}%
\else\if\member f\relax
\PutBondLine(-56,332)(-95,153){\thinLineWidth}%
\else\if\member g%left aromatic circle
\PutBondLine(-95,153)(13,28){\thinLineWidth}%
\fi\fi\fi\fi\fi\fi\fi%
}%
%%%%%%%%%%%%%%%%%
%skeletal bonds%
%%%%%%%%%%%%%%%%%
{\resetbdsw%
```

```
\@bond@@omit{#6}%
\ifx\@aaa\empty\else
\PutBondLine(0,0)(200,0){\thinLineWidth}\fi%bond a (1--2)
\ifx\@bbb\empty\else
\PutBondLine(200,0)(325,157){\thinLineWidth}\fi%bond b (2--3)
\ifx\@ccc\empty\else
\PutBondLine(325,157)(281,352){\thinLineWidth}\fi%bond c(3--4)
\ifx\@ddd\empty\else
\PutBondLine(281,352)(100,439){\thinLineWidth}\fi%bond d (4--5)
\ifx\@eee\empty\else
\PutBondLine(100,439)(-81,352){\thinLineWidth}\fi%bond e (5--6)
\ifx\@fff\empty\else
\PutBondLine(-81,352)(-125,157){\thinLineWidth}\fi%bond f (6--7)
\ifx\@ggg\empty\else
\PutBondLine(-125,157)(0,0){\thinLineWidth}\fi%bond g (7--1)
}%
%%%%%%%%%%%%%%%%
%skeletal atoms%
%%%%%%%%%%%%%%%%
{\@tempcnta=-#3\relax
\@forsemicol\member:=#5\do{%
\ifx\member\empty \relax\else%
\expandafter\@m@mb@r\member;\relax%
\expandafter\twoch@r\@membera{}\relax%
\if\@tmpb s\relax
\let\PutAtomRotatedR=\PutAtomRotatedRb
\let\PutAtomRotatedL=\PutAtomRotatedLb
\else
\let\PutAtomRotatedR=\PutAtomRotatedRa
\let\PutAtomRotatedL=\PutAtomRotatedLa
\fi
\ifcase\@tmpa \relax%
\or%position 1
\PutAtomRotatedL(0,0){\the\@tempcnta}{\@memberb}%
\or%position 2
\PutAtomRotatedR(200,0){\the\@tempcnta}{\@memberb}%
\or%position 3
\PutAtomRotatedR(325,157){\the\@tempcnta}{\@memberb}%
\or%position 4
\PutAtomRotatedR(281,352){\the\@tempcnta}{\@memberb}%
\or%position 5
\PutAtomRotatedR(100,439){\the\@tempcnta}{\@memberb}%
\or%position 6
\PutAtomRotatedL(-81,352){\the\@tempcnta}{\@memberb}%
\or%position 7
\PutAtomRotatedL(-125,157){\the\@tempcnta}{\@memberb}%
\fi\fi}}%
\end{picture}}%
}
\makeatother
```

The above source list of `\SevenCycle` has the same construction as that of `\FiveCycle`. Thus, the processing of the arguments ⟨refpoint⟩ (`(#1,#2)`) and ⟨rotdegree⟩ (`#3`) are conducted by using the common commands defined in Section 31.1. The processing of the ⟨bondlist⟩ (`#4`) is based on the LaTeX command `\@tfor`, which is a common way to the XeLaTeX system. The processing of the ⟨aromlist⟩ (`#5`) is conducted by using the XeLaTeX command `\@forsemicol`, which is a list-treating command with considering a

semicolon as a delimiter. The processing of the optional argument ⟨delbdlist⟩ (#6) is based on the XyMTEX command \@bond@@omit, which detects skeletal bonds to be deleted.

As found in the syntax on page 537, the command \SevenCycle lacks the argument ⟨subslist⟩ in a similar way to FiveCycle (cf. the syntax on page 529), Hence, a substituent with a bond is attached to the seven-membered ring through the ⟨atomlist⟩ by virtue of the atom replacement (an improper application of the replacement technique).

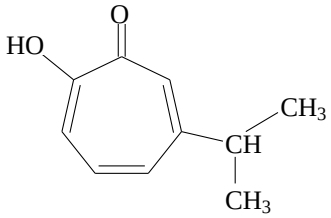
31.3.3 Examples of Using \SevenCycle

Monocyclic Compounds

Example 31.13. The structure of hinokitiol (cf. **30-4** in Section30.2) is drawn by using the newly-defined command \SevenCycle. Three substituents are specified by the replacement technique (not by the substitution technique), as found in the code:

```
\begin{XyMcompd}(1100,800)(-300,-150){cpd:hinokitiolX}{}
\SevenCycle(0,0){0}[acf]{%
5s==\exodoublebond{0};5==\put(0,160){O};%
6s==\exosinglebond{51};6==\put(-150,130){HO};%
3s==\exosinglebond{-103};%
3==\put(180,0){\Utrigonal{3==(yl);0==CH;1==CH$_{3}$;2==CH$_{3}$}}}
\end{XyMcompd}
```

where a set of a linking bond and a substituent is input by using the ⟨atomlist⟩ of the command \SevenCycle. The rotation angle 51° for the hydroxyl is calculated to be 180 − 129, while the rotation angle 103° for the isopropyl is calculated to be 13 + 90. This code generates an equivalent structure of hinokitiol:

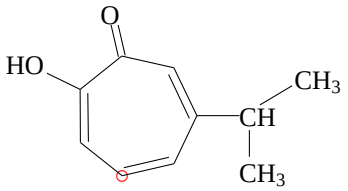


31-9

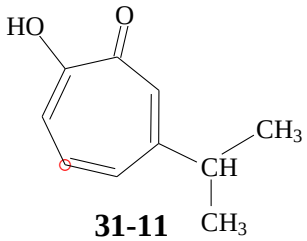
The following codes depict two diagrams after rotation:

```
\begin{XyMcompd}(1100,800)(-300,-150){cpd:hinokitiolY}{}
\put(0,0){\redx{\circle{40}}}
\SevenCycle(0,0){13}[acf]{%
5s==\exodoublebond{0};5==\put(0,160){O};%
6s==\exosinglebond{51};6==\put(-150,130){HO};%
3s==\exosinglebond{-103};%
3==\put(180,0){\Utrigonal{3==(yl);0==CH;1==CH$_{3}$;2==CH$_{3}$}}}
\end{XyMcompd}
\qquad
\begin{XyMcompd}(1100,800)(-300,-150){cpd:hinokitiolZ}{}
\put(0,0){\redx{\circle{40}}}
\SevenCycle(0,0){-13}[acf]{%
5s==\exodoublebond{0};5==\put(0,160){O};%
6s==\exosinglebond{51};6==\put(-150,130){HO};%
3s==\exosinglebond{-103};%
3==\put(180,0){\Utrigonal{3==(yl);0==CH;1==CH$_{3}$;2==CH$_{3}$}}}
\end{XyMcompd}
```

where each isopropyl group retains its original output of vertical direction (in particular, see the vertical downward methyl group):



31-10

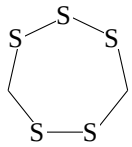


31-11

□

Example 31.14. The structure **31-12** of lenthionine is drawn by the code:

```
\begin{XyMcompd}(400,500)(-120,-20){cpd:lenthionine}{}
\SevenCycle(0,0){0}{1==S;2==S;4==S;5==S;6==S}
\end{XyMcompd}
```



31-12

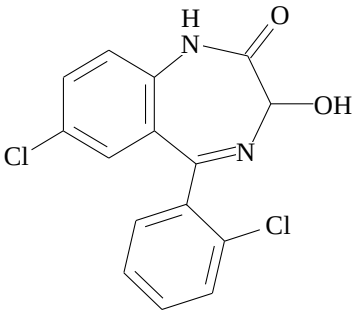
□

Fused and Spiro Ring Systems

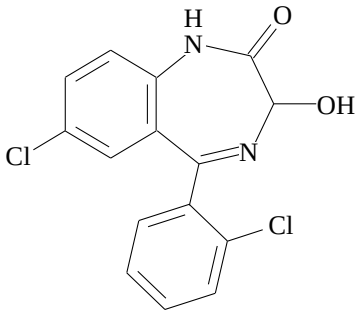
Example 31.15. The structure of lorazepam (Wypax®) is drawn in two ways. The left diagram **31-13** is drawn by the addition technique, where `\SevenCycle` is declared in the ⟨bondlist⟩ of `\sixheterov`. Note that the nested structure due to `\SevenCycle` is regarded as a fusing unit, as found in the first code. On the other hand, the left diagram **31-14** is drawn by an improper application of the replacement technique, where `\SevenCycle` is declared in the ⟨atomlist⟩ of `\sixheterov`. Thus, the nested structure due to `\SevenCycle` is regarded as a hypothetical skeletal atom in the second code, but it results in ring fusion under the diagrammatic condition at issue.

```
\begin{XyMcompd}(1250,1200)(0,-350){cpd:lorazepamA}{}
\sixheterov[bdf%
{B\SevenCycle(-125,157){13}[a]{%
2==N;5==\put(0,50){\upnobond{N}{H}};%
4s==\exodoublebond{-51};4==\put(160,120){O};%
3s==\exosinglebond{-103};3==\put(200,-50){OH};%
1s==\exosinglebond{154};%
1s==\put(-70,-140){\rotatebox{-26}{\benzenev{1==(yl);2==\rotatebox{13}{Cl}}}}%
}[f]}]{}{5==Cl}
\end{XyMcompd}
\qquad
\begin{XyMcompd}(1250,1200)(0,-350){cpd:lorazepamB}{}
\sixheterov[bdf]{%
3s==\SevenCycle(-125,157){13}[a]{%
2==N;5==\put(0,50){\upnobond{N}{H}};%
4s==\exodoublebond{-51};4==\put(160,120){O};%
3s==\exosinglebond{-103};3==\put(200,-50){OH};%
1s==\exosinglebond{154};%
1s==\put(-70,-140){\rotatebox{-26}{\benzenev{1==(yl);2==\rotatebox{13}{Cl}}}}%
}[f]}{5==Cl}
\end{XyMcompd}
```

The angle $-51°$ is calculated to be $129 - 180$, the angle $-103°$ is calculated to be $-(90 + 13)$, and the angle $154°$ is calculated to be $90 + 128.6/2$. These codes generate equivalent diagrams of lorazepam:



31-13



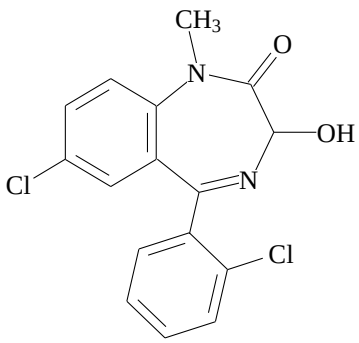
31-14

□

Example 31.16. The structure **31-15** of lormetazepam (Evamyl®) can be drawn by a slight modification of the code for drawing **31-14** (an improper application of the replacement technique), where the moiety NH is changed into N—CH_3. Thus, the code:

```
\begin{XyMcompd}(1250,1300)(0,-350){cpd:lormetazepam}{}
\sixheterov[bdf]{%
3s==\SevenCycle(-125,157){13}[a]{%
5s==\exosinglebond{0};5==\put(0,200){CH$_{3}$};%
2==N;5==N;%
4s==\exodoublebond{-51};4==\put(160,120){O};%
3s==\exosinglebond{-103};3==\put(200,-50){OH};%
1s==\exosinglebond{154};%
1s==\put(-70,-140){\rotatebox{-26}{\benzenev{1==(yl);2==\rotatebox{13}{Cl}}}}%
}[f]}{5==Cl}
\end{XyMcompd}
```

generates the following diagram:



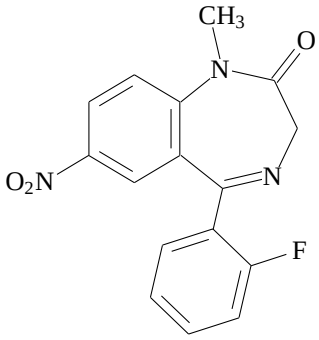
31-15

□

Example 31.17. The structure **31-16** of flunitrazepam (Silece®, Rohypnol®) is drawn by a similar code, where several substituents are changed in comparison with lormetazepam **31-15**. Thus the code:

```
\begin{XyMcompd}(1150,1300)(-50,-350){cpd:flunitrazepam}{}
\sixheterov[bdf]{%
3s==\SevenCycle(-125,157){13}[a]{%
5s==\exosinglebond{0};5==\put(0,200){CH$_{3}$};%
2==N;5==N;%
4s==\exodoublebond{-51};4==\put(160,120){O};%
1s==\exosinglebond{154};%
1s==\put(-70,-140){\rotatebox{-26}{\benzenev{1==(yl);2==\rotatebox{13}{F}}}}%
}[f]}{5==O$_{2}$N}
\end{XyMcompd}
```

generates the following diagram:

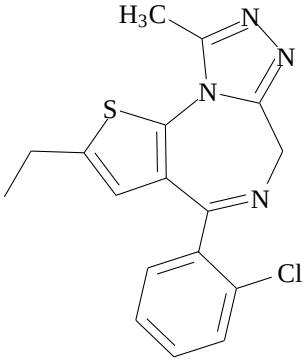


31-16 □

Example 31.18. The structure **31-17** of etizolam (Depas®) is drawn by the code:

```
\begin{XyMcompd}(1100,1350)(-450,-600){cpd:etizolam}{}
\FiveCycle(0,0){19}[be]{4==S;%
5s==\rotatebox{10}{\trimethylene{}{3==(yl)}};%
2s==\SevenCycle(-125,157){-6}[a]{%
2==\rotatebox{-19}{N};%
5s==\FiveCycle(0,0){-25}[bd]{%
3==\rotatebox{-13}{N};4==\rotatebox{-13}{N};%
5s==\exosinglebond{72};%
5==\put(-180,50){\rotatebox{-13}{\llap{H$_{3}$}C}}%
}[a];%
5==\rotatebox{-19}{N};%
1s==\exosinglebond{154};%
1s==\put(-70,-140){\rotatebox{-26}{\benzenev{1==(yl);2==\rotatebox{13}{Cl}}}}%
}[f]}
\end{XyMcompd}
```

where several rotation angles are determined by trial and error. This code generates the following diagram:

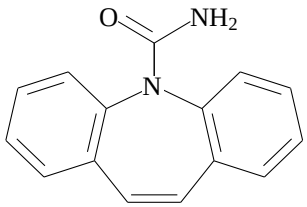


31-17 □

Example 31.19. The structural formula of carbamazepin, which has been shown in Section 30.2.2 (**30-7**) is alternatively drawn by the new commands defined in this chapter. Thus, the code:

```
\begin{XyMcompd}(1050,750)(-450,0){cpd:carbamazepinZ}{}
\SevenCycle(0,0){0}[a]{%
5s==\exosinglebond{0};%
5s==\put(0,160){\trimethylenei[a]{1==O;3==NH$_{2}$}{2==(yl);2==\null}};
5==N;%
3s==\rotatebox{13}{\sixfusev[ace]{}{}{e}};%
7s==\rotatebox{-13}{\sixfusev[bdf]{}{}{B}}}
\end{XyMcompd}
```

generates an equivalent structural formula **31-18** of carbamazepin as follows:



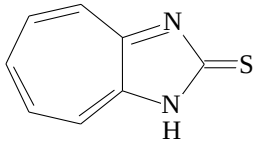
31-18

□

Example 31.20. The structural formula **31-19** of 1,3-diazaazulene-2(1*H*)-thione is drawn by the code:

```
\begin{XyMcompd}(850,550)(-50,-100){cpd:diazulene}{}
\SevenCycle(0,0){-13}[beg]{%
3s==\FiveCycle(0,0){-5}[d]{%
2==\rotatebox{13}{\raisebox{-4pt}{\downnobond{\SetTwoAtomx{N}}{H}}};%
4==\rotatebox{13}{N};%
3s==\exodoublebond{-72};3==\put(160,50){\rotatebox{13}{S}}}}[c]
\end{XyMcompd}
```

which adopts the fusion of type 7 ← 5. This code generates the following diagram:

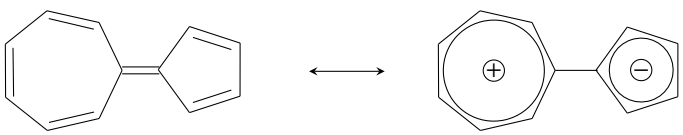


31-19

□

Example 31.21. The structure **31-20** of sesquifulvalene (cyclopentadienylidenecycloheptratriene) [1,2] and its ionic structure **31-21** can be drawn by inputting the codes:

```
\begin{XyMcompd}(800,500)(-100,0){cpd:sesquifulvalene}{}
\SevenCycle(0,0){13}[adf]{%                          %7-membered ring
3s==\exodoublebond{-103};%                           %= exocyclic double bond
3s==\put(133,-28){\FiveCycle(-62,190){5}[ac]{}}%     %5-membered ring
}
\end{XyMcompd}
\qquad\reactlrarrow{5pt}{1cm}{}{}\qquad
\makeatletter
\begin{XyMcompd}(800,500)(-100,0){cpd:sesquifulvaleneion}{}
\SevenCycle(0,0){13}{%                                 %7-membered ring
5s==\Put@oCircle(0,-231){380};%
5s==\Put@oCircle(0,-231){80};%
5s==\put(0,-231){\rotatebox{-13}{\makebox(0,0){$+$}}};%
3s==\exosinglebond{-103};%                             %= exocyclic single bond
3s==\put(150,-34){\FiveCycle(-62,190){5}{%             %5-membered ring
4s==\Put@oCircle(0,-170){240};%
4s==\Put@oCircle(0,-170){80};%
4s==\put(0,-170){\rotatebox{-18}{\makebox(0,0){$-$}}}%
}}}%
\end{XyMcompd}
\makeatother
```



31-20 **31-21**

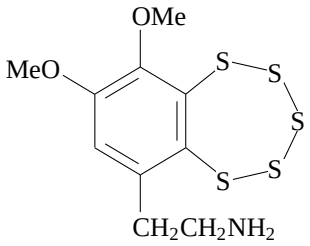
□

Several Natural Products with Seven-Membered Rings

Example 31.22. Varacin **31-22** is a product of marine origin, which has a 1,2,3,4,5-pentathiepin moiety. The structure **31-22** of varacin is drawn by the code:

```
\begin{XyMcompd}(1100,1000)(-100,-50){cpd:varacin}{}
\sixheterov[bdf%
{B\SevenCycle(-125,157){13}{%
1==S;2==S;3==S;4==S;5==S}[f]}%
]{}{1==OMe;6==MeO;4==CH$_{2}$CH$_{2}$NH$_{2}$}
\end{XyMcompd}
```

where the ring fusion is based on the addition technique. This mode of drawing is essentially parallel to the one of drawing **31-13**. The above code generates the following formula:



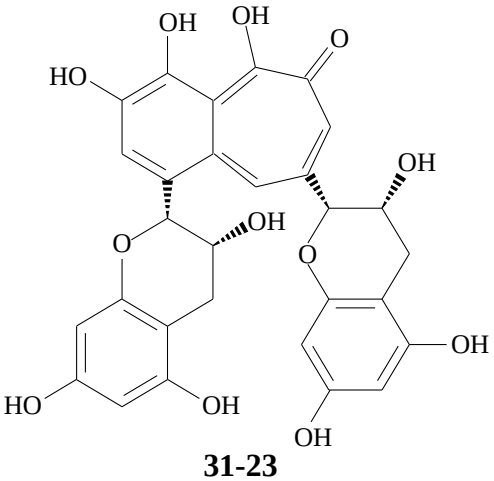
31-22

Note that the same structure can be drawn according to an improper application of the replacement technique in a parallel way to **31-14**. □

Example 31.23. Theaflavin is an antioxidant polyphenol formed during the enzymatic oxidation of tea leaves. The structure **31-23** of theaflavin is drawn by the code:

```
\begin{XyMcompd}(1750,1700)(-200,-750){cpd:theaflavin}{}
\wedgehashedwedge
\sixheterov[df]{%
4s==\put(0,-140){\decaheterovt[fhk]{1==O}{2==(yl);2A==\null;3A==OH;5==OH;7==HO}};
3s==\SevenCycle(-125,157){13}[beg]{%
5s==\exosinglebond{0};5==\put(0,200){OH};%
4s==\exodoublebond{-51};4==\put(160,120){O};%
2s==\put(50,-140){\rotatebox{-13}{\decaheteroh[fhk]{1==O}{2==(yl);2A==\null;%
3A==OH;5==OH;7==OH}}}%
}[f]}{1==OH;6==HO}
\end{XyMcompd}
```

where `\decaheterovt` is not rotated but `\decaheteroh` is rotated clockwise by 13°.



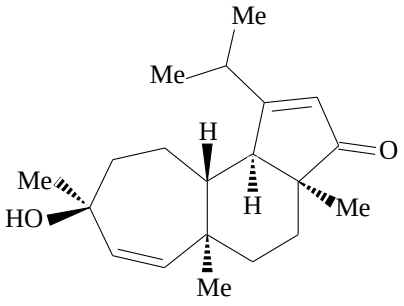
31-23

Note that the ⟨subslist⟩ of `\decaheterovt` (or `\decaheteroh`) contains a rather irregular specification, `2==(yl);2A==\null`. This specification indicates that the (yl)-function (due to `2==(yl)`) shifts the reference point to the 2-position of `\decaheterovt` (or `\decaheteroh`), to which a hashed-wedged bond (due to `2A==\null`) is attached as an apparently dimensionless object. □

Example 31.24. A total synthesis of (+)-cyanthiwigin U, which is a tricyclic terpene, has been reported [3]. For the methodology (cascade reactions) of total synthesis, see [4]. The structure **31-24** of (+)-cyanthiwigin U is drawn by the code:

```
\begin{XyMcompd}(1400,1150)(-500,100){cpd:cyanthiwiginU}{}
\wedgehashedwedge
\sixheterov{%six-membered ring
1s==\HashWedgeAsSubstX(0,-10)(0,-140);%
1s==\put(0,-160){\makebox(0,0)[t]{H}};%
5s==\SevenCycle(325,157){-13}[a]{%seven-membered ring
7s==\HashWedgeAsSubstX(-14,7)(-140,70);%
7s==\put(-160,70){\rotatebox{13}{\makebox(0,0)[r]{Me}}};
7s==\WedgeAsSubstX(0,0)(-140,-80);%
7s==\put(-160,-80){\rotatebox{13}{\makebox(0,0)[r]{HO}}}}[c];%
2s==\FiveCycle(0,0){42}[c]{%five-membered ring
4s==\rotatebox{-55}{%
\trimethylene{1==\rotatebox{13}{Me}}{3==(yl);2==\rotatebox{13}{Me}}};%
2s==\exodoublebond{-140};2s==\put(80,-140){\rotatebox{-40}{O}}[e]%
}{5FA==Me;6GB==H;2GA==Me}
\end{XyMcompd}
```

where `\SevenCycle` and `\FiveCycle` are declared in the ⟨atomlist⟩ of the outer command `\sixheterov` according to improper applications of the replacement technique (not the addition technique). This code generates the following formula:



31-24

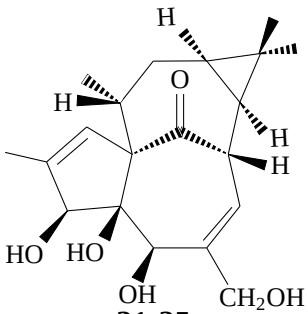
□

Example 31.25. Ingenol 3-angelate is a medicine for solar keratosis. A total synthesis of ingenol has been reported [5]. The structure **31-25** of ingenol is drawn by inputting the code:

```
\begin{XyMcompd}(1100,1150)(-550,-200){cpd:ingenol}{}
\wedgehashedwedge
\SevenCycle(0,0){0}[b]{%seven-membered ring
5s==\exodoublebond{0};5s==\put(0,160){\makebox(0,0)[b]{O}};%
4s==\HashWedgeAsSubstX(0,0)(-181,87);%
6s==\HashWedgeAsSubstX(0,0)(181,87);%
4s==\SevenCycle(200,0){26}{%seven-membered ring
6s==\HashWedgeAsSubstX(0,0)(-80,140);%
6s==\WedgeAsSubstX(0,0)(-140,80);%
6s==\put(-160,80){\rotatebox{-26}{\makebox(0,0)[r]{H}}};%
3s==\rotatebox{-18}{\threefusev{}{%
1SA==\raisebox{5pt}{\rotatebox{-5}{~~H}};%
3Sd==\raisebox{5pt}{\rotatebox{-5}{H}};%
2SA==\null;2SB==\null}{C}}
```

```
}[ag];%
4s==\WedgeAsSubstX(0,0)(140,-40);4s==\put(160,-40){\makebox(0,0)[l]{H}};%
1s==\WedgeAsSubstX(0,0)(-60,-120);1s==\put(-60,-140){\makebox(0,0)[t]{OH}};%
7s==\WedgeAsSubstX(0,0)(-60,-120);7s==\put(-60,-140){\makebox(0,0)[tr]{HO}};%
2s==\exosinglebond{-150};%
2s==\put(80,-150){\makebox(0,0)[t]{C\rlap{H$_{2}$OH}}};%
7s==\FiveCycle(200,0){5}[d]{%five-membered ring
1s==\WedgeAsSubstX(0,0)(-100,-100)[12];%
1s==\put(-100,-120){\rotatebox{-5}{\makebox(0,0)[tr]{HO}}};%
5s==\exosinglebond{72}}[b]%
}[de]
\end{XyMcompd}
```

where \SevenCycle and \FiveCycle are declared in the ⟨atomlist⟩ of the outer command \SevenCycle according to improper applications of the replacement technique (not the addition technique). The inner \SevenCycle is further fused by a three-membered ring. This code generates the following formula:



31-25

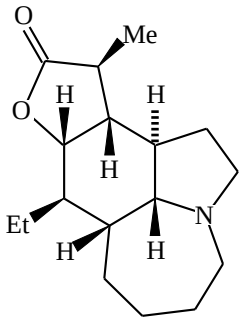
Note that the skeletal bonds of the inner command \SevenCycle are deleted by declaring ⟨delbdlist⟩, i.e., [ag]. Thereby, the inner bicyclo[4.4.1]undecane part is constructed. □

Example 31.26. An expeditious total synthesis of (±)-stenine has been recently reported [6]. For the methodology (cascade reactions) of total synthesis, see [4]. The structure **31-26** of stenine is drawn by the code:

```
\begin{XyMcompd}(800,1200)(50,-100){cpd:stenine}{}
%\wedgehashedwedge
\def\thinLineWidth{0.8pt}
\def\thickLineWidth{2.8pt}
\sixheterov{%
1s==\WedgeAsSubstX(0,0)(0,-140);%
1s==\put(0,-160){\makebox(0,0)[t]{H}};%
4s==\SevenCycle(-81,352){7}{%seven-membered ring
}[de];%
3s==\FiveCycle(0,0){-18}{%five-membered ring
2==N%
}[e];%
6s==\FiveCycle(0,0){30}{%five-membered ring
5==O;%
3s==\WedgeAsSubstX(0,0)(120,40);%
3s==\put(140,60){\rotatebox{-30}{\makebox(0,0)[l]{Me}}};%
4s==\exodoublebond{0};%
4s==\put(0,160){\rotatebox{-30}{\makebox(0,0)[b]{O}}}%;%
}[a]%
}{2FA==H;3GB==H;4GB==H;5B==Et;6GB==H}
\end{XyMcompd}
```

where one of \SevenCycle and two commands of \FiveCycle are declared in the ⟨atomlist⟩ of the outer command \sixheterov. Note that the declaration \wedgehashedwedge (wedges and hashed wedges)

is commented out to return to the default setting of the XyMTEX system (\wedgehasheddash: wedges and hashed dashes). In addition, \thinLineWidth and \thickLineWidth are changed into 0.8pt (default 0.4pt) and 2.8pt (default 1.6pt). Thereby, we obtain the following formula with wedges and dashed bold bonds.



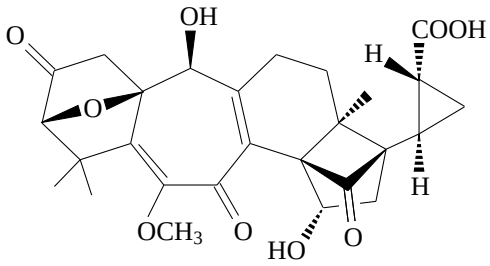
31-26

□

Example 31.27. The structure **31-27** of solanoeclepin A, the total synthesis of which has been recently reported [7], is drawn by the code:

```
\begin{XyMcompd}(1700,1000)(-550,-300){cpd:solanoeclepinA}{}
\wedgehashedwedge
\SevenCycle(0,0){0}[cg]{%seven-membered ring
5s==\WedgeAsSubstX(0,0)(0,140);5s==\put(-40,160){\makebox(0,0)[lb]{OH}};%
2s==\exodoublebond{-150};2s==\put(100,-140){\makebox(0,0)[t]{O}};%
1s==\PutBondLine(0,0)(-60,-120){0.4pt};%
1s==\put(-100,-140){\makebox(0,0)[lt]{OCH$_{3}$}};%
3s==\rotatebox{13}{\sixfusev{%six-membered ring
4s==\FiveCycle(-62,190){-6}{%five-membered ring
1s==\HashWedgeAsSubstX(0,0)(-80,-100);%
1s==\put(-80,-100){\makebox(0,0)[rt]{\rotatebox{-7}{HO}}};%
4s==\put(0,-232){\whitex{\PutBondLine(0,-50)(0,-100){8pt}}};%
4s==\put(0,-232){\exodoublebond{180}};%
4s==\put(0,-392){\makebox(0,0)[t]{\rotatebox{-7}{O}}};%
3s==\WedgeAsSubstX(0,0)(-172,-118);%
5s==\WedgeAsSubstX(0,0)(172,-118);%
4s==\put(0,-232){\exodoublebond{180}};%
3s==\PutBondLine(0,0)(130,42){0.4pt};%
3s==\put(130,42){\rotatebox{-7}{\threeheteroh{}{2==(yl);%
2SA==H;3SB==H;3SA==COOH}}
}[d]%
}{3FA==\null}{e}};%
7s==\rotatebox{-13}{\sixfusev{%six-membered ring
2s==\WedgeAsSubstX(0,0)(-130,-78);%
5s==\WedgeAsSubstX(0,0)(130,78);%
2s==\put(-171,-103){\makebox(0,0){\rotatebox{13}{O}}}%
}{6D==\rotatebox{13}{O};4Sa==\null;4Sb==\null}{B}}}
\end{XyMcompd}
```

which contains all of three- to seven-membered rings. The fused ring system is constructed by the scheme: $6 \to 7 \leftarrow 6 \leftarrow 5$, while the four-membered ring is constructed by low-level commands. The three-membered ring is incorporated as a substituent. This code generates the following structural formula:



31-27 □

31.4 Command for Drawing Rotatable Eight-Membered Rings

In this section, we will define a command named `\EightCycle` for drawing rotatable eight-membered rings.

31.4.1 Syntax of the Command `\EightCycle`

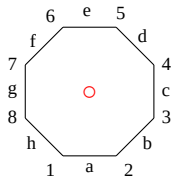
The syntax of the command `\EightCycle` is as follows:

```
\EightCycle(⟨refpoint⟩){⟨rotdegree⟩}[⟨bondlist⟩]{⟨atomlist⟩}[⟨delbdlist⟩]
```

The default coordinates of respective vertices of `\EightCycle` are assigned to be

1 — (−100, −242); 2 — (100, −242); 3 — (242, −100); 4 — (242, 100); 5 — (100, 242);
6 — (−100, 242); 7 — (−242, 100) 8 — (−242, −100)

where the locant numbers are shown bellow:



The center of the regular octagon is located at (100, 208), as marked by a red circle.

The argument ⟨refpoint⟩ denotes the coordinate of a shifted reference point. The original reference point (0, 0) is located at the center of the regular octagon, as shown by a red small circle. The argument ⟨rotdegree⟩ denotes the angle of rotation, the value of which is determined anti-clockwise. The rotation is operated around the shifted reference point. The optional argument ⟨bondlist⟩ is a list of locant alphabets selected from a–g to assign skeletal double bonds, where the syntax is based on the general convention described in Subsection 3.3.1. The argument ⟨atomlist⟩ is a list of skeletal atoms, where the syntax is based on the general convention described in Subsection 3.2.2. The optional argument ⟨delbdlist⟩ is a list of deleted bonds, where the syntax is based on the general convention described in Subsection 3.3.3.

31.4.2 Definition of the Command `\EightCycle`

The definition of the command `\EightCycle` is based on the conventions of the X$\mathfrak{n}$MTEX system. The source list is shown below. Although complicated treatments by `\@ifnextchar` are preliminarily conducted to treat optional arguments, the net command of `\EightCycle` is `\@@EightCycle` with six arguments.

```
\makeatletter
\def\EightCycle(#1,#2)#3{\@ifnextchar[{\@EightCycle(#1,#2){#3}}%
{\@EightCycle(#1,#2){#3}[]}}%
\def\@EightCycle(#1,#2)#3[#4]#5{%
\@ifnextchar[{\@@EightCycle(#1,#2){#3}[#4]{#5}}%
{\@@EightCycle(#1,#2){#3}[#4]{#5}[]}}
```

```
\def\@@EightCycle(#1,#2)#3[#4]#5[#6]{%
\rotatebox{#3}{%
\begin{picture}(0,0)(#1,#2)%
%%%%%%%%%%%%%%%
%double bonds%
%%%%%%%%%%%%%%%
\@tfor\member:=#4\do{%bondlist
\if\member a\relax
\PutBondLine(-88,-212)(88,-212){\thinLineWidth}%
\else\if\member b\relax
\PutBondLine(88,-212)(212,-88){\thinLineWidth}%
\else\if\member c\relax
\PutBondLine(212,-88)(212,88){\thinLineWidth}%
\else\if\member d\relax
\PutBondLine(212,88)(88,212){\thinLineWidth}%
\else\if\member e\relax
\PutBondLine(88,212)(-88,212){\thinLineWidth}%
\else\if\member f\relax
\PutBondLine(-88,212)(-212,88){\thinLineWidth}%
\else\if\member g%left aromatic circle
\PutBondLine(-212,88)(-212,-88){\thinLineWidth}%
\else\if\member h%left aromatic circle
\PutBondLine(-212,-88)(-88,-212){\thinLineWidth}%
\fi\fi\fi\fi\fi\fi\fi\fi%
}%
%%%%%%%%%%%%%%%%
%skeletal bonds%
%%%%%%%%%%%%%%%%
{\resetbdsw%
\@bond@@omit{#6}%
\ifx\@aaa\empty\else
\PutBondLine(-100,-242)(100,-242){\thinLineWidth}\fi%bond a (1--2)
\ifx\@bbb\empty\else
\PutBondLine(100,-242)(242,-100){\thinLineWidth}\fi%bond b (2--3)
\ifx\@ccc\empty\else
\PutBondLine(242,-100)(242,100){\thinLineWidth}\fi%bond c(3--4)
\ifx\@ddd\empty\else
\PutBondLine(242,100)(100,242){\thinLineWidth}\fi%bond d (4--5)
\ifx\@eee\empty\else
\PutBondLine(100,242)(-100,242){\thinLineWidth}\fi%bond e (5--6)
\ifx\@fff\empty\else
\PutBondLine(-100,242)(-242,100){\thinLineWidth}\fi%bond f (6--7)
\ifx\@ggg\empty\else
\PutBondLine(-242,100)(-242,-100){\thinLineWidth}\fi%bond g (7--8)
\ifx\@hhh\empty\else
\PutBondLine(-242,-100)(-100,-242){\thinLineWidth}\fi%bond g (8--1)
}%
%%%%%%%%%%%%%%%%
%skeletal atoms%
%%%%%%%%%%%%%%%%
{\@tempcnta=-#3\relax
\@forsemicol\member:=#5\do{%
\ifx\member\empty \relax\else%
\expandafter\@m@mb@r\member;\relax%
\expandafter\twoch@r\@membera{}\relax%
\if\@tmpb s\relax
\let\PutAtomRotatedR=\PutAtomRotatedRb
```

```
\let\PutAtomRotatedL=\PutAtomRotatedLb
\else
\let\PutAtomRotatedR=\PutAtomRotatedRa
\let\PutAtomRotatedL=\PutAtomRotatedLa
\fi
\ifcase\@tmpa \relax%
\or%position 1
\PutAtomRotatedL(-100,-242){\the\@tempcnta}{\@memberb}%
\or%position 2
\PutAtomRotatedR(100,-242){\the\@tempcnta}{\@memberb}%
\or%position 3
\PutAtomRotatedR(242,-100){\the\@tempcnta}{\@memberb}%
\or%position 4
\PutAtomRotatedR(242,100){\the\@tempcnta}{\@memberb}%
\or%position 5
\PutAtomRotatedR(100,242){\the\@tempcnta}{\@memberb}%
\or%position 6
\PutAtomRotatedL(-100,242){\the\@tempcnta}{\@memberb}%
\or%position 7
\PutAtomRotatedL(-242,100){\the\@tempcnta}{\@memberb}%
\or%position 8
\PutAtomRotatedL(-242,-100){\the\@tempcnta}{\@memberb}%
\fi\fi}%
\end{picture}}%
}
\makeatother
```

The above source list of `\EightCycle` has the same construction as that of `\FiveCycle` or `\SevenCycle`. Thus, the processing of the arguments ⟨refpoint⟩ (`(#1,#2)`) and ⟨rotdegree⟩ (`#3`) are conducted by using the common commands defined in Section 31.1. The processing of the ⟨bondlist⟩ (`#4`) is based on the LaTeX command `\@tfor`, which is a common way to the XyMTeX system. The processing of the ⟨aromlist⟩ (`#5`) is conducted by using the XyMTeX command `\@forsemicol`, which is a list-treating command with considering a semicolon as a delimiter. The processing of the optional argument ⟨delbdlist⟩ (`#6`) is based on the XyMTeX command `\@bond@@omit`, which detects skeletal bonds to be deleted.

As found in the syntax on page 549, the command `\EightCycle` lacks the argument ⟨subslist⟩ in a similar way to `FiveCycle` (cf. the syntax on page 529) or to `SevenCycle` (cf. the syntax on page 537), Hence, a substituent with a bond is attached to the eight-membered ring through the ⟨atomlist⟩ by virtue of the atom replacement (an improper application of the replacement technique).

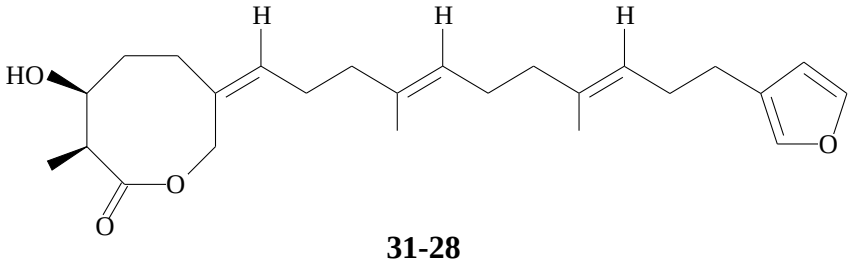
31.4.3 Examples of Using `\EightCycle`

Monocyclic Compounds

Example 31.28. Astakolactin is a sesterterpene isolated from the mediterranean sponge Cacospongia scalaris. The structure **31-28** of astakolactin is drawn by the code:

```
\begin{XyMcompd}(3050,900)(-500,-400){cpd:astakolactin}{}
\EightCycle(0,0){0}{%
1s==\exodoublebond{150};1s==\put(-110,-190){O};2==O;%
7s==\WedgeAsSubst(0,0)(-2,1){140};%
7s==\put(-160,70){\makebox(0,0)[r]{HO}};%
8s==\WedgeAsSubst(0,0)(-2,-1){140};%
4s==\decamethylene[aei]{%
{10}s==\tetramethylenei{%
4s==\FiveCycle(-62,190){0}[ce]{2==O}}{1==(yl)}%
}{1==(yl);2==H;5==\null;6==H;9==\null;{{10}}==H}}
\end{XyMcompd}
```

The linking unit of carbon content 11 is constructed by combining `\decamethylene` (carbon content 10) and `\tetramethylenei` (carbon content 4), where 10 + 4 − 1(joint) − 2(terminals) = 11. The above code generates the following structure:

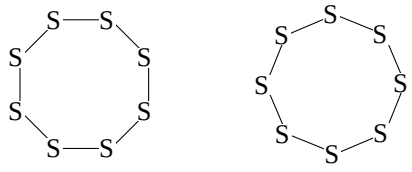


31-28 □

Example 31.29. The following examples exhibit the effects of rotations: Thus, the codes:

```
\begin{XyMcompd}(600,600)(-350,-300){}{}
\EightCycle(0,0){0}{%
1==S;2==S;3==S;4==S;5==S;6==S;7==S;8==S}
\end{XyMcompd}
\qquad
\begin{XyMcompd}(600,600)(-350,-300){}{}
\EightCycle(0,0){23}{%
1==S;2==S;3==S;4==S;5==S;6==S;7==S;8==S}
\end{XyMcompd}
```

generate a diagram of default direction and a rotated one.



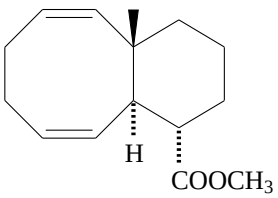
□

Fused and Spiro Ring Systems

Example 31.30. An six-to-eight fused system **31-29** is drawn by the code:

```
\begin{XyMcompd}(1000,750)(-150,-200){cpd:six-eightA}{}
\EightCycle(-100,-242){0}[ae]{%
3s==\sixheterov{}{5==(yl);4A==COOCH$_{3}$;5FA==H;6GB==\null}[e]}
\end{XyMcompd}
```

which is based on an improper application of the replacement technique (not on the addition technique). This code generates the following formula:

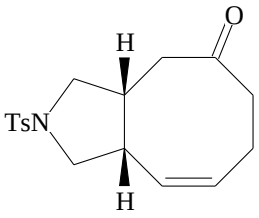


31-29 □

Example 31.31. An six-to-eight fused system **31-30** is drawn by the code:

```
\begin{XyMcompd}(900,800)(-550,-100){cpd:five-eightA}{}
\EightCycle(-100,-242){0}[a]{%
5s==\exodoublebond{-22};5==\put(80,160){O};%
8s==\FiveCycle(200,0){18}{5==\llap{Ts}N}[b];%
7s==\WedgeAsSubst(0,0)(0,1){140};7==\put(0,200){H};%
8s==\WedgeAsSubst(0,0)(0,-1){140};8==\put(0,-200){H}}
\end{XyMcompd}
```

where the ring-fusion is based on an improper application of the replacement technique (not on the addition technique). Substituents on the eight-membered ring are placed by using the ⟨atomlist⟩ (not ⟨subslist⟩) according to the atom-replacement technique. This code generates the following diagram:

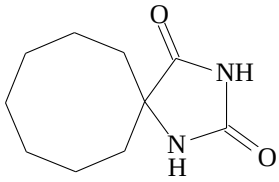


31-30 □

Example 31.32. The structure **31-31** of 1,3-diazaspiro[4.7]dodecane-2,4-dione is drawn by the code:

```
\begin{XyMcompd}(950,700)(-250,-50){cpd:diaza12-47}{}
\EightCycle(-100,-242){23}{%
3s==\FiveCycle(-62,190){-5}{%
1==\put(-15,-80){\rotatebox{-23}{H}};
1==\rotatebox{-23}{N};3==\rotatebox{-23}{\SetTwoAtomx{NH}};%
4s==\exodoublebond{5};4==\put(-10,180){\rotatebox{-23}{O}};%
2s==\exodoublebond{-144};2==\put(110,-150){\rotatebox{-23}{O}}}}
\end{XyMcompd}
```

where the spiro fusion is accomplished by the replacement technique. Thus, `\FiveCycle` is declared in the ⟨atomlist⟩ of `\EightCycle`. This code generates the following formula:



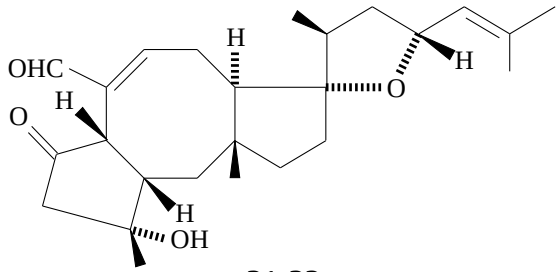
31-31 □

Several Natural Products with Eight-Membered Rings

Example 31.33. A convergent total synthesis of (+)-ophiobolin A has been reported [8]. The structure **31-32** of (+)-ophiobolin A is drawn by the code:

```
\begin{XyMcompd}(2000,1050)(-550,-550){cpd:ophiobolinA}{}
\def\thickLineWidth{3pt}
\EightCycle(0,0){0}[f]{%
7s==\PutBondLine(0,0)(-140,70){0.4pt};%
7s==\put(-160,70){\makebox(0,0)[r]{OHC}};%
1s==\rotatebox{-15}{\fivefusevi{}{1FB==\rotatebox{15}{H};%
2GB==\rotatebox{15}{H};3SB==\null;3SA==\rotatebox{15}{OH};%
5D==\rotatebox{15}{O}}{A}};%
3s==\fivefusev{%
3s==\fiveheterovi{3==\put(-80,0){O};%
2s==\tetramethylene[b]{}{1==(yl);3==\null};%
2s==\PutDashedBond(0,0)(-75,-150){\thickLineWidth};%
4s==\PutDashedBond(0,0)(220,0){\thickLineWidth};%
}{4==(yl);2GB==H;5B==\null}[bc]
}{5FB==\null;4GA==H}{D}
}
\end{XyMcompd}
```

where α-bonds are depicted by using `\PutDashedBond`. The line width of an α-bond is decided to be equal to `\thickLineWidth`, which is change to be 3pt. The above code generates the following diagram:



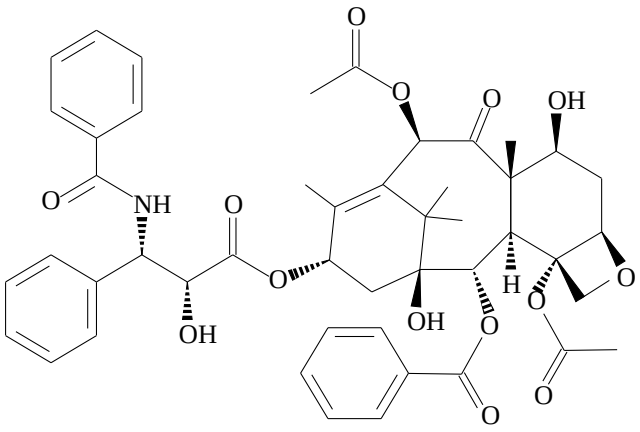
31-32 □

Example 31.34. Paclitaxel (Taxol®) is the most well-known cancer drug of natural source. The structure **31-33** of paclitaxel is drawn by the code:

```
\begin{XyMcompd}(2300,1650)(-1650,-850){cpd:paclitaxel}{}
\wedgehashedwedge
\EightCycle(0,0){0}{%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%replacement of a skeletal bond (f, 6--7)%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
6s==\PutBondLine(0,0)(-140,-165){0.4pt};%
%%%%%%%%%%%%%%%
%substituents%
%%%%%%%%%%%%%%%
5s==\exodoublebond{-22};5==\put(80,160){O};%
6s==\WedgeAsSubstX(0,0)(-60,140)[7];%
6s==\put(-30,200){\trimethylene{3==O}{3==(yl);2D==O}};%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%left (ortho- and peri-fused) six-membered ring%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
1s==\rotatebox{-6}{\sixheterov[f]{}{3==(yl);%
5A==\rotatebox{6}{\pentamethylene{5==O;1s==\benzenev{2==(yl)};%
2s==\put(40,220){%
\trimethylene[a]{3==\null;1==O}{3==(yl);2==\benzenev{4==(yl)}}}}%
{5==(yl);4D==O;3A==OH;2A==NH}};%
2Sa==\null;2Sb==\null;6==\null;3GB==\rotatebox{6}{OH}}};%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%right (ortho-fused) six-membered ring%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
3s==\sixheterov{%
4s==\PutBondLine(90,-150)(200,-80){0.4pt};
4s==\WedgeAsSubstX(0,0)(90,-150);%
}{5==(yl);1B==OH;5FA==H;6GB==\null;
3SB==\put(-30,-30){O};%%4Su==\null;%
4Sd==\put(-100,-50){\rotatebox{-30}{%
\trimethylenei{1==\rotatebox{30}{O}}{1==(yl);2D==\rotatebox{30}{O}}}}};%
%%%%%%%%%%%%%%%
%substituents%
%%%%%%%%%%%%%%%
2s==\HashWedgeAsSubstX(0,0)(60,-160)[7];
2s==\put(100,-220){\rotatebox{30}{%
\trimethylenei{3==\raisebox{3pt}{\rotatebox{-30}{O}};%
1s==\rotatebox{-30}{\benzeneh{4==(yl)}}%
}{3==(yl);2D==\raisebox{3pt}{\rotatebox{-30}{O}}}}}%
}[fgh]
\end{XyMcompd}
```

where two six-membered rings (due to `\sixheterov`) attach to an eight-membered ring (due to `\EightCycle`) in different fashions. The left ring serves as a fusing unit to participate in an ortho- and peri-

fusion (giving a bicyclo[5.3.1]undecane ring), while the right ring serves as a usual fusing unit to participate in an ortho-fusion. The above code generates the following formula:



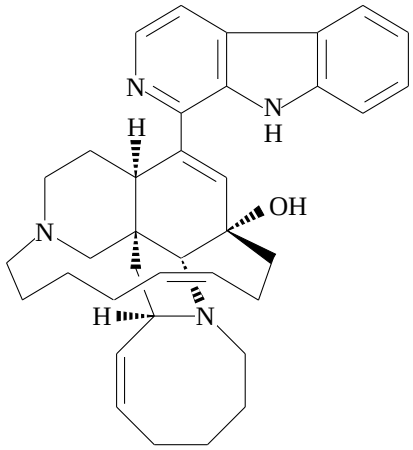
31-33

□

Example 31.35. Total syntheses of manzamine A, which was isolated from a sponge collected in the Okinawa Sea, have been reported extensively[9,10,11]. The structure **31-34** of (+)-manzamine A is drawn by the code:

```
\begin{XyMcompd}(1500,1750)(50,-500){cpd:manzamine}{}
\wedgehashedwedge
\decaheterov[a%
{e\put(0,-140){\PutBondLine(0,0)(70,-180){0.4pt}}}%
{e\put(0,-140){\whitex{\PutBondLine(12,-31)(32,-82){4pt}}}}%
{e\put(70,-320){%
\EightCycle(-100,242){0}[g]{%
5==N;%
6s==\HashWedgeAsSubst(0,0)(-1,0){140};%
6s==\put(-160,0){\makebox(0,0)[r]{H}}}}}
]{%
6s==\PutBondLine(0,0)(-140,-120){0.4pt};%
6s==\PutBondLine(-140,-120)(-80,-260){0.4pt};%
6s==\put(-80,-260){\trimethylene{%
3s==\tetramethylenecap[b]{}{1==(yl)}}{1==(yl)}};%
6==\SetTwoAtomx{N};%
3s==\WedgeAsSubstX(0,0)(171,-103);%
3s==\PutBondLine(171,-103)(116,-260){0.4pt};%
4s==\HashWedgeAsSubstX(0,0)(70,-160)[7];%
4s==\whitex{\PutBondLine(20,-46)(45,-103){6pt}}%
}{3FA==OH;{10}A==H;9A==\null;%
1==\nonaheterov[egj{b\sixfusev[ace]{}{}{e}}]%
{1==\downnobond{N}{H};6==N}{7==(yl)}}
\end{XyMcompd}
```

Note that each background bond incident to the eight-membered ring is erased by a white thick line drawn by using `\whitex{\PutBondLine...}`.

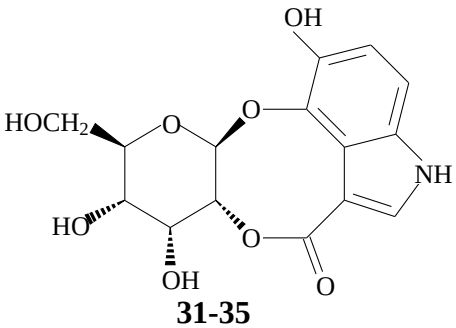


31-34

□

Example 31.36. The structure **31-35** of (−)-ovatolide, a tetracyclic indol alkaloid bearing an eight-membered ether-lactone [12], is drawn as follows:

```
\begin{XyMcompd}(1600,1100)(-950,-200){cpd:ovatolide}{}
\wedgehashedwedge
\EightCycle(-100,-242){0}{%
1==O;6==O;%
8s==\sixheterov{1==O}{3==(yl);4A==OH;5A==HO;6B==HOCH$_{2}$};%
8s==\HashWedgeAsSubst(0,0)(1,-1){100};%
7s==\WedgeAsSubst(0,0)(1,1){100};%
2s==\exodoublebond{-160};%
2==\put(80,-180){O};%
4s==\rotatebox{45}{\sixheterov[ace]{%
4s==\PutBondLine(0,0)(0,-140){0.4pt}}{5==(yl);%
1==\rotatebox{-45}{\raisebox{3pt}{OH}}%
}};%
3s==\FiveCycle(0,0){-18}[a]{3==NH}[cde]%
}[dfgh]
\end{XyMcompd}
```



31-35

□

31.5 Multiple Ring Fusion

Now that we have defined commands for drawing seven- and eight-membered rings, we are ready to draw several complicated compounds of natural source.

31.5.1 Maitotoxin

Maitotoxin **31-39** has attracted extensive interests as the largest and most toxic secondary metabolite known to date. It has a molecular formula $C_{164}H_{256}O_{68}S_2Na_2$, where 32 rings (A to Z and A′ to F′) construct a ladder-like structure [13].

Example 31.37. To avoid an error "TeX capacity exceeded" during TEX/LATEX processing, the structure **31-39** is divided into three domain, i.e., the A-to-M domain, the N-to-V domain, and the W-to-F′ domain.

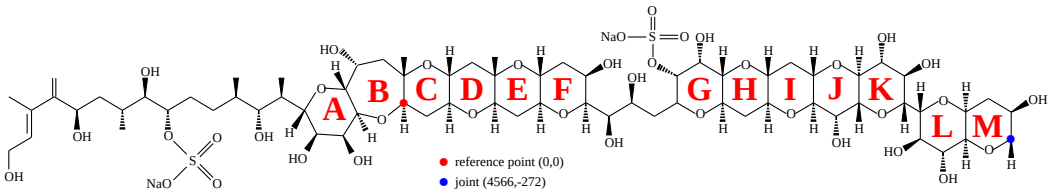
First, a command `\maitotoxinAtoM` is defined to draw the A-to-M domain of maitotoxin, where the C-ring is selected as the outer skeleton.

```
\def\maitotoxinAtoM{%
\begin{picture}(0,0)(0,0)
\sixheterov[%C-ring
%%%%%%%%%%%%%%%%
% right branch %
%%%%%%%%%%%%%%%%
{b\sixfusev[%D-ring
{b\sixfusev[%E-ring
{b\sixfusev[%F-eubf
]{4==O;%
3s==\pentamethylenei{%
5s==\sixheterov[%G-ring
{b\sixfusev[%H-ring
{b\sixfusev[%I-ring
{b\sixfusev[%J-ring
{b\sixfusev%K-ring
{4==O}{2B==OH;3GB==H;1A==OH;%
3==\sixheterov[%L-ring
{b\sixfusev%M-ring
{4==O}{2B==OH;3GB==H}{E}}%end M-ring
]{1==O}{6==(yl);2FA==H;3GA==H;4A==OH;6GB==H;5B==HO}%end L-ring
}{E}}%end K-ring
]{1==O}{2FA==H;3GB==H;4A==OH}{E}}%end J-ring
]{4==O}{2FB==H;3GA==H}{E}}%end I-ring
]{1==O}{2FB==H;3GA==H}{E}}%end H-ring
]{4==O}{5==(yl);1A==OH;2FB==H;3GA==H;%
6A==\lyl(5==O){0==%
\tetrahedral{0==S;3==(yl);1D==O;4D==O;2==NaO}}%end G-ring
}{1==(yl);2B==OH;3B==OH}%
}{2B==OH;3GA==H}{E}}%end F-ring
]{1==O}{2FB==H;3GA==H}{E}}%end E-ring
]{4==O}{2FB==\null;3GA==H}{E}}%end D-ring
%%%%%%%%%%%%%%%%
% left branch %
%%%%%%%%%%%%%%%%
{e\SevenCycle(325,157){-13}{%B-ring
2==O;%
6s==\HashWedgeAsSubstX(0,0)(-140,80);%
6s==\put(-160,80){\rotatebox{13}{\makebox(0,0)[r]{HO}}};%
1s==\rotatebox{40}{\sixfusev%A-ring
{1==\raisebox{2pt}{\rotatebox{-27}{O}};%
6s==\rotatebox{-27}{\octamethylenei{%
1s==\hexamethylene{%
1s==\sixheterov[b]{}{2==(yl);4==OH}[def]%
}{6==(yl);5A==\null;2D==\null;3B==OH}%
}{8==(yl);7B==\null;%
6A==OH;5B==\null;2A==\ryl(0==O){6==%
\squareplanar{4==(yl);0==S;1D==O;2D==O;3==NaO}};%
```

```
1B==OH}}%
}{4B==\rotatebox{-27}{O\rlap{H}};5B==\rotatebox{-27}{\llap{H}O};%
6FB==\raisebox{2pt}{\rotatebox{-27}{H}};2FB==\raisebox{2pt}{\rotatebox{-27}{H}};%
3GA==\rotatebox{-27}{H}}{B}}%end A-ring
}[c]}%end B-ring
]{1==O}{5==(yl);6GB==\null;5FA==H;2FB==H;3GA==H}%end C-ring
\end{picture}}
```

This code contains multiply nested ring fusions, which are shown by pairs of commands such as `%C-ring` and `%end C-ring`. The right branch is drawn by the nested declaration of the D-ring to the M-ring, where the left branch is drawn by the nested declaration of the B-ring and the A-ring (as well as a side chain). Each of the ring fusions is based on the addition technique or an improper application of the replacement technique (B ← A).

The newly-defined command is operated by declaring `\maitotoxinAtoM` so as to generate the following diagram:



31-36 (the A-to-M domain of maitotoxin)

The reference point $(0, 0)$ of the A-to-M domain of maitotoxin **31-36** is located at the leftmost vertex of the C-ring as shown by a red solid circle. On the other hand, a terminal for joint is located at $(4566, -272)$ as shown by a blue solid circle. The x-coordinate of the terminal is calculated to be $171 \times 26 + 120 = 4566$, while the y-coordinate is calculated to be $-(120 \times \frac{103}{171} + 200) = -272$. Note that the value 120 is the x-length of the bond between the K-ring and the L-ring and that the values 171 and 103 are the standard values of a bond with the slope $(5, 3)$ in the XyMTEX system.

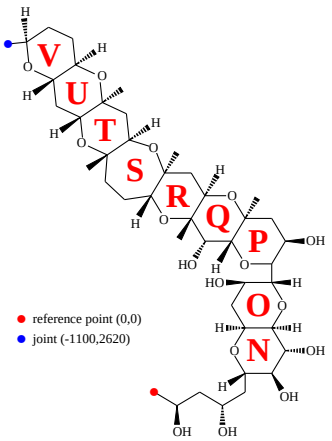
Second, a command `\maitotoxinNtoV` is defined to draw the N-to-V domain of maitotoxin, where the linking unit drawn by `\pentamethylenei` is selected as the outer skeleton.

```
\def\maitotoxinNtoV{%
\begin{picture}(0,0)(0,0)
\pentamethylenei{}{1==(yl);2B==OH;4A==OH;%
5==\sixheteroh[%N-ring
{b\sixfuseh%O-ring
{4==O}{2FB==HO;3GB==H;%
3Sa==\sixheteroh[%P-ring
{a\sixfuseh[%Q-ring
{a\sixfuseh[%R-ring
{a\SevenCycle(325,157){-43}{%S-ring
5==O;%
7s==\rotatebox{18}{\sixfuseh[%T-ring
{a\sixfuseh[%U-ring
{a\sixfuseh[%V-ring
]{6==\rotatebox{25}{O}}{1GA==\put(-50,0){\rotatebox{25}{H}};%
1Sa==\null}{D}}%end V-ring
]{3==\rotatebox{25}{O}}{1FB==\rotatebox{25}{H};%
2GA==\rotatebox{25}{H}}{D}}%end U-ring
]{6==\rotatebox{25}{O}}{1FB==\rotatebox{25}{H};2GA==\null;%
4FA==\rotatebox{25}{H};5GB==\null}{D}}%end T-ring
}[c]}%end S-ring
]{6==O}{1FB==H;2GA==\null}{D}}%end R-ring
]{3==O}{1FB==\null;2GA==H;6A==\lmoiety{HO}}{D}}%end Q-ring
]{6==O}{5==(yl);4B==OH;1FB==H;2GA==\null}%end P-ring
}{E}}%end O-ring
]{1==O}{6==(yl);2FA==H;3GA==H;4A==OH;5B==OH;6SB==H}%end N-Ring
```

```
}%
\end{picture}}
```

This code contains multiply nested ring fusions, which are shown by pairs of commands such as `%N-ring` and `%end N-ring`. Each of the ring fusions is based on the addition technique, an improper application of the replacement technique (the S-ring ← the T-ring), or the substitution technique (the linking unit ← the N-ring and the O-ring ← the P-ring).

The newly-defined command is operated by declaring `\maitotoxinNtoV` so as to generate the following diagram:



31-37 (the N-to-V domain of maitotoxin)

The reference point $(0, 0)$ of the N-to-V domain of maitotoxin **31-37** is located at the terminal vertex of a pentamethylene unit, as shown by a red solid circle. On the other hand, a terminal for joint is located at $(-1100, 2620)$ as shown by a blue solid circle.

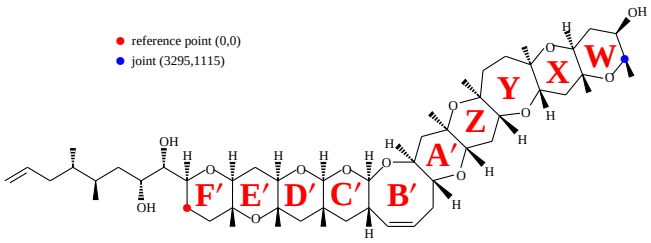
Third, a command `\maitotoxinWtoFp` is defined to draw the W-to-F′ domain of maitotoxin, where the F′-ring drawn by `\sixheterov` is selected as the outer skeleton.

```
\def\maitotoxinWtoFp{%
\begin{picture}(0,0)(0,0)
\sixheterov[%F'-ring
{b\sixfusev[%E'-ring
{b\sixfusev[%D'-ring
{b\sixfusev[%C'-ring
{b\EightCycle(-242,100){0}[a]{%B'-ring
6==O;%
5s==\rotatebox{15}{\sixfuseh[%A'-ring
{c\sixfuseh[%Z-ring
{C\SevenCycle(0,0){-8}{%Y-ring
2==\rotatebox{-15}{O};%
3s==\rotatebox{13}{\sixfusev[%X-ring
{b\sixfusev%W-ring
{4==\rotatebox{-18}{O}}{2B==\put(0,30){\rotatebox{-18}{OH}};3GB==\null}{E}%
}%end W-ring
]{1==\rotatebox{-18}{O}}{6GA==\null;5FB==\rotatebox{-18}{H};%
2FA==\rotatebox{-18}{H};3GB==\null%
}{e}}%end X-ring
}[g]}%end Y-ring
]{2==\rotatebox{-15}{O}}{3FA==\null;4GB==\rotatebox{-15}{H}}{F}}%end Z-ring
]{5==\rotatebox{-15}{O}}{1GA==\rotatebox{-15}{H};6FB==\rotatebox{-15}{H};%
3FA==\null;4GB==\rotatebox{-15}{H}}{F}}%end A'-ring
}[g]}%end B'-ring
]{1==O}{2FA==H;3GB==H}{E}}%end C'-ring
]{1==O}{2FA==H;3GB==\null}{E}}%end D'-ring
]{4==O}{2FA==H;3GB==\null}{E}}%end E'-ring
```

```
]{1==O;%
6s==\nonamethylene[a]{}{9==(yl);8A==OH;7A==OH;5B==\null;4A==\null}%
}{5==(yl);6GA==H;2FA==H;3GB==\null}%end F'-ring
\end{picture}}
```

This code contains multiply nested ring fusions, which are shown by pairs of commands such as `%F'-ring` and `%end F'-ring`. Each of the ring fusions is based on the addition technique or an improper application of the replacement technique (B′ ← A′ and Y ← X as well as the side chain).

The newly-defined command is operated by declaring `\maitotoxinWtoFp` so as to generate the following diagram:



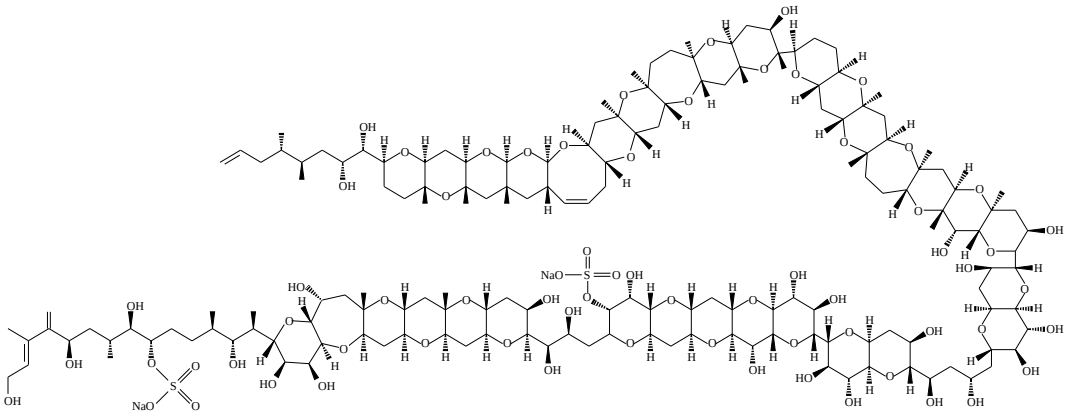
31-38 (the W-to-F′ domain of maitotoxin)

The reference point (0, 0) of the W-to-F′ domain of maitotoxin **31-38** is located at the leftmost vertex of the F′-ring, as shown by a red solid circle. On the other hand, a terminal for joint is located at (3295, 1115) as shown by a blue solid circle.

To draw the structure **31-39** of maitotoxin, the three domains defined above, i.e., `\maitotoxinAtoM`, `\maitotoxinNtoV`, and `\maitotoxinWtoFp`, are finally combined in a `XyMcompd` environment as shown in the code:

```
\begin{tabular}{c}
\scalebox{0.45}{%
\begin{XyMcompd}(8800,3400)(-3050,-650){}{}
\wedgehashedwedge
\def\thinLineWidth{0.8pt}
\put(0,0){\maitotoxinAtoM}
\put(4566,-272){\maitotoxinNtoV}
\put(171,1233){\maitotoxinWtoFp}
\end{XyMcompd}}
\\
\compd\label{cpd:maitotoxin} (Maitotoxin)
\\
\end{tabular}
```

We first put the A-to-M domain at the point (0, 0) of the `XyMcompd` environment by declaring `\put(0,0){\maitotoxinAtoM}`. This means that the reference point (0, 0) of **31-36** is located at the point (0, 0) of the `XyMcompd` environment. As a result, the terminal joint is located at (4566, −272) of the `XyMcompd` environment. In order to combine the N-to-V domain with the A-to-M domain, the reference point (0, 0) of the N-to-V domain (**31-37**) is placed at the (4566, −272) point of the `XyMcompd` environment, i.e., `\put(4566,-272){\maitotoxinNtoV}`. The terminal for joint (−1100, 2620) in the N-to-V domain (**31-37**) is placed now at (3466, 2348) in the `XyMcompd` environment because 4566 − 1100 = 3466 and −272 + 2620 = 2348. To combine the W-to-F′ domain with the N-to-V domain, the terminal (3295, 1115) of the W-to-F′ should be placed on the (3466, 2348) point in the `XyMcompd` environment so that the reference point of the W-to-F′ should be placed on the (171, 1233) point of the `XyMcompd` environment, because 3466 − 3295 = 171 and 2348 − 1115 = 1233. Hence, we should input `\put(171,1233){\maitotoxinWtoFp}`. The completed code described above generates the structure **31-39** of maitotoxin.



31-39 (Maitotoxin)

The above diagram is too small to make out atoms and substituents. A more readable diagram is shown in Fig. 31.3, where it is printed out after rotated by 90°. □

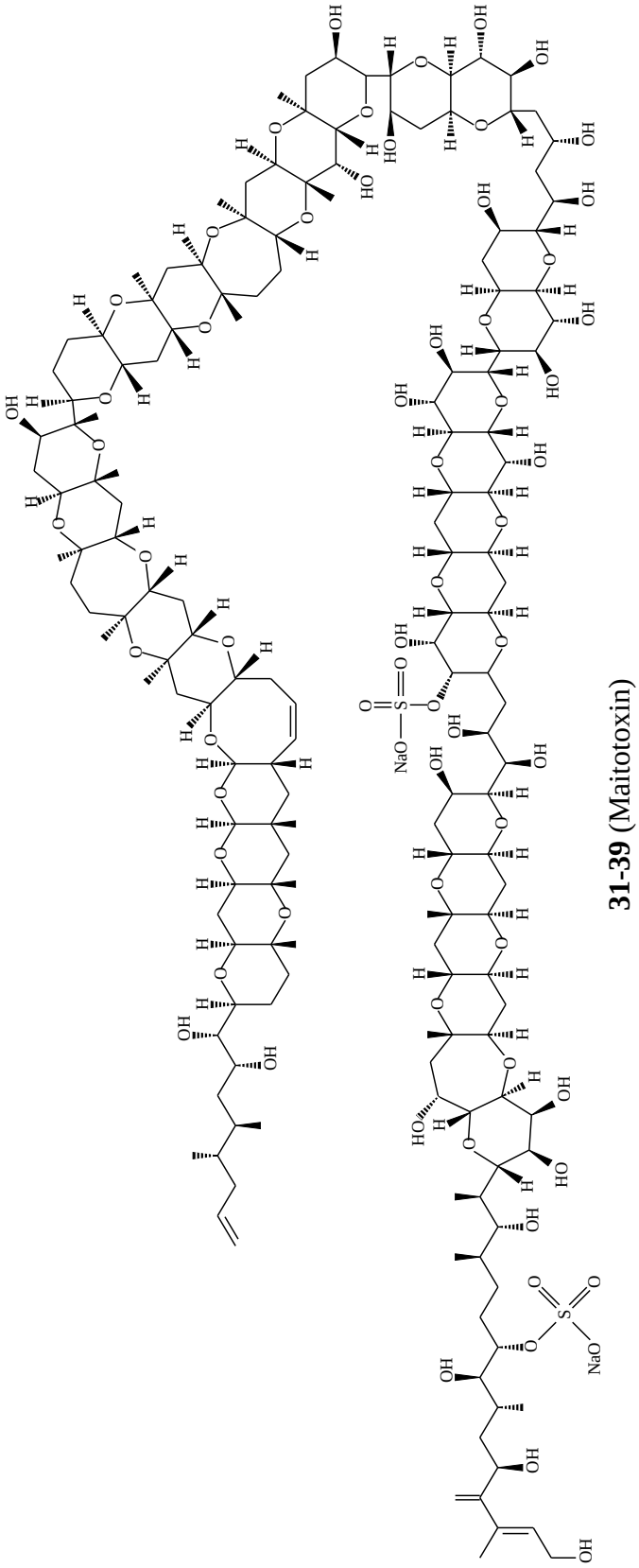
Although several attempts of total synthesis of maitotoxin have been reported, the complete success has not been reached as yet.

31.5.2 Ciguatoxin 1B

Ciguatoxins are a class of organic poisons found in some fish that cause ciguatera. Total syntheses of ciguatoxins have been reported [14,15]. Cigatoxin 1B (**31-40**) has 13 rings whose sizes cover from five to eight. These rings are designated by uppercase alphabets from A to M, among which the rings F and I are eight-membered rings.

Example 31.38. The structure **31-40** of ciguatoxin 1B is drawn by the code:

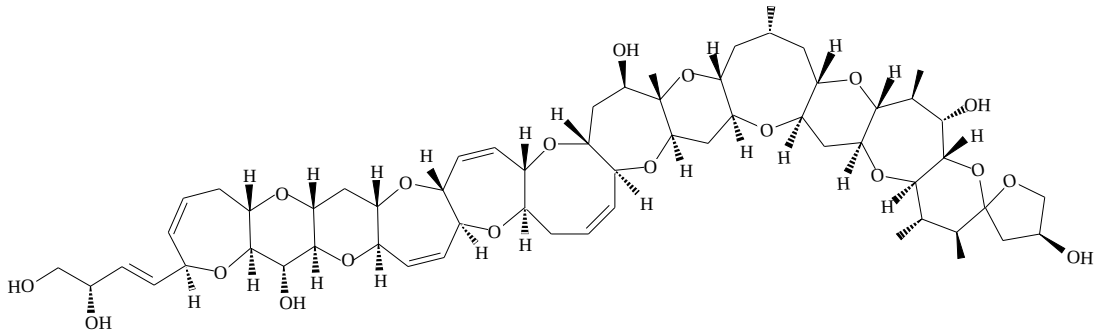
```
\begin{tabular}{c}
\scalebox{0.7}{%
\begin{XyMcompd}(5800,1800)(-2900,-500){}{}
\wedgehashedwedge
\EightCycle(-100,-242){0}[b]{%F-ring
6==O;%
4s==\HashWedgeAsSubstX(0,0)(120,-120);4==\put(180,-180){H};%
5s==\WedgeAsSubstX(0,0)(-120,120);5==\put(-160,160){H};%
7s==\WedgeAsSubstX(0,0)(0,140);7==\put(0,200){H};%
8s==\HashWedgeAsSubstX(0,0)(0,-140);8==\put(0,-200){H};%
%%%%%%%%%%%%%%%
% right part %
%%%%%%%%%%%%%%%
4s==\SevenCycle(0,0){6}{%G-ring
2==O;5s==\WedgeAsSubstX(0,0)(0,140);5==\put(0,200){OH};%
3s==\rotatebox{12}{%H-ring
\sixfusev{1==\rotatebox{-12}{O};%
3s==\EightCycle(-100,-242){-42}{%I
6s==\HashWedgeAsSubstX(0,0)(-50,130)[7];%
2==\rotatebox{-12}{O};%
3s==\rotatebox{30}{%J-ring
\sixheteroh{3==O;%
5s==\SevenCycle(0,0){-68}{%K-ring
2==O;%
5s==\HashWedgeAsSubstX(0,0)(0,140);5==\put(0,180){\rotatebox{-7}{OH}};%
6s==\WedgeAsSubstX(0,0)(-110,110);%
3s==\rotatebox{72}{%L-ring
\sixheterov{2==O;%
3s==\FiveCycle(-62,190){0}{%M-ring
```



31-39 (Maitotoxin)

Figure 31.3. Structure of maitotoxin

```
4==O;%
2s==\WedgeAsSubstX(0,0)(110,-110);2==\put(160,-160){\rotatebox{-11}{OH}}
}%end M-ring
}{6==(yl);1GB==\rotatebox{-8}{H};6FA==\rotatebox{-8}{H};4B==\null;5A==\null
}[f]}%end L-ring
}%end K-ring
}{1==(yl);1FA==\rotatebox{-3}{H};2GB==\rotatebox{-3}{H};%
5GA==\rotatebox{-3}{H};4FB==\rotatebox{-3}{H}%
}[ad]}%end J-ring
}[h]%end I-ring
}{5FA==\rotatebox{-18}{H};6GB==\null;3GA==\rotatebox{-18}{H};%
2FB==\rotatebox{-18}{H}}{e}}%end H-ring
}[g];%end G-ring
%%%%%%%%%%%%
% left part %
%%%%%%%%%%%%
8s==\SevenCycle(325,157){-12}[e]{%E-ring
2==O;%
1s==\SevenCycle(325,157){26}[a]{%D-ring
5==\rotatebox{12}{O};%
3s==\HashWedgeAsSubstX(6,-12)(60,-120)[6];3==\put(80,-180){\rotatebox{12}{H}};%
4s==\WedgeAsSubstX(0,0)(-40,120)[6];4==\put(-40,200){\rotatebox{12}{H}};%
7s==\rotatebox{-12}{%BC-ring
\decaheterov{4==\rotatebox{-2}{O};8==\rotatebox{-2}{O};%
6s==\SevenCycle(325,157){-13}[f]{%A-ring
2==O;%
1s==\HashWedgeAsSubstX(6,-12)(60,-120)[7];1==\put(80,-180){\rotatebox{-1}{H}};%
1s==\rotatebox{12}{\pentamethylenei[c]{}{5==(yl);1W==HO;2A==OH}}%
}%end A-ring
}{3==(yl);2FB==\rotatebox{-2}{H};3GA==\rotatebox{-2}{H};9A==\rotatebox{-2}{H};%
{10}B==\rotatebox{-2}{H};6FA==\rotatebox{-2}{H};7GB==\rotatebox{-2}{H};%
5A==\rotatebox{-2}{OH}%
}[bg]}%endBC-ring
}[c]%end D-ring
}[c]%end E-ring
}%end F-ring
\end{XyMcompd}
}
\\
\compd\label{cpd:ciguatoxin} (Ciguatoxin 1B)
\\
\end{tabular}
```



31-40 (Ciguatoxin 1B)

In the above code, each step of nested fusions is shown by a pair of comments such as `%F-ring` and `%end F-ring`. The eight-membered F-ring is selected as a skeleton, where the right part and the left part are drawn

by the addition technique or an improper application of the replacement technique. The last (terminal) step of the right part is a spiro ring fusion of `\FiveCycle` (the M-ring) according to the replacement technique. The last (terminal) step of the left part is an atom replacement of `\pentamethylene` (as a kind of the replacement technique). □

References

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Chapter 32

Dirty Tricks

32.1 Skeletal Atoms Without Relying on the Atom Lists

32.1.1 Commands for Drawing Front Objects

Skeletal atoms of XyMTEX commands of general use are assigned by the argument ⟨atomlist⟩. Skeletal atoms of XyMTEX commands of specified use (e.g., `\benzenev`) can be assigned by using the corresponding commands of general use if available (e.g., `sixheterov`). The target of this section is how we can do if such corresponding commands of general use are unavailable.

First, we define two commands for setting a front object after erasing background objects.

```
\SetTwoAtoms{⟨frontobject⟩}
\SetTwoAtomx{⟨frontobject⟩}
```

where the command `\SetTwoAtoms` erases background object within a tight box surrounding a front object specified by the argument ⟨frontobject⟩, while the command `\SetTwoAtomx` erases background objects to assure a few space surrounding ⟨frontobject⟩. For this technique, see Chapter 29 as well as Remarks on page 496.

32.1.2 Hetera-adamantanes

Azaadamantane and diazaadamantane are drawn by using `\hadamantane` as examples for drawing skeletal atoms in cases that the ⟨atomlist⟩ is unavailable. For the locant numbers assigned to `\hadamantane`, see Section 12.3. The default coordinates of respective vertices of `\hadamantane` can be obtained from the data of ccycle package (ccycle.dtx) of the XyMTEX system as follows:

1 — (440, 676);	2 — (843, 541);	3 — (843, 181);	4 — (673, −46);	5 — (270, 90);
6 — (0, 0);	7 — (170, 226);	8 — (170, 586);	9 — (270, 450);	10 — (573, 91)

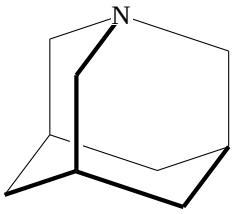
where the reference point is located at the 6-position (the leftmost position).

Example 32.1. 1-Azaadamantane is drawn by the code:

```
\begin{XyMcompd}(800,800)(-400,-700){}{}
\put(0,0){\hadamantane{1==(yl)}}
\put(0,0){\makebox(0,0){\SetTwoAtomx{N}}}
\end{XyMcompd}
```

where the declaration of `1==(yl)` shift the reference point from the 6-position (the leftmost vertex) to 1-position (the top vertex). This means that the 1-position is regarded as a new reference point (0, 0) in the

outer XyMcompd environment. A nitrogen as a front object is then placed at the new reference point by using \SetTwoAtomx. The command \makebox(0,0) makes the front object N a size-less object. Thereby, the above code generates the following structure:

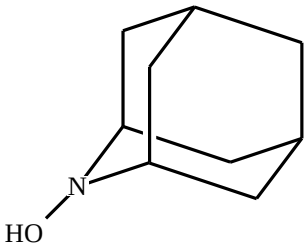


□

Example 32.2. In the case of drawing 2-hydroxy-2-azaadamantane, a new reference point is placed at the 6-position by declaring 6==(yl). The hydroxy substituent is depicted by declaring 6==HO in the ⟨subslist⟩ in a usual way:

```
\begin{XyMcompd}(1050,950)(-240,-224){}{}
\frontthicktothintrue
\def\thinLineWidth{1.2pt}
\put(0,0){\hadamantane{6==(yl);6==HO}}
\put(0,0){\makebox(0,0){\SetTwoAtomx{N}}}%at the 6-position
\end{XyMcompd}
```

This code depicts the following formula:

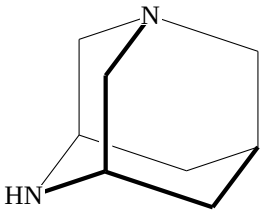


To show feasibilities of the XyMTEX commands, the thin lines and the boldfaced lines are equalized by declaring \frontthicktothintrue (cf. Section 29.5) and the bond thickness is commonly changed into 1.2pt. □

Example 32.3. In a similar way, a new reference point is placed at the 6-position by declaring 6==(yl) in the case of drawing 1,6-Diazaadamantane. Then, the code:

```
\begin{XyMcompd}(800,800)(-40,-24){}{}
\put(0,0){\hadamantane{6==(yl)}}
\put(440,676){\makebox(0,0){\SetTwoAtomx{N}}}%at the 1-position
\put(0,0){\makebox(0,0){\SetTwoAtomx{\llap{H}N}}}%at the 6-position
\end{XyMcompd}
```

generates the following structural formula:



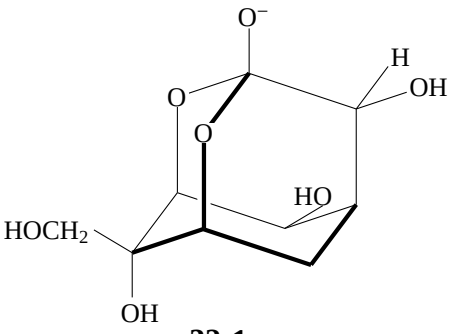
□

Example 32.4. A 2,4-dioxaadamantane derivative having the structural formula **32-1** is drawn by the code:

```
\begin{XyMcompd}(1550,1200)(-450,-250){cpd:dioxaadamantaneX}{}
\put(0,0){\hadamantane{6==(yl);1==O$^{-}$;2a==OH;2b==H;%
6a==OH;6b==HOCH$_{2}$;{10}b==HO}}
```

```
\put(170,586){\makebox(0,0){\SetTwoAtomx{O}}}%oxygen at 8-position
\put(270,450){\makebox(0,0){\SetTwoAtomx{O}}}%oxygen at 9-position
\end{XyMcompd}
```

where two oxygens are placed at the 8- and 9-positions of \hadamantane. Thereby, we obtain:



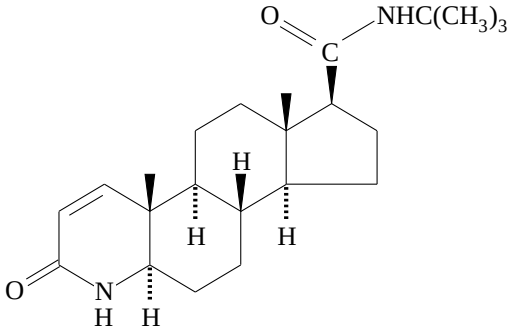
32-1 □

32.1.3 Azasteroids

Example 32.5. Finasteride (propecia®) is an oral medicine for androgenetic alopecia (AGA). The structure **32-2** of finasteride is drawn by the code:

```
\begin{XyMcompd}(1800,1300)(50,100){cpd:finasteride}{}
\steroid[a%
{c\put(0,-30){\makebox(0,0){\downnobond{\SetTwoAtomx{N}}{\SetTwoAtomx{H}}}}}%
]{3D==O;5A==H;8B==H;9A==H;{10}B==\null;{13}B==\null;{14}A==H;%
{17}B==\Utrigonal{1==(yl);0==C;2==\ChemForm{NHC(CH_{3})_{3}};3D==O}}
\end{XyMcompd}
```

which is based on an improper application of the addition technique. The skeletal nitrogen at the 4-position is drawn as a front object by using the command \SetTwoAtomx. The above code generates the following diagram:



32-2 □

32.2 Ring Fusion Without Relying on the Addition Technique

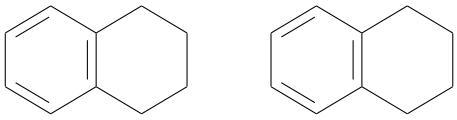
32.2.1 Various Methods for Drawing Fused Rings

The optional argument ⟨bondlist⟩ of such specified commands as \benzenev (\bzdrv) is incapable of serving as a receiver of the addition technique. If there are more general command such as \cyclohexanev or \sixheterov, the addition technique can be operated to their argument ⟨bondlist⟩.

Example 32.6. For example, the codes:

```
\cyclohexanev[bdf{b\sixfusev{}{}{E}}]{} \qquad
\sixheterov[bdf{b\sixfusev{}{}{E}}]{}{}
```

generate the following fused ring systems:

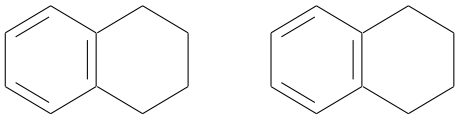


□

Example 32.7. Ring fusion can be depicted if the replacement technique is applied to a fusing unit such as `\sixfusev`. For example, the following codes:

```
\sixheterov[bdf]{2s==\sixfusev{}{}{E}}{} \qquad
\sixheterov[bdf]{2s==\sixheterov{}{6==(yl)}[e]}{}
```

generate equivalent ring systems:

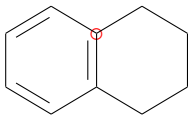


although this technique is rather dirty. □

Example 32.8. A more dirty but versatile technique is available by using (yl)-functions in the `XyMcompd` or `picture` environment. A (yl)-function places the reference point at issue on one of the terminal vertices of a bond to be fused. This means the the terminal vertex is characterized by the coordinates $(0, 0)$. Hence, two commands with a (yl)-function are placed on the same position in the `XyMcompd` or `picture`, so that they result in the depiction of a fused ring system. For example, the code:

```
\begin{XyMcompd}(600,450)(-300,-300){}{}
\put(0,0){\redx{\circle{40}}}%
\put(0,0){\benzenev{2==(yl)}}%
\put(0,0){\cyclohexanev{6==(yl)}[e]}%
\end{XyMcompd}
```

means that the 2-position of a benzene ring is placed at the same location as the 6-position of a cyclohexane ring. Thereby, we obtain an equivalent diagram:



where a red circle is output for the purpose of emphasizing the reference point, at which the two parts are connected. □

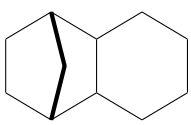
32.2.2 Ring Fusion to Bicyclo[2.2.1]heptanes

This technique for drawing fused rings is effective to the ring fusion of bicyclo[2.2.1]heptane drawn by the command `\bicychepv`, which does not support the addition technique.

Example 32.9. For example, the code

```
\begin{XyMcompd}(600,450)(-300,-300){}{}%
\put(0,0){\bicychepv{2==(yl)}}%
\put(0,0){\cyclohexanev{6==(yl)}[e]}%
\end{XyMcompd}
```

generates the following fused ring:

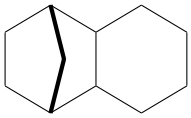


Note that the argument ⟨bondlist⟩ of the command `\bicychepv` does not support the addition technique. □

Example 32.10. The command with a (yl)-function can be used as a fusing unit, although the fusing bond is not deleted. For example, the command `\bicychepv{2==(yl)}` used above can be declared in the ⟨bondlist⟩ of the outer command `\cyclohexanev` according to an improper application of the addition technique.

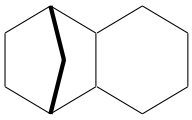
```
\begin{XyMcompd}(600,450)(-80,250){}{}%
\cyclohexanev[%
{E\bicychepv{2==(yl)}}
]{}[e]
\end{XyMcompd}
```

where the last argument `[e]` erases the bond of the outer six-membered ring. This code generates an equivalent structure.



The command `\bicychepv{2==(yl)}` used above can be also declared in the ⟨atomlist⟩ of the outer command `\sixheterov` according to an improper application of the replacement technique.

```
\begin{XyMcompd}(600,450)(-80,250){}{}%
\sixheterov{6s==\bicychepv{2==(yl)}}{}[e]
\end{XyMcompd}
```

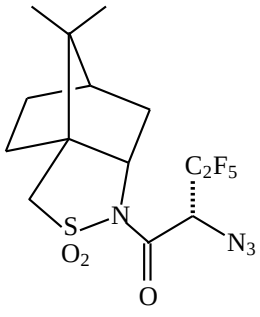


□

Example 32.11. An intermediate **32-3** for synthesizing fluorinated amino acids [1] is drawn by the code:

```
\begin{XyMcompd}(800,1150)(-400,-550){cpd:Faminoachid}{}%
\frontthicktothintrue
\def\thinLineWidth{0.8pt}
\put(0,0){\bornane{3==(yl);7Sa==\null;7Sb==\null}}%
\put(0,0){\rotatebox{-10}{\fiveheterov{1==%
\rotatebox{10}{\downnobond{S}{O$_{2}$}};2==\rotatebox{10}{N}}%
{3==(yl);2==%
\rotatebox{10}{\dimethylene{}{1==(yl);1D==O;2W==N$_{3}$;2A==C$_{2}$F$_{5}$}}%
}[cd]}}%
\put(-225,90){\PutBondLine(0,0)(-150,-230){0.8pt}}%
\end{XyMcompd}
```

where the 3-position of `\bornane` is superposed onto the 3-position of `\fiveheterov`. After deletion of the skeletal bonds 'c' (the fused bond) and 'd' in `\fiveheterov`, the bond 'd' is replaced by the bond drawn by `\PutBondLine`. The coordinate $(-225, 90)$ is calculated from $(462, -43)$ (the 3-position) and $(237, 47)$ (the bridgehead 4-position), which are obtained from the data of the ccycle package (ccycle.dtx) of the XyMTEX system. Thereby, we obtain the following formula:



32-3

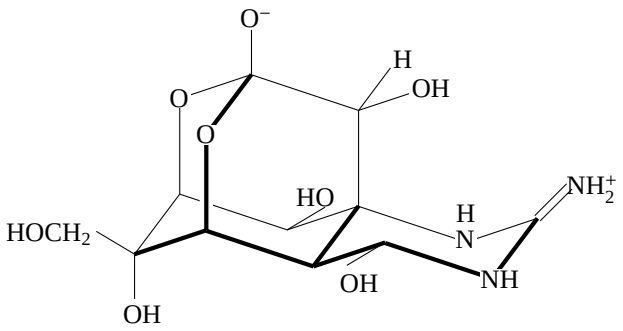
□

32.2.3 Drawing Tetrodotoxin

Example 32.12. Tetrodotoxin is famous as an extremely potent poison contained in a puffer fish. Its structure **32-4** is drawn by a code combining \hadamantane and \chairi after the declaration of (yl)-functions:

```
\begin{XyMcompd}(2200,1200)(-400,-250){cpd:tetrodotoxin}{}
%%%%%%%%%%%%%%%%%
%adamantane part%
%%%%%%%%%%%%%%%%%
\put(0,0){%outer picture environment
\put(0,0){\hadamantane{6==(yl);1==O$^{-}$;2a==OH;2b==H;%
6a==OH;6b==HOCH$_{2}$;{10}b==HO}}
\put(170,586){\makebox(0,0){\SetTwoAtomx{O}}}
\put(270,450){\makebox(0,0){\SetTwoAtomx{O}}}
}
%%%%%%%%%%%%%%%%%
%chair-form part%
%%%%%%%%%%%%%%%%%
\put(673,-46){%outer picture environment
\put(0,0){\chairi{1==(yl);4D==NH$_{2}^{+}$;2Se==OH}}
\put(573,150){\makebox(0,0){\upnobond{\SetTwoAtomx{N}}{H}}}%(573,91) to (573,150)
\put(673,-46){\makebox(0,0){\hbox to0.8em{\SetTwoAtomx{NH}\hss}}}
}
\end{XyMcompd}
```

This code generates the following formula:



32-4

Note that each coordinate appearing in the code for drawing **32-4** is cited above (page 565) from the ccycle package (ccycle.dtx).

1. The reference point $(0, 0)$, which is located at the 6-position of an adamantane skeleton (shifted by declaring 6==(yl) in the ⟨subslist⟩ of \hadamantane), is placed on the original point $(0, 0)$ of the outer picture environment (due to the XyMcompd environment). Two oxygen atom are placed on the vertices, $(170, 586)$ (8-position) and $(270, 450)$ (9-position), which are determined as the inner coordinates of \hadamantane. This part is based on the code for drawing **32-1**.
2. On the other hand, the reference point $(0, 0)$, which is located at the 1-position of a chair skeleton (shifted by declaring 1==(yl) in the ⟨subslist⟩ of \chairi), is placed on the point $(673, -46)$ of the outer picture environment. The point $(673, -46)$ corresponds to 3-point of the adamantane skeleton. Two NH groups are placed on the vertices, $(673, -46)$ (3-position) and $(573, 150)$ (5-position, shifted from $(573, 91)$), which are determined as the inner coordinates of \hadamantane. □

32.3 Substituents Without Relying on Substitution Lists

32.3.1 Using Atom Lists

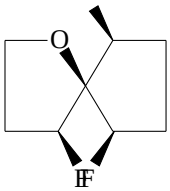
When a XyMTEX command has an ⟨atomlist⟩ argument, the atom-replacement technique described in Section 27.3 can be used to draw the attachment of a substituent. In particular, the commands listed in Subsection

27.3.3, i.e., \PutBondLine and \PutDashedBond; \WedgeAsSubst and \HashWedgeAsSubst; as well as \WedgeAsSubstX and \HashWedgeAsSubstX, are effective to draw substitution which is different from the default drawing based on the substitution technique.

IUPAC Recommendations 2006 discuses stereogenic centers at spiro fusion atoms [2, St-1.3.4]. A simple application of the XyMTEX system results in an insufficient diagram. Thus the code:

```
\begin{XyMcompd}(600,700)(350,0){}{}
\fiveheteroh{2==O;%
1s==\WedgeAsSubst(0,0)(-3,5){80};%
1s==\fiveheterohi{}{1==(yl);2B==\null;5B==F}
}{5B==F}[a]
\end{XyMcompd}
```

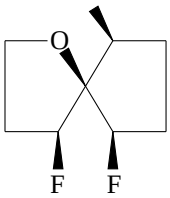
generates the following diagram:



where two fluorine atoms are overlapped.

Example 32.13. Although another simple application avoids the overlap of the two fluorine atoms, the resulting bonds are vertical, so as not to be accepted as a final diagram:

```
\begin{XyMcompd}(600,700)(350,0){}{}
\fiveheteroh{2==O;%
1s==\WedgeAsSubst(0,0)(-3,5){80};%
1s==\fiveheterohi{}{1==(yl);2B==\null;5Su==F}
}{5Su==F}[a]
\end{XyMcompd}
```

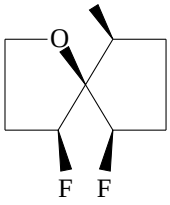


□

Example 32.14. A more sophisticated application provides us with a preferred depiction style:

```
\begin{XyMcompd}(600,750)(350,-50){cpd:atomreplace}{}
\fiveheteroh{2==O;%
1s==\WedgeAsSubst(0,0)(-3,5){80};%
5s==\WedgeAsSubstX(0,0)(30,-150)[4];%
5s==\put(0,-250){F};%
1s==\fiveheterohi{%
5s==\WedgeAsSubstX(0,0)(-30,-150)[4];%
5s==\put(-60,-250){F}%
}{1==(yl);2B==\null}
}{}[a]
\end{XyMcompd}
```

where wedges are depicted by the atom-replacement technique described in Section 27.3. This code provides the following preferred diagram:



32-5

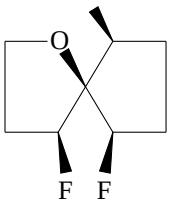
Note that `\WedgeAsSubstX` is used in place of `\WedgeAsSubst` for the purpose of drawing fluorine substitution, because `\WedgeAsSubstX` is capable of adjusting the thickness of wedges in terms of the optional argument '`[4]`' (default '`[10]`'). □

32.3.2 Using Bond Lists

If an optional argument ⟨bondlist⟩ is capable of receiving the addition technique, substituents can be declared in the ⟨bondlist⟩. This convention is regarded as an improper application of the addition technique.

Example 32.15. Thus, the spiro derivative **32-5** is alternatively drawn by this convention as follows:

```
\begin{XyMcompd}(600,750)(350,-50){cpd:addtechspiro}{}
\fiveheteroh[%
{a\WedgeAsSubst(0,0)(-3,5){80}}%
{e\WedgeAsSubstX(0,0)(30,-150)[4]}%
{e\put(0,-250){F}}]%
{2==O;1s==\fiveheterohi[%
{e\WedgeAsSubstX(0,0)(-30,-150)[4]}%
{e\put(-60,-250){F}}]{}{1==(yl);2B==\null}
}{}[a]
\end{XyMcompd}
```



32-6

Note that each wedge produced by `\WedgeAsSubst` or `\WedgeAsSubstX` is regarded as a tentative fusing unit for the improper addition technique. □

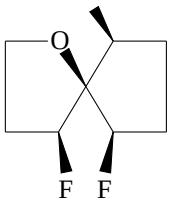
32.3.3 Without Using Substitution, Atom and Bond Lists

The diagram represented by **32-5** and **32-6** can be further drawn by the methodology equivalent to those described in Sections 32.1 and 32.2.

Example 32.16. First, the spiro skeleton is constructed by the replacement technique, where the reference point of the right five-membered ring (`\fiveheterohi`) is shifted to the 1-position by declaring `1==(yl)` and the reference point of the left five-membered ring (`\fiveheteroh`) is shifted to the 1-position also by declaring `1==(yl)`. Then, the new reference point at the spiro position (0, 0) is used to specify the coordinates of substituents, as found in the code:

```
\begin{XyMcompd}(600,750)(-350,-450){cpd:spiroalternative}{}
\put(0,0){\fiveheteroh{2==O;1s==\fiveheterohi{}{1==(yl);2B==\null}}{1==(yl)}[a]}
\put(0,0){\WedgeAsSubst(0,0)(-3,5){80}}%
\put(-103,-171){\put(0,0){\WedgeAsSubstX(0,0)(30,-150)[4]}\put(0,-250){F}}%
\put(103,-171){\put(0,0){\WedgeAsSubstX(0,0)(-30,-150)[4]}\put(-60,-250){F}}
\end{XyMcompd}
```

Note that the coordinate $(-103, -171)$ denotes the adjacent vertex to the spiro atom in the left ring, while the coordinate $(103, -171)$ denotes the adjacent vertex to the spiro atom in the right ring. The above code generates the following diagram:



32-7

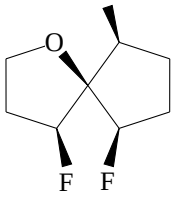
□

32.3.4 Using Regular Pentagons Produced by Low-Level Commands

Example 32.17. By using the command `\FiveCycle` defined in Chapter 31, we are able to change the home-plate forms of the above spiro derivative into regular-pentagonal forms.

```
\begin{XyMcompd}(600,750)(-350,-450){cpd:regpenaspiro}{}
\FiveCycle(-62,190){18}{%right
4s==\WedgeAsSubst(0,0)(0,1){140};%
1s==\WedgeAsSubstX(0,0)(-80,-120);%
1s==\put(-140,-200){\rotatebox{-18}{F}}}
\FiveCycle(262,190){-18}{%left
4==O;%
3s==\WedgeAsSubstX(0,0)(-126,84)[7];%
2s==\WedgeAsSubstX(0,0)(80,-120);%
2s==\put(60,-220){\rotatebox{18}{F}}}[c]
\end{XyMcompd}
```

Note that the coordinate $(-62, 190)$ denotes the 5-position of the right pentagon, while the coordinate $(262, 190)$ denotes the 3-position of the left pentagon. The two positions are regarded as new reference points and superposed to give a spiro position after rotation by $18°$ or $-18°$. The above code generates the following diagram with regular pentagons:



32-8

□

32.4 Partial Deletion of Skeletal Bonds

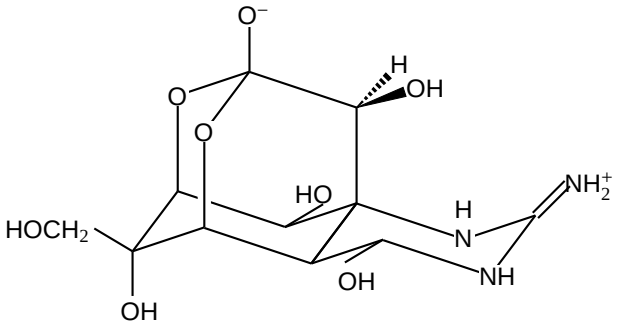
The IUPAC Recommendations 2006 [2, ST-3] deals with the use of perspective to indicate configuration, where a preferred depiction of the adamantane analogue contains no wedges nor hashed wedges, because a single bond crossing (with erasing a background bond) implies the configuration of all four bridgehead atoms.

Example 32.18. According to this convention, the boldfaced bonds in the structure **32-4** are changed into a thin-line bonds (the common thickness: 0.8pt). The configuration at the 2-position is emphasized by a wedge and a hashed wedge. Hence, we obtain the following code:

```
\begin{XyMcompd}(2200,1200)(-400,-250){cpd:tetrodotoxinX}{}
\def\thinLineWidth{0.8pt}
\def\thickLineWidth{0.8pt}
```

```
\let\substfont=\sffamily
\sffamily
%%%%%%%%%%%%%%%%%
%adamantane part%
%%%%%%%%%%%%%%%%%
\put(0,0){%outer picture environment
\put(0,0){\hadamantane{6==(yl);1==O$^{-}$;%
6a==OH;6b==HOCH$_{2}$;{10}b==HO}}%
%added at 2-position
\HashWedgeAsSubst(843,541)(1,1){120}\put(970,670){H}%
\WedgeAsSubst(843,541)(3,1){180}\put(1030,580){OH}%
%skeletal oxygens
\put(170,586){\makebox(0,0){\SetTwoAtomx{O}}}
\put(270,450){\makebox(0,0){\SetTwoAtomx{O}}}
}
%%%%%%%%%%%%%%%%%
%chair-form part%
%%%%%%%%%%%%%%%%%
\put(673,-46){%outer picture environment
\put(0,0){\chairi{1==(yl);4D==NH$_{2}^{+}$;2Se==OH}}
\put(573,150){\makebox(0,0){\upnobond{\SetTwoAtomx{N}}{H}}}%(573,91) to (573,150)
\put(673,-46){\makebox(0,0){\hbox to0.8em{\SetTwoAtomx{NH}\hss}}}
}
\end{XyMcompd}
```

This code generates an improved formula:



32-9

which is preferred in the light of the IUPAC Recommendations 2006 [2, ST-3]. □

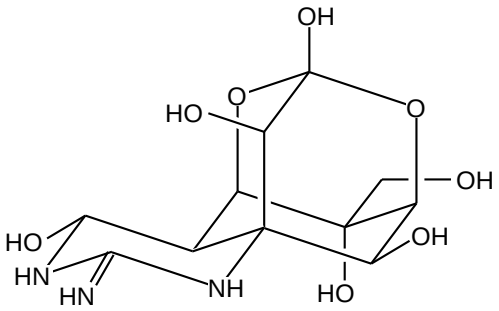
Example 32.19. If the diagram **32-4** or **32-9** is rotated around the vertical axis along the bridgehead C—O bond, there emerges another depiction **32-10** with more sites of bond-crossing, each of which is represented by an appropriate partial erasing of a background bond. The technique of erasing has been discussed in Section 29.5. In particular, see Remarks on page 496.

```
\begin{XyMcompd}(1800,1200)(-700,-250){cpd:tetrodotoxinY}{}
\def\thinLineWidth{0.8pt}
\def\thickLineWidth{0.8pt}
\let\substfont=\sffamily
\sffamily
%%%%%%%%%%%%%%%%%
%adamantane part%
%%%%%%%%%%%%%%%%%
\put(0,0){%outer picture environment
%background object
\put(573,91){\PutBondLine(0,0)(0,-200){\thinLineWidth}%
\whitex{\PutBondLine(0,-80)(0,-130){4pt}}%
\put(0,-210){\makebox(0,0)[t]{\hbox to0.8em{\hss HO}}}}%
```

```
\put(573,91){%
\PutBondLine(0,0)(140,180){\thinLineWidth}%
\PutBondLine(140,180)(400,180){\thinLineWidth}%
\whitex{\PutBondLine(240,180)(300,180){4pt}}%
\put(420,180){\makebox(0,0)[l]{OH}}}
%front object
\put(0,0){\hadamantane{6==(yl);1==OH;4Se==OH}}
\put(843,541){\makebox(0,0){\SetTwoAtomx{O}}}
\put(170,586){\makebox(0,0){\SetTwoAtomx{O}}}
\put(270,450){\whitex{\PutBondLine(-60,20)(-150,50){4pt}}}%
\put(270,450){\PutBondLine(0,0)(-210,70){\thinLineWidth}%
\put(-230,70){\makebox(0,0)[r]{HO}}}%
}
%%%%%%%%%%%%%%%%%
%chair-form part%
%%%%%%%%%%%%%%%%%
\put(0,0){%outer picture environment
%background object
\put(0,0){\replaceSKbond(0,0)(3,1){270}{\white}}%
%front object
\put(0,0){\chairi{5==(yl);6Se==HO}}
\put(100,-137){\makebox(0,0){\hbox to0.8em{\SetTwoAtomx{NH}\hss}}}
\put(-573,-91){\makebox(0,0){\hbox to0.8em{\hss\SetTwoAtomx{HN}}}}
\put(-303,0){\rotatebox{-120}{%carbonyl double bonds
\PutBondLine(8,12)(140,12){\thinLineWidth}%
\PutBondLine(8,-12)(140,-12){\thinLineWidth}}}
\put(-303,0){\put(-200,-200){HN}}
}
\end{XyMcompd}
```

This code contains such declarations as `\whitex{\PutBondLine(0,-80)(0,-130){4pt}}`, which partially erases a background bond by putting a white boldfaced line. Another technique based on `\replaceSKbond` is used to erase a skeletal bond at the fused position. For the definition of `\replaceSKbond`, see Subsection 39.1.2. See page 506 for examples.

The above code generates the following diagram:



32-10 □

32.5 Meisenheimer Complexes

A nucleophilic substitution on a benzene ring includes a so-called Meisenheimer-type complex.

Example 32.20. To draw such an ionic intermediate, we first define `\benzeniumionelement` to draw a pentadienyl anionic species.

```
\def\benzeniumionelement{%
\begin{picture}(0,0)(0,50)
```

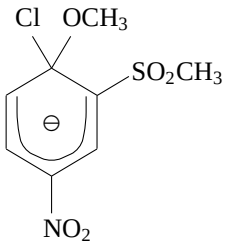
```
\putRoundArrow[-]{(130,300)(130,200)(110,100)(0,50)%
(-110,100)(-130,200)(-130,300)}
\put(0,200){\makebox(0,0){$\ominus$}}
\end{picture}}
```

Note that the command `\putRoundArrow`, which is defined to draw a curved arrow in Section 33.4, can be used to draw a curved line without an arrowhead if the optional argument `[-]` is declared.

The command `\benzeniumionelement` depicts the following element:

Then, this element is designated in the atom list of `\sixheterov`.

```
\sixheterov{4s==\put(0,50){\benzeniumionelement}}{%
1Sb==Cl;1Sa==OCH$_{3}$;2==SO$_{2}$CH$_{3}$;4==NO$_{2}$}
```



□

References

[1] T. Yajima, *Yuki Gosei Kagaku Kyokai-Shi*, **71**, 683–693 (2013).

[2] J. Brecher and IUPAC Chemical Nomenclature and Structure Representation Division, *Pure Appl. Chem.*, **78**, 1897–1970 (2006).

Part VIII

Molecular Formulas and Reaction Schemes

Chapter 33

Arrows

33.1 Arrows of Fixed Lengths

Because longer arrows of fixed lengths are frequently used in chemical equations, they are supported by the chemist (chmst-pdf or chmst-ps) package, which is automatically loaded by calling the X$_{\text{E}}$MT$_{\text{E}}$X system (`\uspackage{xyxmtex}`, `\uspackage{xyxmtexpdf}`, or `\uspackage{xyxmtexps}`).[a] Such commands for drawing longer arrows should be used in an in-text or display math mode (e.g., `$\llongrightarrow$` and `\ChemForm{\llongrightarrow}`), because they are defined as relational operators. The appearances of arrows produced by a command of the same name in chemist and chmst-pdf (or chmst-ps) are different, as summarized in Table 33.1.

The commands for drawing arrows (Table 33.1) can be used in `\ChemForm` as part of a chemical equation. The following list shows several examples, where horizontal spaces before and after each arrow (as a relational operator) are placed automatically.

stoichiometric relationship
`\ChemForm{H_{2}+Br_{2} = 2HBr}` $\mathrm{H_2 + Br_2 = 2HBr}$
forward reaction
`\ChemForm{H_{2}+Br_{2} \llongrightarrow 2HBr}` $\mathrm{H_2 + Br_2 \longrightarrow 2HBr}$
reverse reaction
`\ChemForm{H_{2}+Br_{2} \llongleftarrow 2HBr}` $\mathrm{H_2 + Br_2 \longleftarrow 2HBr}$
equilibrium
`\ChemForm{H_{2}+Br_{2} \equilibarrow 2HBr}` $\mathrm{H_2 + Br_2 \rightleftharpoons 2HBr}$
forward and reverse
`\ChemForm{H_{2}+Br_{2} \Equilibarrow 2HBr}` $\mathrm{H_2 + Br_2 \Longleftrightarrow 2HBr}$
resonance
`\ChemForm{H\sbond Br \llongleftrightarrow H^{+} Br^{-}}` $\mathrm{H{-}Br \longleftrightarrow H^{+}Br^{-}}$

Because the present document is typeset under the PDF-compatible mode (i.e., the use of the chmst-pdf package), such newly-defined arrows as shown above are drawn by using PDF utilities. If you want to print such arrows according to the embodiment of T$_{\text{E}}$X/L$^{\text{A}}$T$_{\text{E}}$X 2$_{\varepsilon}$, you should declare the switching command `\chemistsw` as follows:

[a] Arrows and harpoons produced by chemist and chmst-ps packages have been discussed in Sections 2 and 5 of the on-line manual of versions 4.05 and 4.06 (xymtx405406.pdf). If the combination of xymtexps, chemist, and chmst-ps (the PostScript-compatible mode) is replaced by the combination of xymtexpdf, chemist, chmst-pdf (the PDF-compatible mode), the descriptions of the on-line manual are applicable to the latter combination.

Table 33.1. Arrows of Fixed Lengths Supported by chemist and chmst-pdf

command	chemist	chmst-pdf (chmst-ps)	comment
`\llongrightarrow`	$\longrightarrow$	$\longrightarrow$	
`\llongleftarrow`	$\longleftarrow$	$\longleftarrow$	
`\llongleftrightarrow`	$\longleftrightarrow$	$\longleftrightarrow$	
`\Llongrightarrow`	$\Longrightarrow$	$\Longrightarrow$	
`\Llongleftarrow`	$\Longleftarrow$	$\Longleftarrow$	
`\Llongleftrightarrow`	$\Longleftrightarrow$	$\Longleftrightarrow$	
`\llongleftharpoondown`	$\leftharpoondown$	$\leftharpoondown$	
`\llongrightharpoonup`	$\rightharpoonup$	$\rightharpoonup$	
`\llongleftharpoonup`	($\longleftarrow$)	$\leftharpoonup$	not supported by chemist
`\llongrightharpoondown`	($\longrightarrow$)	$\rightharpoondown$	not supported by chemist
`\equilibarrow`	$\rightleftharpoons$	$\rightleftharpoons$	
`\Equilibarrow`	$\rightleftarrows$	$\rightleftarrows$	
`\lllongrightarrow`	$\longrightarrow$	$\longrightarrow$	
`\lllongleftarrow`	$\longleftarrow$	$\longleftarrow$	
`\lllongleftrightarrow`	$\longleftrightarrow$	$\longleftrightarrow$	
`\Lllongrightarrow`	$\Longrightarrow$	$\Longrightarrow$	
`\Lllongleftarrow`	$\Longleftarrow$	$\Longleftarrow$	
`\Lllongleftrightarrow`	$\Longleftrightarrow$	$\Longleftrightarrow$	
`\lllongleftharpoondown`	$\leftharpoondown$	$\leftharpoondown$	
`\lllongrightharpoonup`	$\rightharpoonup$	$\rightharpoonup$	
`\lllongleftharpoonup`	($\longleftarrow$)	$\leftharpoonup$	not supported by chemist
`\lllongrightharpoondown`	($\longrightarrow$)	$\rightharpoondown$	not supported by chemist
`\equiliblongarrow`	$\rightleftharpoons$	$\rightleftharpoons$	
`\Equiliblongarrow`	$\rightleftarrows$	$\rightleftarrows$	

`\chemistsw`
stoichiometric relationship
`\ChemForm{H_{2}+Br_{2} = 2HBr}` $H_2 + Br_2 = 2HBr$
forward reaction
`\ChemForm{H_{2}+Br_{2} \llongrightarrow 2HBr}` $H_2 + Br_2 \longrightarrow 2HBr$
reverse reaction
`\ChemForm{H_{2}+Br_{2} \llongleftarrow 2HBr}` $H_2 + Br_2 \longleftarrow 2HBr$
equilibrium
`\ChemForm{H_{2}+Br_{2} \equilibarrow 2HBr}` $H_2 + Br_2 \rightleftharpoons 2HBr$
forward and reverse
`\ChemForm{H_{2}+Br_{2} \Equilibarrow 2HBr}` $H_2 + Br_2 \rightleftarrows 2HBr$
resonance
`\ChemForm{H\sbond Br \llongleftrightarrow H^{+} Br^{-}}` $H\text{—}Br \longleftrightarrow H^{+}Br^{-}$

Attention should be focused on arrowheads; these appearances of arrows are inherent to the chemist package (without loading the chmst-pdf or chmst-ps package). To return to the PDF-compatible mode (or the PostScript-compatible mode), the switching command `\chmstpspdfsw` should be declared.

`\chmstpspdfsw`
stoichiometric relationship
`\ChemForm{H_{2}+Br_{2} = 2HBr}` $H_2 + Br_2 = 2HBr$
forward reaction
`\ChemForm{H_{2}+Br_{2} \llongrightarrow 2HBr}` $H_2 + Br_2 \longrightarrow 2HBr$
(omitted)

Example 33.1. A `ChemEquation` environment is used to describe a chemical equation, where chemical compounds are printed in upright fonts. The following code is a typical example containing a chemical

compound and ionic species. Thus, solid limestone ($CaCO_3$) is almost water insoluble, but a very small quantity dissolves in water according to the following process:

```
\begin{ChemEquation}
 CaCO_{3(s)} \llongrightarrow Ca_{(aq)}^{2+} + CO_{3(aq)}^{2-}
\end{ChemEquation}
```

$$\mathrm{CaCO_{3(s)}} \longrightarrow \mathrm{Ca^{2+}_{(aq)}} + \mathrm{CO^{2-}_{3(aq)}} \tag{33.1}$$

The molecular formulas are printed in upright fonts, although they are written directly without using the `\mathrm` command. Compare this output with the following one due to an `equation` environment of LaTeX 2_ε:

```
\begin{equation}
 CaCO_{3(s)} \llongrightarrow Ca_{(aq)}^{2+} + CO_{3(aq)}^{2-}
\end{equation}
```

$$CaCO_{3(s)} \longrightarrow Ca^{2+}_{(aq)} + CO^{2-}_{3(aq)} \tag{33.2}$$

where each molecular formula written without using the `\mathrm` command is printed in italic fonts. □

Further longer arrows are also supported by the chemist (chmst-pdf or chmst-ps) package (Table 33.1). They can be used in the argument of `\ChemForm` as follows:

```
\ChemForm{A\lllongrightarrow B} \ChemForm{A\lllongleftarrow B}
\ChemForm{A\lllongleftrightarrow B} \ChemForm{A\llllongleftrightarrow B}
\ChemForm{A\equiliblongarrow B} \ChemForm{A\Equiliblongarrow B}
```

$$\mathrm{A} \longrightarrow \mathrm{B}\ \mathrm{A} \longleftarrow \mathrm{B}\ \mathrm{A} \longleftrightarrow \mathrm{B}\ \mathrm{A} \longleftrightarrow \mathrm{B}\ \mathrm{A} \rightleftharpoons \mathrm{B}\ \mathrm{A} \rightleftharpoons \mathrm{B}$$

In a parallel way to double-lined arrows supported by TeX/LaTeX 2_ε, i.e., `$\Longrightarrow$` ($\Longrightarrow$) `$\Longleftarrow$` ($\Longleftarrow$) `$\Longleftrightarrow$` ($\Longleftrightarrow$), a set of longer double-lined arrows and a further longer set are supported by the chemist (chmst-pdf or chmst-ps) package (Table 33.1). They can be used in the argument of `\ChemForm` as follows:

```
\ChemForm{A \Llongrightarrow B}
\ChemForm{A \Llongleftarrow B}
\ChemForm{A \Llongleftrightarrow B} \\
\ChemForm{A\Lllongrightarrow B}
\ChemForm{A\Lllongleftarrow B}
\ChemForm{A\Lllongleftrightarrow B}
```

$$\mathrm{A} \Longrightarrow \mathrm{B}\ \mathrm{A} \Longleftarrow \mathrm{B}\ \mathrm{A} \Longleftrightarrow \mathrm{B}$$
$$\mathrm{A} \Longrightarrow \mathrm{B}\ \mathrm{A} \Longleftarrow \mathrm{B}\ \mathrm{A} \Longleftrightarrow \mathrm{B}$$

If the switching command `\chemistsw` is declared, the same commands for drawing double-lined arrows give the corresponding arrows of different appearances:

```
{\chemistsw
\begin{center}
\ChemForm{A \Llongrightarrow B}
\ChemForm{A \Llongleftarrow B}
\ChemForm{A \Llongleftrightarrow B} \\
\ChemForm{A\Lllongrightarrow B}
\ChemForm{A\Lllongleftarrow B}
\ChemForm{A\Lllongleftrightarrow B}
\end{center}
}
```

$$\mathrm{A} \Longrightarrow \mathrm{B}\ \mathrm{A} \Longleftarrow \mathrm{B}\ \mathrm{A} \Longleftrightarrow \mathrm{B}$$
$$\mathrm{A} \Longrightarrow \mathrm{B}\ \mathrm{A} \Longleftarrow \mathrm{B}\ \mathrm{A} \Longleftrightarrow \mathrm{B}$$

33.2 Arrows for Organic Chemistry

In addition of the reaction arrows described in Ref. [1], we have added further reaction arrows shown in Fig. 33.1. They are defined in the package chemist.sty (cf. Section 12.2 of the manual of XyMTEX version 2.00 (xymtx200PS) and [2]). Each arrow command is the following format:

```
\ARROWNAME[⟨xshift⟩]{⟨yshift⟩}{⟨length⟩}{⟨itemover⟩}{⟨itemunder⟩}
```

where \ARROWNAME represents a command name; ⟨xshift⟩ is an optional argument to show a horizontal adjustment value; ⟨yshift⟩ is an argument to show a vertical adjustment value; ⟨length⟩ is an argument to designate the length of the arrow; and the arguments ⟨itemover⟩ and ⟨itemunder⟩ represent items placed over and under the arrow. The name (\ARROWNAME) of each reaction arrow takes the following format:

```
\react...arrow
```

in which the inserted characters (...) is selected from the following list: r = right arrow, l = left arrow, lr = leftright arrow, d = down arrow, u = up arrow, du = down up arrow, eq = equilibrium arrow, veq = vertical equilibrium arrow, deq = down equilibrium arrow, leq = up equilibrium arrow, dlr = down leftright arrow, ulr = up leftright arrow, sw = southwest arrow, se = southeast arrow, nw = northwest arrow, and ne = northeast arrow.

The list of arrows of the manual is cited for convenience, as shown in Fig. 33.1, where the four arrows for representing equilibriums in the fourth row are new matters in the version 5.00 of chemist (chmst-pdf) package [3].[b] The arrows in the fifth row have been renamed into the present names in order to assign the previous names to the arrows in the fourth row. Note that a combination of left and right arrows is used to represent a forward and reverse reaction, while a combination of left and right harpoons is used to represent an equilibrium.

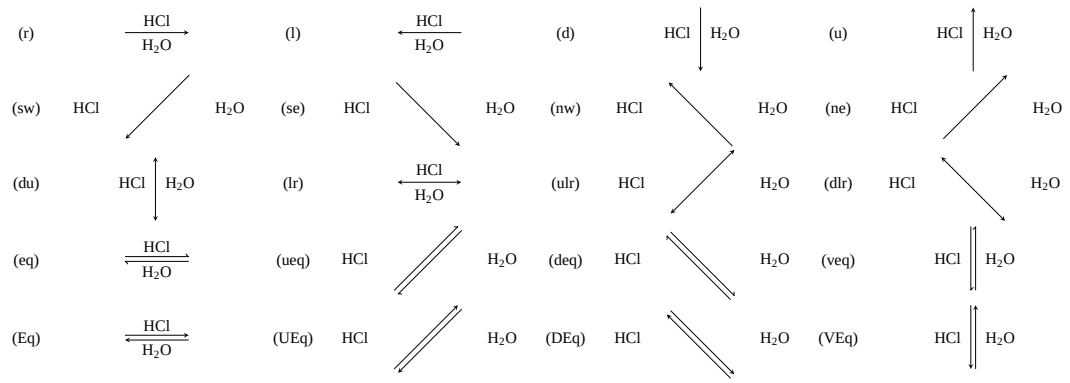


Figure 33.1. Reaction arrows of various types. The character string surrounded by each pair of parenthesis represents inserted characters, e.g., (r) denotes \reactrarrow.

Example 33.2. Arrows for organic chemistry (Fig. 33.1) can also be used for outputting objects over or below arrows in inorganic chemical equations. An equivalent result is obtained by using \reactrarrow, where \scriptsize is declared to adjust the sizes of objects over and below an arrow:

```
\begin{ChemEquation}
Na + Al + 2H_{2}
\reactrarrow{0pt}{3cm}{\scriptsize \ChemForm{THF/140^{\circ}/3\: h}}
{\scriptsize 350~atom}
```

[b] The corresponding summary of chemical arrows produced by chemist and chmst-ps packages have been discussed in Sections 2 and 5 of the on-line manual of versions 4.05 and 4.06 (xymtx405406.pdf) [4].

```
NaAlH_{4}\quad (99\%~yield)
\end{ChemEquation}
```

$$\mathrm{Na + Al + 2H_2} \xrightarrow[350\ \text{atom}]{\text{THF}/140^\circ/3\,\text{h}} \mathrm{NaAlH_4} \quad (99\%\ \text{yield}) \tag{33.3}$$

□

On similar lines, the following set of arrows for organic chemistry can be used to draw reaction equations for inorganic chemistry.

```
\reactrarrow{0pt}{1cm}{A}{B}
\reactlarrow{0pt}{1cm}{A}{B}
\reactlrarrow{0pt}{1cm}{A}{B}
\reacteqarrow{0pt}{1cm}{A}{B}
```

$\xrightarrow[B]{A}$

$\xleftarrow[B]{A}$

$\xleftrightarrow[B]{A}$

$\underset{B}{\overset{A}{\rightleftharpoons}}$

Example 33.3. The following code for writing catalytic reforming:

```
\begin{ChemEquation}
CH_3CH_2CH_2CH_2CH_2CH_3 \quad
\reactrarrow{0pt}{2cm}{catalyst \\[-5pt]}{{}\\[-15pt]heat}
\quad
\begin{XyMcompd}(200,350)(300,280){}{}
\bzdrv[A]{}
\end{XyMcompd} \quad + 4H_2
\end{ChemEquation}
```

gives the following output:

$$\mathrm{CH_3CH_2CH_2CH_2CH_2CH_3} \xrightarrow[\text{heat}]{\text{catalyst}} \bigcirc + 4\mathrm{H_2} \tag{33.4}$$

where the `\reactrarrow` command is used in a `ChemEquation` environment. □

Example 33.4. Another example is shown as follows:

```
\begin{ChemEqnarray*}
\lefteqn{%
CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3 \qquad
\reactrarrow{0pt}{2cm}{heat\\[-5pt]}{{}\\[-15pt]catalyst}} && \\[10pt]
&\hskip40pt& CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3 + CH_2\dbond CH_2 \\
&& \hskip120pt\mbox{and} \\
&& CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3 + CH_3CH\dbond CH_2 \\
&& \hskip120pt\mbox{and} \\
&& CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3 + CH_3CH_2CH_2CH_2CH\dbond CH_2 \\
&& \hskip120pt\mbox{and so on}
\end{ChemEqnarray*}
```

where the \reactrarrow command is used in a ChemEqnarray* environment. This code results in the following output:

$$\mathrm{CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3} \xrightarrow[\text{catalyst}]{\text{heat}}$$

$$\mathrm{CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3 + CH_2{=}CH_2}$$
and
$$\mathrm{CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3 + CH_3CH{=}CH_2}$$
and
$$\mathrm{CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3 + CH_3CH_2CH_2CH_2CH{=}CH_2}$$
and so on

It should be noted that \ChemForm{\mbox{and}} and \ChemForm{and} give equivalent outputs, “and” and “and”. In contrast, \ChemForm{\mbox{and so on}} and \ChemForm{and so on} give different outputs, “and so on” and “andsoon”, where the spaces of the latter are deleted by typesetting mechanism due to the math mode of TEX/LATEX 2ε. □

Example 33.5. As found in the following examples, the status in the third and fourth arguments of \reactrarrow etc. is a text mode (not a mathematical mode).

```
\begin{ChemEqnarray}
A \reactrarrow{0pt}{3cm}{\ChemForm{H^+}}{acid catalysis}
B \reactlarrow{0pt}{2cm}{\ChemForm{H^+}}{\ChemForm{CH_3OH}}
C \reactlrarrow{0pt}{2cm}{\ChemForm{H^+}}{\strut}
D \reacteqarrow{0pt}{2cm}{\ChemForm{H^+}}{equilibrium}  E
\end{ChemEqnarray}
```

$$\mathrm{A} \xrightarrow[\text{acid catalysis}]{\mathrm{H^+}} \mathrm{B} \xleftarrow[\mathrm{CH_3OH}]{\mathrm{H^+}} \mathrm{C} \xleftrightarrow{\mathrm{H^+}} \mathrm{D} \underset{\text{equilibrium}}{\overset{\mathrm{H^+}}{\rightleftharpoons}} \mathrm{E} \tag{33.5}$$

□

Arrows with a double line are drawn by using \schemerarrow, \schemelarrow, and \schemelrarrow. When the chmst-pdf (automatically loaded in the PDF-compatible mode) or chmst-ps package (automatically loaded in the PostScript mode) is loaded after the loading of the chmemist package, the pgf package or the PSTricks package becomes effective so as to print arrows due to pgf or PostScript utilities, as shown in the following examples.

```
\begin{ChemEqnarray}
A \schemerarrow{0pt}{3cm}{\ChemForm{H^+}}{acid catalysis}
B \schemelarrow{0pt}{2cm}{\ChemForm{H^+}}{\ChemForm{CH_3OH}}
C \schemelrarrow{0pt}{2cm}{\ChemForm{H^+}}{\strut} D
\end{ChemEqnarray}
```

$$\mathrm{A} \xRightarrow[\text{acid catalysis}]{\mathrm{H^+}} \mathrm{B} \xLeftarrow[\mathrm{CH_3OH}]{\mathrm{H^+}} \mathrm{C} \xLeftrightarrow{\mathrm{H^+}} \mathrm{D} \tag{33.6}$$

If the chmst-pdf or chmst-ps package is not loaded, the following output is obtained by means of the same code shown above:

$$\mathrm{A} \xRightarrow[\text{acid catalysis}]{\mathrm{H^+}} \mathrm{B} \xLeftarrow[\mathrm{CH_3OH}]{\mathrm{H^+}} \mathrm{C} \xLeftrightarrow{\mathrm{H^+}} \mathrm{D} \tag{33.7}$$

33.3 Further Commands and Techniques for Drawing Arrows

If fine tuning is necessary with respect vertical spaces, the following examples would be helpful:

```
\reactrarrow{0pt}{1cm}{A}{A}
\reactrarrow{0pt}{1cm}{A}{a}
\reactrarrow{0pt}{1cm}{a}{a}
{\reactarrowsep=-1pt \def\reactarrowseprate{1.8}
\reactrarrow{0pt}{1cm}{A}{a}}
{\reactarrowsep=-1pt \def\reactarrowseprate{1.8}
\reactrarrow{0pt}{1cm}{a}{a}}
```

$\xrightarrow[A]{A}$ $\xrightarrow[a]{A}$ $\xrightarrow[a]{a}$ $\xrightarrow[a]{A}$ $\xrightarrow[a]{a}$

where \reactarrowsep is an adjustment value between an upper object and an arrow, while the corresponding value between an arrow and a lower object is determined by multiplying the ratio stored as a letter string (\reactarrowseprate), i.e., \reactarrowseprate × \reactarrowsep.

New commands \reactreqarrow and \reactleqarrow have been defined to show unbalanced equilibrium:

```
\reactreqarrow{0pt}{1cm}{A}{B}
\reactleqarrow{0pt}{1cm}{A}{B}
```

$\xrightarrow[\leftharpoondown]{A}$

$\xleftarrow[\rightharpoonup]{A}$

The ratio of the length of the shorter arrow to that of the longer arrow is specified by \eqlbarrowstretch, which is 0.6 for a default setting. To change the ratio, the following declaration is necessary:

```
{\def\eqlbarrowstretch{0.4} \reactreqarrow{0pt}{1cm}{A}{B}} \qquad
{\def\eqlbarrowstretch{0.6} \reactreqarrow{0pt}{1cm}{A}{B}} \qquad
{\def\eqlbarrowstretch{0.8} \reactreqarrow{0pt}{1cm}{A}{B}}
```

$\xrightarrow[\leftharpoondown]{A}$ $\xrightarrow[\leftharpoondown]{A}$ $\xrightarrow[\leftharpoondown]{A}$

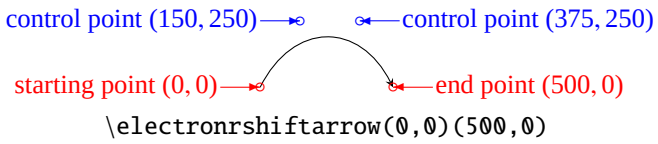
33.4 Curved Arrows for Electron Shifts

To illustrate the mechanisms of organic reactions, curved arrows are used to show an electron shift. The macros for drawing such curved arrows are defined in the chmst-pdf package for the PDF-compatible mode (or the chmst-ps package for the PostScript mode):[c]

```
\electronrshiftarrow[⟨direction⟩](⟨startpoint⟩)(⟨endpoint⟩)
\electronlshiftarrow[⟨direction⟩](⟨endpoint⟩)(⟨startpoint⟩)
```

where the arrowhead is attached at the end point designated by the argument ⟨endpoint⟩. The data of ⟨startpoint⟩ or ⟨endpoint⟩ are given in the form of (x, y), where the values of x- and y-coordinates are determined by the multiples of \unitlength (= 0.1pt). The optional argument ⟨direction⟩ takes 0 for drawing a hat-type curve (default) or 1 for drawing a cup-type curve.

From the data of the starting and end points (⟨startpoint⟩ and ⟨endpoint⟩), the coordinates of two control points are automatically calculated in order to draw a cubic Bézier curve. For example, the data $(0, 0)$ and $(500, 0)$ of the code \electronrshiftarrow(0,0)(500,0) give the coordinates of two control points, i.e., $(150, 250)$ and $(375, 250)$, so that the following cubic Bézier curve is generated.



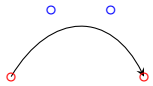
\electronrshiftarrow(0,0)(500,0)

The coordinates of the control points, $(150, 250)$ and $(375, 250)$, are confirmed by the following code:

[c] The chemist package for the TEX/LATEX-compatible mode does not support these commands.

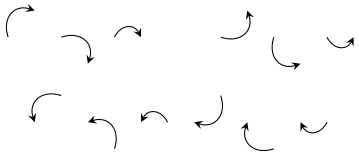
```
\begin{picture}(600,400)(-50,-100)
\ifPSmode
\put(0,0){\psbezier[unit=\unitlength,linewidth=0.4pt]{->}%
(0,0)(150,250)(375,250)(500,0)}
\else\ifPDFmode
\put(0,0){%
\tikznodimension{%
\draw [-stealth,line width=0.4pt]%
(0pt,0pt) .. controls (15pt,25pt) and (37.5pt,25pt) .. (50pt,0pt);}}%
\fi\fi
\put(0,0){\redx{\circle{30}}}
\put(500,0){\redx{\circle{30}}}
\put(150,250){\bluex{\circle{30}}}
\put(375,250){\bluex{\circle{30}}}
\end{picture}
```

where the `\draw` command of the pgf package (for the PDF-compatible mode) or the `\pzbezier` command of the PSTricks package (for the PostScript-compatible mode) is used to draw the cubic Bézier curve:



Several curved arrows generated by these commands are shown as examples:

```
\electronrshiftarrow(0,0)(100,100)\qquad
\electronrshiftarrow(0,0)(100,-100)\qquad
\electronrshiftarrow(0,0)(100,0)\qquad\qquad
\electronrshiftarrow[1](0,0)(100,100)\qquad
\electronrshiftarrow[1](0,0)(100,-100)\qquad
\electronrshiftarrow[1](0,0)(100,0) \\[20pt]
\electronlshiftarrow(0,0)(100,100)\qquad
\electronlshiftarrow(0,0)(100,-100)\qquad
\electronlshiftarrow(0,0)(100,0)\qquad
\electronlshiftarrow[1](0,0)(100,100)\qquad
\electronlshiftarrow[1](0,0)(100,-100)\qquad
\electronlshiftarrow[1](0,0)(100,0)
```



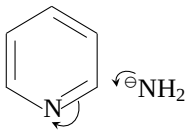
Example 33.6. An attack of an amide anion $^{\ominus}NH_2$ on the 2-position of pyridine is illustrated as follows. According to the specification of the XeLaTeXsystem, the code `1==N` should be placed at the last part of the atom list of `\sixheterovi`.[d]

```
\sixheterovi[ace]{2==\futuresubst{$^{\ominus}$NH$_{2}$};
2s==\electronlshiftarrow(70,0)(140,50);%
1s==\electronlshiftarrow[1](0,-30)(100,50);1==N}{}
```

The command `\futuresubst` is defined to show the amide anion $^{\ominus}NH_2$ that will be involved as a future substituent.

The command `\electronlshiftarrow` for drawing a left curly arrow is designated in the atom list of the command `\sixheterovi`.

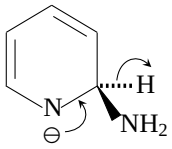
[d] Otherwise, the flag for truncating a vertex is deleted.



33-1 □

Example 33.7. Similarly, the command `\electronrshiftarrow` is used to draw a right curly arrow.

```
\sixheterovi[ce]{%
1s==\electronrshiftarrow[1](50,-70)(100,50);%
2s==\electronrshiftarrow(70,20)(200,70);1==\downnobond{N}{$\ominus$}%
}{2SB==NH$_{2}$;2SA==H}
```



□

In order to explicitly set the two control points of a cubic Bézier curve, let us define a new command `\electronAHshiftBezier`:

```
\makeatletter
\ifPSmode
\def\electronAHshiftBezier{%
\@ifnextchar[{\@electronAHshiftBezier}{%
\@electronAHshiftBezier[->]}}%
\else\ifPDFmode
\def\electronAHshiftBezier{%
\@ifnextchar[{\@electronAHshiftBezier}{%
\@electronAHshiftBezier[-stealth]}}
\fi\fi

\ifPSmode
\def\@electronAHshiftBezier[#1](#2,#3)(#4,#5)(#6,#7)(#8,#9){%
\psbezier[unit=\unitlength,linewidth=0.4pt]{#1}%
(#2,#3)(#4,#5)(#6,#7)(#8,#9)}%
\else\ifPDFmode
\def\@electronAHshiftBezier[#1](#2,#3)(#4,#5)(#6,#7)(#8,#9){%
\tikznodimension{%
\draw [#1,line width=0.4pt]%
(#2\unitlength,#3\unitlength) ..
controls (#4\unitlength,#5\unitlength) and
(#6\unitlength,#7\unitlength) ..
(#8\unitlength,#9\unitlength);}}%
\fi\fi
\makeatother
```

The syntax of the new command is as follows:

```
\electronAHshiftBezier[⟨arrowhead⟩](⟨startpoint⟩)(⟨control1⟩)(⟨control2⟩)(⟨endpoint⟩)
```

where the arrowhead is attached at the end point designated by the argument ⟨endpoint⟩ under a default condition. The type and the direction of the arrowhead can be changed by the optional argument ⟨arrowhead⟩.[e] The two control points, ⟨control1⟩ and ⟨control2⟩, are explicitly declared between ⟨startpoint⟩ or ⟨endpoint⟩.

For example, the codes:

[e] In the PDF-compatible mode, the symbol `-stealth` is adopted as a default setting.

```
\electronAHshiftBezier(0,0)(150,250)(375,250)(500,0)
\electronAHshiftBezier(0,0)(150,350)(375,350)(500,0)
\electronAHshiftBezier(0,0)(150,150)(375,150)(500,0)
\electronrshiftarrow(0,0)(500,0)
```

generate the following curved arrows:

Arrows of the reverse direction are drawn by setting the optional argument ⟨arrowhead⟩, where `<-` (for the PostScript-compatible mode) or `stealth-` (for the PDF-compatible mode) is declared:

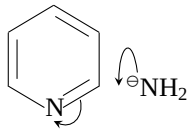
```
\ifPSmode
\electronAHshiftBezier[<-](0,0)(150,250)(375,250)(500,0)
\electronAHshiftBezier[<-](0,0)(150,350)(375,350)(500,0)
\electronAHshiftBezier[<-](0,0)(150,150)(375,150)(500,0)
\electronlshiftarrow(0,0)(500,0)
\else\ifPDFmode
\electronAHshiftBezier[stealth-](0,0)(150,250)(375,250)(500,0)
\electronAHshiftBezier[stealth-](0,0)(150,350)(375,350)(500,0)
\electronAHshiftBezier[stealth-](0,0)(150,150)(375,150)(500,0)
\electronlshiftarrow(0,0)(500,0)
\fi\fi
```

These codes generate the following curved arrows:

Example 33.8. If the right curved arrow of **33-1** is desired to be deeper, the following code can be written:

```
\ifPDFmode
\sixheterovi[ace]{2==\futuresubst{$^{\ominus}$NH$_{2}$};
2s==\electronAHshiftBezier[stealth-](70,0)(70,150)(120,200)(140,50);%
1s==\electronlshiftarrow[1](0,-30)(100,50);1==N}{}
\else\ifPSmode
\sixheterovi[ace]{2==\futuresubst{$^{\ominus}$NH$_{2}$};
2s==\electronAHshiftBezier[<-](70,0)(70,150)(120,200)(140,50);%
1s==\electronlshiftarrow[1](0,-30)(100,50);1==N}{}
\fi\fi
```

where either one should be selected according to the PDF mode or the PostScript mode. This code generates the following formula with a deeper curved arrow:



33-2 □

The commands `\electronshiftArrowr` and `\electronshiftArrowl` have a fixed arrowhead in comparison with the command `\electronAHshiftBezier` with a variable arrowhead. The syntax of the commands are as follows:

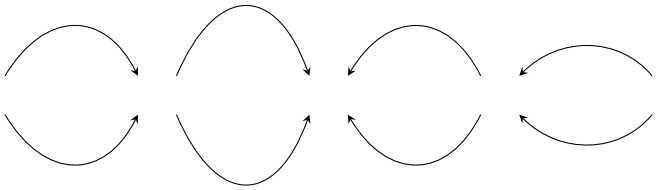
```
\electronshiftArrowr(⟨startpoint⟩)(⟨control1⟩)(⟨control2⟩)(⟨endpoint⟩)
\electronshiftArrowl(⟨startpoint⟩)(⟨control1⟩)(⟨control2⟩)(⟨endpoint⟩)
```

The two control points, ⟨control1⟩ and ⟨control2⟩, are explicitly declared between ⟨startpoint⟩ or ⟨endpoint⟩ in order to draw a cubic Bézier curve.

For example, the codes:

```
\electronshiftArrowr(0,0)(150,250)(375,250)(500,0)
\electronshiftArrowr(0,0)(150,350)(375,350)(500,0)
\electronshiftArrowl(0,0)(150,250)(375,250)(500,0)
\electronshiftArrowl(0,0)(150,150)(375,150)(500,0) \\
\electronshiftArrowr(0,0)(150,-250)(375,-250)(500,0)
\electronshiftArrowr(0,0)(150,-350)(375,-350)(500,0)
\electronshiftArrowl(0,0)(150,-250)(375,-250)(500,0)
\electronshiftArrowl(0,0)(150,-150)(375,-150)(500,0)
```

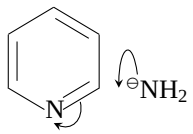
generate the following curved arrows:



Example 33.9. The formula **33-2** can be drawn more simply by the following code using the above-defined command `\electronshiftArrowl`:

```
\sixheterovi[ace]{2==\futuresubst{$^{\ominus}$NH$_{2}$};
2s==\electronshiftArrowl(70,0)(70,150)(120,200)(140,50);%
1s==\electronlshiftarrow[1](0,-30)(100,50);1==N}{}
```

which is effective in the PDF-compatible mode as well as in the PostScript-compatible mode. The resulted arrow is based on a cubic Bézier curve:



33-3

□

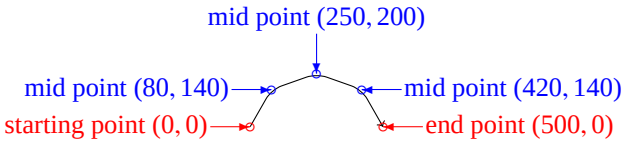
The XeTeX system supports a command of another type, `\putRoundArrow`, where the points for drawing a curved arrow are listed sequentially as arguments. The syntax of the new command is as follows:

```
\putRoundArrow[⟨arrowhead⟩]({⟨startpoint⟩)(⟨point1⟩)(⟨point2⟩) ··· (⟨endpoint⟩)}
```

The curved arrow runs through these listed points. For example, the code:

```
\putRoundArrow{(0,0)(80,140)(250,200)(420,140)(500,0)}
```

generates the following arrow:



where the listed points are shown in red or blue color.

The `\putRoundArrow` is capable of drawing a wavy arrow, as shown in the following example:

```
\putRoundArrow{(0,0)(50,110)(125,140)(200,110)(250,0)%
(300,-110)(375,-140)(450,-110)(500,0)}
```

The command \putRoundArrow takes the optional argument ⟨arrowhead⟩ to specify the type of its arrowhead. The value -stealth (or stealth-) in the PDF-compatible mode provides almost the same effect as -> (or <-) in the PostScript-compatible mode, as shown in the following examples.

```
\ifPDFmode
\putRoundArrow[-stealth]{(0,0)(0,140)(85,150)(100,100)} \qquad
\putRoundArrow[stealth-]{(0,0)(0,140)(85,150)(100,100)}
\else\ifPSmode
\putRoundArrow[->]{(0,0)(0,140)(85,150)(100,100)} \qquad
\putRoundArrow[<-]{(0,0)(0,140)(85,150)(100,100)}
\fi\fi
```

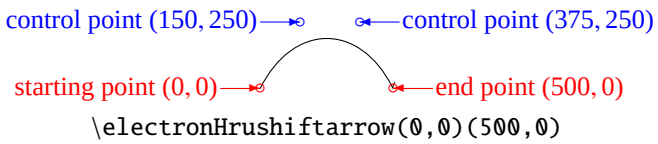
33.5 Curved Harpoons for Electron Shifts

In a parallel way to the commands \electronrshiftarrow and \electronlshiftarrow, the XeTeX system supports commands named \electron···shiftarrow, which are used to draw curved arrows with a harpoon-type arrowhead. The middle symbol ··· denotes a keyword selected from Hru, Hrd, Hlu, and Hld. The first letter H denotes 'harpoon'. The second letter r or l indicates a rightward or leftward harpoon. The third letter u or d indicates an upward or downward barb, when the arrowhead of the harpoon is placed rightwards (for the second letter r) or leftwards (for the second letter l). These commands for drawing such curved harpoons are defined in the chmst-pdf package for the PDF-compatible mode (or the chmst-ps package for the PostScript mode):[f]

```
\electronHrushiftarrow[⟨direction⟩](⟨startpoint⟩)(⟨endpoint⟩})
\electronHrdshiftarrow[⟨direction⟩](⟨endpoint⟩)(⟨startpoint⟩})
\electronHlushiftarrow[⟨direction⟩](⟨startpoint⟩)(⟨endpoint⟩})
\electronHldshiftarrow[⟨direction⟩](⟨endpoint⟩)(⟨startpoint⟩})
```

where the head of each harpoon is attached at the end point designated by the argument ⟨endpoint⟩. The data of ⟨startpoint⟩ or ⟨endpoint⟩ are given in the form of (x, y), where the values of x- and y-coordinates are determined by the multiples of \unitlength (= 0.1pt). The optional argument ⟨direction⟩ takes 0 for drawing a hat-type curve (default) or 1 for drawing a cup-type curve.

The coordinates of two control points for drawing the harpoon as a cubic Bézier curve are automatically calculated in the same way as those of the commands \electronrshiftarrow and \electronlshiftarrow. For example, the code \electronHrushiftarrow(0,0)(500,0) has the coordinates $(0, 0)$ and $(500, 0)$, from which the coordinates of two control points, i.e., $(150, 250)$ and $(375, 250)$, are automatically calculated so that the following cubic Bézier curve is generated.



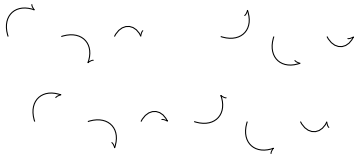
\electronHrushiftarrow(0,0)(500,0)

Several curved harpoons generated by these commands with a middle keyword Hru or Hrd are shown as examples:

```
\electronHrushiftarrow(0,0)(100,100)\qquad
```

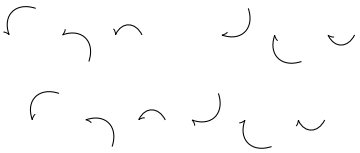
[f] The chemist package for the TeX/LaTeX-compatible mode does not support these commands.

```
\electronHrushiftarrow(0,0)(100,-100)\qquad
\electronHrushiftarrow(0,0)(100,0)\qquad\qquad
\electronHrushiftarrow[1](0,0)(100,100)\qquad
\electronHrushiftarrow[1](0,0)(100,-100)\qquad
\electronHrushiftarrow[1](0,0)(100,0) \\[20pt]
\electronHrdshiftarrow(0,0)(100,100)\qquad
\electronHrdshiftarrow(0,0)(100,-100)\qquad
\electronHrdshiftarrow(0,0)(100,0)\qquad
\electronHrdshiftarrow[1](0,0)(100,100)\qquad
\electronHrdshiftarrow[1](0,0)(100,-100)\qquad
\electronHrdshiftarrow[1](0,0)(100,0)
```



Several curved harpoons generated by these commands with a middle keyword `Hlu` or `Hld` are shown as examples:

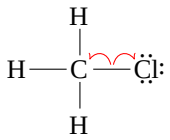
```
\electronHlushiftarrow(0,0)(100,100)\qquad
\electronHlushiftarrow(0,0)(100,-100)\qquad
\electronHlushiftarrow(0,0)(100,0)\qquad\qquad
\electronHlushiftarrow[1](0,0)(100,100)\qquad
\electronHlushiftarrow[1](0,0)(100,-100)\qquad
\electronHlushiftarrow[1](0,0)(100,0) \\[20pt]
\electronHldshiftarrow(0,0)(100,100)\qquad
\electronHldshiftarrow(0,0)(100,-100)\qquad
\electronHldshiftarrow(0,0)(100,0)\qquad
\electronHldshiftarrow[1](0,0)(100,100)\qquad
\electronHldshiftarrow[1](0,0)(100,-100)\qquad
\electronHldshiftarrow[1](0,0)(100,0)
```



Example 33.10. The radical fission of chloromethane is drawn by the substitution technique, where the commands `\electronHlushiftarrow` and `\electronHrushiftarrow` are declared in the ⟨subslist⟩ of the command `\tetrahedral` to draw curved harpoons:

```
\tetrahedral{0==C;%
0==\redx{\electronHlushiftarrow(40,70)(120,50)};%
0==\redx{\electronHrushiftarrow(130,50)(210,70)};%
1==H;2==H;3==H;4==\lonepairA[123]{Cl}}
```

This code generates following formula:



33-4

□

In a parallel way to the commands `\electronshiftArrowr` and `\electronshiftArrowl`, the X$\hat{}$MTEX system supports commands named `\electronshift`$\cdots$, which are used to draw curved arrows with a

harpoon-type arrowhead. The suffix ··· denotes a keyword selected from `Hru`, `Hrd`, `Hlu`, and `Hld`. The syntax of these commands are as follows:

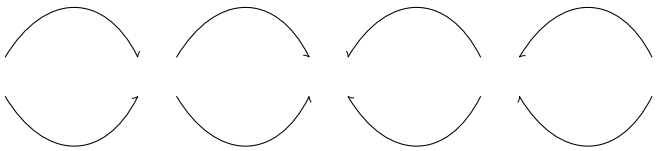
```
\electronshiftHru(⟨startpoint⟩)(⟨control1⟩)(⟨control2⟩)(⟨endpoint⟩)
\electronshiftHrd(⟨startpoint⟩)(⟨control1⟩)(⟨control2⟩)(⟨endpoint⟩)
\electronshiftHlu(⟨startpoint⟩)(⟨control1⟩)(⟨control2⟩)(⟨endpoint⟩)
\electronshiftHld(⟨startpoint⟩)(⟨control1⟩)(⟨control2⟩)(⟨endpoint⟩)
```

The two control points, ⟨control1⟩ and ⟨control2⟩, are explicitly declared between ⟨startpoint⟩ or ⟨endpoint⟩ in order to draw a cubic Bézier curve.

For example, the codes:

```
\electronshiftHru(0,0)(150,250)(375,250)(500,0)
\electronshiftHrd(0,0)(150,250)(375,250)(500,0)
\electronshiftHlu(0,0)(150,250)(375,250)(500,0)
\electronshiftHld(0,0)(150,250)(375,250)(500,0) \\
\electronshiftHru(0,0)(150,-250)(375,-250)(500,0)
\electronshiftHrd(0,0)(150,-250)(375,-250)(500,0)
\electronshiftHlu(0,0)(150,-250)(375,-250)(500,0)
\electronshiftHld(0,0)(150,-250)(375,-250)(500,0)
```

generate the following curved harpoons:

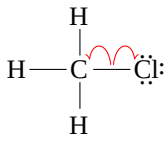


These commands can be used by declaring one control point so that they print harpoons in slightly different manners, as shown below:

```
\electronshiftHru(0,0)(100,50)(200,0)
\electronshiftHru(0,0)(30,80)(170,80)(200,0)
\electronshiftHrd(0,0)(100,-50)(200,0)
\electronshiftHrd(0,0)(30,-80)(170,-80)(200,0)
\electronshiftHlu(0,0)(100,50)(200,0)
\electronshiftHlu(0,0)(30,80)(170,80)(200,0)
\electronshiftHld(0,0)(100,-50)(200,0)
\electronshiftHld(0,0)(30,-80)(170,-80)(200,0)
```

Example 33.11. If the curved harpoons of **33-4** is desired to be deeper, the following code can be written by using the commands `\electronshiftHlu` and `\electronshiftHru`:

```
\tetrahedral{0==C;%
0==\redx{\electronshiftHlu(40,70)(50,140)(110,140)(120,50)};%
0==\redx{\electronshiftHru(130,50)(140,140)(200,140)(210,70)};%
1==H;2==H;3==H;4==\lonepairA[123]{Cl}}
```



33-5 □

33.6 Chemical Conventions for Using Arrows and Harpoons

Chemical conventions use arrows and harpoons differently:

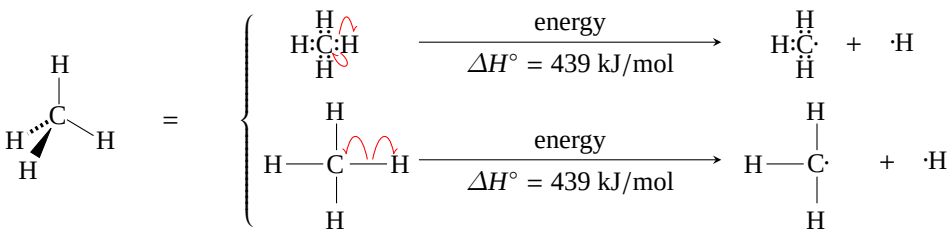
1. A composite of right and left harpoons (⇌) is used to specify an equilibrium equation, while a composite of right and left arrows (⟷) is used to specify a forward-reverse reaction.
2. A right (⇀) or left harpoon (↼) is used to show a shift of an electron, while a right (→) or left arrow (←) is used to show a shift of an electron pair (cf. page 657). These harpoons or arrows are frequently printed in bent (curved) styles to visualize a path of moving an electron or an electron pair.

The first convention can be fulfilled, because the chmst-pdf (chmst-ps or chemist) package has defined harpoons and arrows for using equilibrium equations and forward-reverse reactions (Subsection 33.1). The harpoons defined by the old version of the chmst-ps (chemist) package have been replaced by the newly-defined harpoons in the present version.

Example 33.12. The second convention for using a harpoon is concerned with a radical fission of a covalent bond. For example, the homolysis of the C—H bond of methane is represented by the following scheme.

```
\begin{ChemEquation}
\begin{XyMcompd}(250,400)(150,100){}{}
\dtetrahedralS{0==C;1==H;2==H;3A==H;4B==H}
\end{XyMcompd}
\qquad = \qquad
\left\{%
\begin{array}{ccc}
\begin{XyMcompd}(100,200)(100,-50){}{}
\put(0,0){\LewistetrahedralA{0==C;1==H;2==H;3==H;4==H}}
\redx{\electronshiftHru(185,70)(200,150)(220,160)(240,80)}%
\redx{\electronshiftHlu(160,0)(190,-80)(250,-50)(190,0)}%
\end{XyMcompd}
&
\reactrarrow{0pt}{4cm}{energy}{$\Delta \mathit{H}^{\circ}=439~kJ/mol$}
&
\setbox0=\hbox{\chemradicalA[2]{C}}
\begin{XyMcompd}(100,200)(100,-50){}{}
\LewistetrahedralA{0==\box0;1==H;3==H;4==H}
\end{XyMcompd}
+ \quad \chemradicalA[4]{H} \\
\noalign{\vskip8pt}
\begin{XyMcompd}(350,450)(100,100){}{}
\tetrahedral{0==C;%
0==\redx{\electronshiftHlu(40,70)(60,170)(100,150)(120,50)};%
0==\redx{\electronshiftHru(140,50)(160,150)(200,170)(220,70)};%
1==H;2==H;3==H;4==H}
\end{XyMcompd}
&
\reactrarrow{0pt}{4cm}{energy}{$\Delta \mathit{H}^{\circ}=439~kJ/mol$}
&
\begin{XyMcompd}(350,450)(100,100){}{}
```

```
\tetrahedral{0==\chemradicalA[2]{C};1==H;2==H;3==H}
\end{XyMcompd}
+ \quad \chemradicalA[4]{H} \\
\end{array}\right.
\end{ChemEquation}
```

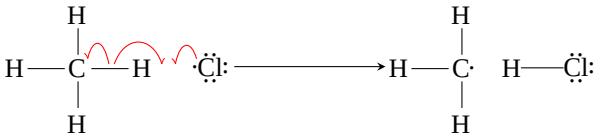


(33.8)

□

Example 33.13. The commands defined above for drawing electron shifts are used in the following equation, where `\redx` is declared to print red harpoons.

```
\begin{ChemEquation}
\begin{XyMcompd}(700,450)(100,100){}{}
\put(0,0){\tetrahedral{0==C;%
0==\redx{\electronshiftHlu(40,70)(60,150)(100,150)(120,50)};%
0==\redx{\electronshiftHru(140,50)(180,160)(280,160)(320,50)};%
0==\redx{\electronshiftHlu(370,50)(390,140)(430,140)(450,70)};%
1==H;2==H;3==H;4==H}}
\put(750,270){\lonepairA[123]{\chemradicalA[4]{Cl}}}
\end{XyMcompd}
\reactrarrow{0pt}{2cm}{}{}
\begin{XyMcompd}(600,450)(100,100){}{}
\put(0,0){\tetrahedral{0==\chemradicalA[2]{C};1==H;2==H;3==H}}
\put(450,270){H\sbond\lonepairA[123]{Cl}}
\end{XyMcompd}
\end{ChemEquation}
```

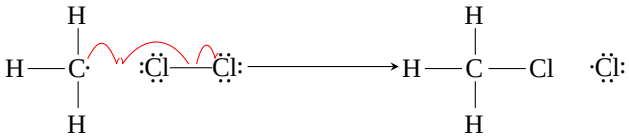


(33.9)

□

Example 33.14. The subsequent propagation step is represented by the following equation:

```
\begin{ChemEquation}
\begin{XyMcompd}(750,450)(100,100){}{}
\put(0,0){\tetrahedral{0==\chemradicalA[2]{C};1==H;2==H;3==H;%
0==\redx{\electronshiftHru(40,70)(80,150)(110,150)(150,50)};%
0==\redx{\electronshiftHlu(170,50)(250,160)(350,160)(420,50)};%
0==\redx{\electronshiftHru(450,50)(470,140)(500,140)(520,70)}%
}}
\put(550,270){\lonepairA[134]{Cl}\sbond\lonepairA[123]{Cl}}
\end{XyMcompd}
\reactrarrow{0pt}{2cm}{}{}
\begin{XyMcompd}(700,450)(100,100){}{}
\put(0,0){\tetrahedral{0==C;1==H;2==H;3==H;4==Cl}}
\put(750,270){\lonepairA[123]{\chemradicalA[4]{Cl}}}
\end{XyMcompd}
\end{ChemEquation}
```

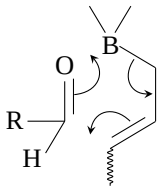


(33.10)

□

Example 33.15. An arrow for representing an electron-pair shift can be drawn by `\electronrshiftarrow` or `\electronrshiftarrow` according to the replacement technique, where these commands are declared in the argument ⟨subslist⟩ of `\sixheterov`.

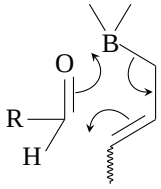
```
\sixheterov[ce]{%
1s==\electronrshiftarrow[1](90,-70)(160,-200);%
3s==\electronlshiftarrow(-250,-50)(-100,0);%
5s==\electronrshiftarrow[1](40,100)(100,250);%
1==B;6==O%
}{1Sa==\null;1Sb==\null;4U==\null;5Sa==R;5Sb==H}[df]
```



□

Example 33.16. The same structure is drawn by the addition technique, where the commands for drawing curved arrows, `\electronrshiftarrow` or `\electronrshiftarrow`, are declared in the argument ⟨atomlist⟩ of `\sixheterov`.

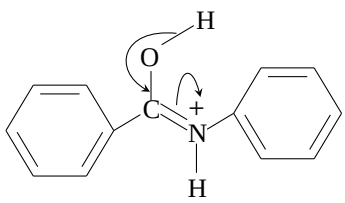
```
\sixheterov[ce%
{a\electronrshiftarrow[1](90,-70)(160,-200)}%
{c\electronlshiftarrow(-250,-50)(-100,0)}%
{e\electronrshiftarrow[1](40,100)(100,250)}%
]{1==B;6==O}{1Sa==\null;1Sb==\null;4U==\null;5Sa==R;5Sb==H}[df]
```



□

Example 33.17. Arrows for representing an electron-pair shift can be also drawn by using the commands `\electronshiftArrowr` and `\electronshiftArrowr`. The usage of these commands is exemplified by the following formula:

```
\begin{XyMcompd}(1100,700)(-400,0){}{}
\dimethylenei[a]{1==C;2==\upnobond{N}{+};%
1==\electronshiftArrowl(-40,100)(-180,180)(-150,340)(60,320);%
1==\electronshiftArrowr(60,50)(70,200)(120,200)(150,80)%
}%
{2==H;2W==\bzdrh{1==(yl)};1W==\bzdrh{4==(yl)};%
1==\Utrigonal{0==O;2==H;1==(yl)}}
\end{XyMcompd}
```



□

References

[1] S. Fujita, “Kagakusha-Seikagakusha no tame no LaTeX (LaTeX for Chemists and Biochemists),” Tokyo Kagaku Dozin, Tokyo (1993).

[2] S. Fujita, XeTeX version 2.00, On-line manual (2001).

[3] S. Fujita, XeTeX version 5.00, On-line manual (2010).

[4] S. Fujita, XeTeX version 4.05/4.06, On-line manual (2009).

Chapter 34

Compound Numbers and Compound Boxes

The XƎMTEX system supports systematic utilities for giving compound numbers and/or derivative numbers to structures drawn by XƎMTEX commands. These numbers are given after compounds are surrounded by compound boxes. This chapter is devoted to explain how to use these utilities.

34.1 Compound Numbers and Derivative Numbers

34.1.1 Compound Numbers and Cross-References

After the chemist (chmst-pdf or chmst-ps) package is loaded, the command `\compd` can be used to print out a sequential compound number. The compound number is capable of usual cross reference of LaTeX 2_ε, where `\label` and `\ref` is used. To print a boldfaced number, the chemist (chmst-pdf or chmst-ps) package supports `\cref` command.

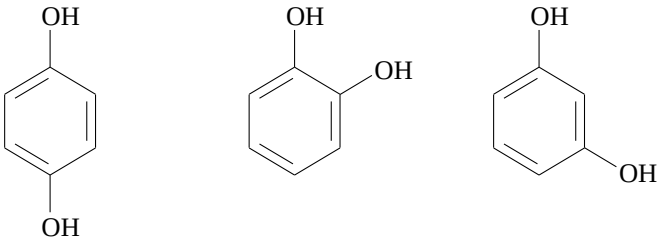
```
\compd\label{⟨refkey⟩}
\compdlabel{⟨refkey⟩}
\cref{⟨refkey⟩}
```

The argument ⟨refkey⟩ indicates an appropriate reference key for referring to the compound number, which is ascribed and printed out by declaring the command `\compd`. The `\compdlabel{...}` command can be used in place of `\compd\label{...}`, where ... is a reference key.

Example 34.1. For example, structural formulas due to the XƎMTEX system are numbered sequentially by writing the following code:

```
\begin{tabular}{ccc}
\bzdrv{1==OH;4==OH} & \bzdrv{1==OH;2==OH} & \bzdrv{1==OH;3==OH} \\
\compd\label{cpd:A1} & \compd\label{cpd:A2} & \compdlabel{cpd:A3} \\
\multicolumn{3}{l}{Compound \cref{cpd:A1} is called hydroquinone
or 1,4-dihyroxybenzene.} \\
\multicolumn{3}{l}{Compound \cref{cpd:A2} is called catechol
or 1,2-dihyroxybenzene.} \\
\multicolumn{3}{l}{Compound \cref{cpd:A3} is called resorcinol
or 1,3-dihydroxybenzene.} \\
\end{tabular}
```

which results in the following output:



34-1 **34-2** **34-3**

Compound **34-1** is called hydroquinone or 1,4-dihyroxybenzene.
Compound **34-2** is called catechol or 1,2-dihyroxybenzene.
Compound **34-3** is called resorcinol or 1,3-dihydroxybenzene. □

34.1.2 Derivative Numbers and Cross-References

The command `\nocompd` gives a sequential compound number to a compound, but the compound number is not output. The compound number can be referred by using `\label` and `\cref` (or `\ref`).

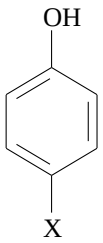
```
\nocompd\label{⟨refkey⟩}
\nocompdlabel{⟨refkey⟩}
\deriv\label{⟨derivrefkey⟩}
\derivlabel{⟨derivrefkey⟩}
```

The command `\nocompdlabel` is an alternative representation of `\nocompd\label`. The command `\nocompd` is combined with the `\deriv` command, which is linked with `\label`. `\derivlabel` is an alternative representation of `\deriv\label`.

Example 34.2. The number assigned by `\nocompd` is maintained in the subsequent `\deriv`, which prints out a subdivided alphabetical labelling, as shown in the following code:

```
\begin{tabular}{cll}
\multicolumn{3}{c}{%
\bzdrv{1==OH;4==X}\nocompd\label{cpd:A4} }\\
\deriv\label{cpd:4a} & \chemform{X = OH} & hydroquinone \\
\deriv\label{cpd:4b} & \chemform{X = F}  & 4-fluorophenol \\
\deriv\label{cpd:4c} & \chemform{X = Cl} & 4-chlorophenol \\
\derivlabel{cpd:4d}  & \chemform{X = Br} & 4-bromophenol \\
\derivlabel{cpd:4e}  & \chemform{X = NO_2} & 4-nitrophenol \\
\derivlabel{cpd:4f}  & \chemform{X = NH_3^+ClO_4^-} &
4-hydroxy-1-anilinium perchlorate \\
\end{tabular}
```

which results in the following output:



34-4a	$X = OH$	hydroquinone
34-4b	$X = F$	4-fluorophenol
34-4c	$X = Cl$	4-chlorophenol
34-4d	$X = Br$	4-bromophenol
34-4e	$X = NO_2$	4-nitrophenol
34-4f	$X = NH_3^+ClO_4^-$	4-hydroxy-1-anilinium perchlorate

The \deriv command gives a derivative number such as **34-4a**, in which the number **34-4** stems from the "compd" counter in the setting due to \nocompd and the alphabet **a** stems from the "deriv" counter in the setting due to \deriv. Each derivative is referred to by \label and \cref. For example, the reference command \cref{cpd:4b} outputs a derivative number **34-4b**. Note that the reference command \cref{cpd:A4} outputs the group number **34-4** of the derivatives, although the group number is not printed below the structure drawn. □

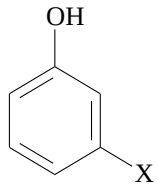
On the other hand, the \derivnum command is used in combination with \compd, where it outputs a net derivative alphabet without a compound (group) number due to \compd.

```
\derivnum\label{⟨derivrefkey⟩}
```

The ⟨derivrefkey⟩ is referred to by using \cref command, which outputs a derivative number as a combination of a compound (group) number and a net derivative alphabet.

Example 34.3. A combined use of \compd and \derivnum is illustrated as follows:

```
\begin{tabular}{cll}
\multicolumn{2}{c}{\bzdrv{1==OH;3==X}}&\\[-15pt]
\multicolumn{2}{c}{\compd\label{cpd:A5}}&\\[10pt]
\derivnum\label{cpd:5a} & \chemform{X = OH} & resorcinol \\
\derivnum\label{cpd:5b} & \chemform{X = F}  & 3-fluorophenol \\
\derivnum\label{cpd:5c} & \chemform{X = Cl} & 3-chlorophenol \\
\derivnum\label{cpd:5d}  & \chemform{X = Br} & 3-bromophenol \\
\derivnum\label{cpd:5e}  & \chemform{X = NO_2} & 3-nitrophenol \\
\derivnum\label{cpd:5f}  & \chemform{X = NH_3^+ClO_4^-} &
3-hydroxy-1-anilinium perchlorate \\
\end{tabular}
```



34-5

a	X = OH	resorcinol
b	X = F	3-fluorophenol
c	X = Cl	3-chlorophenol
d	X = Br	3-bromophenol
e	$X = NO_2$	3-nitrophenol
f	$X = NH_3^+ClO_4^-$	3-hydroxy-1-anilinium perchlorate

The \derivnum command gives a derivative number as a sequential alphabet (**a** etc.) which stems from the "deriv" counter in the setting due to \derivnum. Each derivative is referred to by \label and \cref. For example, \cref{cpd:5a} outputs a derivative number **34-5a**, while \cref{cpd:A5} output the group number **34-5** of the derivatives. □

34.1.3 Changing Modes of Printed Numbers

In this manual, the mode of printed compound numbers is decided by the macro:

```
\def\thecompd{\arabic{chapter}\mbox{-}\arabic{compd}}
```

which is declared in the preamble of this manual. According to this macro, the declaration \cref{cpd:A1}, for example, prints out a compound number **34-1**, where the chapter number ("chapter" counter) and the net compound number ("compd" counter) are linked with a hyphen.

If the chapter number is desired to be omitted in the compound number, the macro \thecompd is redefined as follows in the preamble of a document:

```
\def\thecompd{\arabic{compd}}
```

A typical example is shown below:

```
{
\def\thecompd{\arabic{compd}}%in the preamble
printed out: \compd\label{cpd:temp1} \par
cross reference: \cref{cpd:temp1}
}
```

Thereby, the compound number and its cross reference take the following formats:

printed out: **6**
cross reference: **6**

The definition of `\thecompd` is effective to print out derivative numbers, as found in the following examples:

```
{
\def\thecompd{\arabic{compd}}
(mode A) \\
print out: \nocompd\label{cpd:temp2} (none) and \deriv\label{cpd:temp2a}\\
cross reference: \cref{cpd:temp2} and \cref{cpd:temp2a} \\
(mode B) \\
print out: \compd\label{cpd:temp3} and \derivnum\label{cpd:temp3a}\\
cross reference: \cref{cpd:temp3} and \cref{cpd:temp3a}
}
```

where mode A is a combination of `\nocompd` and `\deriv`, while mode B is a combination of `\compd` and `\derivnum`. These codes give the following results:

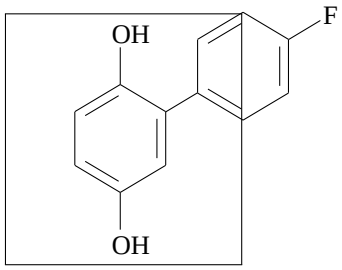
(mode A)
print out: (none) and **7a**
cross reference: **7** and **7a**
(mode B)
print out: **8** and **a**
cross reference: **8** and **8a**

34.2 Boxes for Chemical Structural Formulas

34.2.1 XyMcompd Environment

Each structural formula drawn by the XyMTEX system has its drawing domain, which is decided by its main skeleton. This means that a large substituent sticks out from the domain, as shown in the following formula:

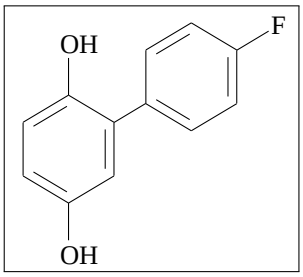
```
\fbox{%
\bzdrv{1==OH;4==OH;2==\bzdrv{5==(yl);2==F}}
}
```



where the domain is surrounded by a frame due to `\fbox`. Note that the tolyl group (produced by declaring a (yl)-function in the ⟨subslist⟩ of `\bzdrv`) has no size. To adjust such a drawing domain to cover the net formula, we use a XyMcompd environment:

```
\begin{XyMcompd}(⟨domainsize⟩)(⟨shift⟩){⟨refkey⟩}{⟨subkey⟩}
(codes for drawing structures)
\end{XyMcompd}
```

The XyMcompd environment is used as follows:



which is drawn by the following code:

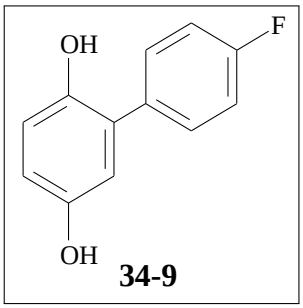
```
\fbox{%
\begin{XyMcompd}(900,900)(250,50){}{}
\bzdrv{1==OH;4==OH;2==\bzdrv{5==(yl);2==F}}
\end{XyMcompd}
}
```

The first argument ⟨domainsize⟩, `(900,900)`, indicates the (width, height) of the domain which is measured by using `\unitlength` (default 0.1 pt) as a unit. The 2nd argument ⟨shift⟩, `(250,50)`, represents a shift value of x, y-coordinates. The 3rd argument ⟨refkey⟩ is a reference key for compound number if necessary. The 4th argument ⟨subkey⟩ is a derivative alphabet (or another character) if necessary.

The 3rd argument ⟨refkey⟩ is used to set a compound number, which is printed out below the structure drawn by the codes at issue. For example, the code:

```
\fbox{%
\begin{XyMcompd}(900,900)(250,50){cpd:XyMcomp1}{}
\bzdrv{1==OH;4==OH;2==\bzdrv{5==(yl);2==F}}
\end{XyMcompd}
}
```

generates the following structure with a compound number:

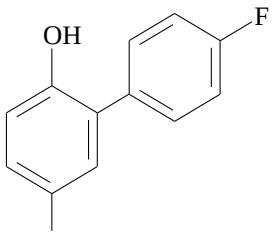


The compound number can be referred to by `\cref{cpd:XyMcomp1}`, which prints out **34-9**.

The 4th argument ⟨subkey⟩ is used to add a suffix to the compound number. For example, the code:

```
\begin{XyMcompd}(900,900)(250,50){cpd:XyMcomp2}{a}
\bzdrv{1==OH;4==OH;2==\bzdrv{5==(yl);2==F}}
\end{XyMcompd}
```

generates the following structure with a compound number, which accompanied by the suffix:

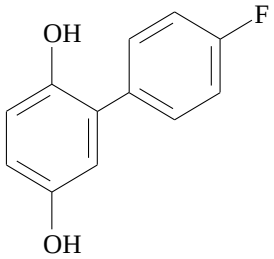


34-10a

The compound number can be referred to by `\cref{cpd:XyMcomp2}\textbf{a}`, which prints out **34-10a**.

If a comment is added below a compound number, the `tablular` environment can be used in addition to the `XyMcompd` environment.

```
\begin{tabular}{c}
\begin{XyMcompd}(900,900)(250,50){}{}
\bzdrv{1==OH;4==OH;2==\bzdrv{5==(yl);2==F}}
\end{XyMcompd} \\
\noalign{\vskip5pt}
\compd\label{cpd:XyMcomp3} \\
(an auxiliary developer)
\end{tabular}
```

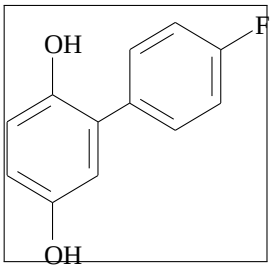


34-11
(an auxiliary developer)

34.2.2 `picture` Environment

The LaTeX picture environment can be used in place of the XyMcompd environment.

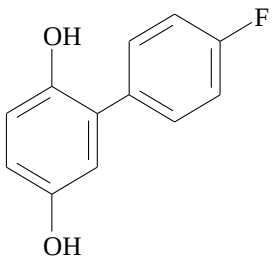
```
\fbox{%
\begin{picture}(900,900)(250,50)
\put(0,0){\bzdrv{1==OH;4==OH;2==\bzdrv{5==(yl);2==F}}}
\end{picture}
}
```



The example for drawing **34-11** can be rewritten as follows:

```
\begin{tabular}{c}
\begin{picture}(900,900)(250,50)
\put(0,0){\bzdrv{1==OH;4==OH;2==\bzdrv{5==(yl);2==F}}}
\end{picture}\\
\noalign{\vskip5pt}
\compd\label{cpd:XyMcomp4} \\
```

```
(an auxiliary developer)
\end{tabular}
```



34-12
(an auxiliary developer)

34.2.3 Commands for Compound Boxes

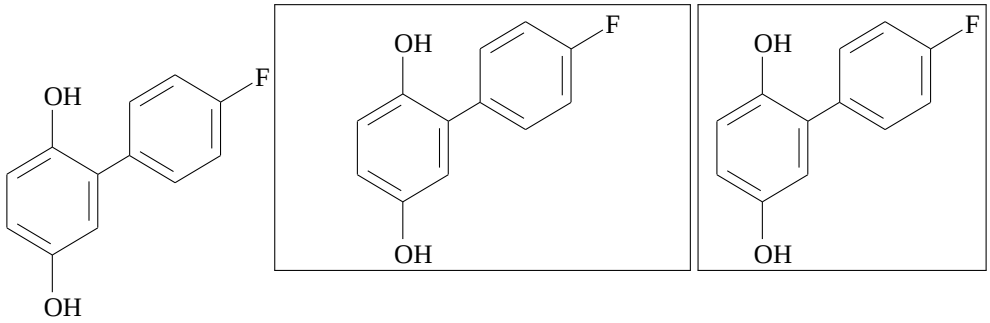
The command `\cdonecell` takes three arguments:

```
\cdonecell{⟨dimenA⟩}{⟨dimenB⟩}{⟨formula⟩}
```

where the structure of the 3rd argument ⟨formula⟩ is drawn with a width of the 2nd argument ⟨dimenB⟩ at a raised position decided by the first argument ⟨dimenA⟩. A similar raised structural formula can be drawn by using the `\raisebox` command of the graphicx package. For example, the following code:

```
\begin{XyMcompd}(900,900)(250,50){}{}
\bzdrv{1==OH;4==OH;2==\bzdrv{5==(yl);2==F}}
\end{XyMcompd}
\fbox{%
\cdonecell{20pt}{150pt}{%
\begin{XyMcompd}(900,900)(250,50){}{}
\bzdrv{1==OH;4==OH;2==\bzdrv{5==(yl);2==F}}
\end{XyMcompd}}}
\fbox{%
\raisebox{20pt}{%
\begin{XyMcompd}(900,900)(250,50){}{}
\bzdrv{1==OH;4==OH;2==\bzdrv{5==(yl);2==F}}
\end{XyMcompd}}}
```

gives the following result:



where the frame of the latter formula is drawn by the `\fbox` command.

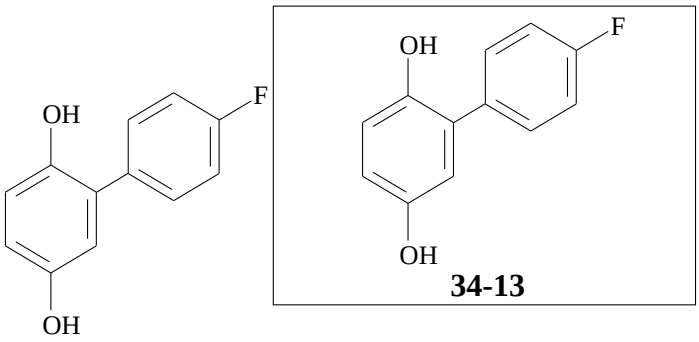
The command `\cdtwocell` takes the following syntax:

```
\cdtwocell{⟨dimenA⟩}{⟨dimenB⟩}{⟨formula⟩}{⟨label⟩}
```

which draws the structure of the 3rd argument ⟨formula⟩ with a width of the 2nd argument ⟨dimenB⟩ at a raised position decided by the first argument ⟨dimenA⟩, where a compound label is written as the fourth argument ⟨label⟩. For example, the following code:

```
\begin{XyMcompd}(900,900)(250,50){}{}
\bzdrv{1==OH;4==OH;2==\bzdrv{5==(yl);2==F}}
\end{XyMcompd}
\fbox{%
\cdtwocell{20pt}{150pt}{%
\begin{XyMcompd}(900,900)(250,50){}{}
\bzdrv{1==OH;4==OH;2==\bzdrv{5==(yl);2==F}}
\end{XyMcompd}}{\compd\label{cpd:7}}}
```

gives the following result:

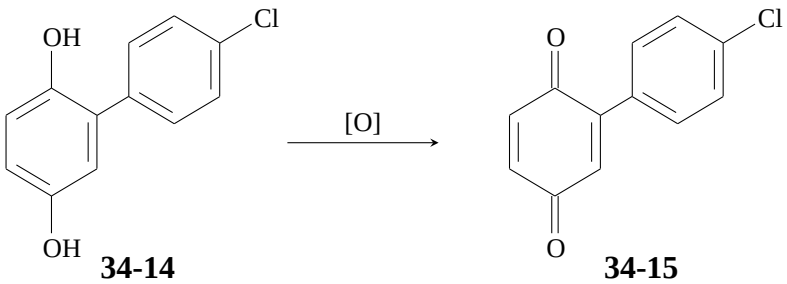


where the frame of the latter formula is drawn by the `\fbox` command.

Example 34.4. As remarked in page 612, the amsmath package has redefined LaTeX display math environments such as the `equation` environment, so that it does not permit multiple usage of the command `\label` in a single display math environment. This restriction can be avoided by declaring `\resetamsmathlabel`, which is defined in page 612.

For example, two compound numbers **34-14** and **34-15** can be declared in a LaTeX `equation` environment after the declaration of `\resetamsmathlabel`.

```
\begin{equation}
\resetamsmathlabel %reset \label from amsmath to LaTeX
\begin{XyMcompd}(950,900)(250,50){cpd:HQClph}{}
\bzdrv{1==OH;4==OH;2==\bzdrv{5==(yl);2==Cl}}
\end{XyMcompd}
\reactrarrow{0pt}{2cm}{[O]}{\strut}\qquad
\begin{XyMcompd}(950,900)(250,50){cpd:QClph}{}
\bzdrv[pa]{1D==O;4D==O;2==\bzdrv{5==(yl);2==Cl}}
\end{XyMcompd}
\end{equation}
```



(34.1)

□

Chapter 35

Commands for Printing Chemical Formulas and Environments for Printing Chemical Equations

Molecular formulas are expressed by roman characters with subscripts and/or superscripts, e.g., $Pb_2^{II}Pb^{IV}O_4$, whereas mathematical terms are expresses in the form of italic characters with subscripts and/or superscripts, e.g., $x_1^2 y_1^2$. This chapter is devoted to compare these two expressions and to introduce convenient utilities for outputting molecular formulas.

35.1 Basic Utilities for Writing Chemical Formulas

Basic utilities are exemplified by using `\ChemForm`. They are common to the three environments (ChemEquation, ChemEqnarray, and ChemEqnarray$*$) supported by the chemist (chmst-pdf or chmst-ps) package.[a]

35.1.1 Basics Due to the `\ChemForm` Command

TEX supports an in-text (in-line) math mode toggled by `$...$`. LATEX 2ε provides us with a facility of the same kind, i.e., `\(...\)`. These in-text math modes (as well as the `equation` environment etc. supported by LATEX 2ε) have the following difficulties in representing molecular formulas.

1. Each text letter in these in-text math modes is typeset in italic form, which is unsuitable to represent molecular formulas. For example, `$H_{2}O$` results in H_2O. Hence, we should input `$\mathrm{H}_{2}\mathrm{O}$` or `$\mathrm{H_{2}O}$` to output an upright formula H_2O. Although the use of `\mathrm` is not tedious in an in-text math mode, the `eqnarray` environment of LATEX 2ε requires a more complicated treatment. Hence, a simpler and integrated method of inputting chemical formulas would be desirable for convenience.

2. In these in-text math modes, the depth of a subscript depends on the presence or absence of the coexisting superscript. For example, the depth of the subscript 2 of C_2 is different from the subscript 2 of O_2^-, as found in the following output.

   `$\mathrm{C}_{2}\mathrm{H}_{3}\mathrm{O}_{2}^{-}$` $C_2H_3O_2^-$

3. The fonts used in such an in-text math mode are italics (for the mathversion normal) or bold italics (for mathversion bold). The use of other fonts (e.g., san serif) would be desirable by a means of a simpler and integrated method.

[a] Because the chmst-ps package loads the chemist package automatically, descriptions on the chemist package are also useful to the chmst-pdf or chmst-ps package throughout the present manual.

Table 35.1. Outputs Due to the ¥ChemForm Command

¥ChemForm		$...$	
`\ChemForm{H_2O}`	H_2O	`$\mathrm{H_2O}$`	H_2O
`\ChemForm{N_{2(g)}}`	$N_{2(g)}$	`$\mathrm{N_{2(g)}}$`	$N_{2(g)}$
`\ChemForm{CrO_{4}^{2-}}`	CrO_4^{2-}	`$\mathrm{CrO}_{4}^{2-}$`	CrO_4^{2-}
`\ChemForm{C_{2}H_{3}% O_{2}^{-}}`	$C_2H_3O_2^-$	`\(\mathrm{C_{2}H_{3}% O_{2}^{-}}\)`	$C_2H_3O_2^-$
`\ChemForm{CuSO_4\cdot% 5H_2 O}`	$CuSO_4 \cdot 5H_2O$	`$\mathrm{CuSO_4\cdot % 5H_2O}$`	$CuSO_4 \cdot 5H_2O$
`\ChemForm{Pb_{2}^{II}% Pb^{IV}O_{4}}`	$Pb_2^{II}Pb^{IV}O_4$	`$\mathrm{Pb_{2}^{II}% Pb^{IV}O_{4}}$`	$Pb_2^{II}Pb^{IV}O_4$
`\ChemForm{^{79}Br^{-}`	$^{79}Br^-$	`$^{79}\mathrm{Br}^{-}$`	$^{79}Br^-$
`\ChemForm{\rho(H_{2}% SO_{4})}`	$\rho(H_2SO_4)$	`$\rho(\mathrm{H_{2}% SO_{4}})$`	$\rho(H_2SO_4)$
`\ChemForm{^{23}Na% (\gamma,\:3n)\:^{20}Na}`	$^{23}Na(\gamma,\ 3n)\ ^{20}Na$	`$^{23}\mathrm{Na}% (\gamma,\:3n)\:^{20}Na}$`	$^{23}Na(\gamma,\ 3n)\ ^{20}Na$

To avoid such difficulties, the previous chemist package (packed in the XeTeX system ≤ version 4.04) has supported the `\chemform` command (as well as the `chemeqn` and the `chemeqnarray` environments). Although this command has cleared Nos. 1 and 2 (by means of the chemical correction) of the above difficulties, it has not yet cleared difficulty No. 3 described above.

The present version of the chemist (chmst-pdf or chmst-ps) package supports the `\ChemForm` command, which gives sufficient results with respect to the difficulties described above.

`\ChemForm{`⟨formula⟩`}`	(satisfying Nos.1–3)
`\chemform{`⟨formula⟩`}`	(satisfying Nos.1 and 2 not No.3)

Table 35.1 summarizes examples which show that the `\ChemForm` command solves difficulties Nos. 1 and 2. With respect to difficulty No. 2 in particular, refer to the rows for $C_2H_3O_2^-$ and $Pb_2^{II}Pb^{IV}O_4$ in Table 35.1. For the solution of No.3, see Subsection 35.1.2.

To obtain the formula H_2O, several codes can be written, e.g., `\ChemForm{H_2O}` (in Table 35.1), `\ChemForm{H_2␣O}` (the symbol ␣ represents a space), and `\ChemForm{H_{2}O}`. Although the first input obeys a TeX standard, it is not so easy to find pauses. The second or third one is redundant but easy to find pauses. For a more complicated example, compare `\ChemForm{C_2H_3O_2^-}` and `\ChemForm{C_2␣H_3␣O_2^-}` (as well as the counterpart listed in Table 35.1), which provide the same output, $C_2H_3O_2^-$.

35.1.2 Fonts for Chemical Formulas

In a normal situation of LaTeX 2ε, `\ChemForm` and `\chemform` give slightly different outputs as follows:[b]

`\ChemForm{N_{2(g)}}`	$N_{2(g)}$
`\chemform{N_{2(g)}}`	$N_{2(g)}$
cf. `$\mathrm{N_{2(g)}}$`	$N_{2(g)}$

In order to change math fonts into san serif fonts, a command `\let\ChemEqFont=\sf` is declared at any place in a tex file. For example, the source code represented by

[b] The font used in `\chemform` is selected by declaring `\mathversion{chem}`. In the present manual, the selected font for `\chemform` is the Computer Modern Roman (`cmr`), while the default font for `\ChemForm` is selected to be the same as the text of this manual. This type of difference in fonts stems from a similar situation to Item No. 3.

```
{\let\ChemEqFont=\sf
\begin{tabular}{lclc}
\verb/\ChemForm{N_{2(g)}}/ & \ChemForm{N_{2(g)}} & & \\
\verb/\chemform{N_{2(g)}}/ & \chemform{N_{2(g)}} & & \\
\hline cf.\ %
\verb/$\mathrm{N_{2(g)}}$/ & $\mathrm{N_{2(g)}}$ &
\verb/$\mathsf{N_{2(g)}}$/ & $\mathsf{N_{2(g)}}$ \\
\end{tabular}
}
```

produces the following output:

`\ChemForm{N_{2(g)}}`	$\mathsf{N_{2(g)}}$		
`\chemform{N_{2(g)}}`	$\mathrm{N_{2(g)}}$		
cf. `$\mathrm{N_{2(g)}}$`	$\mathrm{N_{2(g)}}$	`$\mathsf{N_{2(g)}}$`	$\mathsf{N_{2(g)}}$

It should be noted that the output due to `\ChemForm` obeys the declaration of `\let\ChemEqFont=\sf`, while the output due to `\chemform` does not follow the declaration.

In a similar way, the declaration of `\let\ChemEqFont=\tt` changes fonts due to `\ChemForm` into typewriter fonts.

`\ChemForm{N_{2(g)}}`	$\mathtt{N_{2(g)}}$		
`\chemform{N_{2(g)}}`	$\mathrm{N_{2(g)}}$		
cf. `$\mathrm{N_{2(g)}}$`	$\mathrm{N_{2(g)}}$	`$\mathtt{N_{2(g)}}$`	$\mathtt{N_{2(g)}}$

By the declaration of `\let\ChemEqFont=\bf`, fonts due to `\ChemForm` are changed into boldfaced fonts.

`\ChemForm{N_{2(g)}}`	$\mathbf{N_{2(g)}}$		
`\chemform{N_{2(g)}}`	$\mathrm{N_{2(g)}}$		
cf. `$\mathrm{N_{2(g)}}$`	$\mathrm{N_{2(g)}}$	`$\mathbf{N_{2(g)}}$`	$\mathbf{N_{2(g)}}$

The declaration of `\let\ChemEqFont=\sl` results in slanted fonts printed by `\ChemForm`, although a LaTeX font warning (Command `\sl` invalid in math mode) appears.

`\ChemForm{N_{2(g)}}`	$N_{2(g)}$		
`\chemform{N_{2(g)}}`	$\mathrm{N_{2(g)}}$		
cf. `$\mathrm{N_{2(g)}}$`	$\mathrm{N_{2(g)}}$	`${\@nomath\sl N_{2(g)}}$`	$N_{2(g)}$

By declaring `\let\ChemEqFont=\it`, fonts due to `\ChemForm` are changed into italic fonts, which are slightly different from the default fonts for the math modes of LaTeX 2_ε.

`\ChemForm{N_{2(g)}}`	$N_{2(g)}$		
`\chemform{N_{2(g)}}`	$\mathrm{N_{2(g)}}$		
cf. `$\mathrm{N_{2(g)}}$`	$\mathrm{N_{2(g)}}$	`$\mathit{N_{2(g)}}$`	$N_{2(g)}$
		`$N_{2(g)}$`	$N_{2(g)}$

Finally, the declaration of `\mathversion{bold}` changes the output of `\ChemForm` as well as that of the in-text math mode.

`\mathversion{bold}`	
`\ChemForm{N_{2(g)}}`	$\mathbf{N_{2(g)}}$
`\chemform{N_{2(g)}}`	$\mathrm{N_{2(g)}}$
cf. `$\mathrm{N_{2(g)}}$`	$\mathbf{N_{2(g)}}$

35.1.3 Using Mathematical Symbols

Mathematical symbols supported by TeX/LaTeX 2_ε can be used in the argument of `\ChemForm`. The following examples show the use of `\frac` and `\lg` in the argument of `\ChemForm`.

```
\ChemForm{Fe(CN)_{\frac{6}{2}}} \quad
\ChemForm{\frac{1}{2}O_{2}} \quad
\ChemForm{pH=-\lg[\gamma_{\pm}\mathit{c}(H^{+})/(mol\cdot dm^{-3})]}
```

$$\mathrm{Fe(CN)}_{\frac{6}{2}} \qquad \tfrac{1}{2}\mathrm{O}_2 \qquad \mathrm{pH} = -\lg[\gamma_{\pm} c(\mathrm{H}^+)/(\mathrm{mol}\cdot\mathrm{dm}^{-3})]$$

Inequality symbols (> and <) can be used in \ChemForm, while they should be replaced by the commands \mathgreater and \mathless in \chemform. Thus, thermal stabilities of boron compounds are typeset as follows:

```
\ChemForm{B_{2}(NMe_{2})_{4}>B_{2}(OMe_{2})_{4}>B_{2}(OH)_{4}
>B_{2}F_{4}>B_{2}Cl_{4}>B_{2}Br_{4}} \\
\chemform{B_{2}(NMe_{2})_{4}\mathgreater B_{2}(OMe_{2})_{4}
\mathgreater B_{2}(OH)_{4}
\mathgreater B_{2}F_{4}\mathgreater B_{2}Cl_{4}\mathgreater B_{2}Br_{4}}
```

$$\mathrm{B_2(NMe_2)_4} > \mathrm{B_2(OMe_2)_4} > \mathrm{B_2(OH)_4} > \mathrm{B_2F_4} > \mathrm{B_2Cl_4} > \mathrm{B_2Br_4}$$
$$\mathrm{B_2(NMe_2)_4}>\mathrm{B_2(OMe_2)_4}>\mathrm{B_2(OH)_4}>\mathrm{B_2F_4}>\mathrm{B_2Cl_4}>\mathrm{B_2Br_4}$$

Compare the following examples:

```
(correct) \ChemForm{B_{2}(NMe_{2})_{4}>B_{2}(OMe_{2})_{4}} and
\ChemForm{B_{2}(OMe_{2})_{4}<NMe_{2})_{4}} \\
(incorrect) \chemform{B_{2}(NMe_{2})_{4}>B_{2}(OMe_{2})_{4}} and
\chemform{B_{2}(OMe_{2})_{4}<NMe_{2})_{4}} \\
(correct) \chemform{B_{2}(NMe_{2})_{4}\mathgreater B_{2}(OMe_{2})_{4}} and
\chemform{B_{2}(OMe_{2})_{4}\mathless NMe_{2})_{4}}
```

(correct) $\mathrm{B_2(NMe_2)_4} > \mathrm{B_2(OMe_2)_4}$ and $\mathrm{B_2(OMe_2)_4} < \mathrm{NMe_2)_4}$
(incorrect) $\mathrm{B_2(NMe_2)_4}$ ¿ $\mathrm{B_2(OMe_2)_4}$ and $\mathrm{B_2(OMe_2)_4}$ ¡ $\mathrm{NMe_2)_4}$
(correct) $\mathrm{B_2(NMe_2)_4}>\mathrm{B_2(OMe_2)_4}$ and $\mathrm{B_2(OMe_2)_4}<\mathrm{NMe_2)_4}$

Double inequality symbols (\gg and \ll) can be used in both \ChemForm and \chemform.

```
\ChemForm{SO_{2}\cdot \mathit{n}H_{2}O \rightleftharpoons H_{2}SO_{3}(aq);%
\quad \mathit{K} \ll 10^{-9}} \qquad
\chemform{SO_{2}\cdot \mathit{n}H_{2}O \rightleftharpoons H_{2}SO_{3}(aq);%
\quad \mathit{K} \ll 10^{-9}}
```

$$\mathrm{SO_2}\cdot n\mathrm{H_2O} \rightleftharpoons \mathrm{H_2SO_3(aq)}; \quad K \ll 10^{-9} \qquad \mathrm{SO_2}\cdot n\mathrm{H_2O} \rightleftharpoons \mathrm{H_2SO_3(aq)}; \quad K \ll 10^{-9}$$

35.1.4 Chemical Corrections

As described on page 605 (Item No. 2), a chemical symbol with both a subscript and a superscript has the subscript at a different vertical level from the counterpart of a symbol with a subscript only. For example, the subscript of $\mathrm{M_2^{II}}$ is different in the bottom level from that of $\mathrm{FeO_4}$ in the formula $\mathrm{M_2^{II}FeO_4}$ (cf. [1, Chapter 18]). For aligning the bottoms of such subscripts, we introduce 'chemical corrections' and define a macro \chemform. Compare the following examples with special attention to the printing places of the subscripts.

```
$\mathrm{M_{2}^{II}FeO_{4}}$ (uncorrected)
vs.\
\ChemForm{M_{2}^{II}FeO_{4}} (corrected) and
\chemform{M_{2}^{II}FeO_{4}} (corrected)
```

$\mathrm{M_2^{II}FeO_4}$ (uncorrected) vs. $\mathrm{M_2^{II}FeO_4}$ (corrected) and $\mathrm{M_2^{II}FeO_4}$ (corrected)

Because the \chemform command is defined to take account of the mathversion "chem" automatically, it is unnecessary to use the command \mathrm or \textrm. On the other hand, the \ChemForm command is defined to take another technique for printing roman fonts, so that it is also unnecessary to use the command \mathrm or \textrm.

35.2 Chemical Equations

The command \ChemForm (or \chemform) corresponds to the in-text math mode represented by \$...\$ (TEX) or \(...\) (LATEX 2ε). On the other hand, ChemEquation and like environments correspond to equation and like environments of LATEX 2ε.

35.2.1 Arrows of Fixed Lengths in Chemical Equations

Arrows supported by TEX/LATEX 2ε can be used in \ChemForm, as shown in the following examples:

```
\ChemForm{H_2+Cl_2 \rightarrow 2HCl} \qquad
\ChemForm{H_2+Cl_2 \longrightarrow 2HCl} \\
\ChemForm{H_2+Cl_2 \leftarrow 2HCl} \qquad
\ChemForm{H_2+Cl_2 \longleftarrow 2HCl} \\
\ChemForm{H_2+Cl_2 \rightleftharpoons 2HCl}
```

$$\mathrm{H_2 + Cl_2 \rightarrow 2HCl} \qquad \mathrm{H_2 + Cl_2 \longrightarrow 2HCl}$$
$$\mathrm{H_2 + Cl_2 \leftarrow 2HCl} \qquad \mathrm{H_2 + Cl_2 \longleftarrow 2HCl}$$
$$\mathrm{H_2 + Cl_2 \rightleftharpoons 2HCl}$$

The appearances of arrows produced by a command of the same name in chemist and chmst-pdf (or chmst-ps) are different, as summarized in Table 33.1. For further examples, see Section 33.1.

35.2.2 ChemEquation Environment

In parallel with the equation environment of LATEX 2ε, the chemist package (version 4.05, also chmst-pdf or chmst-ps) supports the ChemEquation environment in addition to the chemeqn environment defined previously (version $\leq$ 4.04). The basic functions described above for \ChemForm are also effective to the ChemEquation environment.

```
\begin{ChemEquation}
(a code for drawing a chemical equation)
\end{ChemEquation}
```

Example 35.1. The following code is a typical example containing a chemical compound and ionic species. Thus, a strong electrolyte (KSO_4) dissolves in water according to the following process:

```
\begin{ChemEquation}
K_{2}SO_{4}(s) \llongrightarrow 2K^{+}(aq) + SO_{4}^{2-}(aq)
\end{ChemEquation}
```

$$\mathrm{K_2SO_4(s) \longrightarrow 2K^+(aq) + SO_4^{2-}(aq)} \tag{35.1}$$

where the molecular formulas are printed in upright fonts, although they are written directly without using the \mathrm command. Compare this output with the following one due to an equation environment of LATEX 2ε:

```
\begin{equation}
K_{2}SO_{4}(s) \llongrightarrow 2K^{+}(aq) + SO_{4}^{2-}(aq)
\end{equation}
```

$$K_2SO_4(s) \longrightarrow 2K^+(aq) + SO_4^{2-}(aq) \tag{35.2}$$

where each molecular formula written without using the \mathrm command is printed in italic fonts. □

The chemeqn environment defined previously (version $\leq$ 4.04) can be also used equivalently when we work in a usual condition, i.e., in the mathversion "normal":

```
\begin{chemeqn}
(a code for drawing a chemical equation)
\end{chemeqn}
```

Example 35.2. Thus, we obtain the following equation:

```
\begin{chemeqn}
K_{2}SO_{4}(s) \llongrightarrow 2K^{+}(aq) + SO_{4}^{2-}(aq)
\end{chemeqn}
```

$$\mathrm{K_2SO_4(s)} \longrightarrow 2\mathrm{K^+(aq)} + \mathrm{SO_4^{2-}(aq)} \tag{35.3}$$

However, the difference between the ChemEquation and the chemeqn environment becomes obvious, when the mathversion “bold” is used:

```
{\mathversion{bold}
\begin{ChemEquation}
K_{2}SO_{4}(s) \llongrightarrow 2K^{+}(aq) + SO_{4}^{2-}(aq)
\end{ChemEquation}
\begin{chemeqn}
K_{2}SO_{4}(s) \llongrightarrow 2K^{+}(aq) + SO_{4}^{2-}(aq)
\end{chemeqn}
}
```

$$\mathbf{K_2SO_4(s)} \longrightarrow \mathbf{2K^+(aq) + SO_4^{2-}(aq)} \tag{35.4}$$

$$\mathrm{K_2SO_4(s)} \longrightarrow 2\mathrm{K^+(aq)} + \mathrm{SO_4^{2-}(aq)} \tag{35.5}$$

□

Example 35.3. On a similar line, when fonts are changed by declaring \let\ChemEqFont=\sf for example, the following difference emerges:

```
{\let\ChemEqFont=\sf
\begin{ChemEquation}
K_{2}SO_{4}(s) \llongrightarrow 2K^{+}(aq) + SO_{4}^{2-}(aq)
\end{ChemEquation}
\begin{chemeqn}
K_{2}SO_{4}(s) \llongrightarrow 2K^{+}(aq) + SO_{4}^{2-}(aq)
\end{chemeqn}
}
```

$$\mathsf{K_2SO_4(s)} \longrightarrow \mathsf{2K^+(aq) + SO_4^{2-}(aq)} \tag{35.6}$$

$$\mathrm{K_2SO_4(s)} \longrightarrow 2\mathrm{K^+(aq)} + \mathrm{SO_4^{2-}(aq)} \tag{35.7}$$

□

Example 35.4. Isotopes can be written in a ChemEquation environment. For example, the code:

```
\begin{ChemEquation}
{}_{~91}^{234}Pa \llongrightarrow {}^{~~0}_{-1}e + {}^{234}_{~92}U
\end{ChemEquation}
```

typesets the following equation:

$$^{234}_{91}\mathrm{Pa} \longrightarrow {}^{0}_{-1}\mathrm{e} + {}^{234}_{92}\mathrm{U} \tag{35.8}$$

□

In addition to arrows of fixed lengths, another set of arrows of variable lengths (for organic structural formulas) is supported by the chemist (chmst-pdf or chmst-ps) package (cf. Section 33.2). Such arrows can be also used in chemical equations of inorganic chemistry.

Example 35.5. For example, the code:

```
\begin{ChemEquation}
 HC_2H_3O_2 \reacteqarrow{0pt}{3cm}{}{} H^+ + C_2H_3O_2^-
\end{ChemEquation}
```

typesets the following equation:

$$\mathrm{HC_2H_3O_2} \rightleftharpoons \mathrm{H^+ + C_2H_3O_2^-} \tag{35.9}$$

where the 2nd argument of the `\reacteqarrow` command specifies the length of the resulting arrow. Note that acetic acid ($\mathrm{HC_2H_3O_2}$) is written as $\mathrm{CH_3COOH}$ in organic chemistry. □

The chemist package itself supports an equilibrium arrow (right and left arrows), while the chmst-pdf package (or the chmst-ps package) supports an equilibrium harpoon (right and left harpoons) by the same name `\reacteqarrow`.

Example 35.6. They are exchanged by declaring `\chemstsw` or `\chmstpdfsw` (or `\chmstpssw`) as follows, when the chmst-pdf package is loaded (the pgf package is necessary but automatically loaded), or when the chmst-ps package is loaded (the PSTricks package is necessary but automatically loaded).

```
\textsf{chemist}: {\chemistsw \reacteqarrow{0pt}{3cm}{}{}
and \reactEqarrow{0pt}{3cm}{}{} (not systematic)}\\
{\ifPDFmode
\textsf{chmst-pdf}: \chmstpdfsw
\else\ifPSmode
\textsf{chmst-ps}: \chmstpssw
\fi\fi
\reacteqarrow{0pt}{3cm}{}{}
and \reactEqarrow{0pt}{3cm}{}{} (systematic)}
```

chemist: $\rightleftharpoons$ and $\rightleftharpoons$ (not systematic)

chmst-pdf: $\rightleftharpoons$ and $\rightleftharpoons$ (systematic)

The chmst-pdf (or chmst-ps) package supports an equilibrium arrow (right and left arrows) by the command name `\reactEqarrow`. Strictly speaking, a more systematic naming is desirable for the chemist package, just as the chmst-pdf (or chmst-ps) package has already realized. □

Example 35.7. The `ChemEquation` environment can be used to write the calculation of an equilibrium constant as follows:

```
\begin{ChemEquation}
\mathit{K_a} = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]}
= \frac{(6.00\times10^{-4}\:mol/L)(6.00\times10^{-4}\:mol/L)}%
{1.94\times10^{-2}\:mol/L}
= 1.86\times10^{-5}\:mol/L
\end{ChemEquation}
```

$$K_a = \frac{[\mathrm{H^+}][\mathrm{C_2H_3O_2^-}]}{[\mathrm{HC_2H_3O_2}]} = \frac{(6.00\times10^{-4}\ \mathrm{mol/L})(6.00\times10^{-4}\ \mathrm{mol/L})}{1.94\times10^{-2}\ \mathrm{mol/L}} = 1.86\times10^{-5}\ \mathrm{mol/L} \tag{35.10}$$

It should be noted that the unit (mol/L) is written directly (i.e., without using the `\mathrm` command) in the `ChemEquation` environment. Moreover, the arguments of `\frac` (i.e., $[\mathrm{H^+}][\mathrm{C_2H_3O_2^-}]$ and $[\mathrm{HC_2H_3O_2}]$) are written directly without toggling by `$...$`. The corresponding output by an in-text math mode can be obtained by the following code, `\ChemForm{\frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]}}`, which produces $\frac{[\mathrm{H^+}][\mathrm{C_2H_3O_2^-}]}{[\mathrm{HC_2H_3O_2}]}$. □

Example 35.8. The following example shows a chemical equation with information on ΔG:

```
\begin{ChemEquation}
SF_{6} + 2SO_{3} \llongrightarrow 2O_{2}SF_{2}; \qquad
\Delta\mathit{G}_{298}^{\circ}=-202\:kJ\cdot mol^{-1}
\end{ChemEquation}
```

where such information (as well as a unit) is written directly in the `ChemEquation` environment. The code typesets as follows:

$$\mathrm{SF_6 + 2SO_3} \longrightarrow \mathrm{2O_2SF_2}; \qquad \Delta G^\circ_{298} = -202\ \mathrm{kJ\cdot mol^{-1}} \tag{35.11}$$

□

Example 35.9. The heat of formation can be directly written in the ChemEquation environment as follows:

```
\begin{ChemEquation}
CuCl(s) + \frac{1}{2}Cl_2(g) \llongrightarrow CuCl_2(s) + 71\:kJ\cdot mol^{-1}
\end{ChemEquation}
```

$$\mathrm{CuCl(s)} + \frac{1}{2}\mathrm{Cl_2(g)} \longrightarrow \mathrm{CuCl_2(s)} + 71\ \mathrm{kJ \cdot mol^{-1}} \tag{35.12}$$

□

Example 35.10. After declaration of \usepackage{amsmath} in a preamble, the command \underset supported by the amsmath package can be used.

```
\begin{ChemEquation}
\underset{Green}{3MnO_{4}^{2-}} + 4H^{+}
\equiliblongarrow%%in place of \rightleftharpoons
\underset{Magenta}{2MnO_{4}^{-}} + MnO_{2} + 2H_{2}O
\end{ChemEquation}
```

where the command \equiliblongarrow supported by the chemist (chmst-pdf or chmst-ps) package is used to output a longer arrow in place of \rightleftharpoons of LaTeX 2_ε. Thereby, we obtain the following result:

$$\underset{\text{Green}}{3\mathrm{MnO_4^{2-}}} + 4\mathrm{H^+} \equiliblongarrow \underset{\text{Magenta}}{2\mathrm{MnO_4^-}} + \mathrm{MnO_2} + 2\mathrm{H_2O} \tag{35.13}$$

□

Example 35.11. The counterpart command \overset for writing an object over a math object is also defined in the amsmath package. Thereby, the disproportionation of dithionates $\mathrm{S_2O_4^{2-}}$ in the presence of water is typeset as follows:

```
\begin{ChemEquation}
2\overset{III}{S}_{2}O_{4}^{2-} + H_{2}O \llongrightarrow
2H\overset{IV}{S}O_{3}^{-} +
\overset{II/VI\mkern-15mu}{SS}O_{3}^{2-}
\end{ChemEquation}
```

where the oxidation state of sulfur in each species is specified explicitly. Thereby, the following output is obtained:

$$2\overset{\text{III}}{\mathrm{S}}_2\mathrm{O_4^{2-}} + \mathrm{H_2O} \longrightarrow 2\mathrm{H}\overset{\text{IV}}{\mathrm{S}}\mathrm{O_3^-} + \overset{\text{II/VI}}{\mathrm{SS}}\mathrm{O_3^{2-}} \tag{35.14}$$

□

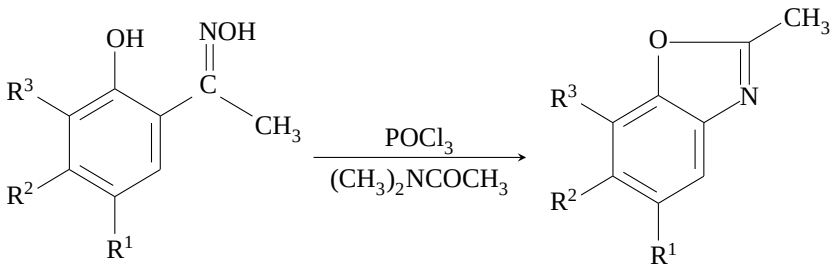
(Remarks) It should be noted that the amsmath package does not permit the multiple setting of the \label commands in an equation-like environment. Because such multiple setting is sometimes required in chemical documentations, the command \resetamsmathlabel is defined as follows:

```
\makeatletter%
\@ifundefined{label@in@display}%
{\let\resetamsmathlabel=\relax}%
{\def\resetamsmathlabel{\let\label\ltx@label}}
\makeatother
```

Example 35.12. The following equation is a typical example which contains the multiple setting of \label commands.

```
\begin{ChemEquation}
\resetamsmathlabel
\begin{tabular}{c}
\begin{XyMcompd}(950,850)(50,50){}{}
```

```
\benzenev{1==OH;4==\ChemForm{R^1};5==\ChemForm{R^2};6==\ChemForm{R^3};%
2==\Dtrigonal{3==(yl);0==C;1D==NOH;2==\ChemForm{CH_3}}}
\end{XyMcompd}
\\
\noalign{\vskip5pt}
\compd\label{cpd:Xphoto1}
\end{tabular}
\reactrarrow{0pt}{80pt}{\ChemForm{POCl_3}}{\ChemForm{(CH_3)_2NCOCH_3}}
\begin{tabular}{c}
\begin{XyMcompd}(950,900)(50,50){}{}
\sixheterov[bdf%
{a\fivefusev[b]{2==N;4==O}{3==\ChemForm{CH_3}}{e}}%
]{}{4==\ChemForm{R^1};5==\ChemForm{R^2};6==\ChemForm{R^3}}%
\end{XyMcompd}
\\
\noalign{\vskip5pt}
\compd\label{cpd:Xphoto2}
\end{tabular}
\label{eq:Xphoto3}
\end{ChemEquation}
```



35-1 **35-2** (35.15)

The compounds **35-1** and **35-2** (referred to by declaring the reference keys: `\cref{cpd:Xphoto1}` and `\cref{cpd:Xphoto2}`) in Eq. 35.15 (referred to by declaring `\ref{eq:Xphoto3}`) are the intermediates of synthesizing photographic dye developers [2, page 462]. □

For the purpose of typesetting a chemical equation with no equation number, the command `\nonumber` is declared in the `ChemEquation` environment or the `chemeqn` environment. Alternatively, we can use the displaymath environment of LaTeX (`\[...\]`) under the mathversion "chem".

Example 35.13. Thus, the following codes:

```
\begin{ChemEquation}
H_{2} + Cl_{2} \rightarrow 2HCl \nonumber
\end{ChemEquation}
\begin{chemeqn}
H_{2} + Cl_{2} \rightarrow 2HCl \nonumber
\end{chemeqn}
{\mathversion{chem}
\[H_{2} + Cl_{2} \rightarrow 2HCl\]}
```

generate almost equivalent equations:[c]

$$H_2 + Cl_2 \rightarrow 2HCl$$

$$H_2 + Cl_2 \rightarrow 2HCl$$

[c] Strictly speaking, the fonts selected by the `ChemEquation` environment is different from those of the latter two environments.

$$\mathrm{H_2 + Cl_2 \rightarrow 2HCl}$$

□

In addition, we can use the `chemmath` environment of the chemist package, which corresponds to the displaymath environment of LaTeX (`\[...\]`). Note that it requires no declaration of the mathversion "chem" by `\mathversion`.

```
\begin{chemmath}
(a code for drawing a chemical equation)
\end{chemmath}
```

```
\begin{chemmath}
H_{2} + Cl_{2} \rightarrow 2HCl
\end{chemmath}
```

$$\mathrm{H_2 + Cl_2 \rightarrow 2HCl}$$

35.2.3 ChemEqnarray and ChemEqnarray∗ Environments

In a parallel way to the `eqnarray` and `eqnarray*` environment of LaTeX 2_ε, the chemist package (after version 4.05, also chmst-pdf or chmst-ps) supports the `ChemEqnarray` and `ChemEqnarray*` environments in addition to the `chemeqnarray` and `chemeqnarray*` environments defined previously (version ≤ 4.04). The basic functions described above for `\ChemForm` are also effective to the `ChemEqnarray` environment:

```
\begin{ChemEqnarray}
(a code for drawing a chemical equation) \\
(a code for drawing a chemical equation) \\
...
\end{ChemEqnarray}
```

and to the `ChemEqnarray*` environment:

```
\begin{ChemEqnarray*}
(a code for drawing a chemical equation) \\
(a code for drawing a chemical equation) \\
...
\end{ChemEqnarray*}
```

where each line (ended by `\\`) is subdivided into three parts so as to be `...&...&...\\`.

Example 35.14. The following example shows a typical output due to the `ChemEqnarray` environment:

```
\begin{ChemEqnarray}
AgBr + 2S_{2}O_{3}^{--} & \rightarrow & Ag(S_{2}O_{3})_{2}^{---} + Br^{-} \\
Ag(S_{2}O_{3})_{2}^{---} & \rightarrow & Ag_{2}S_{2}O_{3}(s) + 3S_{2}O_{3}^{--}
\end{ChemEqnarray}
```

$$\begin{aligned} \mathrm{AgBr + 2S_2O_3^{--}} &\rightarrow \mathrm{Ag(S_2O_3)_2^{---} + Br^-} && (35.16)\\ \mathrm{Ag(S_2O_3)_2^{---}} &\rightarrow \mathrm{Ag_2S_2O_3(s) + 3S_2O_3^{--}} && (35.17) \end{aligned}$$

where the positions of the two chemical equations are aligned at their arrows by using two ampersands (`...&...&...`). □

When a chemical equation number is unnecessary partly, the command `\nonumber` is declared in a similar way to an `eqnarray` environment of LaTeX 2_ε.

Example 35.15. For example, we obtain:

```
\begin{ChemEqnarray}
Fe^{3+}(aq) + {\textstyle \frac{1}{2}}H_{2}
\equiliblongarrow  Fe^{2+}(aq) + H^{+}(aq)
&& \mathit{E}^{\circ} = 0.771\:V \\
&& \Delta \mathit{G}^{\circ} = -74.4\:kJ\cdot mol^{-1} \nonumber
\end{ChemEqnarray}
```

$$\mathrm{Fe^{3+}(aq) + \tfrac{1}{2}H_2 \rightleftharpoons Fe^{2+}(aq) + H^{+}(aq)} \qquad \begin{aligned} E^\circ &= 0.771\ \mathrm{V} \\ \Delta G^\circ &= -74.4\ \mathrm{kJ \cdot mol^{-1}} \end{aligned} \tag{35.18}$$

Note that the command `\textstyle` is declared to output the fraction $\frac{1}{2}$ in an in-text mode. □

Example 35.16. When all chemical equation numbers are unnecessary, the `ChemEqnarray*` environment can be used as follows:

```
\begin{ChemEqnarray*}
{\textstyle \frac{1}{2}}I_{2} + e^{-} & \rightleftharpoons &   I^{-}
\mskip36mu \mathit{E}^{\circ} = 0.536\:V; \quad
\Delta \mathit{G}^{\circ} = -51.5\:kJ\cdot mol^{-1} \\
I_{2} + 2e^{-} & \rightleftharpoons&   2I^{-}
\mskip28mu \mathit{E}^{\circ} = 0.536\:V; \quad
\Delta \mathit{G}^{\circ} = -103.0\:kJ\cdot mol^{-1}
\end{ChemEqnarray*}
```

$$\begin{aligned} \tfrac{1}{2}\mathrm{I_2} + \mathrm{e^-} &\rightleftharpoons \mathrm{I^-} \qquad E^\circ = 0.536\ \mathrm{V}; \quad \Delta G^\circ = -51.5\ \mathrm{kJ \cdot mol^{-1}} \\ \mathrm{I_2} + 2\mathrm{e^-} &\rightleftharpoons 2\mathrm{I^-} \qquad E^\circ = 0.536\ \mathrm{V}; \quad \Delta G^\circ = -103.0\ \mathrm{kJ \cdot mol^{-1}} \end{aligned}$$

□

The difference between the `ChemEqnarray` (or `ChemEqnarray*`) environment and the `chemeqnarray` (or `chemeqnarray*`) environment is parallel to the difference between the `ChemEquation` environment and the `chemeqn` environment (for the mathversions “normal” and “bold”). The syntax of the `chemeqnarray` environment:

```
\begin{chemeqnarray}
(a code for drawing a chemical equation) \\
(a code for drawing a chemical equation) \\
...
\end{chemeqnarray}
```

and that of the `chemeqnarray*` environment:

```
\begin{chemeqnarray*}
(a code for drawing a chemical equation) \\
(a code for drawing a chemical equation) \\
...
\end{chemeqnarray*}
```

are shown for the sake of convenience.

Example 35.17. Two or more chemical equations are aligned by using the `chemeqnarray` environment of the chemist package of the XeLaTeX system, which corresponds to the `eqnarray` environment of LaTeX.

```
\begin{chemeqnarray}
Me_{3}B + LiMe & \rightarrow & Me_{4}B^{-}Li^{+} \\
Ph_{5}B + LiPh & \rightarrow & Ph_{6}B^{-}Li^{+}
\end{chemeqnarray}
```

$$\begin{aligned} \mathrm{Me_3B + LiMe} &\rightarrow \mathrm{Me_4B^-Li^+} && (35.19)\\ \mathrm{Ph_5B + LiPh} &\rightarrow \mathrm{Ph_6B^-Li^+} && (35.20) \end{aligned}$$

They are also typeset by using the chemeqnarray$*$ environment of the chemist package without numbering. This corresponds to the eqnarray$*$ environment of LaTeX.

```
\begin{chemeqnarray*}
Me_{3}B + LiMe & \rightarrow & Me_{4}B^{-}Li^{+} \\
Ph_{5}B + LiPh & \rightarrow & Ph_{6}B^{-}Li^{+}
\end{chemeqnarray*}
```

$$\begin{aligned} \mathrm{Me_3B + LiMe} &\rightarrow \mathrm{Me_4B^-Li^+}\\ \mathrm{Ph_5B + LiPh} &\rightarrow \mathrm{Ph_6B^-Li^+} \end{aligned}$$

□

The mode of numbering can be changed by using the `chemeqnarraya` environment of of the chemist package, which corresponds to the `eqnarraya` environment of the mathchem package [3].

```
\begin{chemeqnarraya}
(a code for drawing a chemical equation) \\
(a code for drawing a chemical equation) \\
...
\end{chemeqnarraya}
```

Example 35.18. The `chemeqnarraya` environment supports equation numbers with grouping.

```
\begin{chemeqnarraya}
Me_{3}B + LiMe & \rightarrow & Me_{4}B^{-}Li^{+}
 \label{chemenv:a3} \\
Ph_{5}B + LiPh & \rightarrow & Ph_{6}B^{-}Li^{+}
\end{chemeqnarraya}
```

$$\begin{aligned} \mathrm{Me_3B + LiMe} &\rightarrow \mathrm{Me_4B^-Li^+} && (35.21a)\\ \mathrm{Ph_5B + LiPh} &\rightarrow \mathrm{Ph_6B^-Li^+} && (35.21b) \end{aligned}$$

Sub-numbering references can be referred by using such a command as `\ref{chemenv:a3}`, which results in, e.g., 35.21a. □

35.2.4 Cross References

The equation numbers of the ChemEquation (chemeqn) and ChemEqnarray (chemeqnarray) environments supported by the chemist (chmst-pdf or chmst-ps) package are given by using the `equation` counter which is used in the `equation` and `eqnarray` environments of LaTeX 2_ε. They are all referred to by means of the cross reference mechanism of LaTeX 2_ε (`\label` and `\ref`).

Example 35.19. The following example illustrates the cross reference mechanism supported by the ChemEquation and related environments.

```
A chemical equation which is produced by a \texttt{ChemEquation} environment
to represent balanced molecular formulas in the both sides:
\begin{ChemEquation}
3NaOH + FeCl_{3} \rightarrow Fe(OH)_{3} + 3NaCl \label{ce:01}
\end{ChemEquation}
and a balanced complete ionic equation which is
produced by a \texttt{ChemEqnarray} environment:
\begin{ChemEqnarray}
\lefteqn{3Na^{+}(aq) + 3OH^{-}(aq) + Fe^{3+}(aq) + 3Cl^{-}(aq)} && \nonumber \\
& \rightarrow & Fe(OH)_{3}(s) + 3Na^{+}(aq) + 3Cl^{-}(aq) \label{ce:02}
\end{ChemEqnarray}
are commonly referred to as follows: Equations \ref{ce:01} and \ref{ce:02}.
```

A chemical equation having balanced molecular equations which is produced by a `ChemEquation` environment:

$$3NaOH + FeCl_3 \rightarrow Fe(OH)_3 + 3NaCl \tag{35.22}$$

and a balanced complete ionic equation which is produced by a `ChemEqnarray` environment:

$$\begin{aligned} &3Na^{+}(aq) + 3OH^{-}(aq) + Fe^{3+}(aq) + 3Cl^{-}(aq) \\ &\rightarrow \quad Fe(OH)_3(s) + 3Na^{+}(aq) + 3Cl^{-}(aq) \end{aligned} \tag{35.23}$$

are commonly referred to as follows: Equations 35.22 and 35.23. □

35.3 Creation of New Environments for Chemical Equations

When the amsmath package is loaded, several environments for printing multiline display equations are available. These mathematical environments can be converted into chemical versions by using the `\newchemenvironment` command supported by the present chemist (chmst-pdf or chmst-ps) package, which is automatically loaded by the XƎMTEX system.

```
\newchemenvironment{⟨NewChemEnv⟩}{⟨OriginalMathEnv⟩}
```

35.3.1 Creation of the `chemmultline` Environment

The `multline` environment of the amsmath package provides us with a mathematical tool for folding a long display equation into a multiline display equation in accord with the text width to be set up:

```
\begin{minipage}{0.6\textwidth}
\begin{multline}
Cu^{2+}(aq) + SO_{4}^{2-}(aq) + 2Li^{+}(aq) + 2OH^{-}(aq) \rightarrow \\
Cu(OH)_{2}(s) + 2Li^{+}(aq) + SO_{4}^{2-}(aq)
\end{multline}
\end{minipage}
```

$$\begin{aligned} &Cu^{2+}(aq) + SO_4^{2-}(aq) + 2Li^{+}(aq) + 2OH^{-}(aq) \rightarrow \\ &\qquad Cu(OH)_2(s) + 2Li^{+}(aq) + SO_4^{2-}(aq) \end{aligned} \tag{35.24}$$

Note that the `minipage` environment reduces the text width to emphasize the function of the `multiline` environment. Each molecular formula in the `multline` environment is printed in italic fonts on a similar line to `equation` and like environments of LATEX 2_ε.

We are able to create a chemical version of the `multline` environment of the amsmath package by declaring

```
\newchemenvironment{chemmultline}{multline}
```

Thereby, the newly-defined `chemmultline` environment is substituted for the `multline` environment shown above, so that italic fonts in the `multline` environment are replaced by roman fonts in the `chemmultline` environment without using the `\mathrm` command explicitly (cf. Item No. 1 at page 605). The syntax of the `chemmultline` environment is as follows:

```
\begin{chemmultline}
(a code for drawing a chemical equation) \\
(a code for drawing a chemical equation) \\
...
\end{chemmultline}
```

Example 35.20. After the creation of the `chemmultline` environment, we are able to obtain the following multiline equation:

```
\begin{minipage}{0.6\textwidth}
\begin{chemmultline}
Cu^{2+}(aq) + SO_{4}^{2-}(aq) + 2Li^{+}(aq) + 2OH^{-}(aq) \rightarrow \\
Cu(OH)_{2}(s) + 2Li^{+}(aq) + SO_{4}^{2-}(aq) \label{eq:chmult}
\end{chemmultline}
\end{minipage}
```

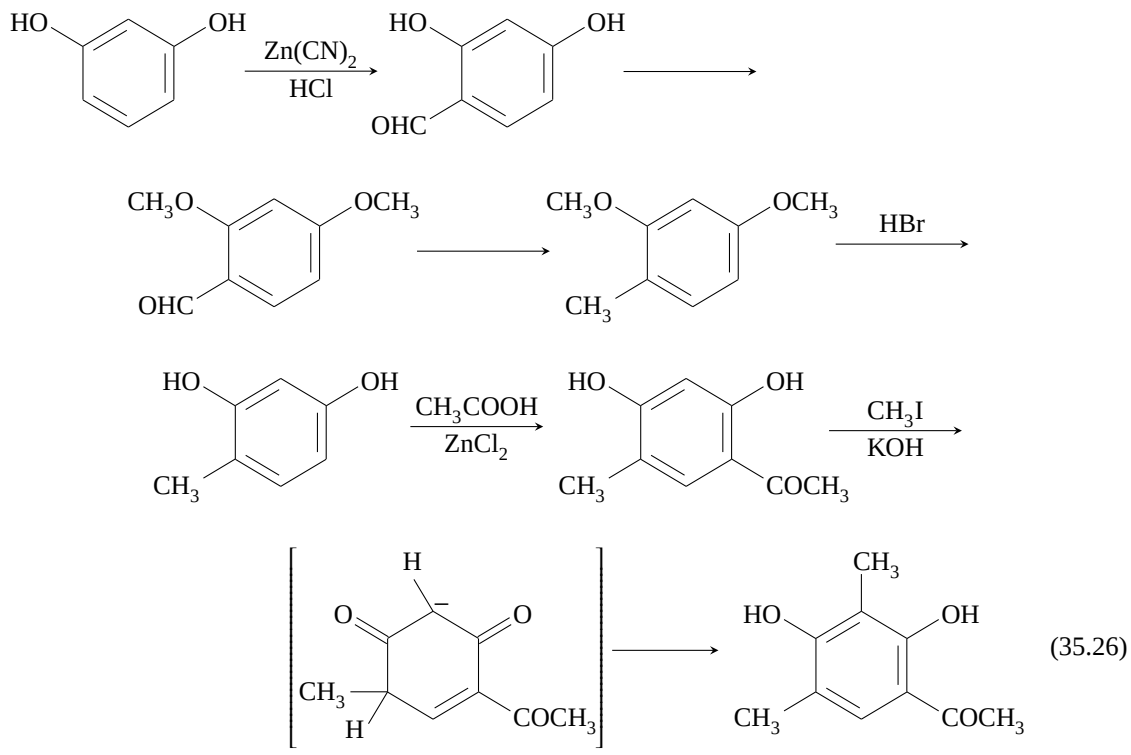
$$\begin{aligned} \mathrm{Cu^{2+}(aq) + SO_4^{2-}(aq) + 2Li^{+}(aq) + 2OH^{-}(aq)} &\rightarrow \\ \mathrm{Cu(OH)_2(s) + 2Li^{+}(aq) + SO_4^{2-}(aq)} \quad (35.25) \end{aligned}$$

□

Example 35.21. The `chemmultline` environment is convenient to draw a multi-step reaction scheme. The following scheme is a typical example:

```
\begin{chemmultline}
\begin{XyMcompd}(750,450)(0,250){}{}
\benzenev{2==OH;6==HO}
\end{XyMcompd}
\reactrarrow{0pt}{50pt}{\ChemForm{Zn(CN)_{2}}}{HCl}
\begin{XyMcompd}(750,450)(0,250){}{}
\benzenev{2==OH;6==HO;5==OHC}
\end{XyMcompd}
\reactrarrow{0pt}{50pt}{}{} \\
\noalign{\vskip15pt}
\begin{XyMcompd}(900,450)(-50,250){}{}
\benzenev{2==\ChemForm{OCH_{3}};6==\ChemForm{CH_{3}O};5==OHC}
\end{XyMcompd}
\reactrarrow{0pt}{50pt}{}{}
\begin{XyMcompd}(900,450)(-50,250){}{}
\benzenev{2==\ChemForm{OCH_{3}};6==\ChemForm{CH_{3}O};%
5==\ChemForm{CH_{3}}}
\end{XyMcompd}
\reactrarrow{0pt}{50pt}{HBr}{\strut} \\
\noalign{\vskip15pt}
\begin{XyMcompd}(850,450)(-50,250){}{}
\benzenev{2==OH;6==HO;5==\ChemForm{CH_{3}}}
\end{XyMcompd}
\reactrarrow{0pt}{50pt}{\ChemForm{CH_{3}COOH}}{\ChemForm{ZnCl_{2}}}
```

```
\begin{XyMcompd}(900,450)(-50,250){}{}
\benzenev{2==OH;6==HO;5==\ChemForm{CH_{3}};3==\ChemForm{COCH_{3}}}
\end{XyMcompd}
\reactrarrow{0pt}{50pt}{\ChemForm{CH_{3}I}}{KOH} \\
\noalign{\vskip10pt}
\left[
\begin{XyMcompd}(1000,750)(-50,150){}{}
\sixheterov[c]{1s==\put(0,0){\ChemForm{-}}}%
{1Sb==H;2D==O;6D==O;5Sa==\ChemForm{CH_{3}};%
5Sb==H;3==\ChemForm{COCH_{3}}}
\end{XyMcompd}
\right]
\reactrarrow{0pt}{40pt}{}{}
\begin{XyMcompd}(1000,750)(-50,150){}{}
\benzenev{1==\ChemForm{CH_{3}};2==OH;6==HO;%
5==\ChemForm{CH_{3}};3==\ChemForm{COCH_{3}}}
\end{XyMcompd}
\label{chmeq:X01}
\end{chemmultline}
```



(35.26)

Because the the `multiline` environment is based on the TEX alignment technique, the use of `\noalign` is permitted. Thus, the code `\noalign{\vskip15pt}` is inserted to stretch a baseline skip in Eq. 35.26. □

On a similar line, the `multiline*` environment of the amsmath package can be converted into a chemical version named `chemmultiline*`.

```
\newchemenvironment{chemmultline*}{multline*}
```

The newly-defined `chemmultiline*` environment is used in place of the `chemmultiline` environment:

```
\begin{chemmultline*}
(a code for drawing a chemical equation) \\
(a code for drawing a chemical equation) \\
...
\end{chemmultline*}
```

so as to give a multilined chemical equation without printing equation numbers.

Example 35.22. The `chemmultline` environment for typesetting Eq. 35.25 (Example 35.20) is replaced by the `chemmultline*` environment, which results in the following equation:

```
\begin{minipage}{0.6\textwidth}
\begin{chemmultline*}
Cu^{2+}(aq) + SO_{4}^{2-}(aq) + 2Li^{+}(aq) + 2OH^{-}(aq) \rightarrow \\
Cu(OH)_{2}(s) + 2Li^{+}(aq) + SO_{4}^{2-}(aq)
\end{chemmultline*}
\end{minipage}
```

$$\begin{aligned}\mathrm{Cu^{2+}(aq) + SO_4^{2-}(aq) + 2Li^{+}(aq) + 2OH^{-}(aq)} &\rightarrow \\ \mathrm{Cu(OH)_2(s) + 2Li^{+}(aq) + SO_4^{2-}(aq)}&\end{aligned}$$

□

Environments created by `\newchemenvironment` have properties equivalent to `ChemEquation` and like environments, which are originally supported by the chemist (chmst-pdf or chmst-ps) package. Hence, fonts used in such newly-defined environments can be changed by declaring `\let\ChemEqFont=\sf` etc.

Example 35.23. After the declaration `\let\ChemEqFont=\sf`, the same code as shown in Example 35.22 gives following result:

```
\let\ChemEqFont=\sf
\begin{minipage}{0.6\textwidth}
\begin{chemmultline*}
Cu^{2+}(aq) + SO_{4}^{2-}(aq) + 2Li^{+}(aq) + 2OH^{-}(aq) \rightarrow \\
Cu(OH)_{2}(s) + 2Li^{+}(aq) + SO_{4}^{2-}(aq)
\end{chemmultline*}
\end{minipage}
```

$$\begin{aligned}\mathrm{Cu^{2+}(aq) + SO_4^{2-}(aq) + 2Li^{+}(aq) + 2OH^{-}(aq)} &\rightarrow \\ \mathrm{Cu(OH)_2(s) + 2Li^{+}(aq) + SO_4^{2-}(aq)}&\end{aligned}$$

□

35.3.2 Creation of the chemgather Environment

The `chemgather` environment as a chemical version of the `gather` environment of the amsmath package can be created on a similar line by using `\newchemenvironment`.

```
\newchemenvironment{chemgather}{gather}
```

The syntax of the newly-defined `chemgather` environment is as follows:

```
\begin{chemgather}
(a code for drawing a chemical equation) \\
(a code for drawing a chemical equation) \\
...
\end{chemgather}
```

Example 35.24. The following set of chemical equations is a typical example of the `chemgather` environment:

```
\begin{chemgather}
Bi(NO_{3})_{3}\cdot 5H_{2}O \overset{50-60^{\circ}}{\lllongrightarrow}
[Bi_{6}O_{6}]_{2}(NO_{3})_{11}(OH)\cdot 6H_{2}O
\overset{77-130^{\circ}}{\lllongrightarrow} \notag \\
[Bi_{6}O_{6}](NO_{3})_{6}(OH)\cdot 3H_{2}O
\overset{400-450^{\circ}}{\lllongrightarrow}
\alpha\mbox{-}Bi_{2}O_{3} \\
Bi(NO_{3})_{3}\cdot N_{2}O_{4}
\overset{200^{\circ}}{\lllongrightarrow}
Bi_{2}O(NO_{3})_{4}
\overset{415^{\circ}}{\lllongrightarrow}
Bi_{4}O_{5}(NO_{3})_{2}
\end{chemgather}
```

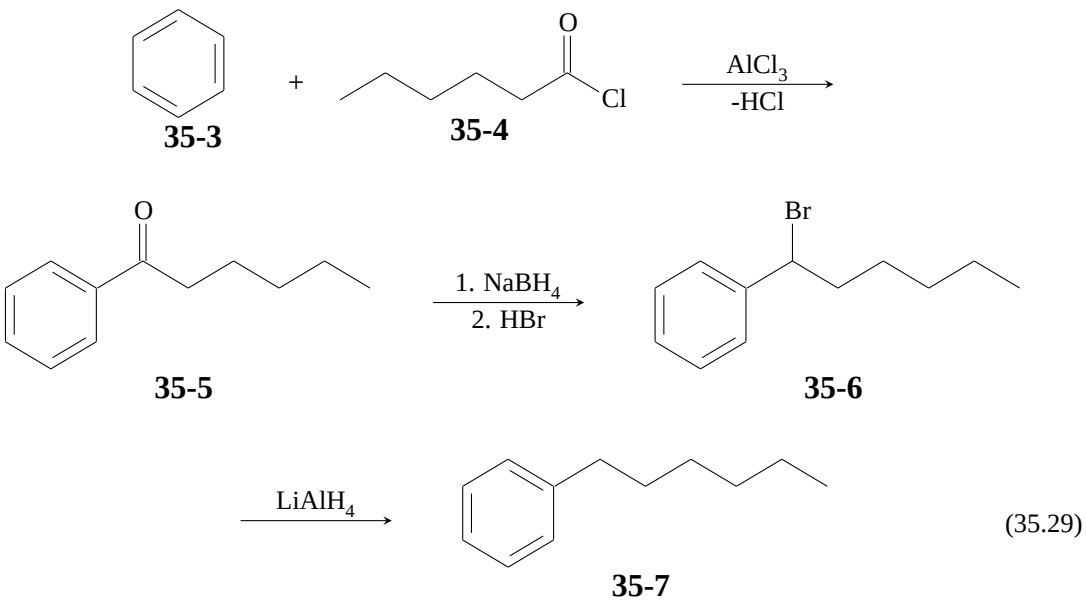
$$\mathrm{Bi(NO_3)_3\cdot 5H_2O} \xrightarrow{50\text{–}60^\circ} \mathrm{[Bi_6O_6]_2(NO_3)_{11}(OH)\cdot 6H_2O} \xrightarrow{77\text{–}130^\circ}$$
$$\mathrm{[Bi_6O_6](NO_3)_6(OH)\cdot 3H_2O} \xrightarrow{400\text{–}450^\circ} \alpha\text{-}\mathrm{Bi_2O_3} \tag{35.27}$$
$$\mathrm{Bi(NO_3)_3\cdot N_2O_4} \xrightarrow{200^\circ} \mathrm{Bi_2O(NO_3)_4} \xrightarrow{415^\circ} \mathrm{Bi_4O_5(NO_3)_2} \tag{35.28}$$

where the equation number of the first line is suppressed by declaring `\notag`. □

Example 35.25. A scheme for synthesizing hexylbenzene **35-7** via **35-5** (given by hexanoylation) and **35-6** (given by reduction) is drawn by using the `chemgather` environment. Compound numbers are attached to respective compounds after the declaration of `\resetamsmathlabel` in each line (cf. Remarks on page 612).

```
\begin{chemgather}
\resetamsmathlabel
\begin{XyMcompd}(350,400)(280,250){cpd:C6-BzA}{}
\benzenev{}
\end{XyMcompd}
\quad + \quad
\begin{XyMcompd}(950,350)(250,150){cpd:C6-BzB}{}
\hexamethylene{}{6D==O;6W==Cl}
\end{XyMcompd}
\qquad \reactrarrow{0pt}{2cm}{\ChemForm{AlCl_3}}{-HCl} \qquad \notag \\
\noalign{\vskip10pt} \resetamsmathlabel
\begin{XyMcompd}(1300,650)(250,250){cpd:C6-BzC}{}
\sixheterov[ace]{2s==\heptamethylene{}{1==(yl);2D==O}}{}
\end{XyMcompd}
\qquad \reactrarrow{0pt}{2cm}{1. \ChemForm{NaBH_4}}{2. HBr} \qquad
\begin{XyMcompd}(1300,650)(250,250){cpd:C6-BzD}{}
\sixheterov[ace]{2s==\heptamethylene{}{1==(yl);2==Br}}{}
\end{XyMcompd}
\notag \\
\noalign{\vskip10pt} \resetamsmathlabel
\qquad \reactrarrow{0pt}{2cm}{\ChemForm{LiAlH_4}}{\strut} \qquad
```

```
\begin{XyMcompd}(1300,450)(250,250){cpd:C6-BzE}{}
\sixheterov[ace]{2s==\heptamethylene{}{1==(yl)}}{}
\end{XyMcompd}
\end{chemgather}
```



(35.29)

□

35.3.3 Creation of the chemalign Environment

The chemalign environment can be created as a chemical version of the align environment of the amsmath package. What you have to do is only to declare as follows:

```
\newchemenvironment{chemalign}{align}.
```

The syntax of the newly-defined chemalign environment is as follows:

```
\begin{chemalign}
(a code for drawing a chemical equation) \\
(a code for drawing a chemical equation) \\
...
\end{chemalign}
```

where each row contains an ampersand (&) to specify an alignment position.

Example 35.26. Just as the align environment of the amsmath package is based on the alignment mechanism of TEX, the present chemalign environment succeeds in functions due to the alignment mechanism. Hence, such commands as \noalign can be used in the chemalign environment so as to give the following output:

```
\begin{chemalign}
5Fe^{2+} & \llongrightarrow 5Fe^{3+} + 5e^{-} \notag \\
MnO_{4}^{-} + 5e^{-} + 8H^{+} & \llongrightarrow Mn^{2+} + 4H_{2}O \notag \\
\noalign{\vskip-8pt}
\noalign{\hfil\hbox to9cm{\hrulefill\kern0.5cm}\hfil}
\noalign{\vskip-4pt}
```

```
MnO_{4}^{-} + 5Fe^{2+} + 8H^{+} & \llongrightarrow Mn^{2+} + 5Fe^{3+} + 4H_{2}O
\end{chemalign}
```

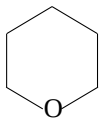
$$\begin{aligned} 5Fe^{2+} &\longrightarrow 5Fe^{3+} + 5e^- \\ MnO_4^- + 5e^- + 8H^+ &\longrightarrow Mn^{2+} + 4H_2O \\ \hline MnO_4^- + 5Fe^{2+} + 8H^+ &\longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O \end{aligned} \tag{35.30}$$

□

Example 35.27. Schemes of synthesizing cyclic ethers are drawn by the `chemalign` environment, which contains both molecular formulas (or rational formulas) and structural formulas.

```
\begin{chemalign}
HOCH_2CH_2Br + HO^- & \llongrightarrow
\begin{XyMcompd}(100,200)(350,250){}{}
\threeheterov{1==O}{}
\end{XyMcompd}
+ Br^- + HOH \\
HO(CH_2)_4CH_2Br + HO^- & \llongrightarrow
\begin{XyMcompd}(300,400)(250,250){}{}
\sixheterovi{1==O}{}
\end{XyMcompd}
+ Br^- + HOH
\end{chemalign}
```

$$HOCH_2CH_2Br + HO^- \longrightarrow \text{  } + Br^- + HOH \tag{35.31}$$

$$HO(CH_2)_4CH_2Br + HO^- \longrightarrow \text{  } + Br^- + HOH \tag{35.32}$$

□

On a similar line, the `chemalign*` environment corresponding to the `align*` environment of the amsmath package can be created by declaring as follows:

```
\newchemenvironment{chemalign*}{align*}.
```

The syntax of the newly-defined `chemalign*` environment is as follows:

```
\begin{chemalign*}
(a code for drawing a chemical equation) \\
(a code for drawing a chemical equation) \\
...
\end{chemalign*}
```

where each row contains an ampersand (&) to specify an alignment position.

Example 35.28. The following set of equations is a typical example:

```
\begin{chemalign*}
Co(CN)_{6}^{4-} & \equilibarrow Co(CN)_{6}^{3-} + e^{-} \\
Fe(CN)_{6}^{4-} & \equilibarrow Co(CN)_{6}^{3-} + e^{-}
\end{chemalign*}
```

$$\mathrm{Co(CN)_6^{4-} \rightleftharpoons Co(CN)_6^{3-} + e^-}$$
$$\mathrm{Fe(CN)_6^{4-} \rightleftharpoons Co(CN)_6^{3-} + e^-}$$

□

35.3.4 Creation of the chemalignat Environment

The chemalignat environment can be created as a chemical version of the alignat environment of the amsmath package by declaring

```
\newchemenvironment{chemalignat}{alignat}.
```

The syntax of the newly-defined chemalignat environment is as follows:

```
\begin{chemalignat}{⟨unitNo⟩}
(a code for drawing a chemical equation) \\
(a code for drawing a chemical equation) \\
...
\end{chemalignat}
```

where the argument ⟨unitNo⟩ is a positive integer n. Each row contains n units due to a number $2n-1$ of ampersands (&), so that each unit contains one ampersand and such two units are separated by an ampersand (&), as shown below:

$$\underbrace{\cdots\&\cdots}_{\text{unit 1}} \quad \& \quad \underbrace{\cdots\&\cdots}_{\text{unit 2}} \quad \& \quad \cdots \quad \& \quad \underbrace{\cdots\&\cdots}_{\text{unit } n} \quad \backslash\backslash$$

Example 35.29. The usage of the newly-defined chemalignat environment is exemplified as follows:

```
\begin{chemalignat}{2}
\mbox{Solution of zinc oxide:} \qquad
& ZnO + 2H^{+}  & \longrightarrow\quad & Zn^{2+} + H_{2}O \\
\mbox{Cathode reaction:} \qquad
& Zn^{2+} + 2e^{-} &\longrightarrow\quad & Zn \\
\mbox{Anode reaction:} \qquad
& H_{2}O  & \longrightarrow\quad &
{\textstyle\frac{1}{2}}O_{2} + 2H^{+} + 2e^{-} \\
\mbox{Over-all reaction:} \qquad
& ZnO  & \longrightarrow\quad  & Zn + {\textstyle\frac{1}{2}}O_{2}
\end{chemalignat}
```

$$\begin{aligned}
\text{Solution of zinc oxide:} \quad & \mathrm{ZnO + 2H^+ \longrightarrow Zn^{2+} + H_2O} && (35.33)\\
\text{Cathode reaction:} \quad & \mathrm{Zn^{2+} + 2e^- \longrightarrow Zn} && (35.34)\\
\text{Anode reaction:} \quad & \mathrm{H_2O \longrightarrow \tfrac{1}{2}O_2 + 2H^+ + 2e^-} && (35.35)\\
\text{Over-all reaction:} \quad & \mathrm{ZnO \longrightarrow Zn + \tfrac{1}{2}O_2} && (35.36)
\end{aligned}$$

□

Example 35.30. Rational formulas are alternatively called “condensed formulas”, where a main chain of carbons are drawn in horizontal direction. The simplest expressions are bond-line formulas, where a main carbon chain is drawn in a zigzag fashion. They are illustrated in a chemalignat environment as follows:

```
\begin{chemalignat}{3}
CH_3CH_2CH_3 & \quad
```

```
\begin{XyMcompd}(200,100)(100,200){}{}
\trimethylene{}{}
\end{XyMcompd}
& \quad & \quad &
CH_3\shortstack{B\rlap{r} \\ \rule{0.4pt}{5pt} \\ C}HCH_2CH_2Br & \quad
\begin{XyMcompd}(600,300)(250,200){}{}
\tetramethylene{}{2==Br;4W==Br}
\end{XyMcompd}
\\
CH_3\shortstack{O \\ \rule{0.4pt}{5pt}\,\rule{0.4pt}{5pt} \\ C}CH=CH_2 & \quad
\begin{XyMcompd}(400,300)(250,200){}{}
\tetramethylene[c]{}{2D==O}
\end{XyMcompd}
& \quad & \quad &
HOCH_2CH_2OH & \quad
\begin{XyMcompd}(550,150)(-150,180){}{}
\dimethylene{3==O}{1W==HO;2W==OH}
\end{XyMcompd}
\end{chemalignat}
```

$$\mathrm{CH_3CH_2CH_3} \qquad \mathrm{CH_3CHCH_2CH_2Br} \tag{35.37}$$

$$\mathrm{CH_3\overset{\displaystyle O}{\overset{\|}{C}}CH=CH_2} \qquad \mathrm{HOCH_2CH_2OH} \tag{35.38}$$

□

35.3.5 The Use of the split Environment

The split environment supported by the amsmath package is originally used in combination with equation (redefined in amsmath), gather, etc.

split Environment in the ChemEquation Environment

Because the ChemEquation environment of the present chemist (chmst-pdf or chmst-ps) package has been tuned to the setting of the amsmath package, it can be used in combination with the split environment.

Example 35.31. This example shows the split environment in the ChemEquation Environment:

```
\begin{ChemEquation}
\begin{split}
 [(\eta^{5}\mbox{-}C_{5}H_{5})(CO)_{2}MnSbPhI_{2}]
& + [(\eta^{5}\mbox{-}C_{5}H_{5})Mn(CO)_{2}]\cdot THF \\
& \reactrarrow{0pt}{3cm}{\scriptsize K/THF}{\scriptsize [18]crown-6}
[PhSb\{Mn(CO)_{2}(\eta^{5}\mbox{-}C_{5}H_{5})\}_{2}] + 2KI + \cdots \\
& \mbox{and further lines}
\end{split}
\end{ChemEquation}
```

$$[(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{CO})_2\mathrm{MnSbPhI_2}] + [(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Mn(CO)_2}]\cdot\mathrm{THF} \xrightarrow[\text{[18]crown-6}]{\text{K/THF}} [\mathrm{PhSb\{Mn(CO)_2}(\eta^5\text{-}\mathrm{C_5H_5})\}_2] + 2\mathrm{KI} + \cdots \quad \text{and further lines} \tag{35.39}$$

where an ampersand is used to mark an alignment point. Note that the equation number is centered vertically on the height of the split environment. □

Example 35.32. To print the equation number at the end of the display equation, the switching command `\ctagsplit@false` is declared as follows:

```
{\makeatletter
\ctagsplit@false
\begin{ChemEquation}
\begin{split}
 [(\eta^{5}\mbox{-}C_{5}H_{5})(CO)_{2}MnSbPhI_{2}]
& + [(\eta^{5}\mbox{-}C_{5}H_{5})Mn(CO)_{2}]\cdot THF \\
& \reactrarrow{0pt}{3cm}{\scriptsize K/THF}{\scriptsize [18]crown-6}
[PhSb\{Mn(CO)_{2}(\eta^{5}\mbox{-}C_{5}H_{5})\}_{2}] + 2KI + \cdots \\
& \mbox{and further lines}
\end{split}
\end{ChemEquation}
\makeatother
}
```

$$[(\eta^5\text{-}C_5H_5)(CO)_2MnSbPhI_2] + [(\eta^5\text{-}C_5H_5)Mn(CO)_2]\cdot THF \xrightarrow[\text{[18]crown-6}]{\text{K/THF}} [PhSb\{Mn(CO)_2(\eta^5\text{-}C_5H_5)\}_2] + 2KI + \cdots$$
$$\text{and further lines} \tag{35.40}$$

□

`split` Environment in the `chemalign` Environment

The `chemalign` environment defined by `\newchemenvironment{chemalign}{align}` can be combined with the `split` environment.

Example 35.33. The following example shows the use of the `split` environment in the `chemalign` environment.

```
\begin{chemalign}
\begin{split}
H_{2}O + H_{2}SO_{4} & \equilibarrow  H_{3}O^{+} + HSO_{4}^{-}; \\
& \mathit{K}_{H_{2}O}(25^{\circ}) =
\frac{[H_{3}O^{+}][HSO_{4}^{-}]}{[H_{2}O]} \sim 1
\end{split} \\
SO_{3} + H_{2}SO_{4} & \equilibarrow  H_{2}S_{2}O_{7} \\
\begin{split}
H_{2}S_{2}O_{7} + H_{2}SO_{4} & \equilibarrow
H_{3}SO_{4}^{+} + HS_{2}O_{7}^{-}; \\
& \mathit{K}_{H_{2}S_{2}O_{7}}(25^{\circ})
= \frac{[H_{3}SO_{4}^{+}][HS_{2}O_{7}^{-}]}{[H_{2}S_{2}O_{7}]} =
1.4 \times 10^{-2}
\end{split}
\end{chemalign}
```

$$\begin{aligned} H_2O + H_2SO_4 &\rightleftharpoons H_3O^+ + HSO_4^-; \\ K_{H_2O}(25^\circ) &= \frac{[H_3O^+][HSO_4^-]}{[H_2O]} \sim 1 \end{aligned} \tag{35.41}$$

$$SO_3 + H_2SO_4 \rightleftharpoons H_2S_2O_7 \tag{35.42}$$

$$\begin{aligned} H_2S_2O_7 + H_2SO_4 &\rightleftharpoons H_3SO_4^+ + HS_2O_7^-; \\ K_{H_2S_2O_7}(25^\circ) &= \frac{[H_3SO_4^+][HS_2O_7^-]}{[H_2S_2O_7]} = 1.4 \times 10^{-2} \end{aligned} \tag{35.43}$$

□

`split` Environment in the `chemgather` Environment

The `chemgather` environment defined above is capable of containing the `split` environment (the amsmath package) and the `chemalign*` environment (defined above) at the same time.

Example 35.34. The following example exemplifies such a nested specification of chemical equations:

```
\begin{chemgather}
\begin{split}
[Cr(CO)_{6}] & \overset{A}{\llongrightarrow}
\underset{yellow}{[Cr(CO)_{5}(AsPhH_{2})]} \overset{B}{\llongrightarrow} \\
& \underset{orange}{[Cr(CO)_{5}(AsPhLi_{2})]} \overset{C}{\llongrightarrow}
\underset{\text{dark violet} ~(mp ~104^{\circ})}{[\{Cr(CO)_{5}\}_{2}AsPh]}
\end{split} \\
\begin{chemalign*}
A:\qquad & PhAsH_{2} \\
B:\qquad & LiBu \\
C:\qquad & \text{cyclohexyl-}NCl_{2}
\end{chemalign*}
\end{chemgather}
```

$$\begin{aligned}
&[Cr(CO)_6] \xrightarrow{A} \underset{\text{yellow}}{[Cr(CO)_5(AsPhH_2)]} \xrightarrow{B} \\
&[Cr(CO)_5(AsPhLi_2)] \xrightarrow{C} \underset{\text{dark violet (mp 104°)}}{[\{Cr(CO)_5\}_2AsPh]} \\
&\qquad\qquad \underset{\text{orange}}{} \qquad\qquad\qquad\qquad
\end{aligned} \tag{35.44}$$

A : $PhAsH_2$
B : LiBu
C : cyclohexyl-NCl_2

□

35.4 Objects Placed Over or Under Arrows

35.4.1 Combination of Commands

Example 35.35. The command `\overset` of the amsmath package is applicable to place an object over an arrow:

```
\begin{ChemEquation}
CCl_{4} + HF \overset{SbFCl_{4}}{\lllongrightarrow}
CFCl_{3} + HCl
\end{ChemEquation}
```

$$CCl_4 + HF \xrightarrow{SbFCl_4} CFCl_3 + HCl \tag{35.45}$$

□

Example 35.36. The command `\stackrel` of LaTeX 2ε can be also applied to a similar target as follows:

```
\begin{ChemEquation}
CFCl_{3} + HF
\stackrel{SbFCl_{4}}{\lllongrightarrow}
CF_{2}Cl_{2} + HCl
\end{ChemEquation}
```

$$CFCl_3 + HF \xrightarrow{SbFCl_4} CF_2Cl_2 + HCl \tag{35.46}$$

□

Example 35.37. A nested usage of `\underset` and `\overset` comes out well in placing objects under and over an arrow.

```
\begin{ChemEquation}
Na + Al + 2H_{2}
\underset{350~atom}{\overset{THF/140^{\circ}/3\: h}{\lllongrightarrow}}
NaAlH_{4}\quad (99\%~yield)
\end{ChemEquation}
```

$$\mathrm{Na + Al + 2H_2} \xrightarrow[350\ \mathrm{atom}]{\mathrm{THF/140^\circ/3\,h}} \mathrm{NaAlH_4} \quad (99\%\ \text{yield}) \tag{35.47}$$

□

35.4.2 Application of Arrows for Organic Chemistry

Example 35.38. Because default positions of objects placed by such arrows for organic chemistry (Section 33.2) are adjusted to meet large structural formulas in organic chemistry, they are sometimes unsuitable if they are combined with rather small inorganic formulas, as found in the following equation:

```
\begin{ChemEquation}
\alpha Na(NH_4)HPO_4
\reactrarrow{0pt}{1cm}{\scriptsize $\Delta$}{\ChemStrut}
(NaPO_3)_{\alpha }
+ \alpha NH_3\uparrow + \alpha H_2O
\end{ChemEquation}
```

$$\alpha\mathrm{Na(NH_4)HPO_4} \xrightarrow{\Delta} (\mathrm{NaPO_3})_\alpha + \alpha\mathrm{NH_3}\uparrow + \alpha\mathrm{H_2O} \tag{35.48}$$

□

Example 35.39. The position of Δ over an arrow is adjustable by means of `\reactarrowsep` in the chemist package (version 4.05).

```
{\reactarrowsep=-2pt
\begin{ChemEquation}
\alpha Na(NH_4)HPO_4
\reactrarrow{0pt}{1cm}{\scriptsize $\Delta$}{\ChemStrut}
(NaPO_3)_{\alpha }
+ \alpha NH_3\uparrow + \alpha H_2O
\end{ChemEquation}
}
```

$$\alpha\mathrm{Na(NH_4)HPO_4} \xrightarrow{\Delta} (\mathrm{NaPO_3})_\alpha + \alpha\mathrm{NH_3}\uparrow + \alpha\mathrm{H_2O} \tag{35.49}$$

Note that `\ChemStrut` is used to adjust the up and down position of the arrow. □

Example 35.40. The following example shows texts over and under an arrow:

```
\def\degC{\char'27C}
\begin{ChemEquation}
2Ph_{3}GeBr + 2Na
\reactrarrow{0pt}{2cm}{boling}{xylene}
2NaBr + Ge_{2}Ph_{6} \quad (mp\: 340\degC)
\end{ChemEquation}
```

$$\mathrm{2Ph_3GeBr + 2Na} \xrightarrow[\text{xylene}]{\text{boiling}} \mathrm{2NaBr + Ge_2Ph_6} \quad (\text{mp } 340^\circ\mathrm{C}) \tag{35.50}$$

Although the command `\degC` is defined in the chemist package, the font width of `\char'27` (˚) depends upon the selected font family. Hence, the redefinition of the command `\degC` is necessary in the present on-line document. □

Example 35.41. The ChemEquation environment is capable of accommodating structural formulas produced by the XyMTEX system. The following example shows that the command \tetrahedral of the XyMTEX system is used to demonstrate an organo-metallic compound of rhenium:

```
\begin{ChemEquation}
Me_{3}SnCl_{2} + 2NaRe(CO)_{5}
\reactrarrow{0pt}{3cm}{Metathesis}{\ChemStrut} \quad
\begin{XyMcompd}(1050,400)(-200,100){}{}
\tetrahedral{0==Sn;1==Me;2==(CO)$_{5}$Re;3==Me;4==Re(CO)$_{5}$}
\end{XyMcompd}
+ 2NaCl
\end{ChemEquation}
```

$$\mathrm{Me_3SnCl_2} + 2\mathrm{NaRe(CO)_5} \xrightarrow{\text{Metathesis}} \begin{array}{c}\mathrm{Me}\\ |\\ \mathrm{(CO)_5Re-Sn-Re(CO)_5}\\ |\\ \mathrm{Me}\end{array} + 2\mathrm{NaCl} \qquad (35.51)$$

where the XyMcompd environment is supported in the chemist package (cf. Section 34.2). □

Example 35.42. The following example shows the use of \ChemForm in an argument of the \reactrarrow:

```
\begin{ChemEquation}
Na[Mn(CO)_{5}]
\reactrarrow{0pt}{2cm}{\ChemForm{C_{3}H_{5}Cl}}{\ChemStrut}
[Mn(CO)_{5}(\eta^{1}\mbox{-}C_{3}H_{5})]
\reactrarrow{0pt}{2cm}{$\mathit{h}\nu$}{or 80$^{\circ}$C}
[Mn(CO)_{4}(\eta^{3}\mbox{-}C_{3}H_{5})] + CO
\end{ChemEquation}
```

$$\mathrm{Na[Mn(CO)_5]} \xrightarrow{\mathrm{C_3H_5Cl}} \mathrm{[Mn(CO)_5(\eta^1\text{-}C_3H_5)]} \xrightarrow[\text{or } 80^\circ\mathrm{C}]{h\nu} \mathrm{[Mn(CO)_4(\eta^3\text{-}C_3H_5)]} + \mathrm{CO} \qquad (35.52)$$

where η^1-allyl (η^1-C_3H_5) is converted into η^3-allyl (η^3-C_3H_5). □

35.5 Bonds and Relevant Representations

Because the original definition of \tbond or \dbond depend upon the font family selected, each bond thickness of a triple bond or a double bond is sometimes insufficient (too thin). The following redefinition is suitable to use \tbond or \dbond in chemical equations and chemical structural formulas:

```
\def\triplebond{\leavevmode\kern.2pt\raisebox{.2ex}{%
\hbox{\vbox{\hrule height0.4pt width1em\kern.4ex
\hrule height0.4pt width1em\kern.4ex
\hrule height0.4pt width1em}}\hskip.4pt}
\def\doublebond{\leavevmode\kern.2pt\raisebox{.3ex}{%
\hbox{\vbox{\hrule height0.4pt width1em\kern.6ex
\hrule height0.4pt width1em}}\hskip.4pt}
\let\tbond=\triplebond
\let\dbond=\doublebond
```

Example 35.43. Triple bonds are drawn by \tbond in a ChemEquation or like environment:

```
\begin{ChemEquation}
RC\tbond CH + e_{am}^{-} \llongrightarrow RC\tbond C^{-} +
{\textstyle \frac{1}{2}}H_{2}
\end{ChemEquation}
```

$$\mathrm{RC{\equiv}CH} + \mathrm{e^-_{am}} \longrightarrow \mathrm{RC{\equiv}C^-} + \tfrac{1}{2}\mathrm{H_2} \qquad (35.53)$$

where the subscript am of e^-_{am} indicates that the electron is solvated by liquid ammonia. □

Example 35.44. Double bonds are drawn by `\dbond` in a `ChemEquation` or like environment:

```
\begin{ChemEquation}
CH_{2}\dbond CH_{2} + PhH
\reactrarrow{0pt}{2cm}{\scriptsize \ChemForm{AlCl_{3}}}{\ChemStrut}
PhEt
\end{ChemEquation}
```

$$\mathrm{CH_2{=}CH_2 + PhH \xrightarrow{AlCl_3} PhEt} \tag{35.54}$$

□

Example 35.45. Single bonds are drawn by `\sbond` in a `ChemEquation` or like environment:

```
\begin{ChemEquation}
PhN\dbond O + 2e_{am}^{-} \llongrightarrow PhN^{-}\sbond O^{-}
\end{ChemEquation}
```

$$\mathrm{PhN{=}O + 2e^-_{am} \longrightarrow PhN^-{-}O^-} \tag{35.55}$$

□

Example 35.46. Lone pairs around an atom can be typeset by using the `\lonepairA` command, which is supported by X$\overset{\frown}{\text{E}}$MTEX version 4.05 (the lewisstruc package, cf. on-line document (xymtx405A.pdf)). The following example shows that a cuprous chloride ion ($CuCl_2^-$) involves two covalent bonds between Cu and Cl and lone pairs around each chlorine atom.

```
\begin{ChemEquation}
CuCl_{4}^{2-} + Cu \llongrightarrow
2\bigl[\:\lonepairA[134]{Cl}\sbond Cu\sbond\lonepairA[123]{Cl}\:\bigr]^{-}
\end{ChemEquation}
```

$$\mathrm{CuCl_4^{2-} + Cu \longrightarrow 2[:\ddot{\underset{\cdot\cdot}{\text{C}}}l{-}Cu{-}\ddot{\underset{\cdot\cdot}{\text{C}}}l:]^-} \tag{35.56}$$

□

References

[1] D. E. Knuth, “The TEXbook,” Addison-Wesley, Reading (1984).

[2] S. Fujita, “Organic Chemistry of Photography,” Springer-Verlag, Berlin-Heidelberg (2004).

[3] S. Fujita, “Kagakusha-Seikagakusha no tame no LATEX (LATEX for Chemists and Biochemists),” Tokyo Kagaku Dozin, Tokyo (1993).

Chapter 36

Formatting Reaction Schemes

This chapter is devoted to show how to construct reaction schemes on the basis of the XeLaTeX system. Structural formulas, which are drawn by using XeLaTeX commands, are are regarded as TeX boxes. They are aligned in a selected environment so as to construct a reaction scheme.

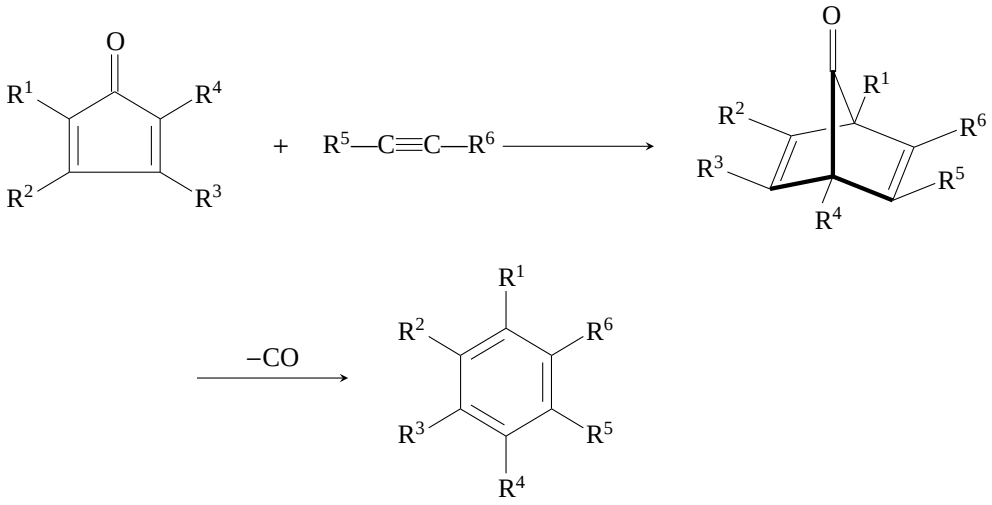
36.1 Structural Formulas as TeX Boxes

Structural formulas typeset by the XeLaTeX system are regarded as TeX boxes; hence, they obey the typesetting rule of TeX/LaTeX in the same way as usual TeX boxes. In the following example, XeLaTeX boxes are aligned consecutively so as to construct a reaction scheme, where vertical adjustment is carried out by using the `\cdonecell` command of the chemist package, which is automatically loaded in the TeX/LaTeX-compatible mode, the PDF-compatible mode, or the PostScript-compatible mode.

Example 36.1. The following code generates TeX-boxes by using `\cdonecell` (involving a structural formula), `\reactrarrow`, `\cdonecell` (involving a structural formula), `\reactrarrow`, and `\cdonecell` (involving a structural formula). These TeX-boxes are aligned on the basis of the typesetting mechanism of TeX, just as words are typeset to give a sentence after they are regarded as TeX-boxes.

```
\cdonecell{0pt}{4cm}{%
\cyclopentanevi[bd]{1D==O;2==R$^{4}$;3==R$^{3}$;%
4==R$^{2}$;5==R$^{1}$}} + \hskip10pt
\mbox{R$^{5}$---C\tbond C---R$^{6}$}
\reactrarrow{0pt}{2cm}{}{}
\cdonecell{10pt}{5cm}{%
\bornane[be]{7D==O;1==R$^{1}$;4==R$^{4}$;%
2==R$^{6}$;3==R$^{5}$;5==R$^{3}$;6==R$^{2}$}} \par
\hspace*{3cm}
\reactrarrow{0pt}{2cm}{$-$CO}{\strut}
\cdonecell{0pt}{4cm}{%
\bzdrv{1==R$^{1}$;4==R$^{4}$;%
2==R$^{6}$;3==R$^{5}$;5==R$^{3}$;6==R$^{2}$}}
```

In this code, a new paragraph is started by declaring the command `\par`. In the situation of the present document, page clearing occurs at the place designated by the `\par`. For the command `\cdonecell`, see Subsection 34.2.3. For the command `\reactrarrow`, see Section 33.2. The above code written as a paragraph directly after this sentence generates the following scheme:



□

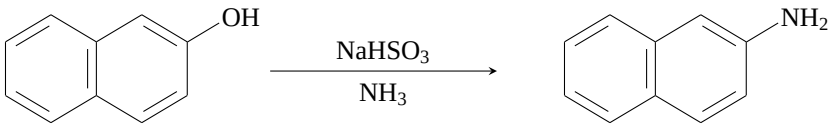
36.2 Centering and “Flushing” Reaction Schemes

36.2.1 Reaction Schemes in the `center` Environment

A reaction scheme can be typeset by using the `center` environment.

Example 36.2. The Bucherer reaction (replacement of a hydroxy group by an amino group) is typeset by using the `\naphdrv` command in the `center` environment. The arrow between the substrate and the product is drawn by means of the `\reactrarrow` command (Section 33.2), where reagents used are designated on the upper side and lower side of the arrow.

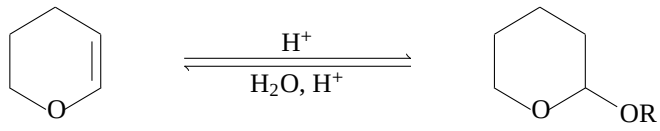
```
\begin{center}
\naphdrv{2==OH}
\reactrarrow{40pt}{3cm}{NaHSO$_{3}$}{NH$_{3}$}
\naphdrv{2==NH$_{2}$}
\end{center}
```



□

Example 36.3. If you want to use cross-reference, a compound number can be attached to each formula by means of a one-column tabular environment. Because the `tabular` environment causes the vertical centering of the formula included, no vertical adjustment is necessary to shift the arrow produced by the `\reacteqarrow` command (Section 33.2); thus, its first argument is 0pt.

```
\begin{center}
\begin{tabular}{c}
\sixheterovi[b]{1==O}{} \\[-.5cm] \compd \label{cpd:reac:c1} \\
\end{tabular}
\reacteqarrow{0pt}{3cm}{H$^{+}$}{H$_{2}$O, H$^{+}$}
\begin{tabular}{c}
\sixheterovi[]{1==O}{2==OR} \\[-.5cm] \compd \label{cpd:reac:c2} \\
\end{tabular}
\end{center}
```

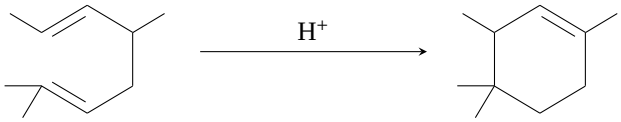


36-1 **36-2**

To refer to **36-1** or **36-2**, the reference key assigned by the command `\label` is declared in the form of `\cref{cpd:reac:c1}` or `\cref{cpd:reac:c2}`. □

Example 36.4. The `\shortstack` command supported by the LaTeX `picture` environment can be used for the same purpose. This method requires the vertical adjustment of placing the arrow produced by `\reactrarrow`.

```
\begin{center}
\shortstack{%
\sixheterov[df]{}{2==;6==;5Sa==;5Sb==}[e]
\\[-.5cm] \compd \label{cpd:reac:c3}}
\reactrarrow{40pt}{3cm}{H$^{+}$}{\strut}
\shortstack{%
\cyclohexanev[a]{2==;6==;5Sa==;5Sb==}
\\[-.5cm] \compd \label{cpd:reac:c4}}
\end{center}
```

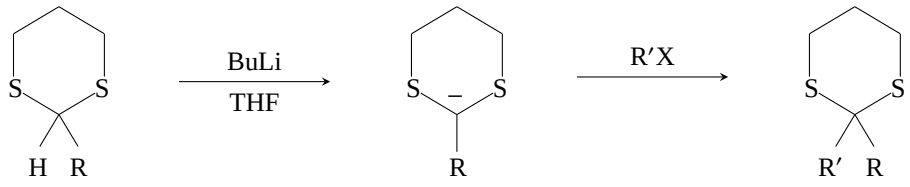


36-3 **36-4**

□

Example 36.5. An alternative method of numbering compounds is to use the `\cdtwocell` command (Subsection 34.2.3). It is applied to draw a scheme of alkylation of 1,3-dithianes.

```
\begin{center}
\cdtwocell{0pt}{3cm}{%
 \sixheterovi[]{2==S;6==S}{1Sa==R;1Sb==H}}%
 {\compd \label{cpd:reac:c5}}
\reactrarrow{0pt}{2cm}{BuLi}{THF}
\cdtwocell{0pt}{3cm}{%
 \sixheterovi[H{1{{\lower1ex\hbox{$-$}}}}]{2==S;6==S}{1==R}}%
 {\compd \label{cpd:reac:c6}}
\reactrarrow{0pt}{2cm}{R$^{\prime}$X}{\strut}
\cdtwocell{0pt}{3cm}{%
 \sixheterovi[]{2==S;6==S}{1Sa==R;1Sb==R$^{\prime}$}}%
 {\compd \label{cpd:reac:c6a}}
\end{center}
```



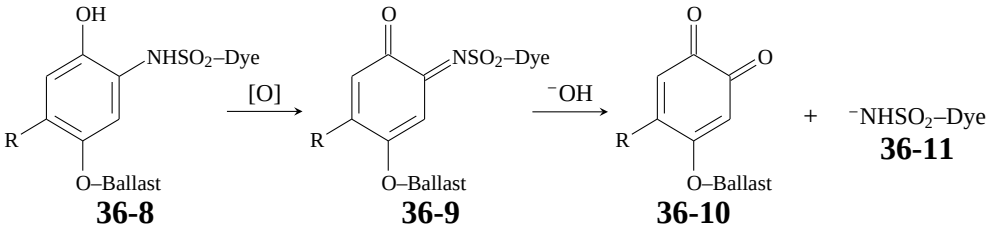
36-5 **36-6** **36-7**

The minus charge on the 2-carbon atom of 1,3-dithiane is printed by using the ⟨bondlist⟩ argument of the `\sixheterovi` command, where a dummy argument 'H' is necessary to obtain a correct result. □

Example 36.6. A more systematic way for assigning compound numbers is to use the `XyMcompd` environment (Subsection 34.2.1). Among representative processes of instant color photography, the dye transfer process based on *o*-sulfonamidophenol dye releaser (**36-8**) consists of an oxidation step (**36-8** → **36-9**) and a subsequent hydrolysis step (**36-9** → **36-10** + **36-11**) [1, page 112]. After each structure with a compound number is generated in the `XyMcompd` environment of the XyMTEX system, the total reaction scheme is drawn by inputting the following code based on the LaTeX `center` environment.

```
\begin{center}
\changeunitlength{0.08pt}\small
\begin{XyMcompd}(1000,900)(100,0){cpd:dyereleaser1}{}
\benzenev{1==OH;2==NHSO$_2$--Dye;4==O--Ballast;5==R}
\end{XyMcompd}
\reactrarrow[-10pt]{0pt}{1cm}{[O]}{\strut}
\begin{XyMcompd}(1000,900)(100,0){cpd:dyereleaser2}{}
\benzenev[oa]{1D==O;2D==NSO$_2$--Dye;4==O--Ballast;5==R}
\end{XyMcompd}
\reactrarrow[-10pt]{0pt}{1cm}{$^{-}$OH}{\strut}
\begin{XyMcompd}(600,900)(100,0){cpd:dyereleaser3}{}
\benzenev[oa]{1D==O;2D==O;4==O--Ballast;5==R}
\end{XyMcompd}
\quad + \quad
\raisebox{-14pt}{%
\shortstack{$^{-}$NHSO$_2$--Dye \\ \compd\label{cpd:dyereleaser4}}}
\end{center}
```

The command `\changeunitlength{0.08pt}` is declared in order to reduce the sizes of structural formulas. Note that the default value of unit length is equal to 0.1pt throughout the XyMTEX system. The command `\small` is declared to reduce the font size of the formula $^{-}NHSO_2$–Dye. The command `\shortstack` is supported by the LaTeX system. The command `\raisebox` is supported by the graphicx package. The above code generates the following scheme:



The symbol 'Dye' denotes a dye moiety, and the symbol 'Ballast' is a large moiety for giving a non-diffusible property to the dye releaser. The resulting $^{-}NHSO_2$–Dye is diffusible to give a photographic picture [1, Chapter 19]. □

36.2.2 Reaction Schemes in the `flushleft` Environment

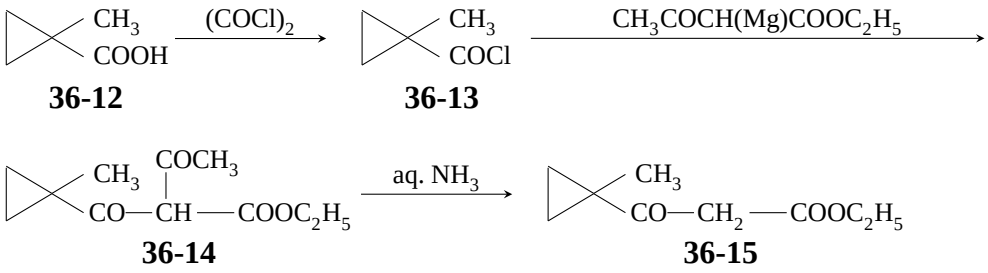
When indent in each line of a reaction scheme is unnecessary, the LaTeX `flushright` environment can be applied as follows.

Example 36.7. A cyclopropene-*β*-ketoester (**36-15**) is an intermediate for synthesizing a two-equivalent yellow coupler for color photography [1, page 243]. The reaction scheme of synthesizing **36-15** is drawn by declaring XyMTEX commands in the `flushleft` environment of the LaTeX system, as shown in the following code:

```
\begin{flushleft}
\begin{XyMcompd}(500,300)(250,200){cpd:cycpro1}{}
\cyclopropaneh{1Sa==COOH;1Sb==\ChemForm{CH_3}}
```

```
\end{XyMcompd}
\reactrarrow{5pt}{2cm}{\ChemForm{(COCl)_{2}}}{\strut} \quad
\begin{XyMcompd}(500,300)(250,200){cpd:cycpro2}{}
\cyclopropaneh{1Sa==COCl;1Sb==\ChemForm{CH_3}}
\end{XyMcompd}
\reactrarrow{5pt}{6cm}{\ChemForm{CH_{3}COCH(Mg)COOC_{2}H_{5}}}{\strut} \\
\bigskip
\begin{XyMcompd}(1200,300)(250,200){cpd:cycpro3}{}
\cyclopropaneh{1Sa==%
\ryl(4==CO){4==\tetrahedral{2==(yl);0==CH;1==\ChemForm{COCH_{3}};%
4==\ChemForm{COOC_{2}H_{5}}};1Sb==\ChemForm{CH_3}}
\end{XyMcompd}
\reactrarrow{5pt}{2cm}{aq.\ \ChemForm{NH_{3}}}{\strut} \quad
\begin{XyMcompd}(1200,300)(250,200){cpd:cycpro4}{}
\cyclopropaneh{1Sa==%
\ryl(4==CO){4==\tetrahedral{2==(yl);0==\ChemForm{CH_{2}};%
4==\ChemForm{COOC_{2}H_{5}}};1Sb==\ChemForm{CH_3}}
\end{XyMcompd}
\end{flushleft}
```

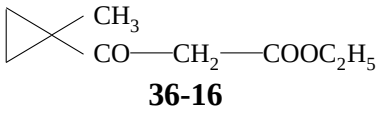
Note that the command \\ in the `flushleft` environment is declared to start a new line. The command `\bigskip` is declared after the command \\ in order to assure an appropriate vertical skip. Both `\ChemForm{COCH_{3}}` (`_{3}` surrounded by a pair of braces) and `\ChemForm{CH_3}` (`_3` with no braces) are permissible to specify a subscript. The above code generates the following scheme:



Each line of the above scheme is printed out in a “flushleft” fashion, where no indent appears. Compare this scheme with the scheme drawn by the `quote` environment in the next subsection.

To draw **36-15**, a simpler code is possible as follows:

```
\begin{XyMcompd}(1250,300)(250,200){cpd:cycpro4a}{}
\cyclopropaneh{1Sa==%
\ChemForm{CO\sbond CH_{2}\sbond COOC_{2}H_{5}};1Sb==\ChemForm{CH_3}}
\end{XyMcompd}
```



□

36.2.3 Reaction Schemes in the `quote` Environment

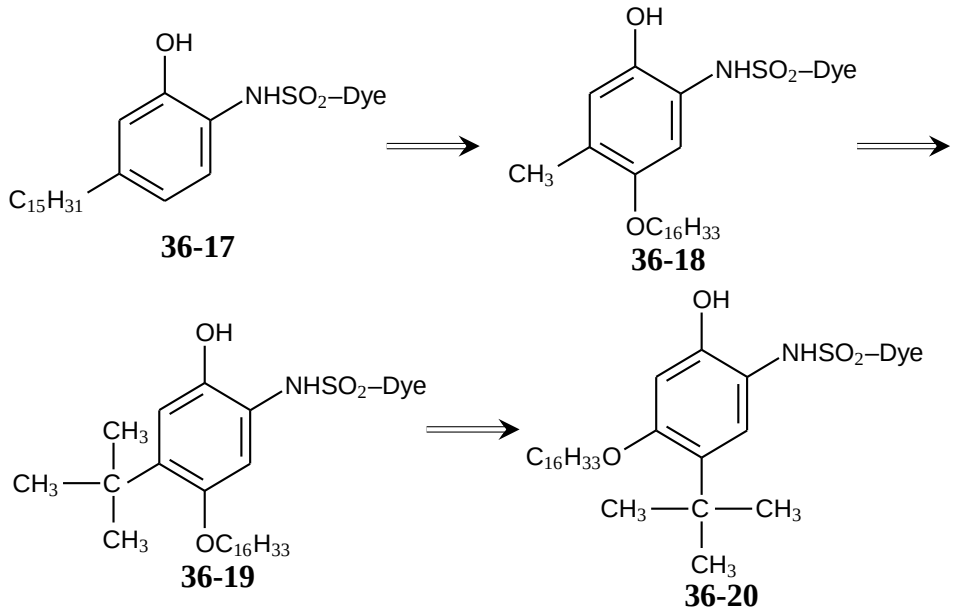
To assure indent in each line of a reaction scheme, the LaTeX `quote` environment can be applied as follows.

Example 36.8. This example is concerned with the targets designed for the R&D of *o*-sulfonamidophenol dye releasers in instant color photography [1, page 458].

```
\begin{quote}
\let\substfont=\sffamily
\def\thinLineWidth{0.8pt}
\begin{XyMcompd}(1250,800)(-100,150){cpd:osulforeleaser1}{}
```

```
\benzenev{1==OH;2==NHSO$_2$--Dye;5==C$_{15}$H$_{31}$}
\end{XyMcompd}
$\Lllongrightarrow$
\begin{XyMcompd}(1250,900)(-100,0){cpd:osulforeleaser2}{}
\benzenev{1==OH;2==NHSO$_{2}$--Dye;4==OC$_{16}$H$_{33}$;5==CH$_{3}$}
\end{XyMcompd}
$\Lllongrightarrow$ \\
\begin{XyMcompd}(1400,950)(-250,0){cpd:osulforeleaser3}{}
\benzenev{1==OH;2==NHSO$_{2}$--Dye;4==OC$_{16}$H$_{33}$;%
5==\tetrahedral{4==(yl);0==C;2==CH$_{3}$;3==CH$_{3}$;1==CH$_{3}$}}
\end{XyMcompd}
\raisebox{10pt}{$\Lllongrightarrow$}
\begin{XyMcompd}(1350,1100)(-200,-200){cpd:osulforeleaser4}{}
\benzenev{1==OH;2==NHSO$_{2}$--Dye;5==C$_{16}$H$_{33}$O;%
4==\tetrahedral{1==(yl);0==C;2==CH$_{3}$;3==CH$_{3}$;4==CH$_{3}$}}
\end{XyMcompd}
\end{quote}
```

In this code, the declaration of `\let\substfont=\sffamily` is done to change the font used in structural formulas (cf. Section 6.1). On the other hand, the declaration of `\def\thinLineWidth{0.8pt}` aims at changing the thickness of bonds, where the default thickness of bonds in the XyMTEX system is decided to be 0.4pt (cf. Section 6.2). The above code generates the following indented reaction scheme:



Each line of the above scheme appears with indent. Compare this scheme with the scheme drawn by the `fulshleft` environment in the preceding subsection. □

36.3 Tabular Schemes

36.3.1 Reaction Schemes in the `tabular` Environment

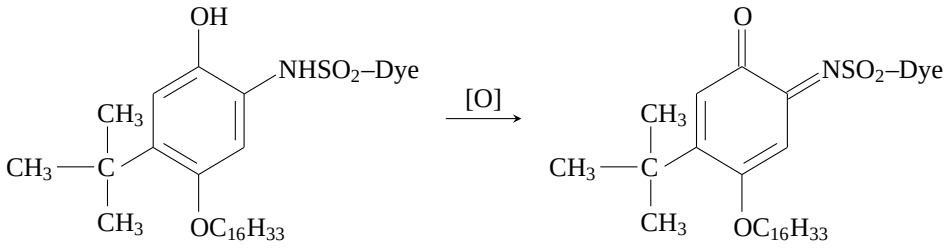
Alignment due to the LaTeX `tabular` environment is useful to format reaction schemes generated by the XyMTEX commands.

Example 36.9. The following example [1, page 452] shows the alignment of structures coupled with the alignment of compounds numbers in a `tabular` environment.

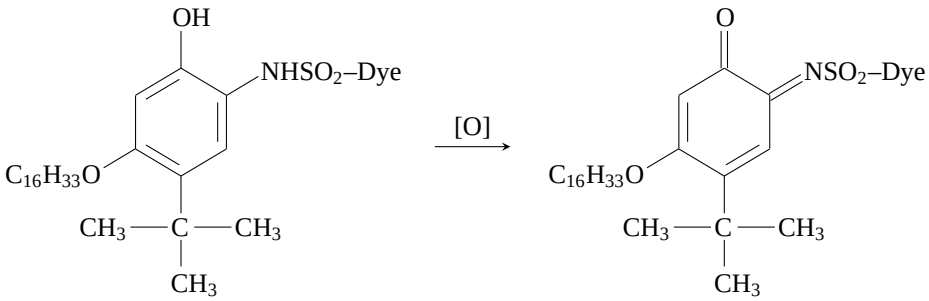
```
\begin{center}
\begin{tabular}{ccc}
```

```
\begin{XyMcompd}(1400,900)(-250,0){}{}
\benzenev{1==OH;2==NHSO$_{2}$--Dye;4==OC$_{16}$H$_{33}$;%
5==\tetrahedral{4==(yl);0==C;2==CH$_{3}$;3==CH$_{3}$;1==CH$_{3}$}}
\end{XyMcompd}
&\reactrarrow{0pt}{1cm}{[O]}{\strut}&
\begin{XyMcompd}(1400,900)(-250,0){}{}
\benzenev[oa]{1D==O;2D==NSO$_{2}$--Dye;4==OC$_{16}$H$_{33}$;%
5==\tetrahedral{4==(yl);0==C;2==CH$_{3}$;3==CH$_{3}$;1==CH$_{3}$}}
\end{XyMcompd}
\\
\noalign{\vskip5pt}
\compd\label{cpd:dyedevoxi1a} &&\compd\label{cpd:dyedevoxi1b} \\[10pt]
\begin{XyMcompd}(1350,1100)(-200,-200){}{}
\benzenev{1==OH;2==NHSO$_{2}$--Dye;5==C$_{16}$H$_{33}$O;%
4==\tetrahedral{1==(yl);0==C;2==CH$_{3}$;3==CH$_{3}$;4==CH$_{3}$}}
\end{XyMcompd}
&\reactrarrow{0pt}{1cm}{[O]}{\strut}&
\begin{XyMcompd}(1350,1100)(-200,-200){}{}
\benzenev[oa]{1D==O;2D==NSO$_{2}$--Dye;5==C$_{16}$H$_{33}$O;%
4==\tetrahedral{1==(yl);0==C;2==CH$_{3}$;3==CH$_{3}$;4==CH$_{3}$}}
\end{XyMcompd}
\\
\noalign{\vskip5pt}
\kern-10pt\compd\label{cpd:dyedevoxi2a} &&
\kern-10pt\compd\label{cpd:dyedevoxi2b} \\
\end{tabular}
\end{center}
```

In the above code, the tabular line of compounds numbers is printed out differently from the tabular line of a reaction scheme, where the printing of the compounds numbers is accomplished by using `\compd` and `\label` (no use of the argument of the `XyMcompd` environment). Note that the printed positions of the compounds numbers (**36-23** and **36-24**) in the last row are adjusted by declaring `\kern-10pt`. The baseline skips are adjusted by declaring `\noalign{\vskip5pt}`. The above code generates the following scheme:



36-21 **36-22**



36-23 **36-24**

□

Alignment due to the LaTeX `tabular` environment is useful to draw a diagram with arrows running to four diagonal directions.

Example 36.10. The following example shows a stereoselective synthesis [2].

```
\begin{figure}
\begin{center}
\tabcolsep=0pt
\begin{tabular}{ccccc}
\begin{XyMcompd}(750,600)(50,-50){}{}%{cpd:osulforeleaser4}{}
\pentamethylenei[d]{}{1W==H;1D==O;2SA==\null;2SB==Ph;3SA==H;3SB==Ph}
\end{XyMcompd}
&&&&
\begin{XyMcompd}(750,600)(50,-50){}{}%{cpd:osulforeleaser4}{}
\pentamethylenei[d]{}{1W==H;1D==O;2SB==\null;2SA==Ph;3SA==H;3SB==Ph}
\end{XyMcompd}
\\
& \reactnwarrow{5pt}{2cm}{%
\llap{\shortstack{\mbox{}\\[10pt]Chiral Ir catalyst 1 \\
Chiral amine 2}\kern-20pt}
}{} &
& \reactnearrow{0pt}{2cm}{}{%
\rlap{\kern-20pt\shortstack{Chiral Ir catalyst 1 \\ Chiral amine 1}}
} & \\
\noalign{\vskip-3pt}
&&
\makebox(0,600){\framebox(1700,600){%
\begin{XyMcompd}(500,500)(-100,50){}{}%{cpd:osulforeleaser4}{}
\dimethylenei{}{1W==H;1D==O;2==\null;2W==Ph}
\end{XyMcompd}
\quad + \quad
\begin{XyMcompd}(500,500)(-150,0){}{}%{cpd:osulforeleaser4}{}
\trimethylenei[b]{}{1==OH;1W==Ph}
\end{XyMcompd}}}
&&\\
\noalign{\vskip-10pt}
& \reactswarrow{0pt}{2cm}{%
\llap{\shortstack{\mbox{}\\[-20pt]Chiral Ir catalyst 2 \\
Chiral amine 2}\kern-40pt}
}{} &
& \reactsearrow{5pt}{2cm}{}{
\rlap{\kern-40pt\shortstack{Chiral Ir catalyst 2 \\ Chiral amine 1}}
} & \\
\begin{XyMcompd}(750,600)(50,-50){}{}%{cpd:osulforeleaser4}{}
\pentamethylenei[d]{}{1W==H;1D==O;2SA==\null;2SB==Ph;3SB==H;3SA==Ph}
\end{XyMcompd}
&&&&
\begin{XyMcompd}(750,600)(50,-50){}{}%{cpd:osulforeleaser4}{}
\pentamethylenei[d]{}{1W==H;1D==O;2SB==\null;2SA==Ph;3SB==H;3SA==Ph}
\end{XyMcompd}
\\
\end{tabular}
\end{center}
\caption{Reaction Scheme in a \texttt{tabular} Environment}
\label{tt:RSintabularEnv}
\end{figure}
```

For the four commands for drawing diagonal arrows, see Section 33.2. The commands `\makebox`, `\framebox`, and `\shortstack`, which are originally supported by the LaTeX `picture` environment, can be used in the `tabular` environment. The net size of the central domain is decided to be 0pt by declaring `\makebox(0,600)`, although the width of the frame box is drawn to be 170pt by means of the command

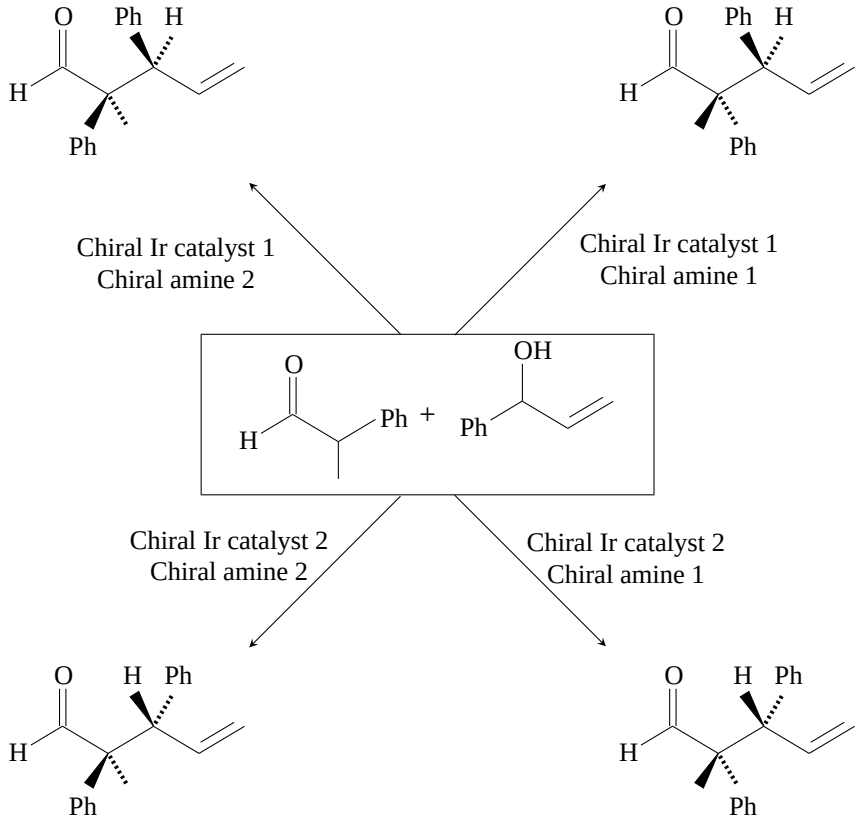


Figure 36.1. Reaction scheme in a `tabular` environment

`\framebox(1700,600)`. Totally, the above code is surrounded by the `figure` environment, so that the resulting scheme is printed out as a floating object, as found in Fig. 36.1. □

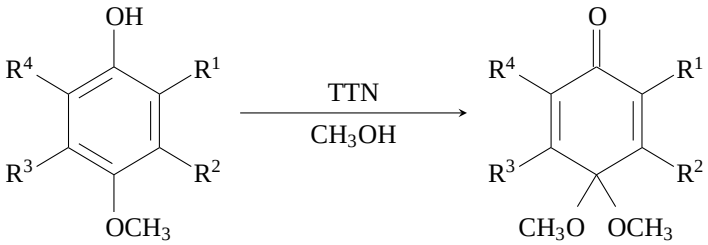
Example 36.11. Another example of using `\cdtwocell` and `\noderiv` is the following table cited from *Yuki Gosei Kagaku Kyokai-Shi* [3].

```
\begin{table}
\begin{quotation}
McKillop reported a method of preparing quinone monoacetals (\cref{cpd:cmb12})
by the oxidation of $p$-methoxyphenols (\cref{cpd:cmb11}) with
thallium(III) nitrate (TTN)/methanol.  The method can be
applied to the preparation of a wide vaiety of quinone monoacetals.
The reactions of
the quinone monoacetal with no subsituents (\cref{cpd:cmb12a})
with nucleophilic reagents have been examined in detail.
\end{quotation}

\caption{The preparation of quinone monoacetals}
\label{tt:chen01}
\begin{center}
\cdtwocell{0pt}{90pt}{\bzdrv{1==OH;4==OCH$_3$;%
 2==R$^1$;3==R$^2$;5==R$^3$;6==R$^4$}}{\compd\label{cpd:cmb11}%
 \noderiv\label{cpd:cmb11a}
 \noderiv\label{cpd:cmb11b}\noderiv\label{cpd:cmb11c}
 \noderiv\label{cpd:cmb11d}\noderiv\label{cpd:cmb11e}
 \noderiv\label{cpd:cmb11f}\noderiv\label{cpd:cmb11g}\noderiv\label{cpd:cmb11h}}
 \reactrarrow{10pt}{3cm}{TTN}{CH$_3$OH}
\cdtwocell{0pt}{90pt}{\bzdrv[pa]{1D==O;4Sa==OCH$_3$;4Sb==CH$_3$O;%
  2==R$^1$;3==R$^2$;5==R$^3$;6==R$^4$} }{\compd\label{cpd:cmb12}%
```

McKillop reported a method of preparing quinone monoacetals (**36-26**) by the oxidation of *p*-methoxyphenols (**36-25**) with thallium(III) nitrate (TTN)/methanol. The method can be applied to the preparation of a wide variety of quinone monoacetals. The reactions of the quinone monoacetal with no substituents (**36-26a**) with nucleophilic reagents have been examined in detail.

Table 36.1. The preparation of quinone monoacetals



36-25 **36-26**

substituents	derivatives							
	36-26a	**36-26b**	**36-26c**	**36-26d**	**36-26e**	**36-26f**	**36-26g**	**36-26h**
R^1	H	CH_3	CH_3	$C(CH_3)_3$	H	H	Cl	Br
R^2	H	H	H	H	OCH_3	OCH_3	H	H
R^3	H	H	H	H	OCH_3	OCH_3	H	H
R^4	H	H	CH_3	$C(CH_3)_3$	H	$OCOCH_3$	H	H
yields (%)	97	89	87	96	95	92	97	91

```
  \noderiv\label{cpd:cmb12a}\noderiv\label{cpd:cmb12b}\noderiv\label{cpd:cmb12c}
  \noderiv\label{cpd:cmb12d}\noderiv\label{cpd:cmb12e}
  \noderiv\label{cpd:cmb12f}\noderiv\label{cpd:cmb12g}\noderiv\label{cpd:cmb12h}}
 \\[10pt]
\begin{tabular}{cccccccccc}
\hline
\bury{substituents} & \multicolumn{8}{c}{derivatives} \\
\cline{2-9}
& \cref{cpd:cmb12a} & \cref{cpd:cmb12b} &
\cref{cpd:cmb12c} & \cref{cpd:cmb12d} & \cref{cpd:cmb12e} &
\cref{cpd:cmb12f} & \cref{cpd:cmb12g} & \cref{cpd:cmb12h} \\
\hline
R$^1$ & H & CH$_3$ & CH$_3$ & C(CH$_3$)$_3$ & H       &H      &Cl&Br\\
R$^2$ & H &  H     &  H     &  H            & OCH$_3$ &OCH$_3$ &H &H\\
R$^3$ & H &  H     &  H     &  H            & OCH$_3$ &OCH$_3$ &H &H\\
R$^4$ & H &  H     &CH$_3$  & C(CH$_3$)$_3$ & H   &OCOCH$_3$  &H &H\\
\hline
yields (\%) & 97& 89 & 87     &    96         & 95      &92  & 97 & 91\\
\hline
\end{tabular}
\end{center}
\end{table}
```

Note that a set of `\noderiv` commands along with `\label` commands are declared after the `\compd` command for each of the structural formulas; thereby, only compound numbers with no derivative numbers are typeset there. On the other hand, a set of `\cref` commands are used in the tabular environment to print compound numbers. The command `\bury` supported by the chemist package (automatically loaded) is used to lower a printed object by the half of a baseline skip. The output is shown in Table 36.1. □

36.3.2 Reaction Schemes in the XyMtab Environment

Tabular schemes containing structural formulas and reaction arrows are drawn by using the XyMtab environment of the chemist package, which is automatically loaded in any modes of the XeLaTeX system (the TeX/LaTeX-compatible mode, the PDF-compatible mode, and the PostScript-compatible mode).

Example 36.12. For example, the code,

```
\begin{figure}
\begin{XyMtab}{cccccc}
\begin{XyMcompd}(400,750)(220,200){cpd:AAPHCL}{}
\bzdrv{{1}==Cl;}
\end{XyMcompd}&
\reactrarrow[10\unitlength]{60\unitlength}{600\unitlength}
{\strut{}H\mbox{$_{2}$}O\\}{\strut{}High press.\\}&
\begin{XyMcompd}(400,750)(220,200){cpd:AAPHOH}{}
\bzdrv{{1}==OH;}
\end{XyMcompd}&
\reactrarrow[10\unitlength]{60\unitlength}{500\unitlength}
{\strut{}CH\mbox{$_{3}$}I\\}{\strut{}NaOH\\}&
\begin{XyMcompd}(400,750)(220,200){cpd:AAPHOME}{}
\bzdrv{{1}==OCH\mbox{$_{3}$};}
\end{XyMcompd} &\\
&&&&
\reactdarrow[0\unitlength]{300\unitlength}{400\unitlength}
{HNO\mbox{$_{3}$}\\}{\kern30pt}& \\
&&&&
\begin{XyMcompd}(400,850)(220,0){APHNO2}{}
\bzdrv{{1}==OH;{4}==NO\mbox{$_{2}$};}
\end{XyMcompd}
&\\
\end{XyMtab}
\caption{Reaction scheme in the \texttt{XyMtab} environment}
\label{ff:RSinXyMtab}
\end{figure}
```

generates a tabular scheme, as shown in Fig. 36.2. Note that the printed reaction scheme due to the XyMtab environment is centered automatically. □

36.4 Structural Formulas in Display Math Environments

36.4.1 Reaction Schemes in the equation-like Environments

In the equation Environment

As remarked in page 612, the amsmath package has redefined LaTeX display math environments such as the equation environment, so that it does not permit multiple usage of the command \label in a single display math environment. However, such multiple usage of reference commands is sometimes required in chemical documentations. The command \resetamsmathlabel has been defined to assure the cooperation of the XeLaTeX system and the amsmath package (cf. Remarks on page 612).

Example 36.13. Display formulas containing structural formulas and reaction arrows are drawn by using the equation-like environments of LaTeX or of the amsmath package. For example, the code based on the equation environment:

```
\begin{equation}
\resetamsmathlabel %reset \label from amsmath to LaTeX
\begin{XyMcompd}(400,750)(220,200){cpd:BPHOH}{}
\bzdrv{1==OH}
```

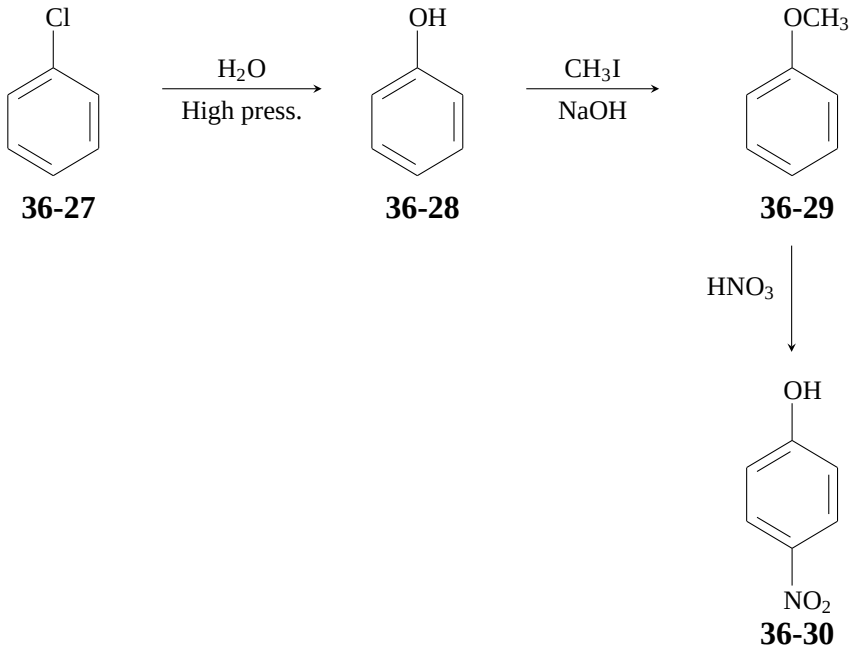
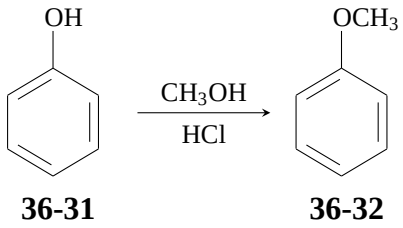


Figure 36.2. Reaction Scheme in the `XyMtab` environment

```
\end{XyMcompd}
\reactrarrow[10\unitlength]{-20\unitlength}{500\unitlength}
{CH\mbox{$_{3}$}OH}{HCl}
\begin{XyMcompd}(400,750)(220,200){cpd:PHOME}{}
\bzdrv{1==OCH\mbox{$_{3}$}}
\end{XyMcompd}
\label{eq:EQ1}
\end{equation}
```

produces the following display formula:



(36.1)

where the command `\resetamsmathlabel` is declared directly after `\begin{equation}`. The compound numbers **36-31** and **36-32** can be referred to by setting `\cref{cpd:BPHOH}` and `\cref{cpd:PHOME}`, while the equation number, i.e., Eq. 36.1, can be referred to by setting `Eq.\ \ref{eq:EQ1}`. □

In the eqnarray Environment

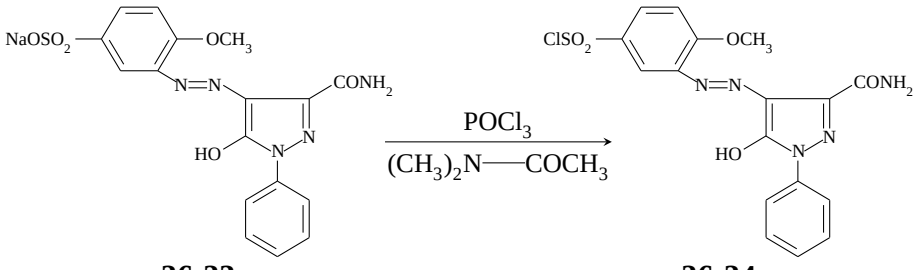
XƎMTEX commands can be declared in the LaTeX `chemeqn` environment. The declaration command `\resetamsmathlabel` should be declared to permit multiply-declared compounds numbers, where the `\label` of the amsmath package is replaced by the LaTeX-original `\label` (cf. Remarks on page 612).

Example 36.14. The chemoselective syntheses of pyrazolone azo dyes **36-33** and **36-34** from a common starting compound **36-35** [1, page483] are drawn by using the LaTeX `chemeqn` environment.

```
%definition of a common skeleton
\def\pyrazolonedye#1#2#3{%
{\changeunitlength{#1}%
\begin{XyMcompd}(1950,1400)(-1000,-300){}{}
```

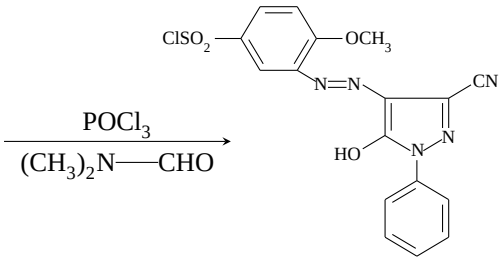
```
\pyrazolev{1==\benzenev{1==(yl)};3==#2;5==HO;%
4==\lyl(4==N\dbond N){3==\benzeneh{5==(yl);4==\ChemForm{OCH_{3}};%
1==#3}}}
\end{XyMcompd}}}
%LaTeX eqnarray environment
\begin{eqnarray}
\resetamsmathlabel %reset \label from amsmath to LaTeX
\begin{tabular}{c}
\pyrazolonedye{0.07pt}{\ChemForm{CONH_{2}}}{\ChemForm{NaOSO_{2}}} \\
\compd\label{cpd:pyrazodye1} \\
\end{tabular} &
\reactrarrow[-20pt]{0pt}{3cm}%
{\ChemForm{POCl_{3}}}{\ChemForm{(CH_{3})_{2}N\sbond COCH_{3}}}
& \kern-50pt
\begin{tabular}{c}
\pyrazolonedye{0.07pt}{\ChemForm{CONH_{2}}}{\ChemForm{ClSO_{2}}} \\
\compd\label{cpd:pyrazodye2} \\
\end{tabular} \label{eq:pyrazodyeA} \\
& \reactrarrow[-20pt]{0pt}{3cm}%
{\ChemForm{POCl_{3}}}{\ChemForm{(CH_{3})_{2}N\sbond CHO}}
& \kern-50pt
\begin{tabular}{c}
\pyrazolonedye{0.07pt}{CN}{\ChemForm{ClSO_{2}}} \\
\compd\label{cpd:pyrazodye3} \\
\end{tabular} \label{eq:pyrazodyeB}
\end{eqnarray}
```

A macro `\pyrazolonedye` for drawing the common skeleton is defined to take three arguments, so that it is capable of assigning a unit length (the argument `#1`) and reactive sites (the arguments `#2` and `#3`). Then, the three structures are aligned by using the `tabular` environment in a LaTeX `chemeqn` environment. The above code generates the following reaction scheme:



36-33 **36-34**

(36.2)



36-35

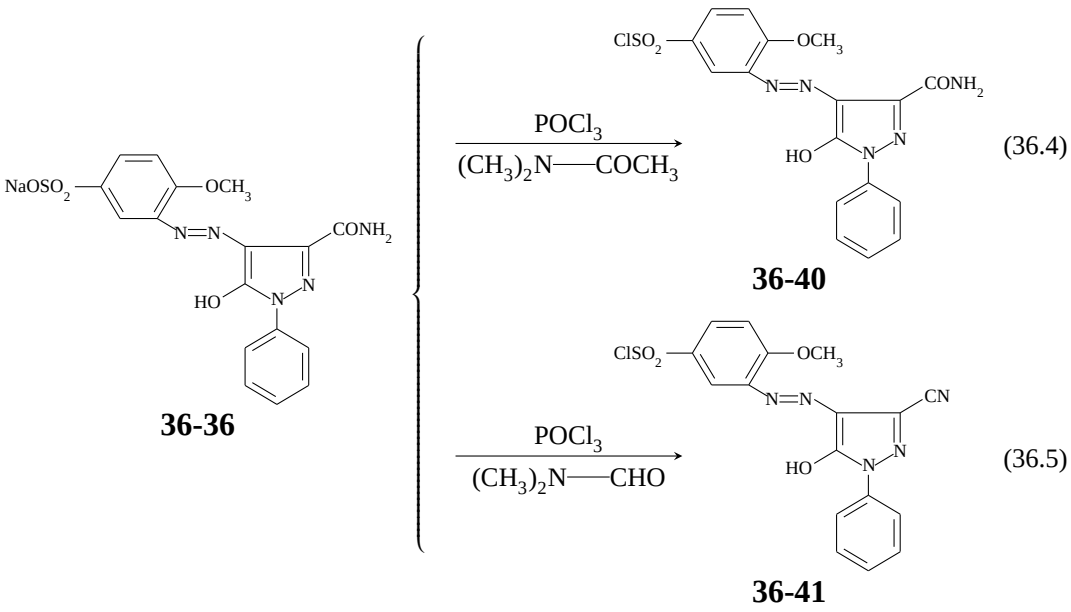
(36.3)

□

Example 36.15. To add a large brace for bind up two processes (Eqs. 36.2 and 36.3), the structural formula **36-33** should be vertically lowered to fit in with the center of the large brace. This task is done by using `\bury` (cf. the code for drawing Table 36.1), where an appropriate depth is declared as an optional argument, e.g., `\bury[55pt]{⟨object⟩}`. Note that the `eqnarray` environment is based on the TEX alignment technique, which is also a basis of the `tabular` environment. The large brace is printed out by declaring

`$\left\{\rule{0pt}{100pt}\right.$`, where `\rule` is to draw a rule of a given width (0pt) and a given height (100pt). The pair `\left\{` and `\right.` is to draw a starting brace (coupled with no ending brace).

```
\begin{eqnarray}
\resetamsmathlabel %reset \label from amsmath to LaTeX
\bury[55pt]{%
\begin{tabular}{c}
\pyrazolonedye{0.07pt}{\ChemForm{CONH_{2}}}{\ChemForm{NaOSO_{2}}}\\
\compd\label{cpd:pyrazodye1X} \\
\end{tabular}$\left\{\rule{0pt}{100pt}\right.$}
&
\reactrarrow[0pt]{0pt}{3cm}%
{\ChemForm{POCl_{3}}}{\ChemForm{(CH_{3})_{2}N\sbond COCH_{3}}}
& \kern-50pt
\begin{tabular}{c}
\pyrazolonedye{0.07pt}{\ChemForm{CONH_{2}}}{\ChemForm{ClSO_{2}}} \\
\compd\label{cpd:pyrazodye2X} \\
\end{tabular} \label{eq:pyrazodyeAX} \\
& \reactrarrow[0pt]{0pt}{3cm}%
{\ChemForm{POCl_{3}}}{\ChemForm{(CH_{3})_{2}N\sbond CHO}}
& \kern-50pt
\begin{tabular}{c}
\pyrazolonedye{0.07pt}{CN}{\ChemForm{ClSO_{2}}} \\
\compd\label{cpd:pyrazodye3X} \\
\end{tabular} \label{eq:pyrazodyeBX}
\end{eqnarray}
```



□

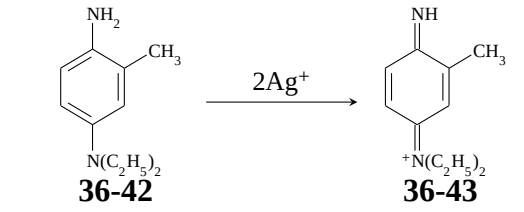
36.4.2 Reaction Schemes in the `align`-like Environments

The `align` environment of the amsmath package can be used to draw reaction schemes, where inner `split` environments are useful. To avoid erroneous results of the amsmath package, the command `\resetamsmathlabel` is multiply declared if necessary. The declaration of `\ctagsplit@false` is necessary to print an equation number at the end of a display equation due to the `split` environment (cf. page 626).

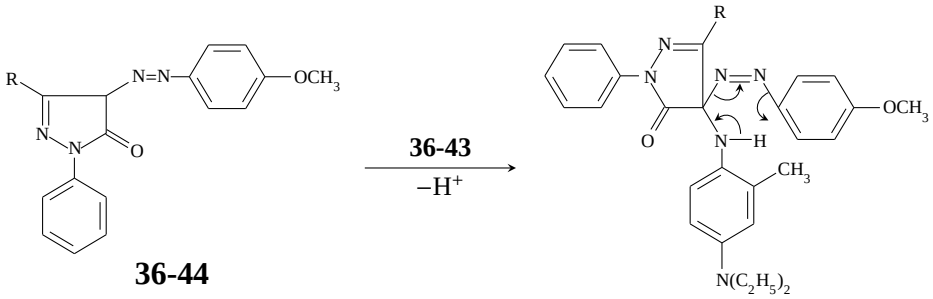
Example 36.16. The following example (Eq. 36.7) is concerned with the reaction of an azo dye (**36-44**) with an oxidized color developer (**36-43**), which is produced by Eq. 36.6. This reaction is basic to color masking due to colored couplers [1, page 250].

```
{\changeunitlength{0.07pt}
\makeatletter
\ctagsplit@false
\makeatother
\begin{align}
\begin{split}
\resetamsmathlabel %reset \label from amsmath to LaTeX
\begin{tabular}{c}
\begin{XyMcompd}(550,900)(250,0){}{}
\benzenev{1==\ChemForm{NH_2};2==\ChemForm{CH_{3}};4==\ChemForm{N(C_2H_5)_2}}
\end{XyMcompd}
\\
\compd\label{cpd:azocoupler1}
\end{tabular}
\reactrarrow{0pt}{2cm}{\ChemForm{2Ag^{+}}}{\strut}
&
\resetamsmathlabel %reset \label from amsmath to LaTeX
\begin{tabular}{c}
\begin{XyMcompd}(550,900)(250,0){}{}
\benzenev[pa]{1D==NH;2==\ChemForm{CH_{3}};%
4D==\ChemForm{\llap{$^+$}N(C_2H_5)_2}}
\end{XyMcompd}
\\
\compd\label{cpd:azocoupler2}
\end{tabular}
\end{split}
\label{eq:azocouplerA}
\\
\begin{split}
\resetamsmathlabel %reset \label from amsmath to LaTeX
\begin{tabular}{c}
\begin{XyMcompd}(1650,1150)(100,-300){}{}
\fiveheterov[d]{1==N;5==N}{1==\benzenev{1==(yl)};2D==O;4==R;%
3==\ryl(5==N=N){4==\benzeneh{1==(yl);4==\ChemForm{OCH_{3}}}}}
\end{XyMcompd}
\\
\compd\label{cpd:azocoupler3}
\end{tabular}
&
\reactrarrow{0pt}{2cm}{\cref{cpd:azocoupler2}}{\ChemForm{-H^{+}}}
\resetamsmathlabel %reset \label from amsmath to LaTeX
\begin{tabular}{c}
\begin{XyMcompd}(1950,1550)(-250,-750){}{}
\fiveheterohi[b]{1==N;2==N;%
4s==\sixheteroh[b]{%
1s==\electronrshiftarrow[1](60,70)(200,130);%
3s==\electronrshiftarrow(50,-90)(50,-240);%
5s==\electronlshiftarrow(-240,100)(-100,30);%
2==N;3==N;6==N;5==H;%
4s==\benzeneh{1==(yl);4==\ChemForm{OCH_{3}}}}%
{1==(yl);6Sa==\benzenev{1==(yl);%
2==\ChemForm{CH_{3}};4==\ChemForm{N(C_2H_5)_2}}}[d]%
}{1==\benzeneh{4==(yl)};5D==O;3==R}%
```

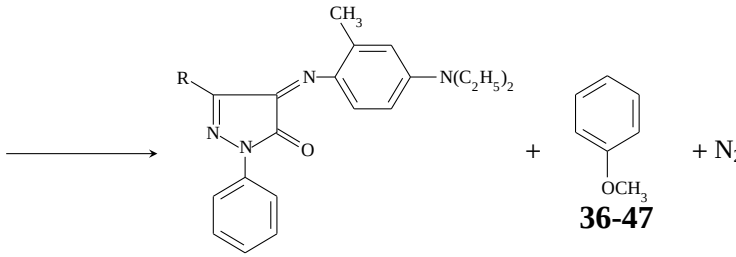
```
\end{XyMcompd}
\\
\compd\label{cpd:azocoupler4}
\end{tabular}
\\
\reactrarrow{0pt}{2cm}{}{}
&
\resetamsmathlabel %reset \label from amsmath to LaTeX
\begin{tabular}{c}
\begin{XyMcompd}(1600,1300)(100,-300){}{}
\fiveheterov[d]{1==N;5==N}{1==\benzenev{1==(yl)};2D==O;4==R;%
3D==\ryl(5==N){4==\benzeneh{1==(yl);2==\ChemForm{CH_{3}};%
4==\ChemForm{N(C_2H_5)_2}}}}
\end{XyMcompd}
\\
\compd\label{cpd:azocoupler5}
\end{tabular}
+
\begin{tabular}{c}
\begin{XyMcompd}(400,700)(250,0){}{}
\benzenev{4==\ChemForm{OCH_{3}}}
\end{XyMcompd}
\\
\compd\label{cpd:azocoupler6}
\end{tabular}
+
\mathrm{N}_2
\end{split}
\label{eq:azocouplerB}
\end{align}
}
```



36-42 **36-43** (36.6)



36-44 **36-45**



36-46 **36-47** (36.7)

Anisole (**36-47**) is detected as a byproduct. The resulting azomethine dye (**36-46**) is a magenta-colored dye for color photography. □

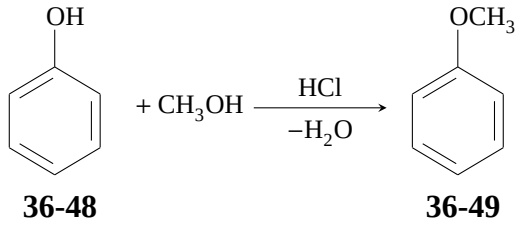
36.5 Structural Formulas in Display Chem Environments

36.5.1 Reaction Schemes in the ChemEquation-like Environments

If the molecular formula CH_3OH written above the reaction arrow in Eq. 36.1 is desired to be drawn in the display line, it is convenient to use the `ChemEquation` environment.

Example 36.17. As found in this example, the code `CH_{3}OH` can be directly declared in place of `\mbox{CH$_{3}$OH}` or `\mathrm{CH}_{3}\mathrm{OH}`, which would be required in the `equation` environment.

```
\begin{ChemEquation}
\resetamsmathlabel %reset \label from amsmath to LaTeX
\begin{XyMcompd}(400,750)(220,200){cpd:BPHOH2}{}
\bzdrv{1==OH}
\end{XyMcompd}
+ CH_{3}OH
\reactrarrow[10\unitlength]{-20\unitlength}{500\unitlength}
{HCl}{\ChemForm{-H_{2}O}}
\begin{XyMcompd}(400,750)(220,200){cpd:PHOME2}{}
\bzdrv{1==\ChemForm{OCH_{3}}}
\end{XyMcompd}
\label{eq:EQ2}
\end{ChemEquation}
```



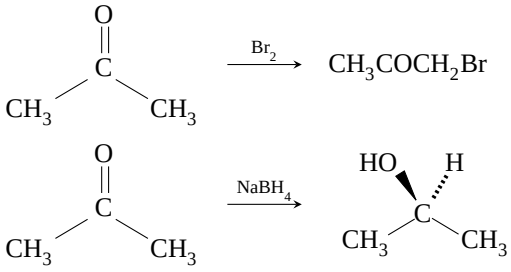
36-48 **36-49** (36.8)

□

Example 36.18. Non-selectivity of the homotopic methyl groups in acetone (Eq. 36.9) and non-selectivity of the homotopic faces in acetone (Eq. 36.9) [4, page 7] are drawn by the code based on the `ChemEqnarray` environment:

```
\begin{ChemEqnarray}
\begin{XyMcompd}(600,450)(0,100){}{}
\Dtrigonal{0==C;1D==O;2==\ChemForm{CH_3};3==\ChemForm{CH_3}}
\end{XyMcompd}
& \overset{Br_2}{\llongrightarrow} & CH_3COCH_2Br \label{eq:acetone1} \\
\begin{XyMcompd}(600,450)(0,100){}{}
\Dtrigonal{0==C;1D==O;2==\ChemForm{CH_3};3==\ChemForm{CH_3}}
\end{XyMcompd}
& \overset{NaBH_4}{\llongrightarrow} &
\begin{XyMcompd}(600,400)(0,150){}{}
\htetrahedralS{0==C;3A==H;4B==HO;1==\ChemForm{CH_3};2==\ChemForm{CH_3}}
\end{XyMcompd}
\label{eq:acetone2}
\end{ChemEqnarray}
```

The command `\overset` is supported by the amsmath package, which should be loaded in combination of the XyMTEX system. This code generates the following scheme:



(36.9) (36.10)

□

36.6 Reaction Schemes in the `picture` Environment

A structural formula prepared by XyMTEX is a TEX box containing inner picture environments. It can be placed in an outer picture environment.

Example 36.19. The following example is cited from *Bull. Chem. Soc. Jpn* [5].

```
\begin{figure}
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
\def\bmC{\mbox{\boldmath $C$}}
\def\bmD{\mbox{\boldmath $D$}}
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
Example:
\begin{quotation}
```

Example:

The pair with [6,6,0,0] and $\boldsymbol{D}_{3d}$-symmetry represents a r-1,t-2,c-3,t-4,c-5,t-6-hexasubstituted cyclohexane. The pattern of substitution of the six Xs and the six hydrogens in the pair strictly complies with the equation which predicts the appearance of two six-membered orbits. Since the pseudo-point group $\boldsymbol{D}_{3d}$ is anisoenergetic, the starting molecule (**36-50a**) is diastereomeric to the product molecule (**36-50b**). The diastereomeric nature stems from the fact that the six Xs are all equatorial in **36-50a** and all axial in **36-50b**. In the light of the present notation, such an anisoenergetic pseudo-point group is easily recognized, since it is represented by a symbol without a hat.

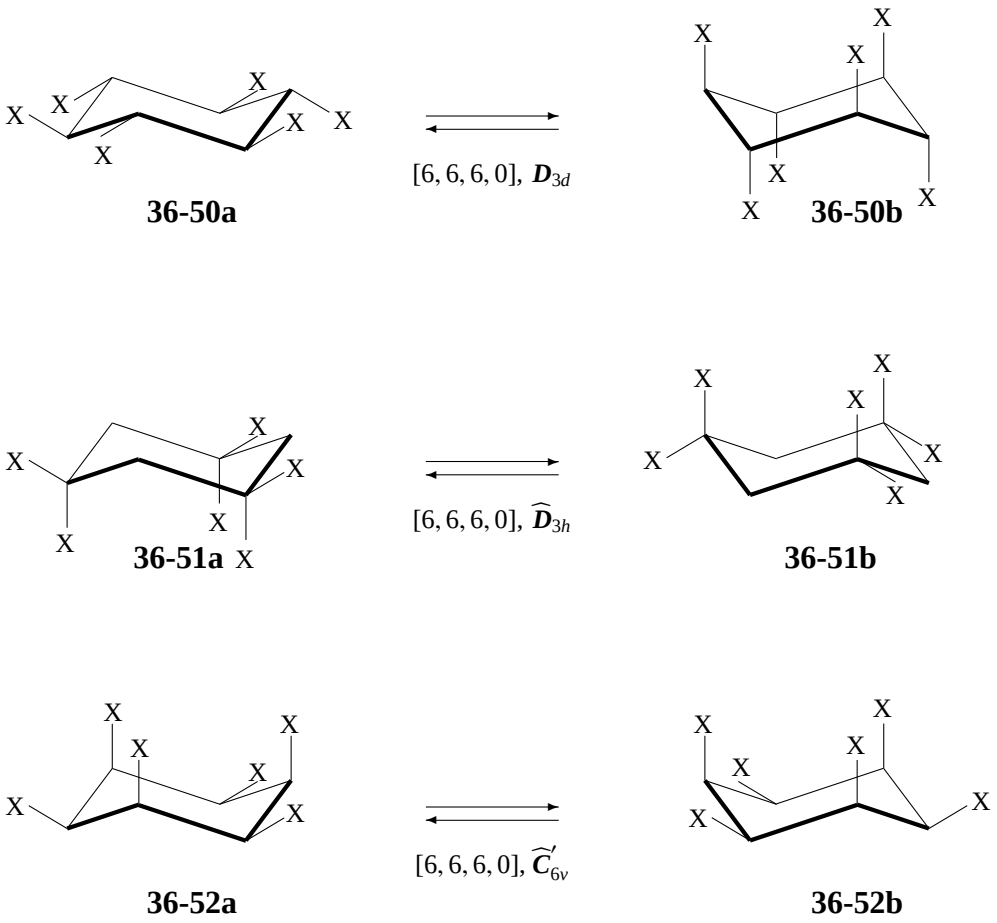


Figure 36.3. [6,6,0,0]-Cyclohexane Derivatives of Higher Symmetries

S. Fujita, *Bull. Chem. Soc. Jpn*, **67**, 2935 (1994)

```
The pair with [6,6,0,0] and $\bmD_{3d}$-symmetry
represents a r-1,t-2,c-3,t-4,c-5,t-6-hexasub\-stituted cyclohexane.
The pattern of substitution of the six Xs and the six hydrogens
in the pair strictly complies with the equation
which predicts the appearance of two six-membered orbits.
Since the pseudo-point group $\bmD_{3d}$ is anisoenergetic,
the starting molecule (\cref{cf:107a}) is
diastereomeric to the product molecule (\cref{cf:107b}).
The diastereomeric nature stems from the fact that
the six Xs are all equatorial in \cref{cf:107a} and
all axial in \cref{cf:107b}.
In the light of the present notation,
such an anisoenergetic pseudo-point group is
```

```
easily recognized, since it is represented by a symbol without a hat.
\end{quotation}

\begin{center}
\begin{picture}(4100,3500)(0,0)
\put(0,2600){\chairi{1Se==X;2Se==X;3Se==X;4Se==X;5Se==X;6Se==X}}
\nocompd
\put(700,2600){\derivlabel{cf:107a}}
\put(1750,3000){\vector(1,0){500}}
\put(2250,2950){\vector(-1,0){500}}
\put(1750,2750){\hbox to50pt{%
 \hss$[6,6,6,0]$, $\bmD_{3d}$\hss}}
\put(2400,2600){\chair{1Sa==X;2Sa==X;3Sa==X;4Sa==X;5Sa==X;6Sa==X}}
\put(3200,2600){\derivlabel{cf:107b}}
%
\put(0,1300){\chairi{1Se==X;1Sa==X;3Se==X;3Sa==X;5Se==X;5Sa==X}}
\nocompd
\put(650,1300){\derivlabel{cf:108a}}
 \put(1750,1700){\vector(1,0){500}}
\put(2250,1650){\vector(-1,0){500}}
\put(1750,1450){\hbox to50pt{\hss$[6,6,6,0]$, $\widehat{\bmD}_{3h}$\hss}}
\put(2400,1300){\chair{1Se==X;1Sa==X;3Se==X;3Sa==X;5Se==X;5Sa==X}}
\put(3100,1300){\derivlabel{cf:108b}}
%
\put(0,0){\chairi{1Se==X;2Sa==X;3Se==X;4Sa==X;5Se==X;6Sa==X}}
\nocompd
\put(700,0){\derivlabel{cf:109a}}
\put(1750,400){\vector(1,0){500}}
\put(2250,350){\vector(-1,0){500}}
\put(1750,150){\hbox to50pt{%
 \hss$[6,6,6,0]$, $\widehat{\bmC}_{6v}^{\prime}$\hss}}
\put(2400,0){\chair{1Sa==X;2Se==X;3Sa==X;4Se==X;5Sa==X;6Se==X}}
\put(3200,0){\derivlabel{cf:109b}}
\end{picture}%
\end{center}
\caption{[6,6,0,0]-Cyclohexane Derivatives of Higher Symmetries}
\label{ff:105}
\bigskip
\rightline{S. Fujita, {\it Bull. Chem. Soc. Jpn}, {\bf 67}, 2935 (1994)}
\end{figure}
```

This code generates Fig. 36.3. □

36.7 Reaction Schemes in Framed Boxes

36.7.1 Simple Framed Boxes

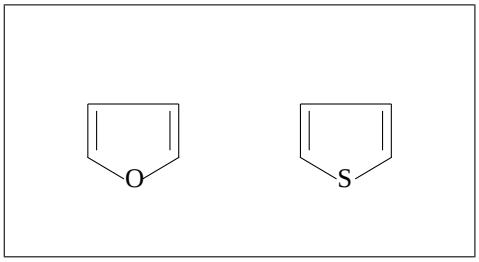
The `frameboxit` environment of the chemist (chmst-pdf or chmst-ps) package has one argument ⟨boxwidth⟩ for specifying the width of the resulting box.

```
\begin{frameboxit}{⟨boxwidth⟩}
(text)
\end{frameboxit}
```

Example 36.20. For example, you write a statement such as

```
\begin{frameboxit}{6cm}
\centering
\fiveheterov[bd]{1==O}{}
\fiveheterov[bd]{1==S}{}
\end{frameboxit}
```

Then, you obtain the following result.

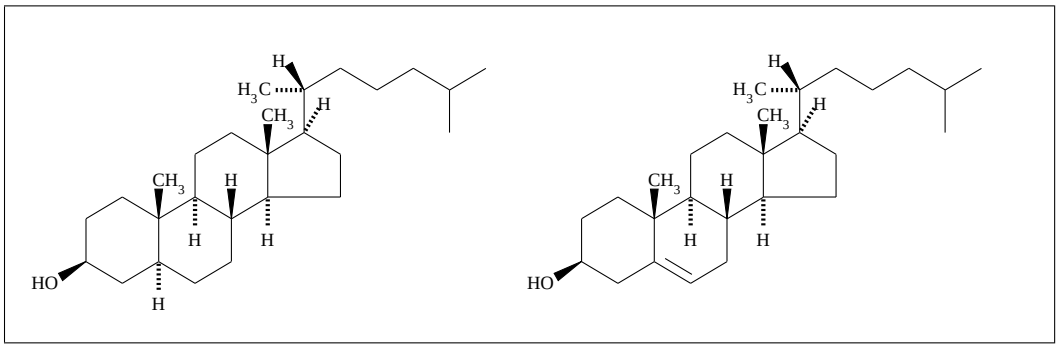


Note that each structural formula drawn by XyMTEX has a space around itself, which will be used for typesetting possible substituents. □

Example 36.21. The argument ⟨boxwidth⟩ is also given as the multiple of the width of text (`\textwidth`).

```
\begin{frameboxit}{0.9\textwidth}
\changeunitlength{0.08pt}
\let\substfontsize=\scriptsize
\centering
\cholestaneAlpha{3B==HO}
\cholestane[e]{3B==HO}
\end{frameboxit}
```

Then, you obtain the following result.



The dimension register `\textwidth` stores the width of the printed domain of a page. The command `\changeunitlength{0.08pt}` reduces the size of each structural formulas drawn by XyMTEX. The setting `\let\substfontsize=\scriptsize` due to XyMTEX changes the font size of each substituent. The command `\centering` of LaTeX 2ε results in the centering of objects within the `frameboxit` environment. □

The `frameboxit` environment is based on the `fr@meboxit` environment of the chemist (chmst-pdf or chmst-ps) package, which can specify the line thickness of the frame (⟨linethickness⟩) and the margin (⟨framesep⟩) around the text included in addition to the with of the resulting box (⟨boxwidth⟩):

```
\begin{fr@meboxit}{⟨linethickness⟩}{⟨framesep⟩}{⟨boxwidth⟩}
(text)
\end{fr@meboxit}
```

In the definition of `\framebox`, the default values of the former two arguments are set to be equal to those of the `\fbox` command of LaTeX: 0.4pt for ⟨linethickness⟩ and 3pt for ⟨framesep⟩.

Example 36.22. The following example shows the use of the `fr@meboxit` environment with changes of such parameters.

```
\makeatletter
\begin{frameboxit}{5cm}
Default Parameters are selected to be 0.4pt for the line thickness and
3pt for the margin space.
The box width can be selected according to your choice.
\end{frameboxit}
\begin{fr@meboxit}{1pt}{10pt}{7cm}
Parameters are changed into 1pt for the line thickness and
10pt for the margin space.
The box width can be selected according to your choice.
\end{fr@meboxit}
\makeatother
```

Note that the commands `\makeatletter` and `\makeatother` should be used for the special treatment of the `@` character. This statement produces the following result.

Default Parameters are selected to be 0.4pt for the line thickness and 3pt for the margin space. The box width can be selected according to your choice.

Parameters are changed into 1pt for the line thickness and 10pt for the margin space. The box width can be selected according to your choice.

□

36.7.2 Oval Boxes

The `miniscreen` environment of the chemist (chmst-pdf or chmst-ps) package has one argument specifying the width of the resulting box.

```
\begin{miniscreen}{⟨boxwidth⟩}
(text)
\end{miniscreen}
```

Example 36.23. For example, by writing a statement such as

```
\begin{miniscreen}{7cm}
\begin{center}
$\displaystyle e^{x}  =  1 + \frac{x}{1!} + \frac{x^{2}}{2!} +
\frac{x^{3}}{3!} + \cdots$ \qquad
$\displaystyle \sin x  =  \frac{x}{1!} - \frac{x^{3}}{3!} +
\frac{x^{5}}{5!} - \frac{x^{7}}{7!} + \cdots$
\end{center}
\end{miniscreen}
```

you obtain the following result.

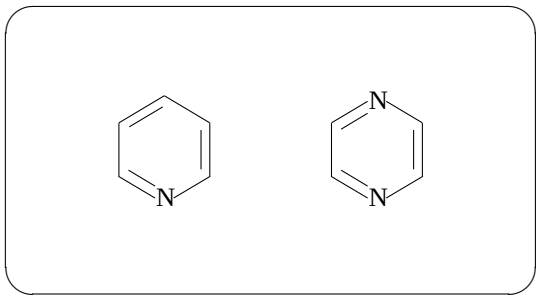
$$e^x = 1 + \frac{x}{1!} + \frac{x^2}{2!} + \frac{x^3}{3!} + \cdots$$
$$\sin x = \frac{x}{1!} - \frac{x^3}{3!} + \frac{x^5}{5!} - \frac{x^7}{7!} + \cdots$$

□

Example 36.24. In a similar way, structural formulas drawn by the XyMTEX commands can be included in the `miniscreen` environment as follows:

```
\begin{miniscreen}{7cm}
\centering
\pyridinevi{}
\pyrazinev{}
\end{miniscreen}
```

Thereby, you obtain the following result.



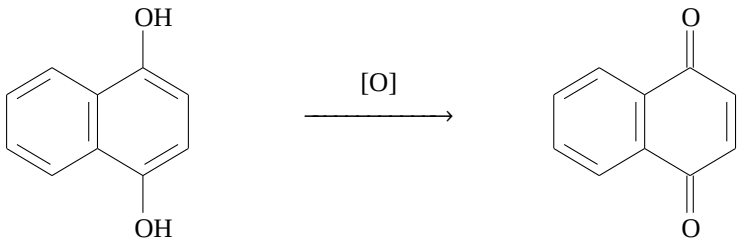
□

When the argument of the `miniscreen` environment is specified to be `\textwidth`, the resulting box generated a framed text of width `\textwidth`. The resulting frame is equivalent to the one generated by the `screen` environment of the package ascmac.sty. It follows that the `screen` environment can be redefined on the basis of the definition of the `miniscreen` environment described above.[a]

```
\begin{screen}
(text)
\end{screen}
```

Example 36.25. The redefined `screen` environment can be used as follows.

```
\begin{screen}
\begin{center}
\begin{tabular}{c}
\naphdrv{1==OH;4==OH} \\[.3cm] \compd \label{box:a2} \\
\end{tabular}
\begin{tabular}{c}
[O] \\ \parbox{2cm}{\rightarrowfill} \\[1cm] \mathstrut \\
\end{tabular}
\begin{tabular}{c}
\naphdrv[p]{1D==O;4D==O} \\[.3cm] \compd \label{box:a3} \\
\end{tabular}
\end{center}
\end{screen}
```



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□

[a] Hence, the `screen` environment is redefined in the chemist package, which is automatically loaded in the XƎMTEX system.

The tboxminiscreen environment of the chemist (chmst-pdf or chmst-ps) package is used to generate a box with a heading title (the default title is “Output”), where the width of the generated box can be specified by its argument.

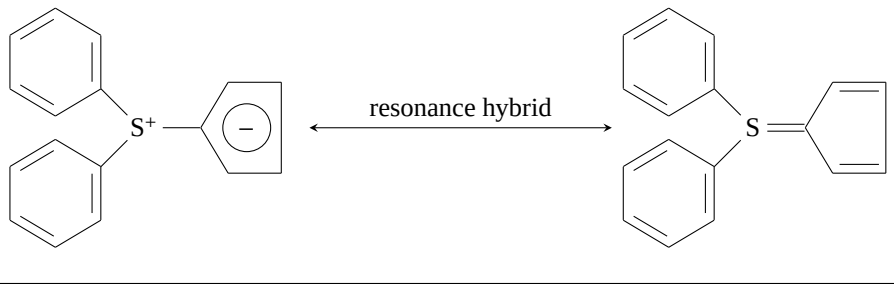
```
\begin{tboxminiscreen}{⟨boxwidth⟩}
(text)
\end{tboxminiscreen}
```

Example 36.26. For example, by writing such a statement as

```
\begin{tboxminiscreen}{0.9\textwidth}
\begin{center}
\begin{XyMcompd}(1000,900)(-150,-150){}{}
\ltrigonal{0==S$^{+}$;2==\bzdrv{3==(yl)};3==\bzdrv{2==(yl)};
1==\cyclopentanehi[A{0{$-$}}]{1==(yl)}}
\end{XyMcompd}
\reactlrarrow{0pt}{4cm}{resonance hybrid}{\strut}
\begin{XyMcompd}(1000,900)(-150,-150){}{}
\ltrigonal{0==S;2==\bzdrv{3==(yl)};3==\bzdrv{2==(yl)};
1D==\cyclopentanehi[bd]{1==(yl)}}
\end{XyMcompd}
\end{center}
\end{tboxminiscreen}
```

you obtain the following result.

Output



□

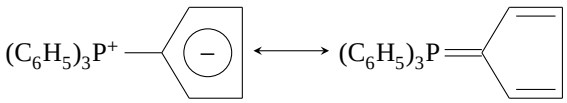
In the next example, the frame and the heading title of the tboxminiscreen environment is colored in blue. For the purpose of changing the heading title, you redefine the control sequence \tboxtitle by means of the command \def or \renewcommand.

Example 36.27. Let us change the title into “Memorandum”:

```
{\def\tboxtitle{Memorandum}
\blue
\begin{tboxminiscreen}{0.8\textwidth}
\black \centering
\begin{XyMcompd}(800,350)(-300,250){}{}
\cyclopentanehi[A{0{$-$}}]{1=={\ChemForm{(C_{6}H_{5})_{3}P^{+}}}}
\end{XyMcompd}
\reactlrarrow{0pt}{1cm}{}{}
\begin{XyMcompd}(750,350)(-250,250){}{}
\cyclopentanehi[bd]{1D=={\ChemForm{(C_{6}H_{5})_{3}P}}}
\end{XyMcompd}
\end{tboxminiscreen}
}
```

Thereby, you obtain the following result.

Memorandum



□

As found easily, this coloring technique is applicable to any other frame-printing commands described in this chapter.

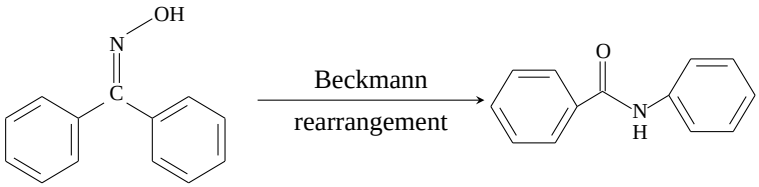
Example 36.28. The following is another example of the usage of the `tboxminiscreen` environment, which contains sentences as well as a reaction scheme:

```
\def\tboxtitle{\bf Summary Notes}
\begin{tboxminiscreen}{0.8\textwidth}
The Beckmann rearrangement is a transformation of
an oxime into an amide under an acidic condition.
Since a substrate oxime can be easily obtained from
a ketone (or aldehyde) and hydroxylamine,
the Beckmann rearrangement is important as one of
valuable industrial processes.
\par \medskip
\begin{center}
\changeunitlength{0.08pt}
\begin{XyMcompd}(1000,850)(-150,-150){}{}
\Ethylenev{1==C;2==N}{3==OH;2==\bzdrv{6==(yl)};1==\bzdrv{2==(yl)}}
\end{XyMcompd}
\reactrarrow{0pt}{3cm}{Beckmann}{rearrangment}
\begin{XyMcompd}(1100,500)(-400,0){}{}
\dimethylenei{2==\downnobond{N}{H}}{2W==\bzdrh{1==(yl)};1W==\bzdrh{4==(yl)};1D==O}
\end{XyMcompd}
\end{center}
\end{tboxminiscreen}
```

This code typesets the following miniscreen box with a changed title.

Summary Notes

The Beckmann rearrangement is a transformation of an oxime into an amide under an acidic condition. Since a substrate oxime can be easily obtained from a ketone (or aldehyde) and hydroxylamine, the Beckmann rearrangement is important as one of valuable industrial processes.



□

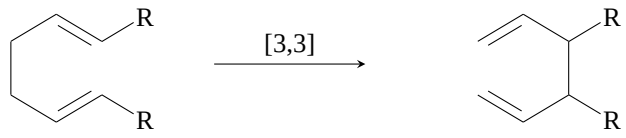
The `tboxscreen` environment provides a frame spreading for `\textwidth`.

```
\begin{tboxscreen}
(text)
\end{tboxscreen}
```

Example 36.29. This example shows a scheme of a [3,3]sigmatropic rearrangement surrounded by a frame box due to the `tboxscreen` environment.

```
\def\tboxtitle{\bf [3,3]Sigmatropic Rearrangement}
\begin{tboxscreen}
\centering
\cdonecell{0pt}{4cm}{\sixheterov[ac]{}{2==R;3==R}[b]}
\reactrarrow{0pt}{2cm}{[3,3]}{\strut}
\cdonecell{0pt}{4cm}{\sixheterov[df]{}{2==R;3==R}[e]}
\end{tboxscreen}
```

[3,3]Sigmatropic Rearrangement



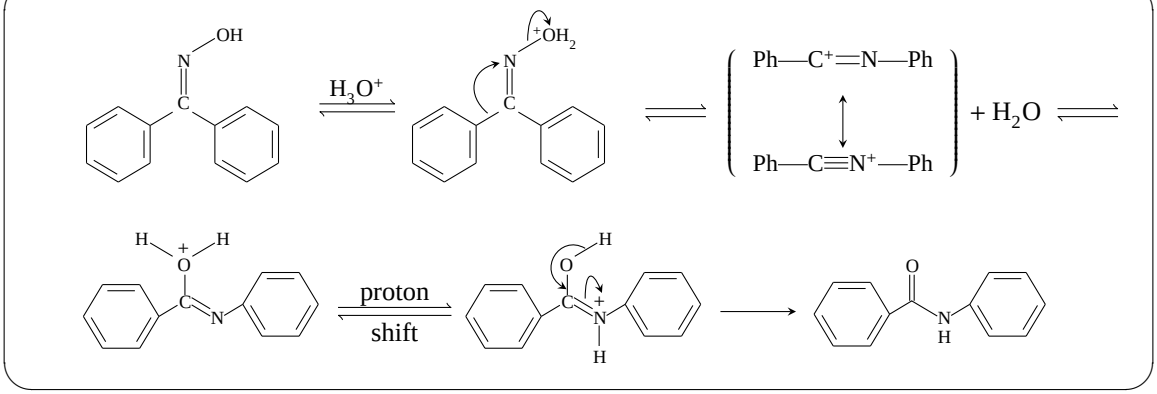
□

Example 36.30. The following example shows that a ChemEqnarray∗ environment can be used in a tboxscreen environment to give a reaction scheme exhibiting the multi-step mechanism of the Beckmann Rearrangement.

```
\def\tboxtitle{\bf Beckmann Rearrangement}
\begin{tboxscreen}
\changeunitlength{0.07pt}
\begin{ChemEqnarray*}
&&
\begin{XyMcompd}(1000,850)(-150,-150){}{}
\Ethylenev{1==C;2==N}{3==OH;2==\bzdrv{6==(yl)};1==\bzdrv{2==(yl)}}
\end{XyMcompd}
\mskip6mu \reacteqarrow{0pt}{1cm}{\small H$_{3}$O$^{+}$}{\strut} \mskip6mu
\begin{XyMcompd}(1000,850)(-150,-150){}{}
\Ethylenev{1==C;2==N;%
1==\electronrshiftarrow(-85,-20)(-20,250);%
2==\electronshiftArrowr(130,140)(130,300)(200,350)(250,220)%
}{3==\llap{$^{+}$}OH$_{2}$;2==\bzdrv{6==(yl)};1==\bzdrv{2==(yl)}}
\end{XyMcompd}
\mskip6mu \reacteqarrow{0pt}{0.8cm}{}{} \mskip6mu
\left\lgroup
\begin{tabular}{c}
\small Ph\sbond C$^{+}$\dbond N\sbond Ph \\
\reactduarrow{0pt}{20pt}{}{} \\
\small Ph\sbond C\tbond N$^{+}$\sbond Ph \\
\end{tabular}
\right\rgroup
+ H_{2}O
\mskip6mu \reacteqarrow{0pt}{0.8cm}{}{}
\\ \noalign{\vskip20pt}
& &
\begin{XyMcompd}(1100,500)(-400,0){}{}
\dimethylenei[a]{1==C;2==N}{2W==\bzdrh{1==(yl)};1W==\bzdrh{4==(yl)};%
1==\Utrigonal{0==\upnobond{O}{+};3==H;2==H;1==(yl)}}
\end{XyMcompd}
\mskip6mu \reacteqarrow{0pt}{1.5cm}{proton}{shift} \mskip6mu
\begin{XyMcompd}(1100,500)(-400,0){}{}
\dimethylenei[a]{1==C;2==\upnobond{N}{+};%
```

```
1==\electronshiftArrowl(-40,100)(-200,200)(-80,400)(60,320);%
1==\electronshiftArrowr(60,50)(60,200)(100,200)(150,80)}%
{2==H;2W==\bzdrh{1==(yl)};1W==\bzdrh{4==(yl)};%
1==\Utrigonal{0==O;2==H;1==(yl)}}
\end{XyMcompd}
\mskip6mu \reactrarrow{0pt}{1cm}{}{} \mskip6mu
\begin{XyMcompd}(1100,500)(-400,0){}{}
\dimethylenei{2==\downnobond{N}{H}}{2W==\bzdrh{1==(yl)};1W==\bzdrh{4==(yl)};1D==O}
\end{XyMcompd}
\end{ChemEqnarray*}
\end{tboxscreen}
```

Beckmann Rearrangement



□

Note that the commands \sbond, \dbond, and \tbond are supported by the chemist packages to draw single (——), double (═), and triple bonds (≡). For the curved arrows, see Section 33.4.

36.7.3 Frames with Shadows

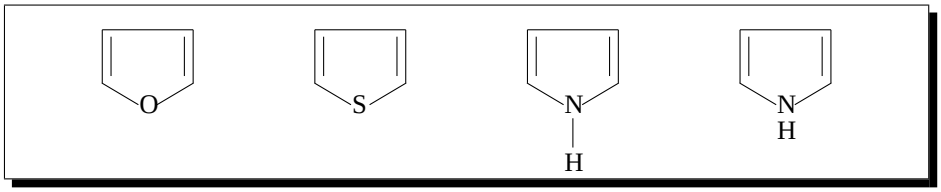
The rshfboxit Environment

The rshfboxit (right-shadow-frame-box-it) environment provides a framed box with right and bottom shadows, where the width of the box can be specified by its argument ⟨boxwidth⟩.

```
\begin{rshfboxit}{⟨boxwidth⟩}
(text)
\end{rshfboxit}
```

Example 36.31. The following example shows a list of commands for drawing five-membered heterocycles, which is surrounded by such a framed box.

```
\begin{rshfboxit}{12cm}
\centering
\begin{XyMcompd}(2700,550)(250,50){}{}
\furanv{} \thiophenev{} \pyrrolev{1==H}
\fiveheterov[bd]{1==\downnobond{N}{H}}{}
\end{XyMcompd}
\end{rshfboxit}
```



□

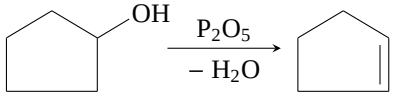
The grshfboxit environment may contain sentences along with structural formulas.

Example 36.32. For example, you write such a statement such as

```
\begin{rshfboxit}{0.8\textwidth}
The dehydration of cyclopentanol (\cref{cpd:C5OH}) gives
cyclopentene (\cref{cpd:C5ene}).
\begin{center}
\begin{XyMcompd}(500,350)(250,300){cpd:C5OH}{}
\cyclopentanevi{2==OH}
\end{XyMcompd}
\reactrarrow{10pt}{1.5cm}{P$_{2}$O$_{5}$}{$-$ H$_{2}$O}
\begin{XyMcompd}(300,350)(250,300){cpd:C5ene}{}
\cyclopentanevi[b]{}
\end{XyMcompd}
\end{center}
\end{rshfboxit}
```

Then, you obtain

The dehydration of cyclopentanol (**36-55**) gives cyclopentene (**36-56**).



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□

The rshfboxit environment is based on the rshfr@meboxit environment of the chemist package. Hence, we can use the latter inner environment to change parameters.

```
\begin{rshfr@meboxit}{⟨hshadow⟩}{⟨vshadow⟩}{⟨framesep⟩}{⟨boxwidth⟩}
(text)
\end{rshfr@meboxit}
```

Note that the line thickness of the frame is fixed to be 0.4pt, while changeable parameters are the thickness of the horizontal shadow (⟨hshadow⟩), the thickness of the vertical shadow (⟨vshadow⟩), and the margin spacing (⟨framesep⟩) around the text included.

Example 36.33. The following example shows changes of such parameters.

```
\makeatletter
\begin{rshfboxit}{5cm}
Default Parameters are selected
3pt for the thickness of the horizontal shadow,
3pt for the thickness of the vertical shadow, and
3pt for the margin space.
\end{rshfboxit}
\qquad
\begin{rshfr@meboxit}{10pt}{5pt}{10pt}{5cm}
Parameters are changed into
10pt for the thickness of the horizontal shadow,
5pt for the thickness of the vertical shadow, and
10pt for the margin space.
\end{rshfr@meboxit}
\makeatother
```

This statement produces the following result.

Default Parameters are selected 3pt for the thickness of the horizontal shadow, 3pt for the thickness of the vertical shadow, and 3pt for the margin space.

Parameters are changed into 10pt for the thickness of the horizontal shadow, 5pt for the thickness of the vertical shadow, and 10pt for the margin space.

□

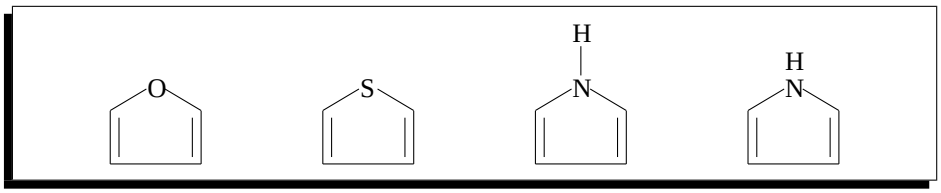
The `lshfboxit` Environment

In a similar way, an `lshfboxit` (left-shadow-frame-box-it) environment provides a framed box with left and bottom shadows, where the width of the box can be specified by its argument ⟨boxwidth⟩.

```
\begin{lshfboxit}{⟨boxwidth⟩}
(text)
\end{lshfboxit}
```

Example 36.34. The following example shows another list of commands for drawing five-membered heterocycles, which is surrounded by such a framed box.

```
\begin{lshfboxit}{12cm}
\centering
\begin{XyMcompd}(2700,550)(250,350){}{}
\furanvi{} \thiophenevi{} \pyrrolevi{1==H}
\fiveheterovi[bd]{1==\upnobond{N}{H}}{}
\end{XyMcompd}
\end{lshfboxit}
```



□

The `grshfboxit` environment may contain sentences along with structural formulas.

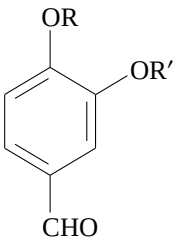
Example 36.35. For example, you write the statement which contains objects of these types:

```
\begin{lshfboxit}{0.8\textwidth}
Representative derivatives of 3,4-dihydroxybenzaldehyde (\cref{cpd:va:a3}) are
shown below, e.g., valillin (\cref{cpd:va:a3a}),
veratraldehyde (\cref{cpd:va:a3b}), and
ethyl vanillin (\cref{cpd:va:a3b}).
\begin{center}
\begin{tabular}{c}
\bzdrv{1==OR;4==CHO;2==OR$^{\prime}$} \\ \compd \label{cpd:va:a3} \\
\end{tabular}
\begin{tabular}{lll}
\deriva \label{cpd:va:a3a} &
 R = H, R$^{\prime}$ = CH$_{3}$ & vanillin \\
\deriva \label{cpd:va:a3b} &
 R = = CH$_{3}$, R$^{\prime}$ = CH$_{3}$ & veratraldehyde \\
\deriva \label{cpd:va:a3c} &
```

```
 R = H, R$^{\prime}$ = CH$_{2}$CH$_{3}$ & ethyl vanillin \\
\end{tabular}
\end{center}
\end{lshfboxit}
```

Then, you obtain the following result.

Representative derivatives of 3,4-dihydroxybenzaldehyde (**36-57**) are shown below, e.g., vanillin (**36-57a**), veratraldehyde (**36-57b**), and ethyl vanillin (**36-57b**).



36-57

a	R = H, R′ = CH_3	vanillin
b	R = = CH_3, R′ = CH_3	veratraldehyde
c	R = H, R′ = CH_2CH_3	ethyl vanillin

□

The `lshfboxit` environment is based on the `lshfr@meboxit` environment of the chemist package.

```
\begin{lshfr@meboxit}{⟨hshadow⟩}{⟨vshadow⟩}{⟨framesep⟩}{⟨boxwidth⟩}
(text)
\end{lshfr@meboxit}
```

Hence, we can use the latter inner environment to change the thickness of the horizontal shadow (⟨hshadow⟩), the thickness of the vertical shadow (⟨vshadow⟩), and the margin spacing (⟨framesep⟩) around the text included. Note that the line thickness of the frame is fixed to be 0.4pt.

Example 36.36. The following example shows changes of such parameters.

```
\makeatletter
\begin{lshfboxit}{5cm}
Default Parameters are selected
3pt for the thickness of the horizontal shadow,
3pt for the thickness of the vertical shadow, and
3pt for the margin space.
\end{lshfboxit}
\qquad
\begin{lshfr@meboxit}{5pt}{10pt}{10pt}{5cm}
Parameters are changed into
5pt for the thickness of the horizontal shadow,
10pt for the thickness of the vertical shadow, and
10pt for the margin space.
\end{lshfr@meboxit}
\makeatother
```

This statement produces the following result.

Default Parameters are selected 3pt for the thickness of the horizontal shadow, 3pt for the thickness of the vertical shadow, and 3pt for the margin space.

Parameters are changed into 5pt for the thickness of the horizontal shadow, 10pt for the thickness of the vertical shadow, and 10pt for the margin space.

□

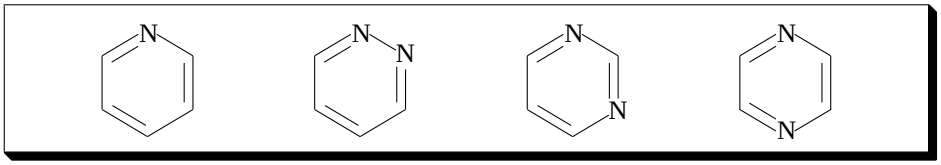
The grshfboxit Environment

A grshfboxit (gradient-right-shadow-frame-box-it) environment provides a framed box with right and bottom gradient shadows, where the width of the box can be specified by its argument ⟨boxwidth⟩.

```
\begin{grshfboxit}{⟨boxwidth⟩}
(text)
\end{grshfboxit}
```

Example 36.37. The following example shows a list of commands for drawing six-membered heterocycles, which is surrounded by such a framed box.

```
\begin{grshfboxit}{12cm}
\centering
\begin{XyMcompd}(2700,450)(250,250){}{}
\pyridinev{} \pyridazinev{} \pyrimidinev{} \pyrazinev{}
\end{XyMcompd}
\end{grshfboxit}
```



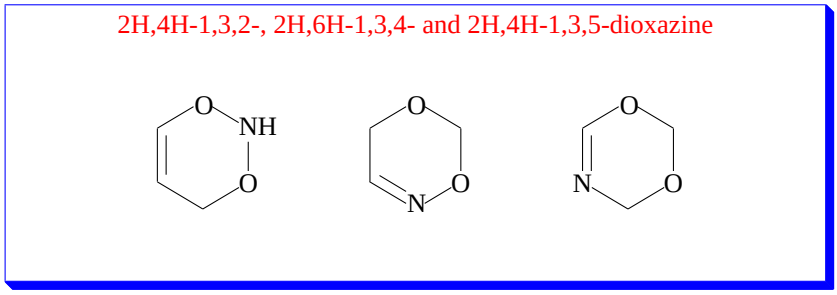
□

The grshfboxit environment may contain a sentence along with structural formulas.

Example 36.38. For example, you write such a statement such as

```
\begin{center}
\blue
\begin{grshfboxit}{0.7\textwidth}
\centering\black
{\red 2H,4H-1,3,2-, 2H,6H-1,3,4- and 2H,4H-1,3,5-dioxazine} \\
\sixheterov[e]{1==O;2==NH;3==O}{}
\sixheterov[d]{1==O;3==O;4==N}{}
\sixheterov[e]{1==O;3==O;5==N}{}
\end{grshfboxit}
\end{center}
```

Then, you obtain the following result:



where the frame is colored in blue, the name is colored in red, and the structural formulas are printed out in black. □

The grshfboxit environment is based on the grshfr@meboxit environment of the chemist package. Hence, we can use the latter inner environment to change parameters.

```
\begin{grshfr@meboxit}{⟨hshadow⟩}{⟨vshadow⟩}{⟨framesep⟩}{⟨boxwidth⟩}
(text)
\end{grshfr@meboxit}
```

Note that the line thickness of the frame is fixed to be 0.4pt, while changeable parameters are the thickness of the horizontal shadow (⟨hshadow⟩), the thickness of the vertical shadow (⟨vshadow⟩), and the margin spacing (⟨framesep⟩) around the text included.

Example 36.39. The following example shows changes of such parameters.

```
\makeatletter
\begin{grshfboxit}{5cm}
Default Parameters are selected
3pt for the thickness of the horizontal shadow,
3pt for the thickness of the vertical shadow, and
3pt for the margin space.
\end{grshfboxit}
\qquad
\begin{grshfr@meboxit}{10pt}{5pt}{10pt}{5cm}
Parameters are changed into
10pt for the thickness of the horizontal shadow,
5pt for the thickness of the vertical shadow, and
10pt for the margin space.
\end{grshfr@meboxit}
\makeatother
```

This statement produces the following result.

Default Parameters are selected 3pt for the thickness of the horizontal shadow, 3pt for the thickness of the vertical shadow, and 3pt for the margin space.

Parameters are changed into 10pt for the thickness of the horizontal shadow, 5pt for the thickness of the vertical shadow, and 10pt for the margin space.

□

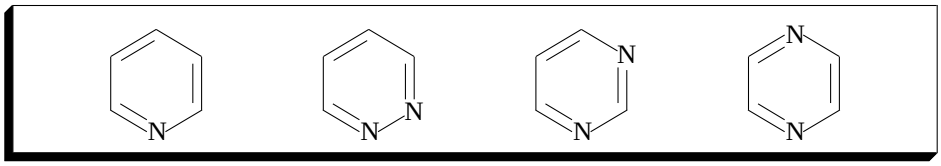
The `glshfboxit` Environment

In a similar way, a `glshfboxit` (gradient-left-shadow-frame-box-it) environment provides a framed box with gradient shadows locating at left and bottom positions, where the width of the box can be specified by its argument ⟨boxwidth⟩.

```
\begin{glshfboxit}{⟨boxwidth⟩}
(text)
\end{glshfboxit}
```

Example 36.40. The following example shows another list of commands for drawing six-membered heterocycles, which is surrounded by such a framed box.

```
\begin{glshfboxit}{12cm}
\centering
\begin{XyMcompd}(2700,450)(250,250){}{}
\pyridinevi{} \pyridazinevi{} \pyrimidinevi{} \pyrazinevi{}
\end{XyMcompd}
\end{glshfboxit}
```



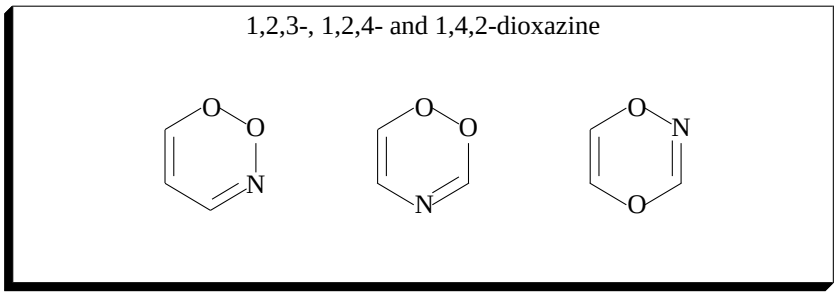
□

The `glshfboxit` environment may contain a sentence along with structural formulas.

Example 36.41. For example, the following code:

```
\begin{glshfboxit}{0.7\textwidth}
\centering
1,2,3-, 1,2,4- and 1,4,2-dioxazine \\
\sixheterov[ce]{1==O;2==O;3==N}{}
\sixheterov[ce]{1==O;2==O;4==N}{}
\sixheterov[be]{1==O;2==N;4==O}{}
\end{glshfboxit}
```

generates such a sentence as accompanied with structural formulas:



□

The `glshfboxit` environment is based on the `glshfr@meboxit` environment of the chemist package. Hence, we can use the latter inner environment to change the thickness of the horizontal shadow (⟨hshadow⟩), the thickness of the vertical shadow (⟨vshadow⟩), and the margin spacing (⟨framesep⟩) around the text included.

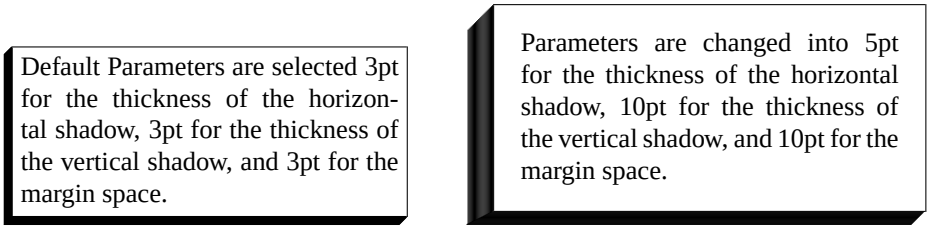
```
\begin{glshfr@meboxit}{⟨hshadow⟩}{⟨vshadow⟩}{⟨framesep⟩}{⟨boxwidth⟩}
(text)
\end{glshfr@meboxit}
```

Note that the line thickness of the frame is fixed to be 0.4pt.

Example 36.42. The following example shows the way of changing such parameters.

```
\makeatletter
\begin{glshfboxit}{5cm}
Default Parameters are selected
3pt for the thickness of the horizontal shadow,
3pt for the thickness of the vertical shadow, and
3pt for the margin space.
\end{lshfboxit}
\qquad
\begin{glshfr@meboxit}{5pt}{10pt}{10pt}{5cm}
Parameters are changed into
5pt for the thickness of the horizontal shadow,
10pt for the thickness of the vertical shadow, and
10pt for the margin space.
\end{lshfr@meboxit}
\makeatother
```

This statement produces the following result.



It should be noted that two large values assigned to ⟨hshadow⟩ and ⟨vshadow⟩ may result in printing jagged edges, because the sloped edges consist of a fixed number of lines drawn repeatedly. □

36.7.4 Commands for Framed Boxes

The `\fboxit` command is used for surrounding a text of one line with a frame,

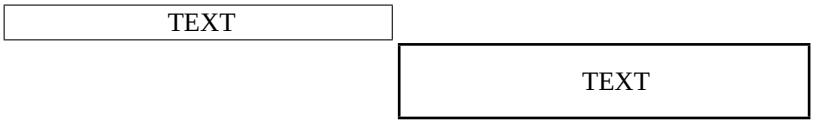
```
\fboxit{⟨boxwidth⟩}{⟨text⟩}
```

where the argument ⟨boxwidth⟩ represent the width of the frame box. This command is based on the inner command `\fb@xit` having changeable parameters.

```
\fb@xit{⟨linethickness⟩}{⟨framesep⟩}{⟨boxwidth⟩}{⟨text⟩}
```

where the argument ⟨linethickness⟩ represents line thickness, the argument ⟨framesep⟩ represents spacing around the text, and the argument ⟨boxwidth⟩ represents the width of the box.

```
\makeatletter
\fboxit{5cm}{\centering TEXT} \qquad
\fb@xit{1pt}{10pt}{5cm}{\centering TEXT}
\makeatother
```



The `\rightshframe` command is used for surrounding a text of one line with a frame having a right-hand shadow,

```
\rightshframe{⟨boxwidth⟩}{⟨text⟩}
```

where the argument ⟨boxwidth⟩ represent the width of the frame box.

On the other hand, The `\rightshfbox` command generates a frame having a right-hand shadow in accordance with the length of the text included.

```
\rightshfbox{⟨text⟩}
```

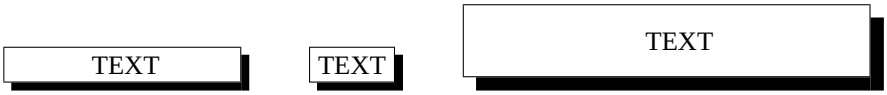
These commands are based on the inner command `\rightshfr@me` having changeable parameters.

```
\rightshfr@me{⟨swidth⟩}{⟨framesep⟩}{⟨boxwidth⟩}{⟨text⟩}
```

where ⟨swidth⟩ represents the thickness of a shadow, ⟨framesep⟩ represents spacing around the text, and ⟨boxwidth⟩ represents the width of the box.

Example 36.43. The following examples show the difference between these box-generating commands.

```
\makeatletter
\rightshframe{3cm}{\centering TEXT} \qquad
\rightshfbox{\centering TEXT} \qquad
\rightshfr@me{5pt}{10pt}{5cm}{\centering TEXT}
\makeatother
```



□

The `\leftshframe` command is used for surrounding a text of one line with a frame having a left-hand shadow,

```
\leftshframe{⟨boxwidth⟩}{⟨text⟩}
```

where ⟨boxwidth⟩ represent the width of the frame box. On the other hand, the `\leftshfbox` command generates a frame having a left-hand shadow in accordance with the length of the text included.

```
\leftshfbox{⟨text⟩}
```

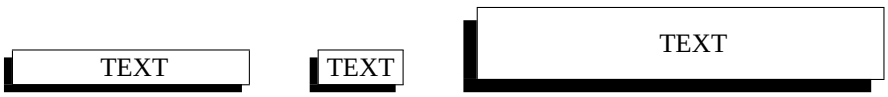
These commands are based on the inner command `\leftshfr@me` having changeable parameters.

```
\leftshfr@me{⟨swidth⟩}{⟨framesep⟩}{⟨boxwidth⟩}{⟨text⟩}
```

where ⟨swidth⟩ represents the thickness of a shadow, ⟨framesep⟩ represents spacing around the text, and ⟨boxwidth⟩ represents the width of the box.

Example 36.44. The following examples show the difference between these box-generating commands.

```
\makeatletter
\leftshframe{3cm}{\centering TEXT} \qquad
\leftshfbox{\centering TEXT} \qquad
\leftshfr@me{5pt}{10pt}{5cm}{\centering TEXT}
\makeatother
```

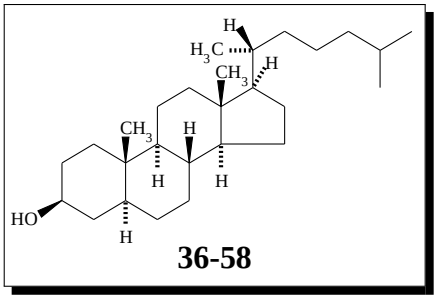


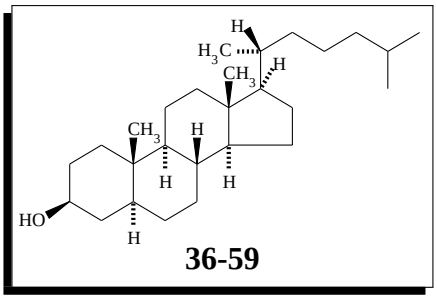
□

These box commands are capable of accommodating structural formulas drawn by the XyMTEX system.

Example 36.45. For example, the commands `\rightshfbox` and `\leftshfbox` are used as follows:

```
\changeunitlength{0.07pt}
\rightshfbox{%
\begin{XyMcompd}(2000,1200)(50,150){cpd:cholestaneA}{}
\cholestaneAlpha{3B==HO}
\end{XyMcompd}}
\qquad
\leftshfbox{%
\begin{XyMcompd}(2000,1200)(50,150){cpd:cholestaneB}{}
\cholestaneAlpha{3B==HO}
\end{XyMcompd}}
```



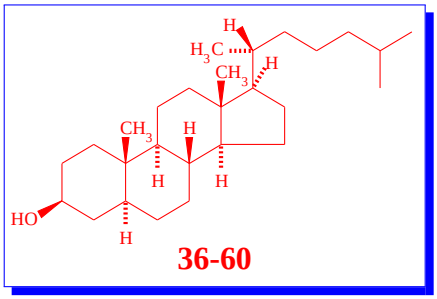


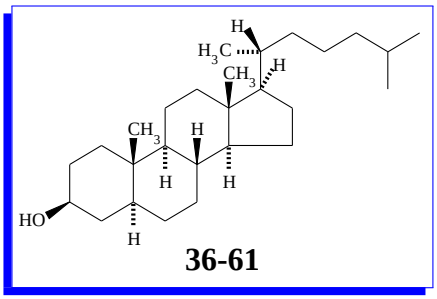
□

Example 36.46. Frames drawn by these box commands can be printed in color. The following examples are representative:

```
\begin{center}
\changeunitlength{0.07pt}
\blue
\rightshfbox{\red
\begin{XyMcompd}(2000,1200)(50,150){cpd:cholestaneAX}{}
\cholestaneAlpha{3B==HO}
\end{XyMcompd}}
\qquad
\leftshfbox{\black
\begin{XyMcompd}(2000,1200)(50,150){cpd:cholestaneBX}{}
\cholestaneAlpha{3B==HO}
\end{XyMcompd}}
\end{center}
```

This code generates the following result:





□

References

[1] S. Fujita, “Organic Chemistry of Photography,” Springer-Verlag, Berlin-Heidelberg (2004).

[2] B. Harford, *Chem & Eng. News*, **91** (Issue 22, June 3), 9 (2013).

[3] S. Fujita, *Yuki Gosei Kagaku Kyokai-Shi*, **40**, 307–320 (1982).

[4] R. S. Ward, “Selectivity in Organic Synthesis,” John Wiley & Sons, Chichester (1999).

[5] S. Fujita, *Bull. Chem. Soc. Jpn.*, **67**, 2935–2948 (1994).

Math Versions

The XeTeX system supports new math versions, “chem” and “boldchem”, in addition to the LaTeX-default math versions, “normal” and “bold”. These math versions are different in fonts selected in mathematical and chemical equations. A document with even volumes of mathematical equations and chemical ones is recommended to be typeset in the math version “normal” combined with chemical environments such as `ChemEquation`, because the default math version of LaTeX is “normal”. The math version “chem” (or “boldchem”) may be globally declared if you prepare a document with chemical equations and few volumes of mathematical equations. Otherwise it should be locally declared to typeset chemical equations under the global (default) declaration of “normal”.

37.1 General Remarks on Math Versions

37.1.1 Mathematical Typesetting

In a document due to TeX, mathematical equations are typeset in the form of in-text math (`$...$`) or display math objects (`$$...$$`).

Example 37.1. For example, the codes

```
\TeX{} in-text math: $F_2$ \par
\TeX{} display math: $$F_2$$
```

generate th following expressions:

TeX in-text math: F_2
TeX display math:

$$F_2$$

where alphabets are typeset in italic, because they are regarded as representing mathematical functions. □

LaTeX commands or environments for printing mathematical equations are based on the TeX in-text or display math. The expressions of the LaTeX in-text and display math objects are controlled by the mechanism of math versions, “normal” and “bold”. In a default situation of the LaTeX documentation, the math version “normal” (`\mathversion{normal}`) is selected.

Example 37.2. For example, the codes:

```
%\mathversion{normal}%default setting
\LaTeX{} in-text math: \(F_2\) \par
```

```
\LaTeX{} display math: \[F_2\] \par
\LaTeX{} equation environment: \begin{equation} F_2 \end{equation}
```

generate the following expressions:

LaTeX in-text math: F_2
LaTeX display math:

$$F_2$$

LaTeX equation environment:

$$F_2 \tag{37.1}$$

□

By declaring `\mathversion{bold}`, boldfaced fonts are selected in the LaTeX in-text and display math.

Example 37.3. For example, the above examples are changed after the declaration of `\mathversion{bold}`. Thus, the codes:

```
\mathversion{bold}
\LaTeX{} in-text math: \(F_2\) \par
\LaTeX{} display math: \[F_2\] \par
\LaTeX{} equation environment: \begin{equation} F_2 \end{equation}
```

generate the following expressions:

LaTeX in-text math: $\boldsymbol{F_2}$
LaTeX display math:

$$\boldsymbol{F_2}$$

LaTeX equation environment:

$$\boldsymbol{F_2} \tag{37.2}$$

Note that alphabets are typeset in boldfaced italic, because they are also regarded as representing mathematical functions. □

37.1.2 Chemical Typesetting

The `\mathrm` Command

For the purpose of chemical documentation, an alphabet with a subscript should be regarded as representing a molecular formula after the alphabet is printed in roman, e.g., $\mathrm{F_2}$ for a fluorine molecule. This task can be accomplished by using the LaTeX command `\mathrm`.

Example 37.4. For example, the codes written in a default situation (math version "normal"):

```
%\mathversion{normal}%default setting
\LaTeX{} in-text math: \(\mathrm{F_2}\) \par
\LaTeX{} display math: \[\mathrm{F_2}\] \par
\LaTeX{} equation environment: \begin{equation} \mathrm{F_2} \end{equation}
```

generate the following expressions:

LaTeX in-text math: $\mathrm{F_2}$
LaTeX display math:

$$\mathrm{F_2}$$

LaTeX equation environment:

$$\mathrm{F_2} \tag{37.3}$$

□

Example 37.5. The roman fonts in the above examples are changed into boldfaced roman after the declaration of `\mathversion{bold}`. Thus, the codes:

```
\mathversion{bold}
\LaTeX{} in-text math: \(\mathrm{F_2}\) \par
\LaTeX{} display math: \[\mathrm{F_2}\] \par
\LaTeX{} equation environment: \begin{equation} \mathrm{F_2} \end{equation}
```

generate the following expressions:

LaTeX in-text math: $\mathbf{F_2}$
LaTeX display math:

$$\mathbf{F_2}$$

LaTeX equation environment:

$$\mathbf{F_2} \tag{37.4}$$

□

Example 37.6. The command `\mathrm` is capable of surrounding the whole equation in an `equation` environment:

```
math version ‘‘bold’’ \mathversion{bold}
\begin{equation}
\mathrm{2H_2 + O_2 \longrightarrow 2H_2O}
\end{equation}
math version ‘‘normal’’ (default) \mathversion{normal}
\begin{equation}
\mathrm{2H_2 + O_2 \longrightarrow 2H_2O}
\end{equation}
```

This code generates the following expression:

math version “bold”

$$\mathbf{2H_2 + O_2 \longrightarrow 2H_2O} \tag{37.5}$$

math version “normal” (default)

$$2H_2 + O_2 \longrightarrow 2H_2O \tag{37.6}$$

Note that the command `\mathrm` selects boldfaced letters (not roman letters), when the math version “bold” is selected. □

However, this method cannot be extended in case of an `eqnarray` environment. The command `\mathrm` must be declared in each portion separated by an ampersand.

Example 37.7. Thus, the codes:

```
math version ‘‘bold’’ \mathversion{bold}
\begin{eqnarray}
\mathrm{2H_2 + O_2} & \longrightarrow & \mathrm{2H_2O} \\
\mathrm{C + O_2} & \longrightarrow & \mathrm{CO_2}
\end{eqnarray}
math version ‘‘normal’’ (default) \mathversion{normal}
\begin{eqnarray}
\mathrm{2H_2 + O_2} & \longrightarrow & \mathrm{2H_2O} \\
\mathrm{C + O_2} & \longrightarrow & \mathrm{CO_2}
\end{eqnarray}
```

generate the following expressions:

math version “bold”

$$\mathbf{2H_2 + O_2 \longrightarrow 2H_2O} \tag{37.7}$$

$$\mathbf{C + O_2 \longrightarrow CO_2} \tag{37.8}$$

math version “normal” (default)

$$2H_2 + O_2 \longrightarrow 2H_2O \tag{37.9}$$

$$C + O_2 \longrightarrow CO_2 \tag{37.10}$$

□

The ChemEquation and ChemEqnarray Environments

By using the ChemEquation environment (Subsection 35.2.2), you can omit the \mathrm command.

Example 37.8. For example, the ChemEquation environment is used in the math version “bold” or “normal” without declaring \mathrm:

```
math version ‘‘bold’’ \mathversion{bold}
\begin{ChemEquation}
2H_2 + O_2 \longrightarrow 2H_2O
\end{ChemEquation}
mathversion ‘‘normal’’ (default) \mathversion{normal}
\begin{ChemEquation}
2H_2 + O_2 \longrightarrow 2H_2O
\end{ChemEquation}
```

These codes generate the following expressions:

math version “bold”

$$\mathbf{2H_2 + O_2 \longrightarrow 2H_2O} \tag{37.11}$$

math version “normal” (default)

$$2H_2 + O_2 \longrightarrow 2H_2O \tag{37.12}$$

It should be noted that fonts selected in the the ChemEquation environment depend upon the selected math version, “bold” or “normal”. □

The ChemEqnarray environment (Subsection 35.2.3) enables us to omit the command \mathrm in a similar way to the ChemEquation environment.

Example 37.9. Thus, the codes:

```
math version ‘‘bold’’ \mathversion{bold}
\begin{ChemEqnarray}
2H_2 + O_2 & \longrightarrow & 2H_2O \\
C + O_2 & \longrightarrow & CO_2
\end{ChemEqnarray}
math version ‘‘normal’’ (default) \mathversion{normal}
\begin{ChemEqnarray}
2H_2 + O_2 & \longrightarrow & 2H_2O \\
C + O_2 & \longrightarrow & CO_2
\end{ChemEqnarray}
```

generate the following expressions:

math version “bold”

$$\mathbf{2H_2 + O_2 \longrightarrow 2H_2O} \tag{37.13}$$

$$\mathbf{C + O_2 \longrightarrow CO_2} \tag{37.14}$$

math version “normal” (default)

$$2H_2 + O_2 \longrightarrow 2H_2O \tag{37.15}$$

$$C + O_2 \longrightarrow CO_2 \tag{37.16}$$

□

As for in-text math expressions, the command `\ChemForm` has been defined in Subsection 35.1.2. For example, the code `\ChemForm{F_2}` prints out F_2.

37.1.3 Math Versions for Cooperating with the XeTeX System

chemist, chmst-ps, and chmst-pdf Packages

According to the three modes of the XeTeX system, there are three sets of math version utilities. The following templates are ready to switch the three sets.

1. **TeX/LaTeX-compatible mode**: The chemist package is loaded automatically, when the XeTeX system is read by the command `\usepackage{xymtex}`, which is declared in the preamble of a tex file, as shown in the following template:

```
\documentclass{article}
\usepackage{xymtex}%%the chemist package loaded automatically
\begin{document}
(text)%default (normal)

\mathversion{bold}
(text)

\mathversion{chem}
(text)

\mathversion{boldchem}
(text)

\mathversion{normal}
(text)%return to the default
\end{document}
```

2. **PostScript-compatible mode**: The chmst-ps package along with the chemist package is loaded automatically to meet PostScript requirements, when the code `\usepackage{xymtexps}` is declared. Note that the xymtexps package provides the PostScript-compatible mode of the XeTeX system.

```
\documentclass{article}
\usepackage{xymtexps}%%the chemist, chmst-ps packages loaded automatically
\begin{document}
(text)%default (normal)

\mathversion{bold}
(text)

\mathversion{chem}
(text)

\mathversion{boldchem}
```

```
(text)

\mathversion{normal}
(text)%return to the default
\end{document}
```

The xymtexps package provides the PostScript-compatible mode of the XyMTEX system. Hence, the resulting dvi file should be converted into a PostScript file by means of an appropriate converter (e.g., dvips). The resulting PostScript file (.ps) can be browsed by Ghostscript. The PostScript file can be further converted into a PDF file by means of an appropriate converter (e.g., Adobe Distiller).

3. **PDF-compatible mode**: The chmst-pdf package along with the chemist package automatically loaded to meet PDF requirements, when the code `\usepackage{xymtexpdf}` is declared. Note that the xymtexpdf package provides the PDF-compatible mode of the XyMTEX system.

```
\documentclass{article}
\usepackage{xymtexpdf}%%the chemist, chmst-pdf packages loaded automatically
\begin{document}
(text)%default (normal)

\mathversion{bold}
(text)

\mathversion{chem}
(text)

\mathversion{boldchem}
(text)

\mathversion{normal}
(text)%return to the default
\end{document}
```

The xymtexpdf package provides the PDF-compatible mode of the XyMTEX system. Hence, the resulting dvi file should be converted into a PDF file by means of an appropriate converter (e.g., dvipdfm(x)). The resulting PDF file can be browsed by Adobe Reader.

New Math Versions: "chem" and "boldchem"

There are two math versions ("normal" and "bold") for mathematical usage in LaTeX 2_ε. The chemist (chmst-pdf or chmst-ps) package provides additional two math versions ("chem" and "boldchem") for chemical usage.

If a math version command is not explicitly declared, the math version "normal" is effective so as to provide usual (default) typesetting inherent in the math mode of LaTeX 2_ε, where letters etc. are typeset by using *italic* fonts. When `\mathversion{bold}` command is declared, the LaTeX 2_ε typesetting is conducted under the math version "bold", where letters etc. are typeset by using ***boldfaced italic*** fonts. The chemist (chmst-pdf or chmst-ps) package provides us with two additional math versions, i.e., "chem" and "boldchem", where letters etc. are typeset by using usual or boldfaced **upright** fonts, which mainly aim at the output of chemical elements or compounds (such as H_2 and H_2O).

Example 37.10. Under the math versions "chem" and "boldchem", the `equation` environment is applicable to print chemical equations.

```
math version ``boldchem'' \mathversion{boldchem}
\begin{equation}
2H_2 + O_2 \longrightarrow 2H_2O
\end{equation}
math version ``chem'' \mathversion{chem}
\begin{equation}
2H_2 + O_2 \longrightarrow 2H_2O
```

```
\end{equation}
math version ‘‘normal’’ (default) \mathversion{normal}
\begin{equation}
2H_2 + O_2 \longrightarrow 2H_2O
\end{equation}
```

These codes generate the following expressions:

math version “boldchem”

$$\mathbf{2H_2 + O_2 \longrightarrow 2H_2O} \tag{37.17}$$

math version “chem”

$$2\mathrm{H_2} + \mathrm{O_2} \longrightarrow 2\mathrm{H_2O} \tag{37.18}$$

math version “normal” (default)

$$2H_2 + O_2 \longrightarrow 2H_2O \tag{37.19}$$

□

Example 37.11. Under the math versions “chem” and “boldchem”, the `eqnarray` environment is applicable to print chemical equations. Thus, the codes:

```
math version ‘‘boldchem’’ \mathversion{boldchem}
\begin{eqnarray}
2H_2 + O_2 & \longrightarrow & 2H_2O \\
C + O_2 & \longrightarrow & CO_2
\end{eqnarray}
math version ‘‘chem’’ \mathversion{chem}
\begin{eqnarray}
2H_2 + O_2 & \longrightarrow & 2H_2O \\
C + O_2 & \longrightarrow & CO_2
\end{eqnarray}
math version ‘‘normal’’ (default) \mathversion{normal}
\begin{eqnarray}
2H_2 + O_2 & \longrightarrow & 2H_2O \\
C + O_2 & \longrightarrow & CO_2
\end{eqnarray}
```

generate the following expressions:

math version “boldchem”

$$\begin{aligned} \mathbf{2H_2 + O_2} &\mathbf{\longrightarrow 2H_2O} && (37.20)\\ \mathbf{C + O_2} &\mathbf{\longrightarrow CO_2} && (37.21) \end{aligned}$$

math version “chem”

$$\begin{aligned} 2\mathrm{H_2} + \mathrm{O_2} &\longrightarrow 2\mathrm{H_2O} && (37.22)\\ \mathrm{C} + \mathrm{O_2} &\longrightarrow \mathrm{CO_2} && (37.23) \end{aligned}$$

math version “normal” (default)

$$\begin{aligned} 2H_2 + O_2 &\longrightarrow 2H_2O && (37.24)\\ C + O_2 &\longrightarrow CO_2 && (37.25) \end{aligned}$$

□

37.2 Usual Math Versions — “normal” and “bold”

This section is devoted to add further comments with examples, where the chemical environments discussed in Chapter 35 are tested under the respective math versions.

37.2.1 Math Version “normal”

The math version “normal” gives outputs of a default mode, which are inherent in LaTeX 2$_\varepsilon$ without any declaration or with declaring `\mathversion{normal}`.

Default Outputs

To show such standard outputs, the listing command `\testmathversion` (Output A) is defined as follows:

```
\def\testmathversion{%for Output A
\[abcdefghijklmnopqrstuvwxyz\imath \jmath ABCDEFGHIJKLMNOPQRSTUVWXYZ\]
\[\alpha\beta\gamma\delta\epsilon\zeta\eta\theta\iota\kappa\lambda
\mu\nu\xi\pi\rho\sigma\tau\upsilon\phi\chi\psi\omega
\varepsilon\vartheta\varpi\varrho\varsigma\varphi
\Gamma\Delta\Theta\Lambda\Xi\Pi\Sigma\Upsilon\Phi\Psi\Omega\]
\[1234567890\]
\[\mathnormal{1234567890}\]
\[\mathcal{ABCDEFGHIJKLMNOPQRSTUVWXYZ}\]
\[\int \sum \prod \coprod \bigcup \bigcap
\bigodot \bigoplus \biguplus \bigotimes \]
\[(, ), [, ], ?, !, \{, \}, =, > (\mathgreater), < (\mathless),
\leftharpoonup, \leftharpoondown, \rightharpoonup, \rightharpoondown,
\ell, \wp, \partial, \flat, \natural, \sharp, \triangleleft, \triangleright,
\smile, \frown, \star, +, -\]
\[\check{x}, \breve{x}, \dot{x}, \vec{x},
\acute{x}, \grave{x}, \ddot{x},  \bar{x},
\tilde{x}, \hat{x}, \widetilde{x}, \widehat{x}\]}
```

Example 37.12. Thereby, the following code using `\testmathversion`:

```
{\def\tboxtitle{\bf Output A due to ‘‘normal’’}
\begin{tboxscreen}
\testmathversion
\end{tboxscreen}}
```

is described in a `tboxtitle` environment (supported by the chemist package) so as to produce:

Output A due to “normal”

$$abcdefghijklmnopqrstuvwxyz\imath\jmath ABCDEFGHIJKLMNOPQRSTUVWXYZ$$

$$\alpha\beta\gamma\delta\epsilon\zeta\eta\theta\iota\kappa\lambda\mu\nu\xi\pi\rho\sigma\tau\upsilon\phi\chi\psi\omega\varepsilon\vartheta\varpi\varrho\varsigma\varphi\Gamma\Delta\Theta\Lambda\Xi\Pi\Sigma\Upsilon\Phi\Psi\Omega$$

$$1234567890$$

$$\mathnormal{1234567890}$$

$$\mathcal{ABCDEFGHIJKLMNOPQRSTUVWXYZ}$$

$$\int \sum \prod \coprod \bigcup \bigcap \bigodot \bigoplus \biguplus \bigotimes$$

$$(,),[,],?,!,\{,\},=,>\ (>),<\ (<),\leftharpoonup,\leftharpoondown,\rightharpoonup,\rightharpoondown,\ell,\wp,\partial,\flat,\natural,\sharp,\triangleleft,\triangleright,\smile,\frown,\star,+,-$$

$$\check{x},\breve{x},\dot{x},\vec{x},\acute{x},\grave{x},\ddot{x},\bar{x},\tilde{x},\hat{x},\widetilde{x},\widehat{x}$$

□

To test `equation` and `eqnarray` environments, the command `\testequation` (Output B) is defined as follows:

```
\def\testequation{%%for Output B
Euler's summation (\texttt{equation}):
\begin{equation}
\sum_{a\leq k < b}f(k)  =  \int_{a}^{b}f(x)\mathrm{d}x
+ \sum_{k=1}^{m}\frac{B_{k}}{k!}f^{(k-1)}(x)\Big|_{a}^{b} + R_{m}.
\end{equation}
The term \(R_{m}\) is represented as follows (\texttt{eqnarray}):
\begin{eqnarray}
R_{m} & = & (-1)^{m+1}\int_{a}^{b}
\frac{B_{m}(\{x\})}{m!}f^{(m)}(x)\mathrm{d}x, \\
      &   &  a\leq b \mbox{~and~} m\geq 1, \nonumber
\end{eqnarray}
where the symbols $a$, $b$, and $m$ represent integers.
}
```

Example 37.13. Thereby, the output produced by `\testequation` shows default outputs of `equation` and `eqnarray` environments in the present math version “normal” as follows:

```
{\def\tboxtitle{\bf Output B due to ``normal''}
\begin{tboxscreen}
\testequation
\end{tboxscreen}}
```

Output B due to “normal”

Euler’s summation (`equation`):

$$\sum_{a\leq k<b} f(k) = \int_a^b f(x)\mathrm{d}x + \sum_{k=1}^{m} \frac{B_k}{k!} f^{(k-1)}(x)\Big|_a^b + R_m. \tag{37.26}$$

The term R_m is represented as follows (`eqnarray`):

$$\begin{aligned} R_m &= (-1)^{m+1} \int_a^b \frac{B_m(\{x\})}{m!} f^{(m)}(x)\mathrm{d}x, \\ &\quad a \leq b \text{ and } m \geq 1, \end{aligned} \tag{37.27}$$

where the symbols a, b, and m represent integers.

□

Convenient Environments for Chemical Equations

To test `equation` and `eqnarray` environments containing chemical formulas, the following test command `\testequationforchemistry` (Output C) is defined as follows:

```
\def\testequationforchemistry{%%for Output C
An \texttt{equation} enviroment:
\begin{equation}
2H_2 + O_2  \rightarrow  2H_2O
\end{equation}
An \texttt{eqnarray} environment:
\begin{eqnarray}
C + O_2 & \rightarrow & CO_2 \\
Na^{+} + Cl^{-} & \rightarrow & NaCl\downarrow
\end{eqnarray}
}%
```

Under the math version “normal”, alphabets in a math mode (such as an equation or eqnarray environment) are typeset by using italic fonts, which do not meet chemical requirements.

Example 37.14. Thus the test command `\testequationforchemistry` defined above gives the following output.

```
{\def\tboxtitle{\bf Output C due to ‘‘normal’’}
\begin{tboxscreen}
\testequationforchemistry
\end{tboxscreen}}
```

Output C due to “normal”

An equation environment:

$$2H_2 + O_2 \rightarrow 2H_2O \tag{37.28}$$

An eqnarray environment:

$$C + O_2 \rightarrow CO_2 \tag{37.29}$$
$$Na^+ + Cl^- \rightarrow NaCl\downarrow \tag{37.30}$$

□

The chemist (chmst-pdf or chmst-ps) package defines chemeqn and chemeqnarray environments in order to support chemical requirements. The following \testchemequation command (Output D) is defined to test the functions of the chemeqn and chemeqnarray environments and related commands.

```
\def\testchemequation{%%for Output D
A \texttt{chemeqn} enviroment:
\begin{chemeqn}
2H_2 + O_2  \rightarrow  2H_2O
\end{chemeqn}
\begin{chemeqn}
abcdefghijklmnopqrstuvwxyz\imath \jmath ABCDEFGHIJKLMNOPQRSTUVWXYZ
\end{chemeqn}
\begin{chemeqn}
\alpha\beta\gamma\delta\epsilon\zeta\eta\theta\iota\kappa\lambda
\mu\nu\xi\pi\rho\sigma\tau\upsilon\phi\chi\psi\omega
\varepsilon\vartheta\varpi\varrho\varsigma\varphi
\Gamma\Delta\Theta\Lambda\Xi\Pi\Sigma\Upsilon\Phi\Psi\Omega
\end{chemeqn}
A \texttt{chemeqnarray} environment:
\begin{chemeqnarray}
C + O_2 & \rightarrow & CO_2 \\
Na^{+} + Cl^{-} & \rightarrow & NaCl\downarrow
\end{chemeqnarray}
A \texttt{chemeqnarray$*$} environment:
\begin{chemeqnarray*}
C + O_2 & \rightarrow & CO_2 \\
Na^{+} + Cl^{-} & \rightarrow & NaCl\downarrow
\end{chemeqnarray*}
In-text chemical formulas: \chemform{2H_2 + O_2  \rightarrow  2H_2O}
and \chemform{C + O_2 \rightarrow CO_2}
}%
```

Under the math version “normal”, alphabets in a chemeqn environment etc. are typeset by using upright fonts.

Example 37.15. Thus the test command \testchemequation defined above gives the following output.

```
{\def\tboxtitle{\bf Output D due to ‘‘normal’’}
\begin{tboxscreen}
\testchemequation
\end{tboxscreen}}
```

Output D due to “normal”

A chemeqn environment:

$$2H_2 + O_2 \rightarrow 2H_2O \tag{37.31}$$

$$\mathrm{abcdefghijklmnopqrstuvwxyz}\imath\jmath\mathrm{ABCDEFGHIJKLMNOPQRSTUVWXYZ} \tag{37.32}$$

$$\alpha\beta\gamma\delta\epsilon\zeta\eta\theta\iota\kappa\lambda\mu\nu\xi\pi\rho\sigma\tau\upsilon\phi\chi\psi\omega\varepsilon\vartheta\varpi\varrho\varsigma\varphi\Gamma\Delta\Theta\Lambda\Xi\Pi\Sigma\Upsilon\Phi\Psi\Omega \tag{37.33}$$

A chemeqnarray environment:

$$\begin{aligned} C + O_2 &\rightarrow CO_2 && (37.34)\\ Na^+ + Cl^- &\rightarrow NaCl\downarrow && (37.35)\end{aligned}$$

A chemeqnarray$*$ environment:

$$\begin{aligned} C + O_2 &\rightarrow CO_2\\ Na^+ + Cl^- &\rightarrow NaCl\downarrow\end{aligned}$$

In-text chemical formulas: $2H_2 + O_2 \rightarrow 2H_2O$ and $C + O_2 \rightarrow CO_2$

□

In addition to the chemeqn and chemeqnarray environments, the latest version of the chemist (chmst-pdf or chmst-ps) package provides another set of commands for chemical requirements, i.e., ChemEquation, ChemEqnarray, and ChemEqnarray$*$ environments as well as \ChemForm command. The following \testChemEquation command (Output E) is defined to test the functions of these newly-defined commands.

```
\def\testChemEquation{%%for Output E
A \texttt{ChemEquation} enviroment:
\begin{ChemEquation}
2H_2 + O_2  \rightarrow  2H_2O
\end{ChemEquation}
\begin{ChemEquation}
abcdefghijklmnopqrstuvwxyz\imath \jmath ABCDEFGHIJKLMNOPQRSTUVWXYZ
\end{ChemEquation}
\begin{ChemEquation}
\alpha\beta\gamma\delta\epsilon\zeta\eta\theta\iota\kappa\lambda
\mu\nu\xi\pi\rho\sigma\tau\upsilon\phi\chi\psi\omega
\varepsilon\vartheta\varpi\varrho\varsigma\varphi
\Gamma\Delta\Theta\Lambda\Xi\Pi\Sigma\Upsilon\Phi\Psi\Omega
\end{ChemEquation}
A \texttt{ChemEqnarray} environment:
\begin{ChemEqnarray}
C + O_2 & \rightarrow & CO_2 \\
Na^{+} + Cl^{-} & \rightarrow & NaCl\downarrow
\end{ChemEqnarray}
A \texttt{ChemEqnarray$*$} environment:
\begin{ChemEqnarray*}
C + O_2 & \rightarrow & CO_2 \\
Na^{+} + Cl^{-} & \rightarrow & NaCl\downarrow
\end{ChemEqnarray*}
In-text chemical formulas: \ChemForm{2H_2 + O_2  \rightarrow  2H_2O}
and \ChemForm{C + O_2 \rightarrow CO_2}
}%
```

Under the math version “normal”, alphabets in a ChemEquation etc. are typeset also by using upright fonts.

Example 37.16. Thus the test command \testChemEquation defined above gives the following output.

```
{\def\tboxtitle{\bf Output E due to ‘‘normal’’}
\begin{tboxscreen}
\testChemEquation
\end{tboxscreen}}
```

Output E due to “normal”

A ChemEquation environment:

$$2H_2 + O_2 \rightarrow 2H_2O \tag{37.36}$$

$$abcdefghijklmnopqrstuvwxyz\imath\jmath ABCDEFGHIJKLMNOPQRSTUVWXYZ \tag{37.37}$$

$$\alpha\beta\gamma\delta\epsilon\zeta\eta\theta\iota\kappa\lambda\mu\nu\xi\pi\rho\sigma\tau\upsilon\phi\chi\psi\omega\varepsilon\vartheta\varpi\varrho\varsigma\varphi\Gamma\Delta\Theta\Lambda\Xi\Pi\Sigma\Upsilon\Phi\Psi\Omega \tag{37.38}$$

A ChemEqnarray environment:

$$\begin{aligned} C + O_2 &\rightarrow CO_2 && (37.39)\\ Na^+ + Cl^- &\rightarrow NaCl\downarrow && (37.40)\end{aligned}$$

A ChemEqnarray* environment:

$$\begin{aligned} C + O_2 &\rightarrow CO_2\\ Na^+ + Cl^- &\rightarrow NaCl\downarrow\end{aligned}$$

In-text chemical formulas: $2H_2 + O_2 \rightarrow 2H_2O$ and $C + O_2 \rightarrow CO_2$

□

(Remarks) It is worthwhile to point out the difference between \chemform (also the environments, chemeqn, chemeqnarray, and chemeqnarray*) and \ChemForm (also the environments, ChemEquation, ChemEqnarray, and ChemEqnarray*) under the default math version “normal” (Table 37.1).

Table 37.1. Fonts Selected in Default Situations

code:	`$Cr_2O_7^{2-}$`	`\chemform{Cr_2O_7^{2-}}`	`{\mathversion{chem}\(Cr_2O_7^{2-}\)}`
print outputs:	$Cr_2O_7^{2-}$	$\mathrm{Cr_2O_7^{2-}}$	$\mathrm{Cr_2O_7^{2-}}$
fonts selected:	math font	math font	math font
chem correction:	–	chem-corrected	–
code:	`$\mathrm{Cr_2O_7^{2-}}$`	`\ChemForm{Cr_2O_7^{2-}}`	`Cr$_2$O$_7^{2-}$`
print outputs:	$\mathrm{Cr_2O_7^{2-}}$	$\mathrm{Cr_2O_7^{2-}}$	$\mathrm{Cr_2O_7^{2-}}$
fonts selected:	in-text font	in-text font	in-text font
chem correction:	–	chem-corrected	–

In usual situations (also in this document), the fonts selected by the math version “normal” (default) are based on the specification of the original TEX (and LATEX), even if the fonts selected in the text is changed to the other fonts (as in this document). For example, the first example of the top section in Table 37.1 shows `$Cr_2O_7^{2-}$` ($Cr_2O_7^{2-}$), where alphabets are printed out in italic. See also Chapter 35.

The command \chemform (also the environments, chemeqn, chemeqnarray, and chemeqnarray*) selects fonts on the basis of the original TEX (and LATEX), as found in the second example of the top section in Table 37.1. Note that the command \chemform adopts the math version “chem” (cf. the third example of the top section in Table 37.1) and the chemical correction (cf. Chapter 35), even if the outer text mode is the math version “normal” as a default. As for the effects of the chemical correction, examine carefully the depths of subscripts 2 and 7 in respective outputs.

On the other hand, the command \mathrm, even in the original mathematical mode of TEX/LATEX, selects the same roman font as selected in the text of a document (the first example of the bottom section in Table 37.1). Examine carefully the letters C, r, and O appearing in the top and bottom sections of Table 37.1.

The command \ChemForm (also the environments, chemeqn, chemeqnarray, and chemeqnarray*) selects the same fonts as selected in the text of a document. Compare the second and third examples of the bottom section in Table 37.1.

37.2.2 Math Version “bold”

The math version “bold” gives outputs of boldfaced fonts, when the switching command \mathversion is explicitly declared. An alternative (rather old) method to enter the math version “bold” is the declaration of \boldmath. For example, {\boldmath x_{i}} produces x_i according to LaTeX2.09. This section is typeset after the declaration of

```
\mathversion{bold}
```

according to LaTeX 2_ε.

Outputs under Math Version “bold”

The math version “bold” gives outputs of “bold” mode, which are inherent in LaTeX 2_ε.

Example 37.17. To show such outputs, the listing command \testmathversion defined above is used after the declaration of \mathversion{bold}. The result is shown as follows:

Output A due to “bold”

$$\boldsymbol{abcdefghijklmnopqrstuvwxyz\imath\jmath ABCDEFGHIJKLMNOPQRSTUVWXYZ}$$

$$\boldsymbol{\alpha\beta\gamma\delta\epsilon\zeta\eta\theta\iota\kappa\lambda\mu\nu\xi\pi\rho\sigma\tau\upsilon\phi\chi\psi\omega\varepsilon\vartheta\varpi\varrho\varsigma\varphi\Gamma\Delta\Theta\Lambda\Xi\Pi\Sigma\Upsilon\Phi\Psi\Omega}$$

$$\boldsymbol{1234567890}$$

$$\boldsymbol{1234567890}$$

$$\boldsymbol{\mathcal{ABCDEFGHIJKLMNOPQRSTUVWXYZ}}$$

$$\boldsymbol{\int\sum\prod\coprod\bigcup\bigcap\bigodot\bigoplus\biguplus\bigotimes}$$

$$\boldsymbol{(,),[,],?,!,\{,\},=,>\ (>),<\ (<),\leftharpoondown,\rightharpoondown,\rightharpoonup,\rightharpoonup,\ell,\wp,\partial,\flat,\natural,\sharp,\triangleleft,\triangleright,\smile,\frown,\star,+,-}$$

$$\boldsymbol{\check{x},\check{x},\dot{x},\vec{x},\acute{x},\grave{x},\ddot{x},\bar{x},\tilde{x},\hat{x},\widetilde{x},\widehat{x}}$$

□

Example 37.18. To test equation and eqnarray environments under the math version “bold”, the above-defined command \testequation is again used here so as to give the following output:

Output B due to “bold”

Euler’s summation (equation):

$$\sum_{a\le k<b} f(k) = \int_a^b f(x)\mathrm{d}x + \sum_{k=1}^{m} \frac{B_k}{k!} f^{(k-1)}(x)\Big|_a^b + R_m. \tag{37.41}$$

The term R_m is represented as follows (eqnarray):

$$\begin{aligned} R_m &= (-1)^{m+1} \int_a^b \frac{B_m(\{x\})}{m!} f^{(m)}(x)\mathrm{d}x, \\ &\quad a \le b \text{ and } m \ge 1, \end{aligned} \tag{37.42}$$

where the symbols a, b, and m represent integers.

□

Environments and Commands for Chemistry

Under the math version “bold”, alphabets in a math mode (such as an equation or eqnarray environment) are typeset by using boldfaced italic fonts.

Example 37.19. Thus the test command `\testequationforchemistry` defined above gives the following output, which does not meet chemical requirements.

Output C due to “bold”

An `equation` environment:

$$\boldsymbol{2H_2 + O_2 \rightarrow 2H_2O} \tag{37.43}$$

An `eqnarray` environment:

$$\boldsymbol{C + O_2 \rightarrow CO_2} \tag{37.44}$$

$$\boldsymbol{Na^+ + Cl^- \rightarrow NaCl\downarrow} \tag{37.45}$$

□

(Remarks) The effect of the command `\mathrm` under the math version “normal” is compared with the counterpart under the math version “bold”.

```
{\mathversion{normal}
mathversion ‘‘normal’’ and \verb/\mathrm/ (\texttt{equation}):
\begin{equation}
\mathrm{2H_2 + O_2 \rightarrow 2H_2O}
\end{equation}}

{\mathversion{bold}
math version ‘‘bold’’ and \verb/\mathrm/ (\texttt{equation}):
\begin{equation}
\mathrm{2H_2 + O_2 \rightarrow 2H_2O}
\end{equation}}
```

math version “normal” and `\mathrm` (`equation`):

$$\mathrm{2H_2 + O_2 \rightarrow 2H_2O} \tag{37.46}$$

math version “bold” and `\mathrm` (`equation`):

$$\mathrm{\boldsymbol{2H_2 + O_2 \rightarrow 2H_2O}} \tag{37.47}$$

Compare these outputs with the following one, which is generated by the command `\mathbf` under the math version “normal”.

```
{\mathversion{normal}
mathversion ‘‘normal’’ and \verb/\mathbf/ (\texttt{equation}):
\begin{equation}
\mathbf{2H_2 + O_2 \rightarrow 2H_2O}
\end{equation}}
```

math version “normal” and `\mathbf` (`equation`):

$$\mathbf{2H_2 + O_2 \rightarrow 2H_2O} \tag{37.48}$$

Even under the math version “bold”, alphabets in a chemeqn environment etc. are typeset by using upright fonts.

Example 37.20. Thus the test command `\testchemequation` defined above gives the following output, which is equivalent to the above output of the math version “normal”.

Output D due to “bold”

A `chemeqn` environment:

$$2\mathrm{H}_2 + \mathrm{O}_2 \rightarrow 2\mathrm{H}_2\mathrm{O} \tag{37.49}$$

$$\mathrm{abcdefghijklmnopqrstuvwxyz}\imath\jmath\mathrm{ABCDEFGHIJKLMNOPQRSTUVWXYZ} \tag{37.50}$$

$$\alpha\beta\gamma\delta\epsilon\zeta\eta\theta\iota\kappa\lambda\mu\nu\xi\pi\rho\sigma\tau\upsilon\phi\chi\psi\omega\varepsilon\vartheta\varpi\varrho\varsigma\varphi\Gamma\Delta\Theta\Lambda\Xi\Pi\Sigma\Upsilon\Phi\Psi\Omega \tag{37.51}$$

A `chemeqnarray` environment:

$$\begin{aligned} \mathrm{C} + \mathrm{O}_2 &\rightarrow \mathrm{CO}_2 && (37.52)\\ \mathrm{Na}^+ + \mathrm{Cl}^- &\rightarrow \mathrm{NaCl}\downarrow && (37.53) \end{aligned}$$

A `chemeqnarray*` environment:

$$\begin{aligned} \mathrm{C} + \mathrm{O}_2 &\rightarrow \mathrm{CO}_2\\ \mathrm{Na}^+ + \mathrm{Cl}^- &\rightarrow \mathrm{NaCl}\downarrow \end{aligned}$$

In-text chemical formulas: $2\mathrm{H}_2 + \mathrm{O}_2 \rightarrow 2\mathrm{H}_2\mathrm{O}$ and $\mathrm{C} + \mathrm{O}_2 \rightarrow \mathrm{CO}_2$

□

In contrast, `ChemEquation`, `ChemEqnarray`, and `ChemEqnarray*` environments as well as a `\ChemForm` command typeset boldfaced alphabets of upright shape under the math version “bold”.

Example 37.21. Thus the test command `\testChemEquation` defined above gives the following output, which is different from the corresponding output of the math version “normal”.

Output E due to “bold”

A `ChemEquation` environment:

$$\mathbf{2H_2 + O_2 \rightarrow 2H_2O} \tag{37.54}$$

$$\mathbf{abcdefghijklmnopqrstuvwxyz}\imath\jmath\mathbf{ABCDEFGHIJKLMNOPQRSTUVWXYZ} \tag{37.55}$$

$$\boldsymbol{\alpha\beta\gamma\delta\epsilon\zeta\eta\theta\iota\kappa\lambda\mu\nu\xi\pi\rho\sigma\tau\upsilon\phi\chi\psi\omega\varepsilon\vartheta\varpi\varrho\varsigma\varphi\Gamma\Delta\Theta\Lambda\Xi\Pi\Sigma\Upsilon\Phi\Psi\Omega} \tag{37.56}$$

A `ChemEqnarray` environment:

$$\begin{aligned} \mathbf{C + O_2} &\mathbf{\rightarrow} \mathbf{CO_2} && (37.57)\\ \mathbf{Na^+ + Cl^-} &\mathbf{\rightarrow} \mathbf{NaCl\downarrow} && (37.58) \end{aligned}$$

A `ChemEqnarray*` environment:

$$\begin{aligned} \mathbf{C + O_2} &\mathbf{\rightarrow} \mathbf{CO_2}\\ \mathbf{Na^+ + Cl^-} &\mathbf{\rightarrow} \mathbf{NaCl\downarrow} \end{aligned}$$

In-text chemical formulas: $\mathbf{2H_2 + O_2 \rightarrow 2H_2O}$ and $\mathbf{C + O_2 \rightarrow CO_2}$

□

37.3 Math Versions for Chemical Equations — “chem” and “boldchem”

The XeTeX system automatically loads the chemist (chmst-pdf or chmst-ps) package, which supports the math versions “chem” and “boldchem”. These math versions give sufficient results with respect to letter outputs for chemical documentation.

37.3.1 Math Version “chem”

This section is typeset after the declaration of

```
\mathversion{chem}
```

Outputs under Math Version “chem”

The math version “chem” gives outputs of “chem” mode, which aim at upright letters for chemical formulas.

Example 37.22. To show such outputs, the listing command `\testmathversion` defined above is used after the declaration of `\mathversion{chem}`. The result is shown as follows:

Output A due to “chem”

$$\mathrm{abcdefghijklmnopqrstuvwxyz\imath\jmath ABCDEFGHIJKLMNOPQRSTUVWXYZ}$$

$$\alpha\beta\gamma\delta\epsilon\zeta\eta\theta\iota\kappa\lambda\mu\nu\xi\pi\rho\sigma\tau\upsilon\phi\chi\psi\omega\varepsilon\vartheta\varpi\varrho\varsigma\varphi\Gamma\Delta\Theta\Lambda\Xi\Pi\Sigma\Upsilon\Phi\Psi\Omega$$

$$1234567890$$

$$\mathbf{1234567890}$$

$$\mathcal{ABCDEFGHIJKLMNOPQRSTUVWXYZ}$$

$$\int\sum\prod\coprod\bigcup\bigcap\bigodot\bigoplus\biguplus\bigotimes$$

$$(,),[,],?,!,\{,\},=,\text{¿}\ (>),\text{¡}\ (<),\leftharpoondown,\rightharpoondown,\rightharpoonup,\rightharpoonup,\ell,\wp,\partial,\flat,\natural,\sharp,\triangleleft,\triangleright,\smile,\frown,\star,+,-$$

$$\check{\mathrm{x}},\breve{\mathrm{x}},\dot{\mathrm{x}},\vec{\mathrm{x}},\acute{\mathrm{x}},\grave{\mathrm{x}},\ddot{\mathrm{x}},\bar{\mathrm{x}},\tilde{\mathrm{x}},\hat{\mathrm{x}},\widetilde{\mathrm{x}},\widehat{\mathrm{x}}$$

□

As found in the first line of Output A due to “chem”, lowercase and uppercase alphabets are typeset upright except $\imath$ and $\jmath$.

Note that the symbols $<$ and $>$ are not properly typeset if they are input directly. The commands `$\mathless$` and `$\mathgreater$` should be used to give correct printing.

Example 37.23. To test equation and eqnarray environments under the math version “chem”, the above-defined command `\testequation` is again used here, although the resulting output is contrary to mathematical conventions:

Output B due to “chem”

Euler’s summation (`equation`):

$$\sum_{a\leq k\text{¡}b} f(k) = \int_a^b f(x)dx + \sum_{k=1}^{m} \frac{B_k}{k!} f^{(k-1)}(x)\Big|_a^b + R_m. \tag{37.59}$$

The term R_m is represented as follows (`eqnarray`):

$$\begin{aligned} R_m &= (-1)^{m+1} \int_a^b \frac{B_m(\{x\})}{m!} f^{(m)}(x)dx, \\ &\quad a \leq b \text{ and } m \geq 1, \end{aligned} \tag{37.60}$$

where the symbols a, b, and m represent integers.

□

Note that the symbols $<$ and $>$ are not properly typeset if they are input directly. Thus, the symbol $<$ in the lower limit of the above summation is erroneously replaced by the symbol ¡. The commands `$\mathless$` and `$\mathgreater$` should be used to give correct printing. For example, the code:

```
\[\sum_{a\leq k \mbox{\scriptsize $\mathless$} b}f(k)\]
```

gives the following output:

$$\sum_{\mathrm{a}\leq \mathrm{k}<\mathrm{b}} \mathrm{f(k)}$$

Because this output does not meet mathematical conventions, it should be written as follows:

```
{\mathversion{normal}
\[\sum_{a\leq k < b}f(k)\]
}
```

which gives the following output:

$$\sum_{a\leq k<b} f(k)$$

Environments and Commands for Chemistry

Under the math version “chem”, alphabets in a math mode (such as an `equation` or `eqnarray` environment) are typeset by using upright fonts.

Example 37.24. Thus the test command `\testequationforchemistry` defined above gives the following output, which meets chemical requirements.

Output C due to “chem”

An `equation` environment:

$$2\mathrm{H_2} + \mathrm{O_2} \rightarrow 2\mathrm{H_2O} \tag{37.61}$$

An `eqnarray` environment:

$$\begin{aligned} \mathrm{C} + \mathrm{O_2} &\rightarrow \mathrm{CO_2} && (37.62)\\ \mathrm{Na^+} + \mathrm{Cl^-} &\rightarrow \mathrm{NaCl}\downarrow && (37.63) \end{aligned}$$

□

Under the math version “chem”, alphabets in a `chemeqn` environment etc. are also typeset by using upright fonts.

Example 37.25. Thus the test command `\testchemequation` defined above gives the following output, which is equivalent to the above output of the math version “normal”.

Output D due to “chem”

A `chemeqn` environment:

$$2\mathrm{H_2} + \mathrm{O_2} \rightarrow 2\mathrm{H_2O} \tag{37.64}$$

$$\mathrm{abcdefghijklmnopqrstuvwxyz}\imath\jmath\mathrm{ABCDEFGHIJKLMNOPQRSTUVWXYZ} \tag{37.65}$$

$$\alpha\beta\gamma\delta\epsilon\zeta\eta\theta\iota\kappa\lambda\mu\nu\xi\pi\rho\sigma\tau\upsilon\phi\chi\psi\omega\varepsilon\vartheta\varpi\varrho\varsigma\varphi\Gamma\Delta\Theta\Lambda\Xi\Pi\Sigma\Upsilon\Phi\Psi\Omega \tag{37.66}$$

A `chemeqnarray` environment:

$$\begin{aligned} \mathrm{C} + \mathrm{O_2} &\rightarrow \mathrm{CO_2} && (37.67)\\ \mathrm{Na^+} + \mathrm{Cl^-} &\rightarrow \mathrm{NaCl}\downarrow && (37.68) \end{aligned}$$

A `chemeqnarray*` environment:

$$\begin{aligned} \mathrm{C} + \mathrm{O_2} &\rightarrow \mathrm{CO_2}\\ \mathrm{Na^+} + \mathrm{Cl^-} &\rightarrow \mathrm{NaCl}\downarrow \end{aligned}$$

In-text chemical formulas: $2\mathrm{H_2} + \mathrm{O_2} \rightarrow 2\mathrm{H_2O}$ and $\mathrm{C} + \mathrm{O_2} \rightarrow \mathrm{CO_2}$

□

On the same line, `ChemEquation`, `ChemEqnarray`, and `ChemEqnarray*` environments as well as a `\ChemForm` command typeset alphabets of upright shape under the math version “chem”.

Example 37.26. Thus the test command `\testChemEquation` defined above gives the following output, which is different from the corresponding output of the math version “bold” but equivalent to the corresponding output of the math version “normal”.

Output E due to “chem”

A `ChemEquation` environment:

$$2H_2 + O_2 \rightarrow 2H_2O \tag{37.69}$$

$$\mathrm{abcdefghijklmnopqrstuvwxyz}\imath\jmath\mathrm{ABCDEFGHIJKLMNOPQRSTUVWXYZ} \tag{37.70}$$

$$\alpha\beta\gamma\delta\epsilon\zeta\eta\theta\iota\kappa\lambda\mu\nu\xi\pi\rho\sigma\tau\upsilon\phi\chi\psi\omega\varepsilon\vartheta\varpi\varrho\varsigma\varphi\Gamma\Delta\Theta\Lambda\Xi\Pi\Sigma\Upsilon\Phi\Psi\Omega \tag{37.71}$$

A `ChemEqnarray` environment:

$$\begin{aligned} C + O_2 &\rightarrow CO_2 && (37.72)\\ Na^+ + Cl^- &\rightarrow NaCl\downarrow && (37.73)\end{aligned}$$

A `ChemEqnarray*` environment:

$$\begin{aligned} C + O_2 &\rightarrow CO_2\\ Na^+ + Cl^- &\rightarrow NaCl\downarrow\end{aligned}$$

In-text chemical formulas: $2H_2 + O_2 \rightarrow 2H_2O$ and $C + O_2 \rightarrow CO_2$

□

37.3.2 Math Version “boldchem”

In addition to the math version “chem” supported by the original version of the chemist (chmst-ps) package (cf. Subsection 17.1 of the manual of XeMTEX version 1.01 (xymtex.pdf)), the latest version of the chemist package packed in XeMTEX version 4.05 supports the math version “boldchem”.

This section is typeset after the declaration of

```
\mathversion{boldchem}
```

Outputs under Math version “boldchem”

The math version “boldchem” gives outputs of “boldchem” mode, which aim at upright letters for chemical formulas.

Example 37.27. To show such outputs, the listing command `\testmathversion` defined above is used after the declaration of `\mathversion{boldchem}`. The result is shown as follows:

Output A due to “boldchem”

$$\mathbf{abcdefghijklmnopqrstuvwxyz\imath\jmath ABCDEFGHIJKLMNOPQRSTUVWXYZ}$$

$$\boldsymbol{\alpha\beta\gamma\delta\epsilon\zeta\eta\theta\iota\kappa\lambda\mu\nu\xi\pi\rho\sigma\tau\upsilon\phi\chi\psi\omega\varepsilon\vartheta\varpi\varrho\varsigma\varphi\Gamma\Delta\Theta\Lambda\Xi\Pi\Sigma\Upsilon\Phi\Psi\Omega}$$

$$\mathbf{1234567890}$$

$$\mathbf{1234567890}$$

$$\boldsymbol{\mathcal{ABCDEFGHIJKLMNOPQRSTUVWXYZ}}$$

$$\boldsymbol{\int\sum\prod\coprod\bigcup\bigcap\bigodot\bigoplus\biguplus\bigotimes}$$

$$\boldsymbol{(,),[,],?,!,\{,\},=,¿\ (>),¡\ (<),\leftharpoondown,\rightharpoondown,\rightharpoonup,\leftharpoonup,\ell,\wp,\partial,\flat,\natural,\sharp,\triangleleft,\triangleright,\smile,\frown,\star,+,-}$$

$$\boldsymbol{\check{x},\check{x},\dot{x},\vec{x},\acute{x},\grave{x},\ddot{x},\bar{x},\tilde{x},\hat{x},\widetilde{x},\widehat{x}}$$

□

As found in the first line of Output A due to “boldchem”, lowercase and uppercase alphabets are typeset in boldfaced upright fonts except $\imath$ and $\jmath$.

Note that the symbols $<$ and $>$ are not properly typeset if they are input directly. The commands `$\mathless$` and `$\mathgreater$` should be used to give correct printing.

Example 37.28. To test `equation` and `eqnarray` environments under the math version “boldchem”, the above-defined command `\testequation` is again used here, although the resulting output is contrary to mathematical conventions:

Output B due to “boldchem”

Euler’s summation (`equation`):

$$\sum_{a\leq k\mathrm{i}b} \mathrm{f(k)} = \int_{\mathrm{a}}^{\mathrm{b}} \mathrm{f(x)dx} + \sum_{\mathrm{k=1}}^{\mathrm{m}} \frac{\mathrm{B_k}}{\mathrm{k!}} \mathrm{f^{(k-1)}(x)}\Big|_{\mathrm{a}}^{\mathrm{b}} + \mathrm{R_m}. \tag{37.74}$$

The term $\mathrm{R_m}$ is represented as follows (`eqnarray`):

$$\begin{aligned} \mathrm{R_m} &= (-1)^{\mathrm{m+1}} \int_{\mathrm{a}}^{\mathrm{b}} \frac{\mathrm{B_m(\{x\})}}{\mathrm{m!}} \mathrm{f^{(m)}(x)dx}, \\ &\quad \mathrm{a} \leq \mathrm{b} \text{ and } \mathrm{m} \geq 1, \end{aligned} \tag{37.75}$$

where the symbols a, b, and m represent integers.

□

Note that the symbols $<$ and $>$ are not properly typeset if they are input directly. Thus, the symbol $<$ in the lower limit of the above summation is erroneously replaced by the symbol ¡. The commands `$\mathless$` and `$\mathgreater$` should be used to give correct printing. For example, the code:

```
\[\sum_{a\leq k \mbox{\scriptsize $\mathless$} b}f(k)\]
```

gives the following output:

$$\sum_{a\leq k<b} \mathrm{f(k)}$$

Because this output does not meet mathematical conventions, it should be written as follows:

```
{\mathversion{bold}
\[\sum_{a\leq k < b}f(k)\]
}
```

which gives the following output:

$$\sum_{\boldsymbol{a\leq k<b}} \boldsymbol{f(k)}$$

Environments and Commands for Chemistry

Under the math version “boldchem”, alphabets in a math mode (such as an `equation` or `eqnarray` environment) are typeset by using upright fonts.

Example 37.29. Thus the test command `\testequationforchemistry` defined above gives the following output, which meets chemical requirements.

Output C due to “boldchem”

An `equation` environment:

$$\mathbf{2H_2 + O_2 \rightarrow 2H_2O} \tag{37.76}$$

An `eqnarray` environment:

$$\begin{aligned} \mathbf{C + O_2} &\rightarrow \mathbf{CO_2} && (37.77) \\ \mathbf{Na^+ + Cl^-} &\rightarrow \mathbf{NaCl\downarrow} && (37.78) \end{aligned}$$

□

Under the math version “boldchem”, alphabets in a `chemeqn` environment etc. are typeset by using upright fonts (not boldfaced).

Example 37.30. Thus the test command `\testchemequation` defined above gives the following output, which is equivalent to the above output of the math version “chem”.

Output D due to “boldchem”

A `chemeqn` environment:

$$2\mathrm{H}_2 + \mathrm{O}_2 \rightarrow 2\mathrm{H}_2\mathrm{O} \tag{37.79}$$

$$\mathrm{abcdefghijklmnopqrstuvwxyz}\imath\jmath\mathrm{ABCDEFGHIJKLMNOPQRSTUVWXYZ} \tag{37.80}$$

$$\alpha\beta\gamma\delta\epsilon\zeta\eta\theta\iota\kappa\lambda\mu\nu\xi\pi\rho\sigma\tau\upsilon\phi\chi\psi\omega\varepsilon\vartheta\varpi\varrho\varsigma\varphi\Gamma\Delta\Theta\Lambda\Xi\Pi\Sigma\Upsilon\Phi\Psi\Omega \tag{37.81}$$

A `chemeqnarray` environment:

$$\begin{aligned} \mathrm{C} + \mathrm{O}_2 &\rightarrow \mathrm{CO}_2 && (37.82)\\ \mathrm{Na}^+ + \mathrm{Cl}^- &\rightarrow \mathrm{NaCl}\downarrow && (37.83) \end{aligned}$$

A `chemeqnarray*` environment:

$$\begin{aligned} \mathrm{C} + \mathrm{O}_2 &\rightarrow \mathrm{CO}_2\\ \mathrm{Na}^+ + \mathrm{Cl}^- &\rightarrow \mathrm{NaCl}\downarrow \end{aligned}$$

In-text chemical formulas: $2\mathrm{H}_2 + \mathrm{O}_2 \rightarrow 2\mathrm{H}_2\mathrm{O}$ and $\mathrm{C} + \mathrm{O}_2 \rightarrow \mathrm{CO}_2$

□

In contrast, `ChemEquation`, `ChemEqnarray`, and `ChemEqnarray*` environments as well as a `\ChemForm` command typeset boldfaced alphabets of upright shape under the math version “boldchem”.

Example 37.31. Thus the test command `\testChemEquation` defined above gives the following output, which is equivalent to the corresponding output of the math version “bold’.

Output E due to “boldchem”

A `ChemEquation` environment:

$$\mathbf{2H_2 + O_2 \rightarrow 2H_2O} \tag{37.84}$$

$$\mathbf{abcdefghijklmnopqrstuvwxyz}\imath\jmath\mathbf{ABCDEFGHIJKLMNOPQRSTUVWXYZ} \tag{37.85}$$

$$\boldsymbol{\alpha\beta\gamma\delta\epsilon\zeta\eta\theta\iota\kappa\lambda\mu\nu\xi\pi\rho\sigma\tau\upsilon\phi\chi\psi\omega\varepsilon\vartheta\varpi\varrho\varsigma\varphi\Gamma\Delta\Theta\Lambda\Xi\Pi\Sigma\Upsilon\Phi\Psi\Omega} \tag{37.86}$$

A `ChemEqnarray` environment:

$$\begin{aligned} \mathbf{C + O_2} &\rightarrow \mathbf{CO_2} && (37.87)\\ \mathbf{Na^+ + Cl^-} &\rightarrow \mathbf{NaCl}\downarrow && (37.88) \end{aligned}$$

A `ChemEqnarray*` environment:

$$\begin{aligned} \mathbf{C + O_2} &\rightarrow \mathbf{CO_2}\\ \mathbf{Na^+ + Cl^-} &\rightarrow \mathbf{NaCl}\downarrow \end{aligned}$$

In-text chemical formulas: $\mathbf{2H_2 + O_2 \rightarrow 2H_2O}$ and $\mathbf{C + O_2 \rightarrow CO_2}$

□

Part IX

Coloring Chemical Compounds and Reaction Schemes

Chapter 38

Coloring Substituents and Substitution Bonds

38.1 Commands for Colors

38.1.1 Base Colors for the XymTEX System

Any of the three modes of the XymTEX system (the TEX/LATEX-compatible mode, the PDF-compatible mode, and the PostScript-compatible mode) automatically calls the xcolor package for coloring objects included in documents. For the purpose of coloring structural formulas drawn by the XymTEX system, it is recommended to select the PDF-compatible mode (`\usepackage{xymtexpdf}`) or the PostScript-compatible mode) (`\usepackage{xymtexps}`).

```
\documentclass{article}
\usepackage{xymtexpdf}%PDF-compatible mode
%\usepackage{xymtexps}%PostScript-compatible mode
\begin{document}
(text)
\end{document}
```

Because the PostScript-compatible mode of the XymTEX system (called by `\usepackage{xymtexps}`) is based on the PSTricks package, such commands as `\red`, `\green`, and `\blue` are defined to generate colored objects, e.g., Red by declaring `{\red Red}`. On the other hand, the pgf package, which is used as a graphical tool in the PDF-compatible mode of the XymTEX system (called by `\usepackage{xymtexpdf}`), lacks these direct commands. Instead of these direct commands, the `\color` command of the xcolor package is used, because the pgf package calls the xcolor package internally as a coloring tool. For example, the code `{\color{red} Red}` generates Red.

For the sake of compatibility, several direct commands are defined for the PDF-compatible mode of the XymTEX system (Table 38.1). Thereby, the codes `{\red Red},{\green Green},and {\blue Blue}` in the PDF-compatible mode generate colored objects such as Red, Green, and Blue in a parallel way to the PostScript-compatible mode.

In addition to the direct commands (declaration-type commands), commands taking an argument (command-type commands), whose names have a suffix '`x`', are also defined as listed in Table 38.1.

38.1.2 Additional Colors

The xcolor package supports further base colors. For example, the code `{\color{brown} Brown}` prints out Brown, where `\color` is a command defined in the xcolor package. Because the XymTEX system automatically loads the xcolor package, these base colors can be used to draw chemical structural formulas by using the `\color` command.

Table 38.1. Declarations and Commands for Coloring Chemical Objects (Base Colors)

declaration-type		command-type	
code	output	code	output
`{\red Red}`	Red	`\redx{Red}`	Red
`{\green Green}`	Green	`\greenx{Green}`	Green
`{\blue Blue}`	Blue	`\bluex{Blue}`	Blue
`{\black Black}`	Black	`\blackx{Black}`	Black
`{\cyan Cyan}`	Cyan	`\cyanx{Cyan}`	Cyan
`{\yellow Yellow}`	Yellow	`\yellowx{Yellow}`	Yellow
`{\magenta Magenta}`	Magenta	`\magentax{Magenta}`	Magenta
`{\white White}`	White	`\whitex{White}`	White

These base colors can be converted into declaration-type commands for using in combination with the XeLaTeX system:

```
\def\brown{\color{brown}}
\def\darkgray{\color{darkgray}}
\def\gray{\color{gray}}
\def\lightgray{\color{lightgray}}
\def\lime{\color{lime}}
\def\olive{\color{olive}}
\def\orange{\color{orange}}
\def\pink{\color{pink}}
\def\purple{\color{purple}}
\def\teal{\color{teal}}
\def\violet{\color{violet}}
```

These definitions should be declared in the preamble of a document to be prepared. Examples of these newly-defined commands of declaration-type are collected in the left-hand column of Table 38.2.

Table 38.2. Declarations and Commands for Coloring Chemical Objects (Additional Colors)

declaration-type		command-type	
code	output	code	output
`{\brown Brown}`	Brown	`\brownx{Brown}`	Brown
`{\darkgray Darkgray}`	Darkgray	`\darkgrayx{Darkgray}`	Darkgray
`{\gray Gray}`	Gray	`\grayx{Gray}`	Gray
`{\lightgray Lightgray}`	Lightgray	`\lightgrayx{Lightgray}`	Lightgray
`{\lime Lime}`	Lime	`\limex{Lime}`	Lime
`{\olive Olive}`	Olive	`\olivex{Olive}`	Olive
`{\orange Orange}`	Orange	`\orangex{Orange}`	Orange
`{\pink Pink}`	Pink	`\pinkx{Pink}`	Pink
`{\purple Purple}`	Purple	`\purplex{Purple}`	Purple
`{\teal Teal}`	Teal	`\tealx{Teal}`	Teal
`{\violet Violet}`	Violet	`\violetx{Violet}`	Violet

In addition to the commands of declaration-type, commands taking an argument (commands of command-type), whose names have a suffix '`x`', can be defined as follows:

```
%\def\xymcolor#1#2{\mbox{\color{#1}#2}}%defined in bondcolor package
\def\brownx#1{\xymcolor{brown}{#1}}
\def\darkgrayx#1{\xymcolor{darkgray}{#1}}
\def\grayx#1{\xymcolor{gray}{#1}}
\def\lightgrayx#1{\xymcolor{lightgray}{#1}}
\def\limex#1{\xymcolor{lime}{#1}}
\def\olivex#1{\xymcolor{olive}{#1}}
```

```
\def\orangex#1{\xymcolor{orange}{#1}}
\def\pinkx#1{\xymcolor{pink}{#1}}
\def\purplex#1{\xymcolor{purple}{#1}}
\def\tealx#1{\xymcolor{teal}{#1}}
\def\violetx#1{\xymcolor{violet}{#1}}
```

These definitions should be declared in the preamble of a document to be prepared. Examples of these newly-defined commands of command-type are shown in the right-hand column of Table 38.2.

The command `\color` of the xcolor package is capable of defining a color explicitly with respect to a given color model, e.g.,

```
{\color[cmyk]{0,0.5,0.5,0}explict CMYK}   explicit CMYK
{\color[gray]{0.1} explict gray}          explicit gray
```

where `cmyk` and `gray` are color models at issue.

In place of such a explicit specification, you can define new color commands, `MyColor` (declaration-type) and `MyColorx` (command-type):

```
\def\MyColor{\color[cmyk]{0,0.5,0.5,0}}
\def\MyColorx#1{\mbox{\color[cmyk]{0,0.5,0.5,0}#1}}
```

These commands are used as follows:

```
{\MyColor CMYK}   CMYK
\MyColorx{CMYK}   CMYK
```

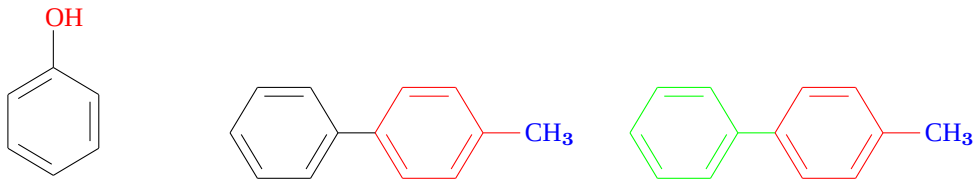
38.2 Coloring Substituents

To color a substituent, the substituent is designated in a ⟨subslist⟩ (substitution list) by adding an appropriate command of coloring.

Example 38.1. For example, the codes:

```
\bzdrv{1==\red OH}}
\bzdrh{4==\red \bzdrh{1==(yl);4==\blue CH$_{3}$}}}} \hskip60pt
{\green \bzdrh{4==\red \bzdrh{1==(yl);4==\blue CH$_{3}$}}}}}
```

produce the following structures:



where the phenyl group designated by a (yl) function is regarded as a substituent to be colored. □

Note

The use of `dvipdfmx` in processing the resulting dvi files containing these coloring codes may result in the appearance of a warning:

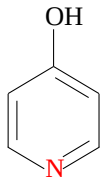
```
** WARNING ** Color stack underflow. Just ignore.
```

In spite of this warning, we can obtain the correct printing of structural formulas. So we just ignore this warning.

(Remarks) Because the above examples involve four troublesome declaration-type commands (except `\green`) in respective arguments ⟨subslist⟩, there appear four warnings of "`Color stack underflow`". In contrast, the warning of "`Color stack underflow`" does not appear when a declaration-type command (e.g., `\red`) is used in the ⟨atomlist⟩ of `\sixheterov`. For example, the code

```
\sixheterov[ace]{4=={\red N}}{1==OH}
```

produces the following structural formula:

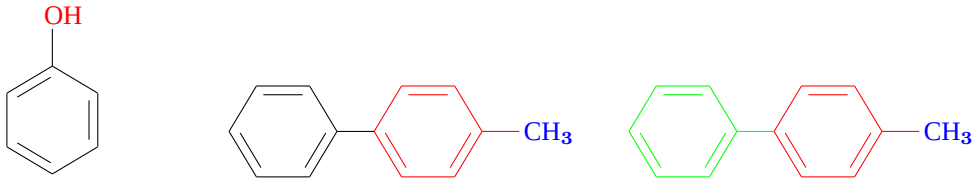


where no warning of “`Color stack underflow`” appears during a conversion process by `dvipdfmx`.

Example 38.2. To avoid the warning of “`Color stack underflow`”, the command `\mbox` is effective as shown below:

```
\bzdrv{1==\mbox{\red OH}}
\bzdrh{4==\mbox{\red \bzdrh{1==(yl);4==\mbox{\blue CH$_{3}$}}}} \hskip60pt
{\green \bzdrh{4==\mbox{\red \bzdrh{1==(yl);4==\mbox{\blue CH$_{3}$}}}}}
```

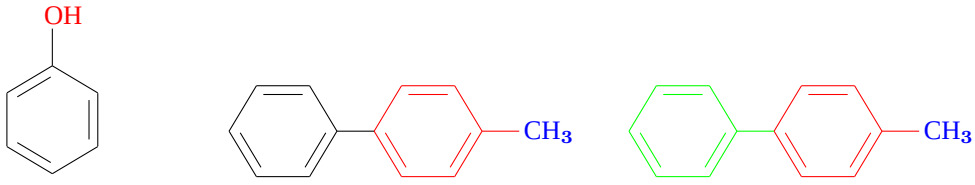
These codes produce the following structures without the warning:



□

Example 38.3. The commands with the suffix ‘`x`’ (Table 38.1) are effective to avoid such a warning even in a case of using ⟨subslist⟩, because these commands contain the command `\mbox` in their definitions (cf. the definition of `\xymcolor` cited above from the bondcolor package). The codes shown above are rewritten as follows:

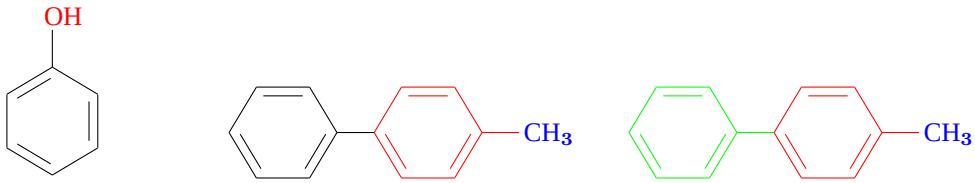
```
\bzdrv{1==\redx{OH}}
\bzdrh{4==\redx{\bzdrh{1==(yl);4==\bluex{CH$_{3}$}}}} \hskip60pt
\greenx{\bzdrh{4==\redx{\bzdrh{1==(yl);4==\bluex{CH$_{3}$}}}}}
```



□

Example 38.4. The command `\textcolor` supported by the xcolor package is also effective to avoid the warning of ‘`Color stack underflow`’.

```
\bzdrv{1==\textcolor{red}{OH}}
\bzdrh{4==\textcolor{red}{\bzdrh{1==(yl);4==\textcolor{blue}{CH$_{3}$}}}}
\hskip60pt
\textcolor{green}{\bzdrh{4==\textcolor{red}{\bzdrh{1==(yl);%
4==\textcolor{blue}{CH$_{3}$}}}}}
```



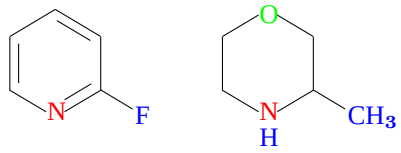
□

A hetero atom in a heterocycle can be colored by adding an appropriate command of coloring.

Example 38.5. For example, the codes:

```
\sixheterovi[ace]{1==\redx{N}}{2==\bluex{F}}
\sixheterovi{1==\downnobond{\redx{N}}{\bluex{H}};%
4==\green{O}}{2==\bluex{CH$_{3}$}}
```

produces the following structure:



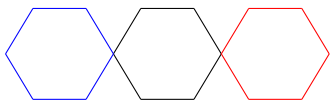
□

Parts of a spiro ring can be colored by adding appropriate commands of coloring in the atomlist.

Example 38.6. For example, the code:

```
\sixheteroh{4s==\redx{\sixheteroh{}{1==(yl)}};%
1s==\bluex{\sixheteroh{}{4==(yl)}}}{}
```

produces the following structure:

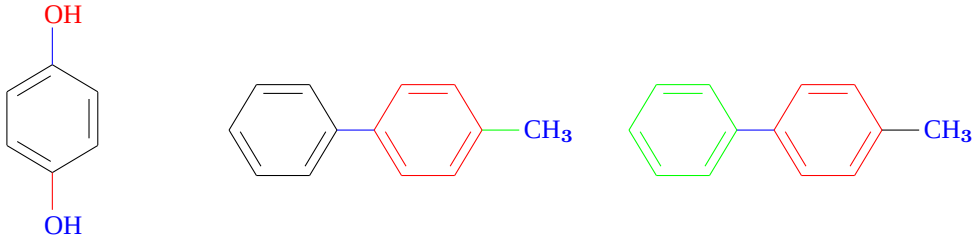


□

In most cases, the color of a substitution bond can be differentiated from the color of the corresponding substituent by using the `\aftergroup` command.

Example 38.7. The formulas drawn above are modified by this technique as follows:

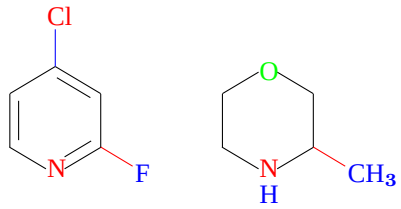
```
\bzdrv{1=={\redx{OH}\aftergroup\blue};4=={\bluex{OH}\aftergroup\red}}
\bzdrh{4=={\redx{\bzdrh{1==(yl);%
4=={\bluex{CH$_{3}$}\aftergroup\green}}}\aftergroup\blue}} \hskip60pt
\greenx{\bzdrh{4=={\redx{\bzdrh{1==(yl);%
4=={\bluex{CH$_{3}$}\aftergroup\black}}}\aftergroup\blue}}}
```



It should be noted that the above codes avoid the warning of '`Color stack underflow`' by declaring `{\redx{OH}\aftergroup\blue}` etc. in place of `{\red\aftergroup\blue OH}` etc, where `\redx` for coloring a substituent is used in place of `\red`, while `\blue` for coloring a bond is used as it is. □

Example 38.8. On the same line, we obtain the following printing of structural formulas, where the color of a substitution bond is differentiated from that of the corresponding substituent.

```
\sixheterovi[ace]{1==\redx{N}}{2=={\bluex{F}\aftergroup\red};%
4=={\redx{Cl}\aftergroup\blue}}
\sixheterovi{1==\downnobond{\redx{N}}{\bluex{H}};4==\greenx{O}}%
{2=={\bluex{CH$_{3}$}\aftergroup\red}}
```



□

38.3 Coloring Substitution Bonds

38.3.1 Systematic Method for Coloring Substitution Bonds

The bondcolor package automatically loaded by the XeLaTeX system (version 5.00 and later) supports the function of coloring substitution bonds. The command `\addbscolor` is defined to specify the color of a substitution bond. It has a format represented by

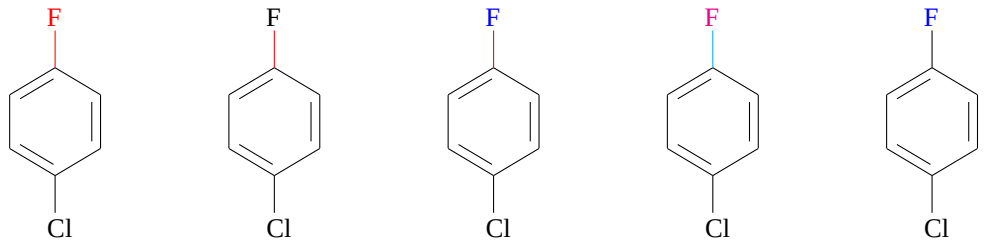
```
\addbscolor{⟨bondcolor⟩}{⟨substituent⟩}
```

where the argument ⟨bondcolor⟩ is a command for specifying color (e.g., `\red` or `\color{red}`) and the second argument ⟨substituent⟩ is a text or a set of commands for drawing a substituent.

Example 38.9. For example, the codes:

```
\bzdrv{1==\addbscolor{\red}{F};4==Cl}
\bzdrv{1==\addbscolor{\red}{\blackx{F}};4==Cl}
\bzdrv{1==\addbscolor{\red}{\bluex{F}};4==Cl}
\bzdrv{1==\addbscolor{\color{cyan}}{\magentax{F}};4==Cl}
\bzdrv{1==\bluex{F};4==Cl}
```

generate the following structural formulas:



The `\addbscolor` command changes the color of a substitution bond as well as that of a substitution, as shown in the first example. If a substitution bond is desired to be solely changed, `\blackx{F}` should be declared as the second argument, as shown in the second example. The third example shows the separate change of the colors of a substitution bond and a substituent. The fourth example shows the use of the `color` command. The last example shows a case in which a substituent is solely changed. □

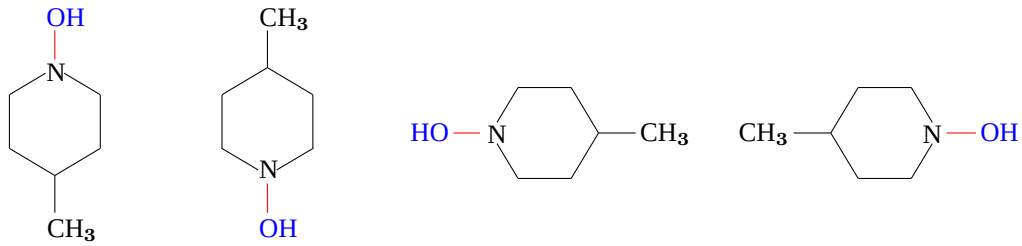
38.3.2 Examples

Other commands defined by the carom package of the XeLaTeX system are also colored by the systematic methods. More low-level commands defined by the hetarom and hetaromh packages of the XeLaTeX system can be colored similarly.

Example 38.10. For example, a six-membered hydroxylamine is drawn in different ways by the codes:

```
\sixheterov{1==N}{1==\addbscolor{\red}{\bluex{OH}};4==CH$_{3}$}
\sixheterovi{1==N}{1==\addbscolor{\red}{\bluex{OH}};4==CH$_{3}$} \qquad
\sixheteroh{1==N}{1==\addbscolor{\red}{\bluex{HO}};4==CH$_{3}$} \qquad\qquad
\sixheterohi{1==N}{1==\addbscolor{\red}{\bluex{OH}};4==CH$_{3}$}
```

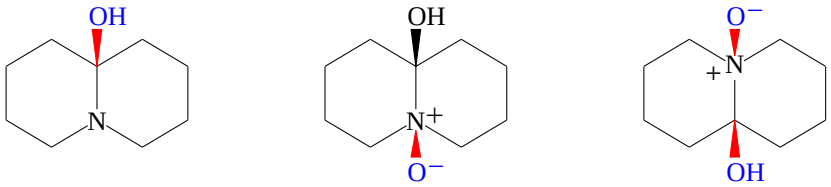
which generate the following structures:



□

Example 38.11. Substitution bonds in fused rings can be colored by the systematic method as follows:

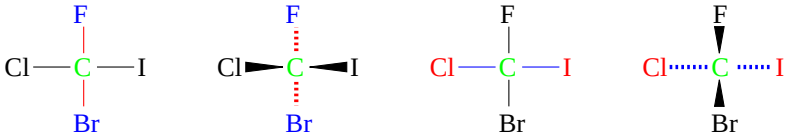
```
\decaheterov{9==N}{{10}B==\addbscolor{\red}{\bluex{OH}}}
\decaheterov{9==N\rlap{$^{+}$}}%
{9B==\addbscolor{\red}{\bluex{O$^{-}$}};{10}B==OH}
\decaheterov[{{10}+}]{{{10}}==N}{9B==\addbscolor{\red}{\bluex{OH}};
{10}B==\addbscolor{\red}{\bluex{O{\normalsize $^{-}$}}}}
```



□

Example 38.12. Commands defined by the aliphat package are also colored by the systematic methods. The following commands shows colored structures produced by `\tetrahedral` command.

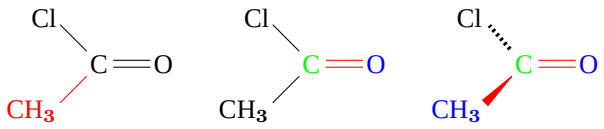
```
\tetrahedral{0==\greenx{C};
1==\addbscolor{\red}{\bluex{F}};%
2==Cl;3==\addbscolor{\red}{\bluex{Br}};4==I} \qquad
\tetrahedral{0==\greenx{C};
1A==\addbscolor{\red}{\bluex{F}};%
2B==Cl;3A==\addbscolor{\red}{\bluex{Br}};4B==I} \qquad
\tetrahedral{0==\greenx{C};1==F;%
2==\addbscolor{\blue}{\redx{Cl}};
3==Br;4==\addbscolor{\blue}{\redx{I}}} \qquad
\tetrahedral{0==\greenx{C};1B==F;2A==\addbscolor{\blue}{\redx{Cl}};%
3B==Br;4A==\addbscolor{\blue}{\redx{I}}}
```



□

Example 38.13. The following commands shows colored structures produced by `\ltrigonal` command.

```
\ltrigonal{0==C;1D==O;2==Cl;3==\addbscolor{\red}{CH$_{3}$}}\qquad
\ltrigonal{0==\greenx{C};1D==\addbscolor{\red}{\bluex{O}};2==Cl;3==CH$_{3}$}\qquad
\ltrigonal{0==\greenx{C};1D==\addbscolor{\red}{\bluex{O}};2A==Cl;%
3B==\addbscolor{\red}{\bluex{CH$_{3}$}}}
```

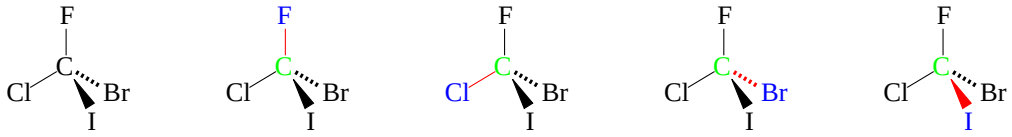


□

Example 38.14. Wedged and dashed bonds for stereochemistry can be colored by the systematic way. For example, the codes:

```
\DtetrahedralS{0==C;1==F;
2==Cl;3A==Br;4B==I} \qquad
\DtetrahedralS{0==\greenx{C};
1==\addbscolor{\red}{\bluex{F}};
2==Cl;3A==Br;4B==I} \qquad
\DtetrahedralS{0==\green{C};1==F;
2==\addbscolor{\red}{\bluex{Cl}};3A==Br;4B==I} \qquad
\DtetrahedralS{0==\green{C};1==F;
2==Cl;3A==\addbscolor{\red}{\bluex{Br}};4B==I} \qquad
\DtetrahedralS{0==\greenx{C};1==F;
2==Cl;3A==Br;4B==\addbscolor{\red}{\bluex{I}}}
```

produce the following colored structures:

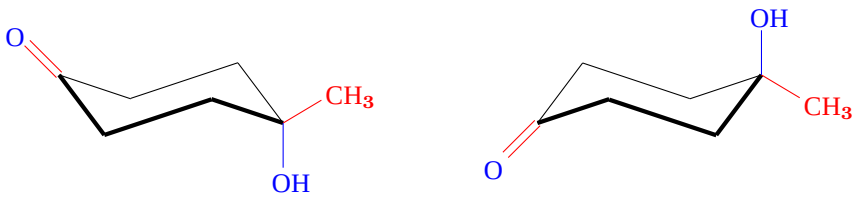


□

Example 38.15. The commands `\chair` and `\chairi` defined in the ccycle package of the XeLaTeX system support a systematic method of coloring substitution bonds. For example, the following code:

```
\chair{1D==\addbscolor{\red}{\bluex{O}};%
4Se==\addbscolor{\red}{CH$_{3}$};4Sa==\addbscolor{\blue}{OH}}\qquad
\chairi{1D==\addbscolor{\red}{\bluex{O}};%
4Se==\addbscolor{\red}{CH$_{3}$};4Sa==\addbscolor{\blue}{OH}}
```

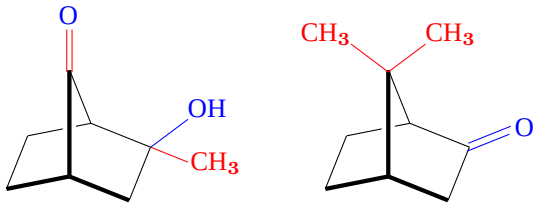
produces a colored structural formula:



□

Example 38.16. The command `\bornane` defined in the ccycle package of the XeLaTeX system also supports a systematic method of coloring substitution bonds.

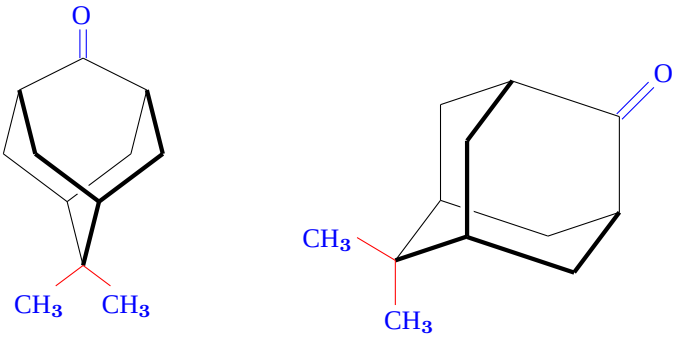
```
\bornane{7D==\addbscolor{\red}{\bluex{O}};%
2Sa==\addbscolor{\red}{CH$_{3}$};2Sb==\addbscolor{\blue}{OH}}\qquad
\bornane{7Sa==\addbscolor{\red}{CH$_{3}$};7Sb==\addbscolor{\red}{CH$_{3}$};%
2D==\addbscolor{\blue}{O}}
```



□

Example 38.17. The following examples show the coloring of substitution bonds by using the `\addbscolor` command in the arguments of the commands `\adamantane` and `\hadamantane`, which are defined in the ccycle package of the XyMTEX system.

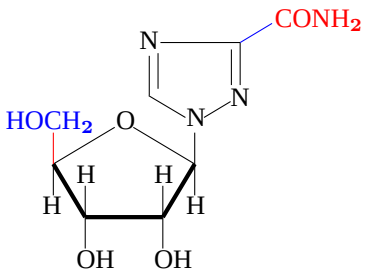
```
\adamantane{2D==\addbscolor{\blue}{O};%
6a==\addbscolor{\red}{\bluex{CH$_{3}$}};%
6b==\addbscolor{\red}{\bluex{CH$_{3}$}}} \qquad
\hadamantane{2D==\addbscolor{\blue}{O};%
6a==\addbscolor{\red}{\bluex{CH$_{3}$}};%
6b==\addbscolor{\red}{\bluex{CH$_{3}$}}}
```



□

Example 38.18. Substitution bonds in a furanose derivative drawn by the command `\furanose` (defined in the hcycle package of the XyMTEX system) can be colored by using the `\addbscolor` command. By applying the method to the example shown in Section 18.2, substitution bonds in the structural formula of ribavirin can be colored, as found in the following result:

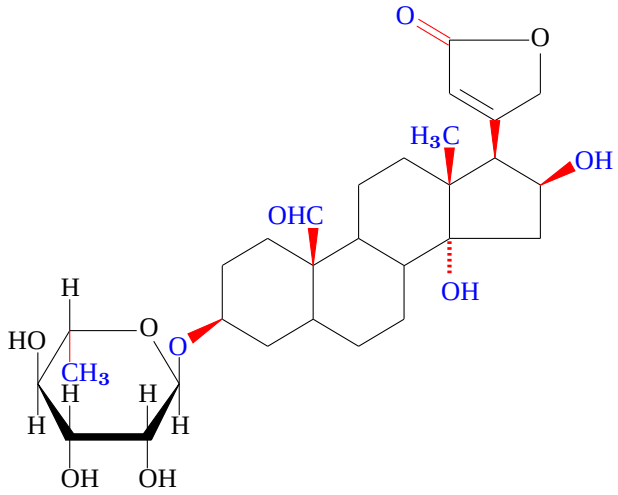
```
\begin{XyMcompd}(1200,1000)(100,0){}{}
\furanose{1Sa==H;2Sb==H;2Sa==OH;3Sb==H;3Sa==OH;4Sa==H;%
4Sb==\addbscolor{\red}{\bluex{HOC\rlap{H$_{2}$}}};
1Sb==\fiveheterov[bd]{1==N;2==N;4==N}{1==(yl);
3==\addbscolor{\blue}{\redx{CONH$_{2}$}}}}
\end{XyMcompd}
```



□

Example 38.19. The command `\pyranosew` defined in the hcycle package of the XyMTEX system supports a systematic method of coloring substitution bonds. The following example shows the use of `\black` in the second argument of the `\addbscolor` command in order to avoid the coloring of a furan skeleton due to `\fiveheterov` and the coloring of a pyranose skeleton due to `\pyranosew`.

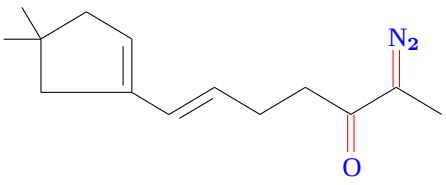
```
\begin{XyMcompd}(2100,1800)(-500,-280){}{}
\steroid{{10}B==\addbscolor{\red}{\bluex{\lmoiety{OHC}}};%
{14}A==\addbscolor{\red}{\bluex{OH}};%
{13}B==\addbscolor{\red}{\bluex{\lmoiety{H$_{3}$C}}};%
{16}B==\addbscolor{\red}{\bluex{OH}};%
{17}B==\addbscolor{\red}{\blackx{%
\fiveheterov[e]{3==O}{4D==\addbscolor{\red}{\bluex{O}};1==(yl)}}};%
3B==\addbscolor{\red}{\blackx{\lyl(3==\bluex{O}){8==%
\pyranosew{1Sb==(yl);1Sa==H;2Sb==H;2Sa==OH;3Sb==H;3Sa==OH;4Sb==HO;%
4Sa==H;5Sb==H;5Sa==\addbscolor{\red}{\bluex{CH$_{3}$}}}}}}}}
\end{XyMcompd}
```



□

Example 38.20. Substitution bonds of polymethylene units defined in the methylene package of the XyMTEX system can be colored by using the `\addbscolor` command. The following structure is drawn by this technique applied to the command `\heptamethylene`.

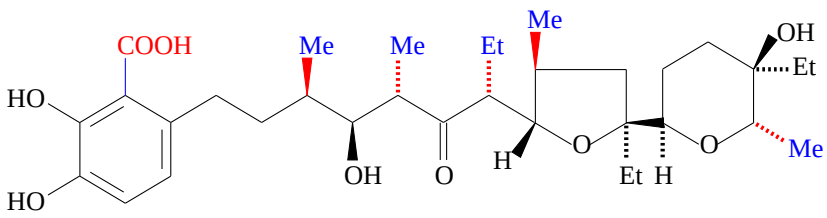
```
\heptamethylene[a]{}{1W==\cyclopentanevi[b]{3==(yl);5Sa==\null;5Sb==\null};%
5D==\addbscolor{\red}{\bluex{O}};6D==\addbscolor{\red}{\bluex{N$_{2}$}}}
```



□

Example 38.21. On a similar line, the following structure is drawn by this technique applied to the command `\nonamethylene`.

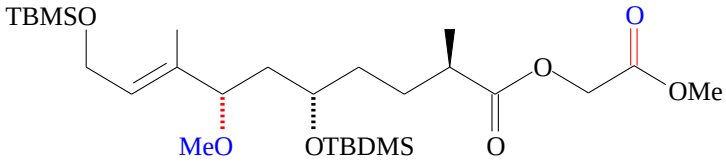
```
\nonamethylene{%
1s==\bzdrv{1==\addbscolor{\blue}{\redx{COOH}};2==(yl);5==HO;6==HO};%
9s==\fiveheterov{1==O}{5==(yl);5SB==H;%
4GB==\addbscolor{\red}{\bluex{Me}};2GA==Et;%
2Su==\sixheterovi{1==O}{6==(yl);6FA==H;3SB==OH;3SA==Et;%
2A==\addbscolor{\red}{\bluex{Me}}}}}%
{4B==\addbscolor{\red}{\bluex{Me}};5B==OH;%
6A==\addbscolor{\red}{\bluex{Me}};7D==O;8A==\addbscolor{\red}{\bluex{Et}}}
```



□

Example 38.22. Further, the following structure is drawn by this technique applied to the command `\decamethylenei`.

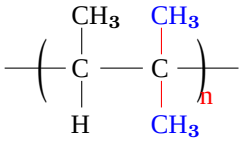
```
\decamethylenei[b]{}{1==\lmoiety{TBMSO};3==\null;%
4A==\addbscolor{\red}{\bluex{\lmoiety{MeO}}};6A==OTBDMS;%
9B==\null;{10}D==O;%
{10}W==\trimethylenei{1==O}{1==(yl);%
3D==\addbscolor{\red}{\bluex{O}};3W==OMe}}
```



□

Example 38.23. The command `\polyethylene` defined in the polymers package of the XyMTEX system supports this technique of bond coloring, as shown in the following example:

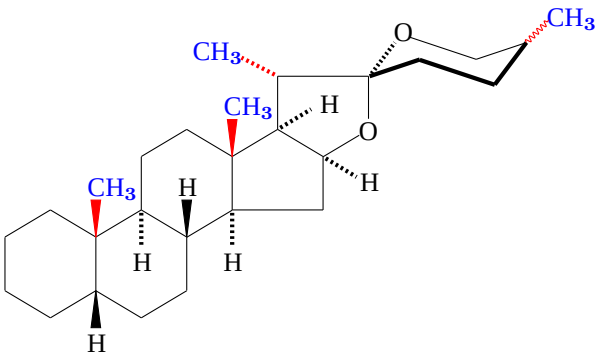
```
\polyethylene{1==C;2==C}%
{1==CH$_{3}$;2==;3==H;4==\addbscolor{\red}{\bluex{CH$_{3}$}};%
5==;6==\addbscolor{\red}{\bluex{CH$_{3}$}};0==\redx{n}}
```



□

Example 38.24. Substitution bonds in a spiro pyranose ring due to `\pyranoseChairi` (defined in the steroid package of the XyMTEX system) as well as in a fused furan ring due to `\fivefusev` are colored by using the `\addbscolor` command, as found in the following example. Note that the bond coloring technique applied to these commands works well even when they are designated in the ⟨bondlist⟩ argument of the command `steroid`.

```
\begin{XyMcompd}(2200,1350)(200,150){}{}
\steroid[%
{s{\fivefusev{2==O;%
3s==\mbox{\changeunitlength{0.07pt}%
\pyranoseChairi{1==(yl);%
4U==\addbscolor{\red}{\bluex{\normalsize CH$_{3}$}}}}}%
{4A==\addbscolor{\red}{\bluex{CH$_{3}$}}}{e}%
}}]{5B==H;{10}B==\addbscolor{\red}{\bluex{CH$_{3}$}};
8B==H;9A==H;{13}B==\addbscolor{\red}{\bluex{CH$_{3}$}};
{14}A==H;{17}GA==H;{16}GA==H}
\end{XyMcompd}
```



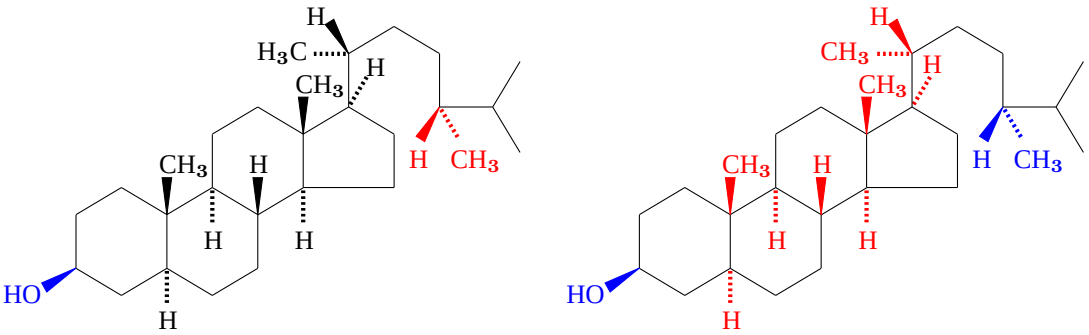
It should be emphasized that wedged bonds, dashed bold bonds, and wavy bonds for stereochemistry are colored by the same technique of bond coloring due to the `\addbscolor` command. □

Commands of high level have a fixed set of substituents, which are not changed by the systematic method described here. For the purpose of coloring the fixed set, you should use the corresponding commands of low level.

Example 38.25. For example, the high-level command `\cholestanealpha` is compared with the low-level command `\steroidchain` as follows:

```
\begin{tabular}{ll}
high-level macro: & low-level macro: \\
\cholestanealpha{3B==\addbscolor{\blue}{HO};
{24}SA==\addbscolor{\red}{CH$_{3}$};{24}SB==\addbscolor{\red}{H}}
&
\steroidchain{3B==\addbscolor{\blue}{HO};
{24}SA==\addbscolor{\blue}{CH$_{3}$};{24}SB==\addbscolor{\blue}{H};
5A==\addbscolor{\red}{H};
8B==\addbscolor{\red}{H};
9A==\addbscolor{\red}{H};
{10}B==\addbscolor{\red}{CH$_{3}$};
{13}B==\addbscolor{\red}{CH$_{3}$};
{14}A==\addbscolor{\red}{H};
{17}SA==\addbscolor{\red}{\raisebox{-3pt}{H}};
{20}SA==\addbscolor{\red}{CH$_{3}$};{20}SB==\addbscolor{\red}{H}}
\\
\end{tabular}
```

high-level macro: low-level macro

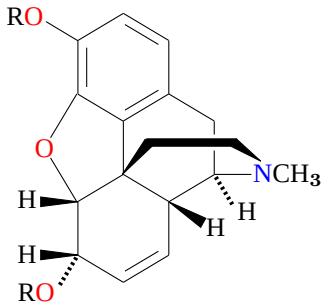


Note that the black bonds in the left structure (or the red bonds in the right structure) indicate the fixed set of substituents for the `\cholestanealpha` command of high level. □

Example 38.26. The fused structure **38-1** of morphine (or heroin) is drawn by the scheme 6 ← 6 ← 6 according to the addition technique. A furan ring and a piperidine ring are added by respective sets of low-level commands such as `\PutBondLine` and `\WedgeAsSubstX`. Hetero atoms (O and N) in morphine **38-1a**

(and in heroin **38-1b**) are colored in a similar way. A white bold line is drawn by \PutBondLine to erase a background bond.

```
\begin{tabular}{lll}
\multicolumn{3}{c}{%
\begin{XyMcompd}(1050,1200)(0,150){}{}
\sixheterov[c%
{a\sixfusev[%
{f\sixfusev[ace]{5s==\PutBondLine(0,0)(-99,-165){0.4pt}}{6==R\redx{O}}{C}}%
]{%
5s==\WedgeAsSubstX(0,0)(100,120)[12];%
5s==\whitex{\PutBondLine(300,120)(400,120){6pt}};%
5s==\PutBondLine(90,120)(432,120){3.2pt};%
3s==\WedgeAsSubstX(171,50)(71,120)[7]%
}{3Sa==\bluex{N}CH$_{3}$;3Sd==H}{D}}%
]{6s==\PutBondLine(0,0)(-99,165){0.4pt};%
6s==\put(-122,203){\makebox(0,0){\redx{O}}}%
}{2GB==H;5Su==H;5Sd==R\redx{O};6Su==H}
\end{XyMcompd}
}
\\
\nocompd\label{cpd:morhero}
\deriv\label{cpd:morphine} & R = H  & (morphine) \\
\deriv\label{cpd:heroin}   & R = COCH$_{3}$ & (heroin) \\
\end{tabular}
```



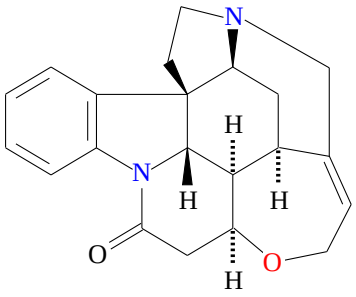
38-1a R = H (morphine)
38-1b R = $COCH_3$ (heroin)

□

Example 38.27. The fused structure **38-2** of strychnine is drawn by the scheme 6 → 6-5 ← 6 (← 7) according to the addition technique and an improper application of the replacement technique (for the seven-membered ring). The seven-membered ring is drawn by using the command \SevenCycle, which has been defined in Section 31.3. Distorted five-membered and six-membered rings are fused by using a low-level command \PutBondLine multiply. Nitrogen atoms (N) in **38-2** are colored in a similar way.

```
\begin{XyMcompd}(1200,1100)(280,-200){cpd:strychnine}{}
\nonaheterov[egj%
{a\sixfusev{6==\bluex{N};%
3s==\SevenCycle(0,0){-40}[d]{2==\redx{O}}[efg]}{2FA==H;3GA==H;5D==O}{f}}%
{b\sixfusev{%
%addition of a distorted 6-membered ring
3s==\PutBondLine(0,0)(188,-33){0.4pt};%
3s==\PutBondLine(188,-33)(188,300){0.4pt};%
3s==\PutBondLine(188,300)(-130,480){0.4pt};%
%addition of a distorted 5-membered ring
6s==\PutBondLine(-70,120)(-20,330){0.4pt};%
6s==\PutBondLine(-20,330)(140,290){0.4pt}%
}{1B==\bluex{N};6SB==\null;3GA==H}{e}[d]}
```

```
]{1==\null}{2GB==H}
\end{XyMcompd}
```



38-2 □

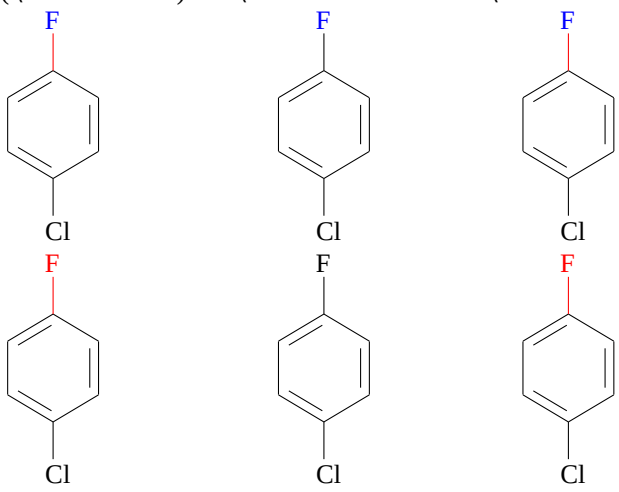
38.3.3 Switches for Coloring Substitution Bonds

The mechanism for coloring substitution bonds relies on a one-by-one procedure of testing whether or not the designation of each substituent contains the `\addbscolor` command. Because this mechanism works even if the `\addbscolor` command is not contained, there are occasionally cases which require prolonged processing times. In particular, multiple nesting of substituents causes such prolongation.

Example 38.28. For the purpose of skipping such prolonged bond coloring, the switch `\bscolorswOFF` is defined. The switch `\bscolorswON` is ready to return to the default mode of coloring.

```
\begin{tabular}{ccc}
default (\verb/\bscolorswON/) & \verb/\bscolorswOFF/ & \verb/\bscolorswON/ \\
\bzdrv{1==\addbscolor{\red}{\blue F};4==Cl} &
\bscolorswOFF \bzdrv{1==\addbscolor{\red}{\blue F};4==Cl} &
\bscolorswON \bzdrv{1==\addbscolor{\red}{\blue F};4==Cl} \\
\bzdrv{1==\addbscolor{\red}{F};4==Cl} &
\bscolorswOFF \bzdrv{1==\addbscolor{\red}{F};4==Cl} &
\bscolorswON \bzdrv{1==\addbscolor{\red}{F};4==Cl} \\
\end{tabular}
```

default (`\bscolorswON`) `\bscolorswOFF` `\bscolorswON`



It should be noted that the designation of each colored substituent (`\bluex{F}`) shown in the first row of structures results in the same effect during such switching of coloring. □

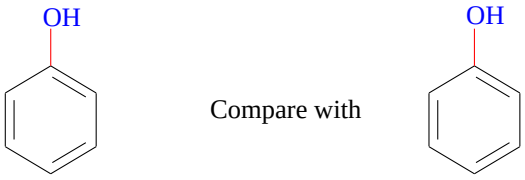
38.3.4 Dirty Techniques for Coloring Substitution Bonds

If no systematic routes to color substitution bonds have been defined with respect to your target command for drawing structures, rather dirty (but versatile) techniques should be tested case by case.

Example 38.29. For example, the \PutBondLine command is used to place a substitution bond, which is colored by adding an appropriate command of coloring. For the simplicity of explanation, let us use the examples described above to discuss such dirty techniques. For example, the codes:

```
\sixheterov[ace]{1s==\redx{\PutBondLine(0,0)(0,140){\thinLineWidth}};%
1s==\bluex{\put(-30,150){OH}}}{}
\qquad \raisebox{45pt}{Compare with}
\sixheterov[ace]{}{1==\addbscolor{\red}{\bluex{OH}}}
```

generate the following structures:

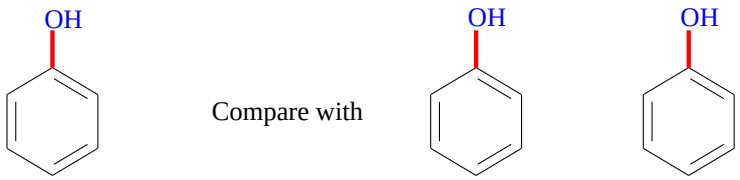


where the argument ⟨atomlist⟩ (the replacement technique) is used in place of the ⟨subslist⟩ (the substitution technique) in order to place the substitution bond at position 1. Compare the left formula with the right formula drawn by the systematic method of bond coloring. □

Example 38.30. By changing \thinLineWidth into \thickLineWidth, the substitution bond appears as a bold-line bond. The same effect can be brought about by the first argument {\red\dashhasheddash \thicklines} of the \addbscolor command. As found in the last example, the declaration of \dashhasheddash and 1B==... also produces an equivalent structure. The codes:

```
\sixheterov[ace]{1s==\redx{\PutBondLine(0,0)(0,140){\thickLineWidth}};%
1s==\bluex{\put(-30,150){OH}}}{}
\qquad \raisebox{45pt}{Compare with}
\sixheterov[ace]{}{1==\addbscolor{\red
\dashhasheddash
\thicklines}{\bluex{OH}}}
{\dashhasheddash
\sixheterov[ace]{}{1B==\addbscolor{\red}{\bluex{OH}}}}
```

generate the following structures:

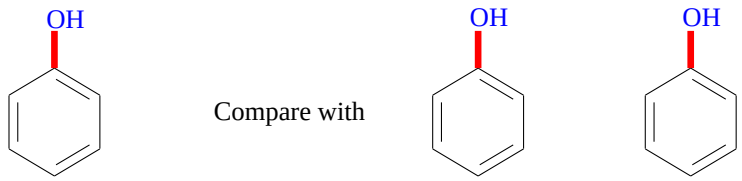


□

Example 38.31. The last argument of \PutBondLine is capable of accommodating a direct designation of bond width, as found in the following example (left). Note that \thinLineWidth is equal to 0.4pt and \thickLineWidth is equal to 1.6pt. As shown in the right example, the same effect is accomplished by designating the first argument of \addbscolor as {\red\dashhasheddash \def\thickLineWidth{2.5pt} \thicklines}. The last example shows that the declaration of \dashhasheddash and 1B==... also produces an equivalent structure if the thickness of bonds is changed by \thickLineWidth.

```
\sixheterov[ace]{1s=={\red \PutBondLine(0,0)(0,140){2.5pt}};%
1s==\bluex{\put(-30,150){OH}}}{}
\qquad \raisebox{45pt}{Compare with}
\sixheterov[ace]{}{1==\addbscolor{\red
\dashhasheddash\def\thickLineWidth{2.5pt}%
```

```
\thicklines}{\bluex{OH}}}
{\dashhasheddash\def\thickLineWidth{2.5pt}%
\sixheterov[ace]{}{1B==\addbscolor{\red}{\bluex{OH}}}}
```

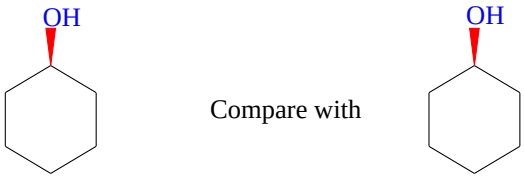


□

Example 38.32. The `\WedgeAsSubst` command is used to place a substitution bond, which is colored by adding an appropriate command of coloring. The systematic way of bond coloring supports this case as a standard usage.

```
\sixheterov{1s==\redx{\WedgeAsSubst(0,0)(0,1){140}};%
1s==\bluex{\put(-30,150){OH}}}{}
\qquad \raisebox{45pt}{Compare with}
\sixheterov{}{1B==\addbscolor{\red}{\bluex{OH}}}
```

generate the following structures:



□

Chapter 39

Coloring Skeletal Bonds and Double Bonds

39.1 Coloring Skeletal Bonds

39.1.1 Systematic Method for Coloring Skeletal Bonds

The bondcolor package of the XeLaTeX version 5.00 and later supports the function of coloring skeletal bonds. The command `\addskbcolor` is defined to specify the color of a skeletal bond, where it has a format represented by

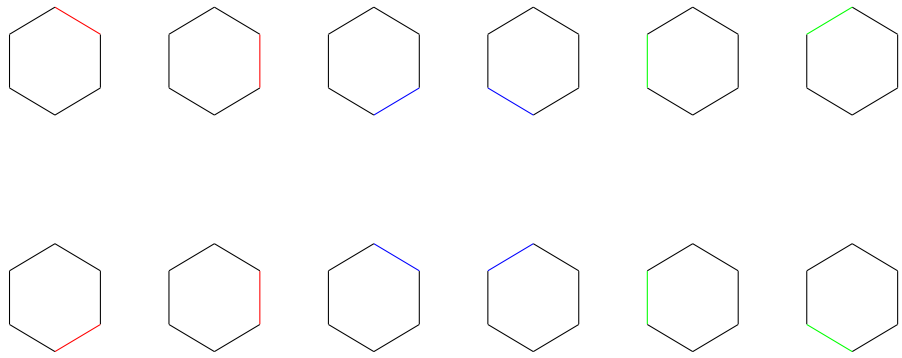
```
\addskbcolor{⟨commandsuffix⟩}{⟨skelbcolor⟩}
```

where the first argument ⟨commandsuffix⟩ is used to specify the vertical or horizontal type of a command. The vacant argument is the same thing as `v` for corresponding to commands of vertical types (suffix `v`) or of inverse vertical type (suffix `vi`). The second argument ⟨skelbcolor⟩ is a command for specifying color (e.g., `\red` or `\color{red}`). The `\addskbcolor` command is designated in the skeletal-bond list (⟨skelbdlist⟩) of each command for drawing a skeleton.

For example, the codes:

```
\sixheterov({a{\addskbcolor{}{\red}}}){}{}\hskip-20pt
\sixheterov({b{\addskbcolor{}{\red}}}){}{}\hskip-20pt
\sixheterov({c{\addskbcolor{}{\blue}}}){}{}\hskip-20pt
\sixheterov({d{\addskbcolor{}{\blue}}}){}{}\hskip-20pt
\sixheterov({e{\addskbcolor{}{\green}}}){}{}\hskip-20pt
\sixheterov({f{\addskbcolor{}{\green}}}){}{} \par
\sixheterovi({a{\addskbcolor{}{\red}}}){}{}\hskip-20pt
\sixheterovi({b{\addskbcolor{}{\red}}}){}{}\hskip-20pt
\sixheterovi({c{\addskbcolor{}{\blue}}}){}{}\hskip-20pt
\sixheterovi({d{\addskbcolor{}{\blue}}}){}{}\hskip-20pt
\sixheterovi({e{\addskbcolor{}{\green}}}){}{}\hskip-20pt
\sixheterovi({f{\addskbcolor{}{\green}}}){}{}
```

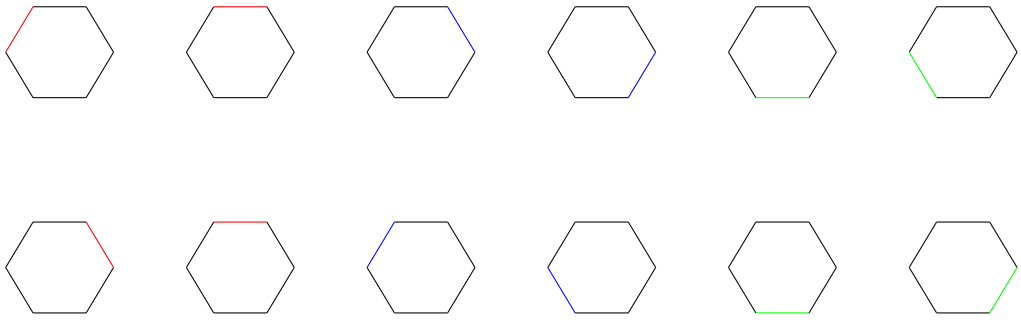
show the use of the `\addskbcolor` command in `\sixheterov` (vertical type) and `\sixheterovi` (inverse vertical type), which generate the following structures:



The use of the \addskbcolor command in \sixheteroh (horizontal type) and \sixheterohi (inverse horizontal type) is illustrated by the following codes:

```
\sixheteroh({a{\addskbcolor{h}{\red}}}){}{}\hskip-20pt
\sixheteroh({b{\addskbcolor{h}{\red}}}){}{}\hskip-20pt
\sixheteroh({c{\addskbcolor{h}{\blue}}}){}{}\hskip-20pt
\sixheteroh({d{\addskbcolor{h}{\blue}}}){}{}\hskip-20pt
\sixheteroh({e{\addskbcolor{h}{\green}}}){}{}\hskip-20pt
\sixheteroh({f{\addskbcolor{h}{\green}}}){}{} \par
\sixheterohi({a{\addskbcolor{h}{\red}}}){}{}\hskip-20pt
\sixheterohi({b{\addskbcolor{h}{\red}}}){}{}\hskip-20pt
\sixheterohi({c{\addskbcolor{h}{\blue}}}){}{}\hskip-20pt
\sixheterohi({d{\addskbcolor{h}{\blue}}}){}{}\hskip-20pt
\sixheterohi({e{\addskbcolor{h}{\green}}}){}{}\hskip-20pt
\sixheterohi({f{\addskbcolor{h}{\green}}}){}{}
```

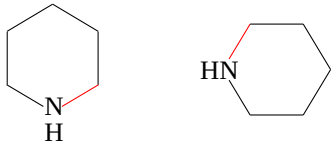
where the first argument {h} of \addskbcolor corresponds to horizontal type or horizontal inverse type. These codes generate structural formulas with colored skeletal bonds:



The presence of a ring atom results in bond shortening, where such a shortened bond can be also colored by the use of the \addskbcolor command. Thus the codes:

```
\sixheterovi({a{\addskbcolor{v}{\red}}}){1==\downnobond{N}{H}}{}
\sixheteroh({a{\addskbcolor{h}{\red}}}){1==HN}{}
```

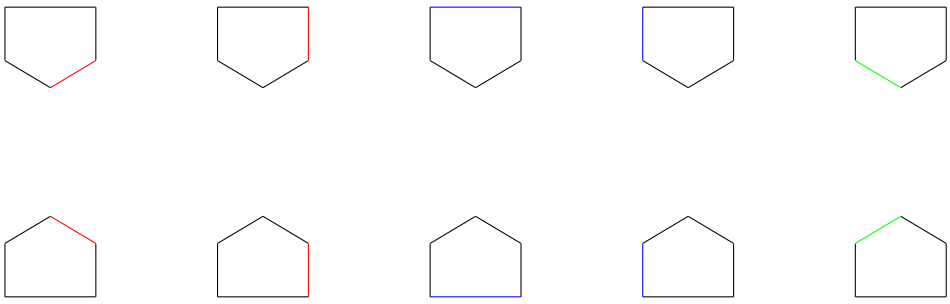
generate structural formulas with colored shortened bonds:



The use of the `\addskbcolor` command in `\fiveheterov` (vertical type) and `\fiveheterovi` (inverse vertical type) as shown in the codes:

```
\fiveheterov({a{\addskbcolor{}{\red}}}){}{}
\fiveheterov({b{\addskbcolor{}{\red}}}){}{}
\fiveheterov({c{\addskbcolor{}{\blue}}}){}{}
\fiveheterov({d{\addskbcolor{}{\blue}}}){}{}
\fiveheterov({e{\addskbcolor{}{\green}}}){}{} \par
\fiveheterovi({a{\addskbcolor{}{\red}}}){}{}
\fiveheterovi({b{\addskbcolor{}{\red}}}){}{}
\fiveheterovi({c{\addskbcolor{}{\blue}}}){}{}
\fiveheterovi({d{\addskbcolor{}{\blue}}}){}{}
\fiveheterovi({e{\addskbcolor{}{\green}}}){}{}
```

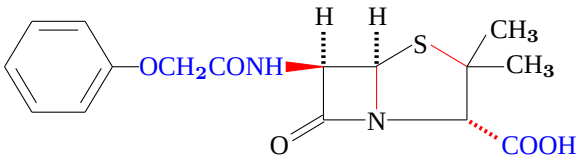
generates the following structures:



Other commands which support a skeletal bond list (⟨skelbdlist⟩) can use the `\addskbcolor` command.

Example 39.1. The following structure is drawn by using `\addskbcolor` commands in `\fourhetero` and `\fivefusevi`.

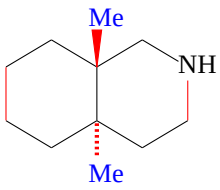
```
\begin{XyMcompd}(2100,600)(-800,100){}{}
\fourhetero({b{\addskbcolor{}{\red}}})%
[{b\fivefusevi({a{\addskbcolor{}{\red}}})%
{1==S;4==\null}{2Sa==CH$_{3}$;2Sb==CH$_{3}$;%
3A==\addbscolor{\red}{\bluex{COOH}}}{d}}]%
{2==N}{1D==O;3FA==H;4GA==H;%
4Su==\addbscolor{\red}{\blackx{%
\lyl(4==\bluex{OCH$_{2}$CONH}){4==\bzdrh{4==(yl)}}}}}
\end{XyMcompd}
```



□

Example 39.2. The following structure is drawn by using `\addskbcolor` commands in `\decaheterov`.

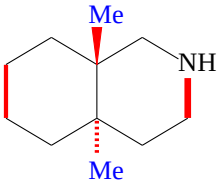
```
\decaheterov({b{\addskbcolor{v}{\red}}}%
{g{\addskbcolor{v}{\red}}}){2==NH}%
{9A==\addbscolor{\red}{\bluex{Me}};{10}B==\addbscolor{\red}{\bluex{Me}}}
```



□

Example 39.3. The line width of a skeletal bond drawn by an `\addskbcolor` command can be changed by the first argument `{\red\thicklines}`. Such a line width can be reset by redefining the line width stored by `\thickLineWidth`, e.g., `\def\thickLineWidth{2.5pt}`.

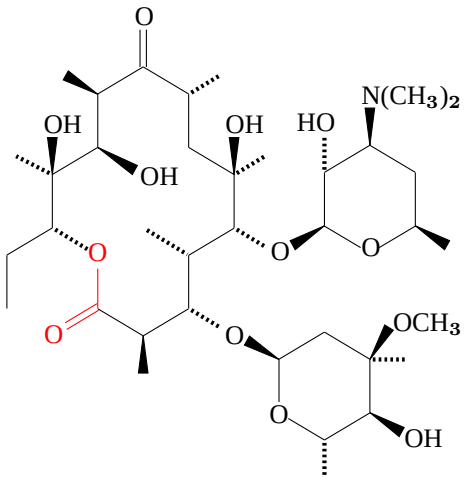
```
\decaheterov({b{\addskbcolor{v}{\red\def\thickLineWidth{2.5pt}\thicklines}}}%
{g{\addskbcolor{v}{\red\thicklines}}}){2==NH}%
{9A==\addbscolor{\red}{\bluex{Me}};{10}B==\addbscolor{\red}{\bluex{Me}}}
```



□

Example 39.4. Erythromycin A **39-1** is a macrolide antibiotic, which has a lactone moiety (colored in red) in a large ring. The skeletal bond of the lactone moiety is colored in red by the command `\addskbcolor`, which is declared in the optional argument ⟨skelbdlist⟩ of the first command `\sixheterov`. The carbonyl group is colored in red by the command `\addbscolor` defined in Section 38.3.

```
\begin{XyMcompd}(1650,1800)(-100,-300){cpd:erythromycinA}{}
\sixheterov({aA}{e{\addskbcolor{v}{\red}}})[%
{e\sixfusev({aA}){2==\null}{}{B}[cd]}%
{f\sixfusev{4==\null;%
1s==\WedgeAsSubst(0,0)(5,-3){140};%
1s==\put(160,-140){OH}}{6A==\null;6GB==OH}{C}[abcd]}%
{a\sixfusev[%
{f\sixfusev{}{1D==O;2A==\null;6B==\null}{C}[cd]}
]{}{2FB==OH;2A==\null;%
3A==\put(220,80){\sixheterov{4==O}{5==(yl);5B==O;3B==\null;%
6GA==\lmoiety{HO};1B==N(CH$_{3}$)$_{2}$}}
}{D}[def]}%
]{6==\redx{O}}{4B==\null;5D==\addbscolor{\red}{O};%
3A==\put(220,-120){\sixheterov{5==O}{6==(yl);6B==O;%
3B==OH;2SB==OCH$_{3}$;2SA==\null;4A==\null}}}[f]
\end{XyMcompd}
```



39-1

□

39.1.2 Dirty Techniques for Coloring Skeletal Bonds

The technique base on `\addskbcolor` cannot be applied to commands which have no skeletal bond list, e.g., `\steroid`. Because an original object can be erased by overwriting a white object in the PDF mode (also in the PostScript mode), the macro `\addPDFLine` (or `\addPSLine`) is defined tentatively to draw a colored skeletal bond.

The `\addPSLine` command for the PostScript mode is defined as follows:

```
\makeatletter
\def\white{\color{white}}
\def\addPSLine{%
\@ifnextchar[{\@ddPSLine}{\@ddPSLine[\thinLineWidth]}}
\def\@ddPSLine[#1](#2,#3)(#4,#5)#6{%
\psline[unit=\unitlength,linewidth=#1,linecolor=white](#2,#3)(#4,#5)%
\put(0,0){#6\PutBondLine(#2,#3)(#4,#5){#1}}}%
\makeatother
```

The optional argument can be applied to change a bond width and the last argument is used to designate a color.

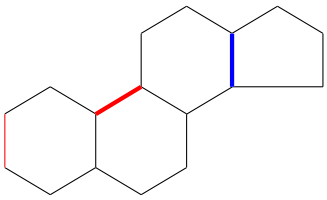
On the other hand, the `\addPDFLine` command for the PDF mode is defined as follows:

```
\makeatletter
\def\white{\color{white}}
\def\addPDFLine{%
\@ifnextchar[{\@ddPDFLine}{\@ddPDFLine[\thinLineWidth]}}
\def\@ddPDFLine[#1](#2,#3)(#4,#5)#6{%
\put(0,0){\white\PutBondLine(#2,#3)(#4,#5){1.6pt}}%
\put(0,0){#6\PutBondLine(#2,#3)(#4,#5){#1}}}%
\makeatother
```

The optional argument can be applied to change a bond width and the last argument is used to designate a color.

Because this document is typeset in the PDF mode, the macro `\addPDFLine` is written in a bond list, as shown in the following example:

```
\steroid[{b{\addPDFLine(0,0)(0,200){\red}}}%
{i{\addPDFLine[1.6pt](0,0)(171,103){\red}}}%
{o{\addPDFLine[1.6pt](0,0)(0,-200){\blue}}}]{}
```



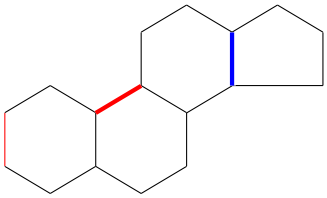
It should be noted that the macro `\addPDFLine` is so local as defined in the PDF mode, because the inner macro `\PutBondLine` depends upon the selected mode. The macro `\addPSLine` for the PostScript mode can be used by replacing `\addPDFLine` by `\addPSLine`.

The command `\replaceSKbond` is defined in the bondcolor package of the XeLaTeX system in order to color skeletal bonds in the PDF mode as well as in the PostScript mode.

```
\replaceSKbond[⟨thickness⟩](⟨startpoint⟩)(⟨slope⟩){⟨bdlength⟩}{⟨skelbcolor⟩})
```

A line to be colored is designated by specifying its starting point (⟨startpoint⟩), slope (⟨slope⟩), and length (⟨bdlength⟩ as the x-axis projection) as the `\replaceSKbond` command. The last argument (⟨skelbcolor⟩) of the `\replaceSKbond` command is set for specifying a bond color. The first optional argument ⟨thickness⟩ specifies the bond width to be drawn, as found in the following example:

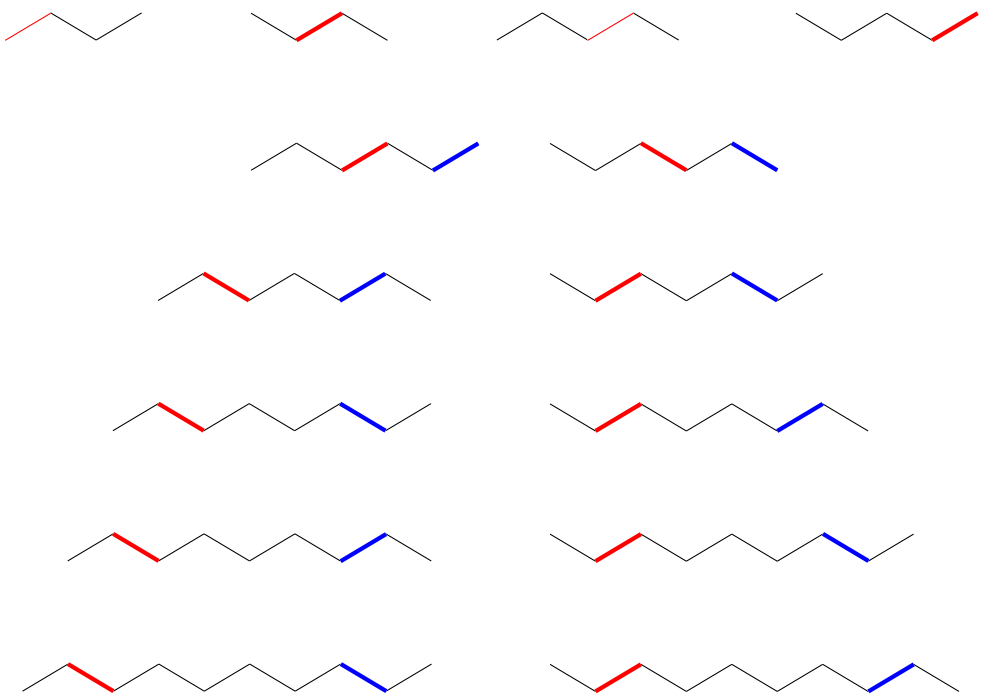
```
\steroid[{b{\replaceSKbond(0,0)(0,1){200}{\red}}}%
{i{\replaceSKbond[1.6pt](0,0)(5,3){171}{\red}}}%
{o{\replaceSKbond[1.6pt](0,0)(0,-1){200}{\blue}}}]{}
```



The command `\replaceSKbond` is effective to color skeletal bonds of polymethylenes, as found in the following list of examples:

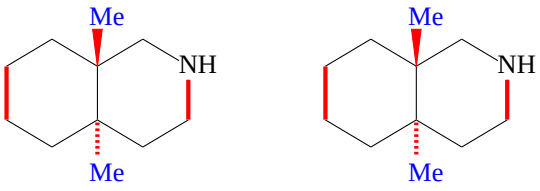
```
\tetramethylene[{a{\replaceSKbond(0,0)(5,3){171}{\red}}}]{}{}
\tetramethylenei[{b{\replaceSKbond[1.6pt](0,0)(5,3){171}{\red}}}]{}{}
\pentamethylene[{c{\replaceSKbond(0,0)(5,3){171}{\red}}}]{}{}
\pentamethylenei[{d{\replaceSKbond[1.6pt](0,0)(5,3){171}{\red}}}]{}{} \par
\hexamethylene[{c{\replaceSKbond[1.6pt](0,0)(5,3){171}{\red}}}%
{e{\replaceSKbond[1.6pt](0,0)(5,3){171}{\blue}}}]{}{}
\hexamethylenei[{c{\replaceSKbond[1.6pt](0,0)(5,-3){171}{\red}}}%
{e{\replaceSKbond[1.6pt](0,0)(5,-3){171}{\blue}}}]{}{} \par
\heptamethylene[{b{\replaceSKbond[1.6pt](0,0)(5,-3){171}{\red}}}%
{e{\replaceSKbond[1.6pt](0,0)(5,3){171}{\blue}}}]{}{}
\heptamethylenei[{b{\replaceSKbond[1.6pt](0,0)(5,3){171}{\red}}}%
{e{\replaceSKbond[1.6pt](0,0)(5,-3){171}{\blue}}}]{}{} \par
\octamethylene[{b{\replaceSKbond[1.6pt](0,0)(5,-3){171}{\red}}}%
{f{\replaceSKbond[1.6pt](0,0)(5,-3){171}{\blue}}}]{}{}
```

```
\octamethylenei[{b{\replaceSKbond[1.6pt](0,0)(5,3){171}{\red}}}%
{f{\replaceSKbond[1.6pt](0,0)(5,3){171}{\blue}}}]{}{} \par
\nonamethylene[{b{\replaceSKbond[1.6pt](0,0)(5,-3){171}{\red}}}%
{g{\replaceSKbond[1.6pt](0,0)(5,3){171}{\blue}}}]{}{}
\nonamethylenei[{b{\replaceSKbond[1.6pt](0,0)(5,3){171}{\red}}}%
{g{\replaceSKbond[1.6pt](0,0)(5,-3){171}{\blue}}}]{}{} \par
\decamethylene[{b{\replaceSKbond[1.6pt](0,0)(5,-3){171}{\red}}}%
{h{\replaceSKbond[1.6pt](0,0)(5,-3){171}{\blue}}}]{}{}
\decamethylenei[{b{\replaceSKbond[1.6pt](0,0)(5,3){171}{\red}}}%
{h{\replaceSKbond[1.6pt](0,0)(5,3){171}{\blue}}}]{}{} \par
```



Example 39.5. The colored structure shown in Page 708 can be alternatively drawn by using the command `\replaceSKbond`. Note that the pair of bond specifiers ‘`b/B`’ or ‘`g/G`’ designates the alternative terminals of a bond to be selected as starting points. With respect to the pair ‘`b/B`’ or ‘`g/G`’, check the slope `(0,1)` or `(0,-1)` specified as the argument of `\replaceSKbond`.

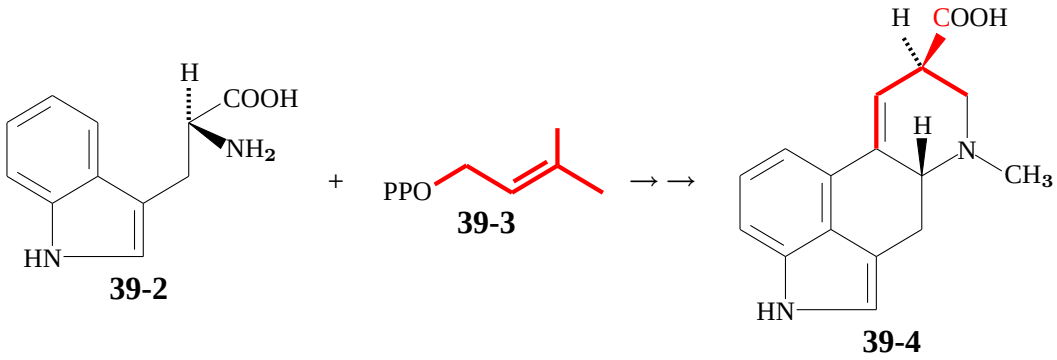
```
\decaheterov[{b{\replaceSKbond[1.6pt](0,-50)(0,-1){150}{\red}}}%
{g{\replaceSKbond[1.6pt](0,0)(0,1){200}{\red}}}]%
{2==NH}%
{9A==\addbscolor{\red}{\bluex{Me}};{10}B==\addbscolor{\red}{\bluex{Me}}}
\decaheterov[{B{\replaceSKbond[1.6pt](0,0)(0,1){150}{\red}}}%
{G{\replaceSKbond[1.6pt](0,0)(0,-1){200}{\red}}}]%
{2==NH}%
{9A==\addbscolor{\red}{\bluex{Me}};{10}B==\addbscolor{\red}{\bluex{Me}}}
```



□

Example 39.6. Lysergic acid **39-4** is a precursor for wide range of ergoline alkaloids. Its dimethylamide (lysergic acid dimethylamide: LSD) is a semisynthetic psychedelic drug of the ergoline family. The red colored moiety of **39-4** stems from DMAPP (dimethylallyl pyrophosphate, **39-3**), which is attached to tryptophan (**39-2**) during the biosynthesis of lysergic acid (**39-4**).

```
\begin{center}
\begin{XyMcompd}(1050,800)(200,0){cpd:tryptophan}{}
\decaheterov[fhk%
{d\fivefusevi[b]{4==HN}{}{A}[e]}%
]{}{2FA==H;2==COOH;2GB==NH$_{2}$}[aj]
\end{XyMcompd}
\quad + \quad
\begin{XyMcompd}(700,300)(-50,150){cpd:DMAPP}{}
\def\thinLineWidth{1.6pt}
\redx{\tetramethylenei[b]{}{1W==\blackx{PPO};3==\null}}
\end{XyMcompd}
\quad $\rightarrow$ $\rightarrow$ \quad
\begin{XyMcompd}(1100,1200)(250,0){cpd:lysergicacid}{}
\decaheterov[fhk%
{a\sixfusev[e%
{a{\replaceSKbond[1.6pt](0,0)(5,-3){171}{\red}}}%
{a{\replaceSKbond[1.6pt](0,0)(-5,-3){171}{\red}}}%
{e{\replaceSKbond[1.6pt](0,0)(0,1){200}{\red}}}%
]{3==N}{3==CH$_{3}$;1Sd==H;1Su==\addbscolor{\red}{C\blackx{OOH}}}{D}}
{d\fivefusevi[b]{4==HN}{}{A}[e]}%
]{}{2FB==H}
\end{XyMcompd}
\end{center}
```



The bold bonds of **39-3** are generated by declaring `\def\thinLineWidth{1.6pt}`. The whole structure generated by `\tetramethylenei` is surrounded by `\redx` so as to be colored in red, except that the character string "PPO" remains to be black by declaring `1W==\blackx{PPO}`. The red skeletal bonds of **39-4** are generated by the command `\replaceSKbond`. □

39.2 Coloring Double Bonds

39.2.1 A Systematic Way

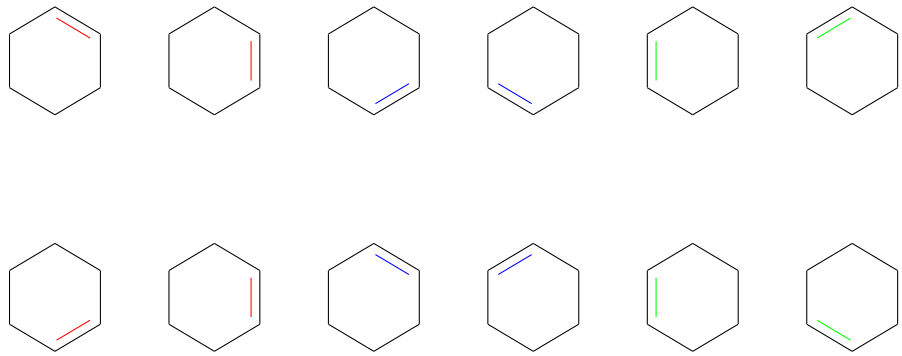
The bondcolor package of the X$\mathfrak{Z}$MTEX version 5.00 and later supports the function of coloring double bonds. The command `\adddbcolor` is defined to specify the color of a double bond, where it has a format represented by

```
\adddbcolor{⟨commandsuffix⟩}{⟨skelbcolor⟩}
```

where the first argument ⟨commandsuffix⟩ is used to specify the vertical or horizontal type of a command, such as `v` for commands of vertical types (suffix `v`), `vi` for commands of inverse vertical types (suffix `vi`), and so on. The second argument ⟨skelbcolor⟩ is a command for specifying color (e.g., `\red` or `\color{red}`). The `\adddbcolor` command is designated in the bond list of each command for drawing a double bond. For example, the codes:

```
\sixheterov[{a{\adddbcolor{v}{\red}}}]{}{}\hskip-20pt
\sixheterov[{b{\adddbcolor{v}{\red}}}]{}{}\hskip-20pt
\sixheterov[{c{\adddbcolor{v}{\blue}}}]{}{}\hskip-20pt
\sixheterov[{d{\adddbcolor{v}{\blue}}}]{}{}\hskip-20pt
\sixheterov[{e{\adddbcolor{v}{\green}}}]{}{}\hskip-20pt
\sixheterov[{f{\adddbcolor{v}{\green}}}]{}{}\par
\sixheterovi[{a{\adddbcolor{vi}{\red}}}]{}{}\hskip-20pt
\sixheterovi[{b{\adddbcolor{vi}{\red}}}]{}{}\hskip-20pt
\sixheterovi[{c{\adddbcolor{vi}{\blue}}}]{}{}\hskip-20pt
\sixheterovi[{d{\adddbcolor{vi}{\blue}}}]{}{}\hskip-20pt
\sixheterovi[{e{\adddbcolor{vi}{\green}}}]{}{}\hskip-20pt
\sixheterovi[{f{\adddbcolor{vi}{\green}}}]{}{}\par
```

generate the following structures with colored double bonds:



Double bonds in polymethylene chains drawn by the macros of the methylen package of the XeLaTeX system can be colored by using the `\adddbcolor` command. For commands of normal type (e.g., `\decamethylene`), the first argument of `\adddbcolor` is set to be vacant. Lowercase bond specifiers `a` to `i` are used in the following examples:

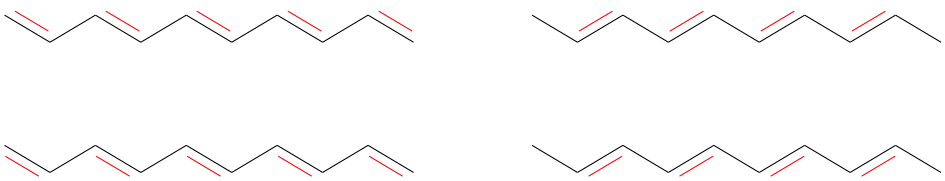
```
\decamethylene[%
{a{\adddbcolor{}{\red}}}%
{c{\adddbcolor{}{\red}}}%
{e{\adddbcolor{}{\red}}}%
{g{\adddbcolor{}{\red}}}%
{i{\adddbcolor{}{\red}}}%
]{}{}
\decamethylene[%
{b{\adddbcolor{}{\red}}}%
{d{\adddbcolor{}{\red}}}%
{f{\adddbcolor{}{\red}}}%
{h{\adddbcolor{}{\red}}}%
]{}{}
```

Uppercase bond specifiers `A` to `I` are used to draw double bonds at the opposite sides in comparison with bond specifiers `a` to `i`.

```
\decamethylene[%
{A{\adddbcolor{}{\red}}}%
{C{\adddbcolor{}{\red}}}%
{E{\adddbcolor{}{\red}}}%
{G{\adddbcolor{}{\red}}}%
{I{\adddbcolor{}{\red}}}%
]{}{}
\decamethylene[%
{B{\adddbcolor{}{\red}}}%
{D{\adddbcolor{}{\red}}}%
{F{\adddbcolor{}{\red}}}%
{H{\adddbcolor{}{\red}}}%
]{}{}
```

For commands of inverse type (e.g., `\decamethylenei`), on the other hand, the first argument of `\adddbcolor` is set to be `i`. Lowercase (`a` to `i`) and uppercase bond specifiers (`A` to `I`) are tested as follows by using the `\decamethylenei` command.

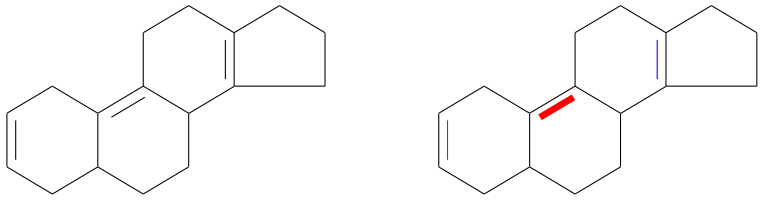
```
\decamethylenei[%
{a{\adddbcolor{i}{\red}}}{c{\adddbcolor{i}{\red}}}%
{e{\adddbcolor{i}{\red}}}{g{\adddbcolor{i}{\red}}}%
{i{\adddbcolor{i}{\red}}}%
]{}{}
\decamethylenei[%
{b{\adddbcolor{i}{\red}}}{d{\adddbcolor{i}{\red}}}%
{f{\adddbcolor{i}{\red}}}{h{\adddbcolor{i}{\red}}}%
]{}{} \par
\decamethylenei[%
{A{\adddbcolor{i}{\red}}}{C{\adddbcolor{i}{\red}}}%
{E{\adddbcolor{i}{\red}}}{G{\adddbcolor{i}{\red}}}%
{I{\adddbcolor{i}{\red}}}%
]{}{}
\decamethylenei[%
{B{\adddbcolor{i}{\red}}}{D{\adddbcolor{i}{\red}}}%
{F{\adddbcolor{i}{\red}}}{H{\adddbcolor{i}{\red}}}%
]{}{}
```



Example 39.7. The following examples show the comparison between a non-color version and a colored version of the same structure.

```
\steroid[bio]{}
\steroid[{b{\adddbcolor{v}{\red}}}%
{i{\adddbcolor{v}{\red
```

```
\dashhasheddash\def\thickLineWidth{2.5pt}%
\thicklines}}}%
{o{\adddbcolor{v}{\blue}}}]{}
```



□

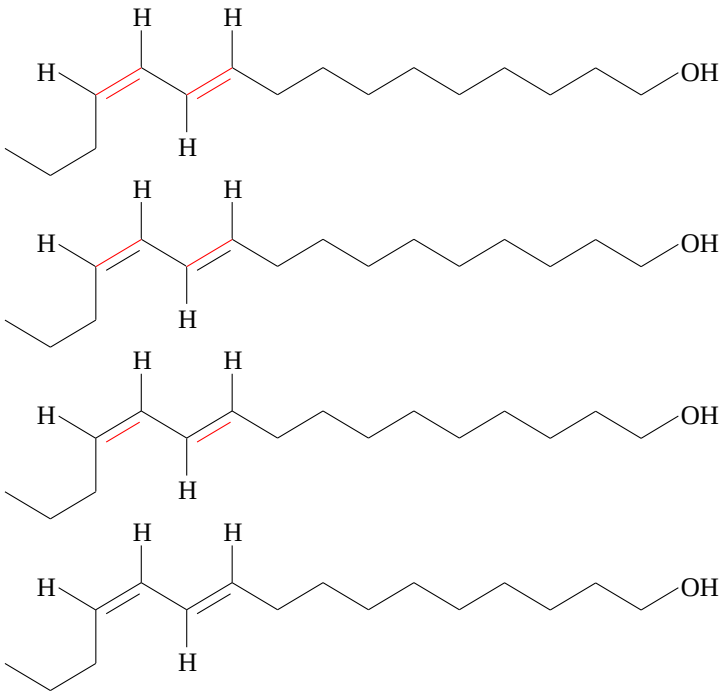
39.3 Coloring Both Skeletal and Double Bonds

The techniques for coloring skeletal bonds (Section 39.1) can be used simultaneously with those for coloring double bonds (Section 39.2).

Example 39.8. Double bonds in bombykol (an insect pheromone of a silkworm moth) are colored in three different versions as follows. The last structure is a non-color version.

```
\begin{XyMcompd}(2600,600)(-100,-100){}{}
\decamethylene[%
{a{\adddbcolor{}{\red}}}%
{c{\adddbcolor{}{\red}}}%
{a{\replaceSKbond(0,0)(5,3){171}{\red}}}%
{c{\replaceSKbond(0,0)(5,3){171}{\red}}}%
]{%
{10}s==\tetramethylenei{}{1==(yl);4W==OH};%
1s==\sixheterov{}{2==(yl)}[aef]%
}{1W==H;2==H;3==H;4==H}
\end{XyMcompd}\par
\begin{XyMcompd}(2600,600)(-100,-100){}{}
\decamethylene[ac%
{a{\replaceSKbond(0,0)(5,3){171}{\red}}}%
{c{\replaceSKbond(0,0)(5,3){171}{\red}}}%
]{%
{10}s==\tetramethylenei{}{1==(yl);4W==OH};%
1s==\sixheterov{}{2==(yl)}[aef]%
}{1W==H;2==H;3==H;4==H}
\end{XyMcompd}\par
\begin{XyMcompd}(2600,600)(-100,-100){}{}
\decamethylene[%
{a{\adddbcolor{}{\red}}}%
{c{\adddbcolor{}{\red}}}%
]{%
{10}s==\tetramethylenei{}{1==(yl);4W==OH};%
1s==\sixheterov{}{2==(yl)}[aef]%
}{1W==H;2==H;3==H;4==H}
\end{XyMcompd}\par
\begin{XyMcompd}(2600,600)(-100,-100){}{}
\decamethylene[ac]{%
{10}s==\tetramethylenei{}{1==(yl);4W==OH};%
```

```
1s==\sixheterov{}{2==(yl)}[aef]%
}{1W==H;2==H;3==H;4==H}
\end{XyMcompd}
```

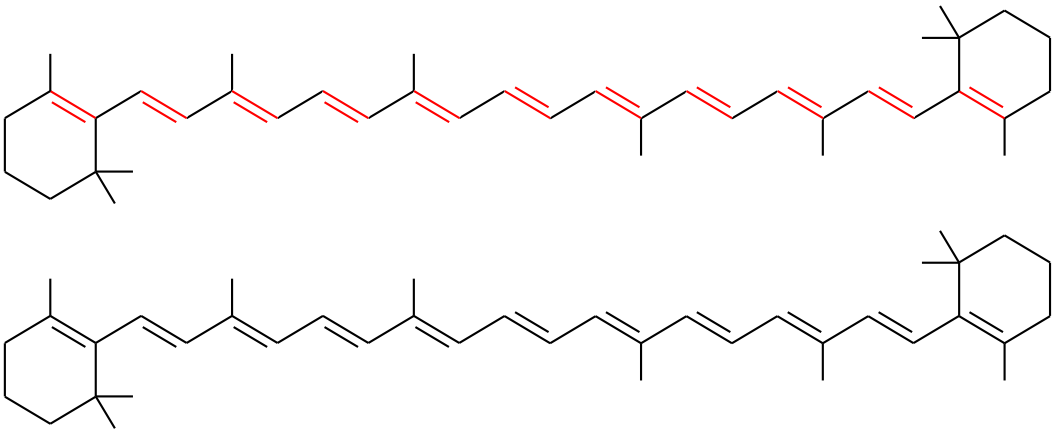


□

Example 39.9. Colored and non-colored structures of β-carotene are drawn by the following codes:

```
%%%%%%%%%%%%%%%%
%color version %
%%%%%%%%%%%%%%%%
{\def\thinLineWidth{0.8pt}
\begin{XyMcompd}(3850,800)(-100,-150){}{}
\decamethylene[%bdfh
{b{\adddbcolor{}{\red}}}%
{d{\adddbcolor{}{\red}}}%
{f{\adddbcolor{}{\red}}}%
{h{\adddbcolor{}{\red}}}%
{b{\replaceSKbond[0.8pt](0,0)(5,-3){171}{\red}}}%
{d{\replaceSKbond[0.8pt](0,0)(5,-3){171}{\red}}}%
{f{\replaceSKbond[0.8pt](0,0)(5,-3){171}{\red}}}%
{h{\replaceSKbond[0.8pt](0,0)(5,-3){171}{\red}}}%
]
{1s==\sixheterov(%
{a{\addskbcolor{v}{\red}}}%
)[%a
{a{\adddbcolor{v}{\red}}}%
]{}{2==(yl);1==\null;3Sa==\null;3Sb==\null};
{10}s==\decamethylenei[%acegi
{a{\adddbcolor{i}{\red}}}%
{c{\adddbcolor{i}{\red}}}%
{e{\adddbcolor{i}{\red}}}%
{g{\adddbcolor{i}{\red}}}%
{i{\adddbcolor{i}{\red}}}%
{a{\replaceSKbond[0.8pt](0,0)(5,-3){171}{\red}}}%
{c{\replaceSKbond[0.8pt](0,0)(5,-3){171}{\red}}}%
{e{\replaceSKbond[0.8pt](0,0)(5,-3){171}{\red}}}%
{g{\replaceSKbond[0.8pt](0,0)(5,-3){171}{\red}}}%
```

```
{i{\replaceSKbond[0.8pt](0,0)(5,-3){171}{\red}}}%
]{{10}s==\dimethylene{%
2s==\sixheterov(%
{d{\addskbcolor{v}{\red}}}%
)[%d
{d{\adddbcolor{v}{\red}}}%
]{}{5==(yl);4==\null;6Sa==\null;6Sb==\null}
}{1==(yl)}}{1==(yl);4==\null;8==\null}}{4==\null;8==\null}
\end{XyMcompd}\par
%%%%%%%%%%%%%%%%%%%%%%%
%non-colored version %
%%%%%%%%%%%%%%%%%%%%%%%
\begin{XyMcompd}(3850,800)(-100,-150){}{}
\decamethylene[bdfh]
{1s==\sixheterov[a]{}{2==(yl);1==\null;3Sa==\null;3Sb==\null};
{10}s==\decamethylenei[acegi]{{10}s==\dimethylene{%
2s==\sixheterov[d]{}{5==(yl);4==\null;6Sa==\null;6Sb==\null}
}{1==(yl)}}{1==(yl);4==\null;8==\null}}{4==\null;8==\null}
\end{XyMcompd}
}
```

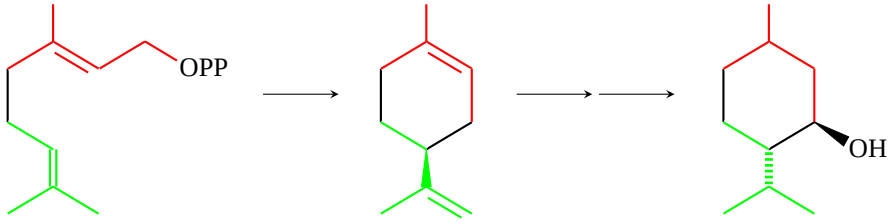


The top declaration `\def\thinLineWidth{0.8pt}` results in printing bold bonds. In accord with this declaration, the command `\replaceSKbond` should take an optional argument `[0.8pt]`. □

Example 39.10. Menthol **39-7** is a monoterpenoid, which contains two isoprene units shown in red and in green. This segmentation is rationalized by the process of biosynthesis via geranyl diphosphate **39-5** and limonene **39-6**.

```
%geranyl diphosphate
\begin{XyMcompd}(750,850)(280,-50){cpd:geranylPP}{}
\def\thinLineWidth{0.8pt}
\sixheterov[%
{a{\adddbcolor{v}{\red}}}%
{a{\replaceSKbond[0.8pt](0,0)(5,-3){171}{\red}}}%
{f{\replaceSKbond[0.8pt](0,0)(5,3){171}{\red}}}%
{d{\replaceSKbond[0.8pt](0,0)(-5,3){171}{\green}}}%
]{2s==\redx{\dimethylene{}{1==(yl);2W==\blackx{OPP}}}
}{1==\addbscolor{\red}{\null};%
4D==\addbscolor{\green}{\trimethylene{}{2==(yl)}}}[bc]
\end{XyMcompd}
\quad \reactrarrow{15pt}{1cm}{}{} \quad
%(-)-limonene
\begin{XyMcompd}(300,850)(280,-50){cpd:limonene}{}
\def\thinLineWidth{0.8pt}
```

```
\sixheterov[%
{a{\adddbcolor{v}{\red}}}%
{a{\replaceSKbond[0.8pt](0,0)(5,-3){171}{\red}}}%
{b{\replaceSKbond[0.8pt](0,0)(0,-1){200}{\red}}}%
{f{\replaceSKbond[0.8pt](0,0)(5,3){171}{\red}}}%
{d{\replaceSKbond[0.8pt](0,0)(-5,3){171}{\green}}}%
]{}{1==\addbscolor{\red}{\null};%
4B==\addbscolor{\green}{\trimethylene[b]{}{2==(yl)}}}
\end{XyMcompd}
\quad \reactrarrow{15pt}{1cm}{}{} \reactrarrow{15pt}{1cm}{}{} \quad
%(-)-menthol
\begin{XyMcompd}(500,850)(280,-50){cpd:menthol}{}
\def\thinLineWidth{0.8pt}
\def\thickLineWidth{3pt}
\sixheterov[%
{a{\replaceSKbond[0.8pt](0,0)(5,-3){171}{\red}}}%
{b{\replaceSKbond[0.8pt](0,0)(0,-1){200}{\red}}}%
{f{\replaceSKbond[0.8pt](0,0)(5,3){171}{\red}}}%
{d{\replaceSKbond[0.8pt](0,0)(-5,3){171}{\green}}}%
]{}{3B==OH;%
1==\addbscolor{\red}{\null};%
4A==\addbscolor{\green}{\trimethylene{}{2==(yl)}}}
\end{XyMcompd}
```



39-5 **39-6** **39-7**

The first code for drawing the structure **39-5** of geranyl diphosphate contains `\adddbcolor` for coloring a double bond, `\replaceSKbond` for coloring a skeletal bond, and `\addbscolor` for coloring a substituent and a linking bond. The second code for drawing the structure **39-6** of (−)-limonene contains the same set of coloring commands. The third code for drawing the structure **39-7** of (−)-menthol contains `\replaceSKbond` for coloring a skeletal bond and `\addbscolor` for coloring a substituent and a linking bond. The widths of bonds are changed by declaring `\def\thinLineWidth{0.8pt}` and/or `\def\thickLineWidth{3pt}`. The latter declaration is effective to thicken the hashed dash bond of **39-7**. □

(Remarks): Commands for coloring skeletal and double bonds are summarized as follows:

Skeletal bonds	`\replaceSKbond`	in a bond list [...]
	`\addskbcolor`	in a skeletal bond list (...)
Double bonds	`\adddbcolor`	in a bond list [...]

39.4 Imaginary Transition Structures

39.4.1 Imaginary Transition Structures and Related Graphs

The author (Fujita) proposed the concept of *imaginary transition structures* (ITSs) for representing chemical reactions [1]. An imaginary transition structure (ITS) is a structural formula with in-bonds, out-bonds, and par-bonds [1]. In this section, a green line is used to denote an in-bond (a bond appearing in a product stage) in place of the symbol —⊖— used in [1]; a red line is used to denote an out-bond (a bond disappearing from a product stage) in place of the symbol —+—; and a black line denotes a par-bond, which is invariant during a reaction (cf. [1, Table 2.1]).

Example 39.11. For example, Fig. 39.1 shows a reaction (a Diels-Alder reaction) and its ITS as well as related diagrams for representing the reaction in various levels of information, i.e, an imaginary transition structure (ITS), a reaction-center graph (RCG), a reaction graph (RG), and a basic reaction graph (BRG). This figure is a modification of [1, Fig. 14.2]. The process denoted by PS is a projection to a starting stage, by which the ITS produces the corresponding starting stage. The process denoted by PP is a projection to a product stage, by which the ITS produces the corresponding product stage.

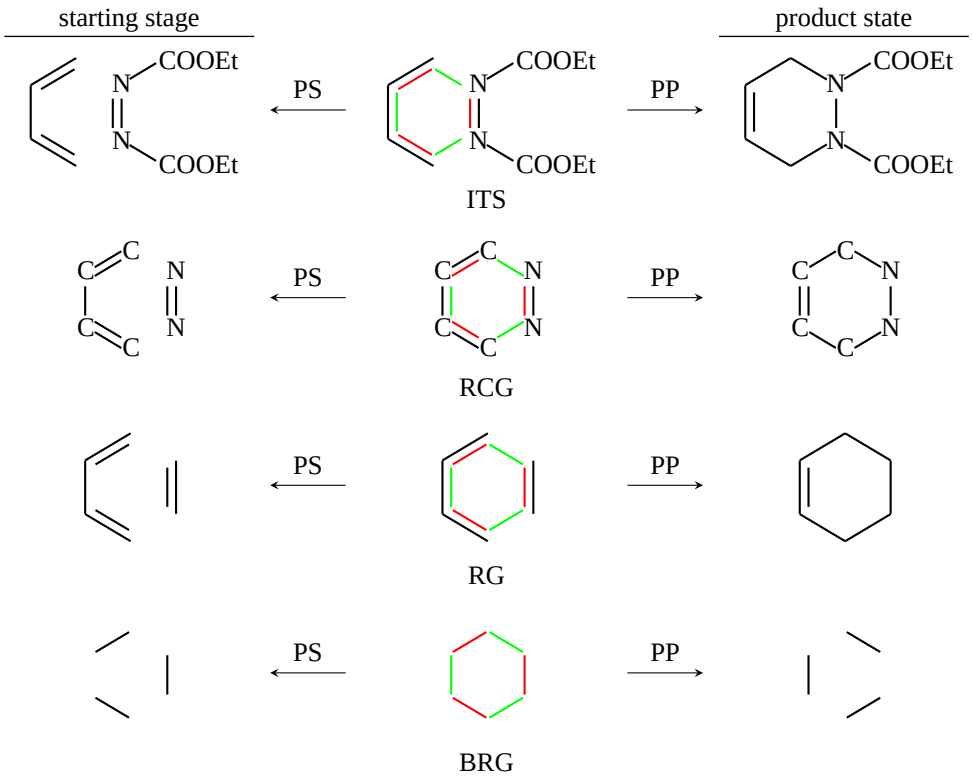


Figure 39.1. An imaginary transition structure (ITS), a reaction-center graph (RCG), a reaction graph (RG), and a basic reaction graph (BRG) for the ITS approach. This figure is a modification of [1, Fig. 14.2].

The scheme contained in Fig. 39.1 is depicted by the following code:

```
\begin{center}
\def\thinLineWidth{0.8pt}
\begin{tabular}{ccccc}
starting stage &&&& product state \\
\cline{1-1}\cline{5-5}
\noalign{\vskip3pt}
\begin{XyMcompd}(700,500)(250,200){}{}
\sixheterov[bdf]{2==N;3==N}{2==COOEt;3==COOEt}[ac]
\end{XyMcompd}
& \reactlarrow{0pt}{1cm}{PS}{\strut} &
\begin{XyMcompd}(700,500)(250,200){}{}
\sixheterov[%
{a{\adddbcolor{v}{\green}}}{b{\adddbcolor{v}{\red}}}%
{c{\adddbcolor{v}{\green}}}{d{\adddbcolor{v}{\red}}}%
{e{\adddbcolor{v}{\green}}}{f{\adddbcolor{v}{\red}}}%
]{2==N;3==N}{2==COOEt;3==COOEt}[ac]
\end{XyMcompd}
& \reactrarrow{0pt}{1cm}{PP}{\strut} &
\begin{XyMcompd}(700,500)(250,200){}{}
\sixheterov[e]{2==N;3==N}{2==COOEt;3==COOEt}
```

```
\end{XyMcompd}
\\
&& ITS && \\
\noalign{\vskip5pt}
\begin{XyMcompd}(350,500)(220,200){}{}
\sixheterov[bdf]{1==C;2==N;3==N;4==C;5==C;6==C}{}[ac]
\end{XyMcompd}
& \reactlarrow{0pt}{1cm}{PS}{\strut} &
\begin{XyMcompd}(350,500)(220,200){}{}
\sixheterov[%
{a{\adddbcolor{v}{\green}}}{b{\adddbcolor{v}{\red}}}%
{c{\adddbcolor{v}{\green}}}{d{\adddbcolor{v}{\red}}}%
{e{\adddbcolor{v}{\green}}}{f{\adddbcolor{v}{\red}}}%
]{1==C;2==N;3==N;4==C;5==C;6==C}{}[ac]
\end{XyMcompd}
& \reactrarrow{0pt}{1cm}{PP}{\strut} &
\begin{XyMcompd}(350,500)(220,200){}{}
\sixheterov[e]{1==C;2==N;3==N;4==C;5==C;6==C}{}
\end{XyMcompd}
\\
&& RCG && \\
\noalign{\vskip5pt}
\begin{XyMcompd}(350,500)(220,200){}{}
\sixheterov[bdf]{}{}[ac]
\end{XyMcompd}
& \reactlarrow{0pt}{1cm}{PS}{\strut} &
\begin{XyMcompd}(350,500)(220,200){}{}
\sixheterov[%
{a{\adddbcolor{v}{\green}}}{b{\adddbcolor{v}{\red}}}%
{c{\adddbcolor{v}{\green}}}{d{\adddbcolor{v}{\red}}}%
{e{\adddbcolor{v}{\green}}}{f{\adddbcolor{v}{\red}}}%
]{}{}[ac]
\end{XyMcompd}
& \reactrarrow{0pt}{1cm}{PP}{\strut} &
\begin{XyMcompd}(350,500)(220,200){}{}
\sixheterov[e]{}{}
\end{XyMcompd}
\\
&& RG && \\
\noalign{\vskip5pt}
\begin{XyMcompd}(350,500)(220,200){}{}
\sixheterov[bdf]{}{}[abcdef]
\end{XyMcompd}
& \reactlarrow{0pt}{1cm}{PS}{\strut} &
\begin{XyMcompd}(350,500)(220,200){}{}
\sixheterov[%
{a{\adddbcolor{v}{\green}}}{b{\adddbcolor{v}{\red}}}%
{c{\adddbcolor{v}{\green}}}{d{\adddbcolor{v}{\red}}}%
{e{\adddbcolor{v}{\green}}}{f{\adddbcolor{v}{\red}}}%
]{}{}[abcdef]
\end{XyMcompd}
& \reactrarrow{0pt}{1cm}{PP}{\strut} &
\begin{XyMcompd}(350,500)(220,200){}{}
\sixheterov[ace]{}{}[abcdef]
\end{XyMcompd}
\\
&& BRG && \\
```

```
\end{tabular}
\end{center}
```

□

39.4.2 Enumeration of Reaction-Center Graphs (RCGs)

Enumeration of reaction-center graphs (RCGs) has been summarized in [1, Chapter 15].

Example 39.12. Fig. 39.2 shows a list of six-membered RCGs with two skeletal nitrogen atoms. This figure is a modification of [1, Fig. 15.3]. For further discussions, see [2].

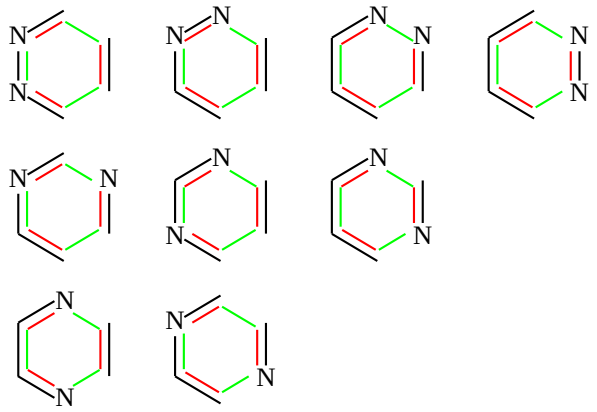


Figure 39.2. Six-membered reaction-center graphs (RCGs) with two skeletal nitrogens. This figure is a modification of [1, Fig. 15.3].

To depict such a enumeration result as shown in Fig. 39.2, we define `\RCgraphAtoms` for the sake of succinct input:

```
\def\RCgraphAtoms#1{%
\begin{XyMcompd}(350,500)(220,200){}{}
\sixheterov[%
{a{\adddbcolor{v}{\green}}}{b{\adddbcolor{v}{\red}}}%
{c{\adddbcolor{v}{\green}}}{d{\adddbcolor{v}{\red}}}%
{e{\adddbcolor{v}{\green}}}{f{\adddbcolor{v}{\red}}}%
]{#1}{}[ac]
\end{XyMcompd}}
```

where the argument succeeds to the ⟨atomlist⟩ of `\sixheterov`. Thereby, the following code generates Fig. 39.2.

```
\begin{center}
\def\thinLineWidth{0.8pt}
\begin{tabular}{cccc}
\RCgraphAtoms{5==N;6==N} &
\RCgraphAtoms{1==N;6==N} &
\RCgraphAtoms{1==N;2==N} &
\RCgraphAtoms{2==N;3==N} \\
\RCgraphAtoms{2==N;6==N} &
\RCgraphAtoms{1==N;5==N} &
\RCgraphAtoms{1==N;3==N} & \\
\RCgraphAtoms{1==N;4==N} &
\RCgraphAtoms{3==N;6==N} & & \\
\end{tabular}
\end{center}
```

□

References

[1] S. Fujita, “Computer-Oriented Representation of Organic Reactions,” Yoshioka-Shoten, Kyoto (2001).
[2] S. Fujita, *J. Math. Chem.*, **7**, 111–133 (1991).

Coloring Chemical Schemes

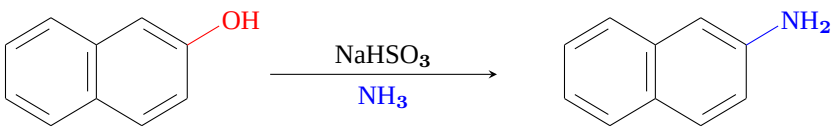
Because Chapters 38 and 39 discuss basic techniques for drawing colored structural formulas, the present chapter is devoted to combine the basic techniques with various environments for drawing equations.

40.1 Coloring in `center` and Related Environments

40.1.1 Bucherer Reaction

Example 40.1. The Bucherer reaction (replacement of a hydroxy group by an amino group) drawn in the `center` environment (Section 36.2) is rewritten to emphasize its reaction sites (OH and NH_2) with color.

```
\begin{center}
\naphdrv{2==\addbscolor{\red}{OH}}
\reactrarrow{40pt}{3cm}{NaHSO$_{3}$}{\bluex{NH$_{3}$}}
\naphdrv{2==\addbscolor{\blue}{NH$_{2}$}}
\end{center}
```



The command `\addbscolor` is used to color a hydroxyl group (or an amino group) and its linking bond. The command `\bluex` is used to color the nucleophile below the reaction arrow. □

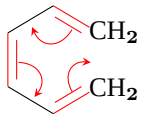
40.1.2 Electrocyclic Reactions

Let us draw electrocyclic reactions, where electron shifts are represented by red-colored curved arrows (cf. [1, Section 14.9].

Example 40.2. First, we define a command named `\sixtriene` for drawing the structure of *cis*-1,3,5-hexatriene which contains red-colored curved arrows. The definition and its output are shown below:

```
\def\sixtriene{%
\begin{XyMcompd}(400,400)(250,250){}{}
\sixheterov(%
{a{\addskbcolor{}{\red}}}%
{c{\addskbcolor{}{\red}}}%
{e{\addskbcolor{}{\red}}}%
)[%
{a{\adddbcolor{v}{\red}}}%
{c{\adddbcolor{v}{\red}}}%
{e{\adddbcolor{v}{\red}}}%
{a{\red\electronlshiftarrow[1](-80,-80)(70,-90)}}%
{c{\red\electronrshiftarrow(-100,-20)(-30,90)}}%
{e{\red\electronrshiftarrow(40,90)(100,-40)}}%
]{2==CH$_{2}$;3==CH$_{2}$}{}[b]
\end{XyMcompd}}
```

\sixtriene

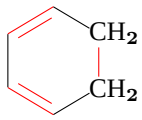


The XyMcompd environment is used to assure the net area for drawing *cis*-1,3,5-hexatriene. As for the command \addskbcolor, see Section 39.1. This command is declared in the optional argument ⟨skelbdlist⟩ of the command \sixheterov. As for the command \adddbcolor, see Section 39.2. This command is declared in the optional argument ⟨bondlist⟩ of the command \sixheterov (the addition technique). As for the commands \electronlshiftarrow and \electronrshiftarrow, see Section 33.4. These commands are declared in the optional argument ⟨bondlist⟩ of the command \sixheterov, where the addition technique is applied as a rather dirty technique.

Second, we define a command named \cyclohexdiene for drawing the structure of 1,3-cyclohexadiene. The definition and its output are shown below:

```
\def\cyclohexdiene{%
\begin{XyMcompd}(400,400)(250,250){}{}
\sixheterov(%
{d{\addskbcolor{}{\red}}}%
{f{\addskbcolor{}{\red}}}%
{b{\addskbcolor{}{\red}}}%
)[%
{d{\adddbcolor{v}{\red}}}%
{f{\adddbcolor{v}{\red}}}%
]{2==CH$_{2}$;3==CH$_{2}$}{}
\end{XyMcompd}}
```

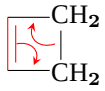
\cyclohexdiene



On the other hand, we define a command named \cyclobutene for drawing the structure of cyclobutene, which contains red-colored curved arrows. The definition and its output are shown below:

```
\def\cyclobutene{%
\begin{XyMcompd}(300,300)(400,200){}{}
\fourhetero(%
{d{\addskbcolor{}{\red}}}%
)[%
{D{\red\PutBondLine(30,30)(30,170){0.4pt}}}%
{c{\red\electronlshiftarrow[1](-100,-20)(-20,-100)}}%
{a{\red\electronrshiftarrow(35,100)(100,20)}}%
]{2==CH$_{2}$;3==CH$_{2}$}{}
\end{XyMcompd}}
```

\cyclobutene

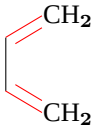


Note that the command \PutBondLine(30,30)(30,170){0.4pt} is used in place of a plausible code {d{\adddbcolor{}{\red}}}, because the latter is not effective to \fourhetero.

Finally, we define a command named \fourdiene for drawing the structure of 1,3-butadiene. The definition and its output are shown below:

```
\def\fourdiene{%
\begin{XyMcompd}(250,400)(250,250){}{}
\sixheterov(%
{d{\addskbcolor{}{\red}}}%
{f{\addskbcolor{}{\red}}}%
%{b{\addskbcolor{}{\red}}}%
)[%
{d{\adddbcolor{v}{\red}}}%
{f{\adddbcolor{v}{\red}}}%
]{1==CH$_{2}$;4==CH$_{2}$}{}[abc]
\end{XyMcompd}}
```

\fourdiene

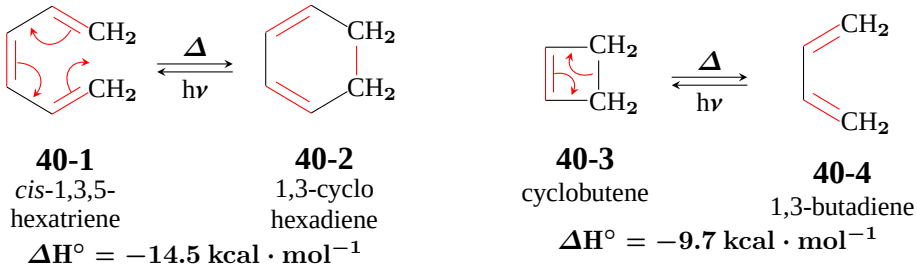


Each of these component structures is attached with a compound number (\compd and \label) and a text (\shortstack) in the tabular environment. Each pair of a starting component and a product component is combined by using \reactEqarrow and the resulting scheme is surrounded by a center environment and an outer minipage environment. The two pairs (surrounded by the minipage environment) are aligned horizontally. The title Electrocyclic Reactions is attached at the top, where the whole diagram is surrounded by an outer center environment after the command \nopagebreak is added to avoid page brake.

```
\def\sixtriene{ (omitted) }
\def\cyclohexdiene{ (omitted) }
\def\cyclobutene{ (omitted) }
\def\fourdiene{ (omitted) }

\begin{center}
\colorbox{olive}{\white Electrocyclic Reactions}
\nopagebreak \\[10pt]
\begin{minipage}[t]{0.45\textwidth}
\begin{center}
\begin{tabular}{c}
\sixtriene \\
\noalign{\vskip10pt}
\compd\label{cpd:sixtriene} \\
\shortstack{\textit{cis}\/-1,3,5- \\ hexatriene} \\
\end{tabular}
\reactEqarrow{20pt}{1cm}{$\Delta$}{h$\nu$}
\begin{tabular}{c}
\cyclohexdiene \\
\noalign{\vskip10pt}
\compd\label{cpd:cyclohexdiene} \\
\shortstack{1,3-cyclo \\ hexadiene} \\
\end{tabular}
\\
$\Delta H^{\circ} = \mathrm{-14.5~kcal\cdot mol^{-1}}$
\end{center}
\end{minipage}
%
\begin{minipage}[t]{0.45\textwidth}
\begin{center}
\begin{tabular}{c}
\cyclobutene \\
\noalign{\vskip10pt}
\compd\label{cpd:cycbutene} \\
cyclobutene \\
\end{tabular}
\reactEqarrow{15pt}{1cm}{$\Delta$}{h$\nu$}
\begin{tabular}{c}
\fourdiene \\
```

```
\noalign{\vskip10pt}
\compd\label{cpd:fourdine} \\
1,3-butadiene \\
\end{tabular}
\\
$\Delta H^{\circ} = \mathrm{-9.7~kcal\cdot mol^{-1}}$
\end{center}
\end{minipage}
\end{center}
```

Electrocyclic Reactions



40-1
cis-1,3,5-hexatriene

40-2
1,3-cyclo hexadiene

$\Delta H^\circ = -14.5\ \mathrm{kcal \cdot mol^{-1}}$

40-3
cyclobutene

40-4
1,3-butadiene

$\Delta H^\circ = -9.7\ \mathrm{kcal \cdot mol^{-1}}$ □

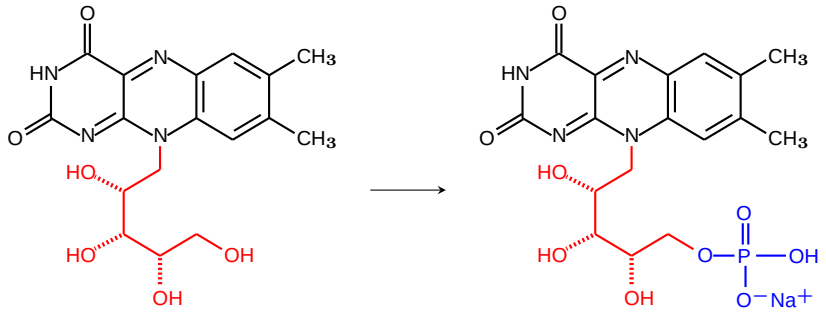
40.1.3 Vitamin B_2 and Related Compounds

Riboflavin (Vitamin B_2) has a benzene-fused 1,3,5,8-tetrazanaphthalene nucleus, which is attached by one ribose unit (colored in red). Flavin mononucleotide (FMN) and flavin adenine dinucleotide (FAD) are derived from riboflavin by introducing phosphate or pyrophosphate linkage.

Example 40.3. The total scheme of derivations is drawn by using the LaTeX quote environment:

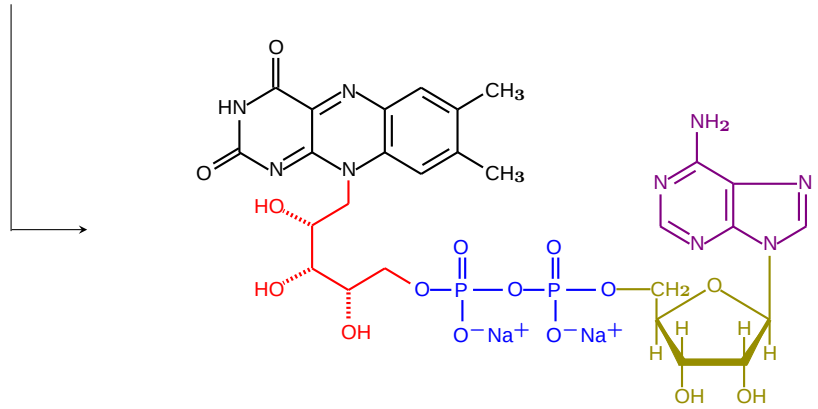
```
\begin{quote}
\changeunitlength{0.08pt}
\def\thinLineWidth{0.8pt}
\let\substfont=\sffamily
\begin{tabular}{c}
\begin{XyMcompd}(1500,1450)(50,-550){}{}
\decaheterov[ej%
{b{\sixfusev[ace]{}{2==CH$_{3}$;3==CH$_{3}$}{E}}}%
]{1==N;4==N;5==N;7==HN}{6D==O;8D==O;%
4==\addbscolor{\red}{\sixheterov{}{1==(yl);4A==OH;5A==HO;6A==HO;3==OH}[ab]}}
\end{XyMcompd} \\
\compd\label{cpd:riboflavin} \\
riboflavin (Vitamin B$_{2}$) \\
\end{tabular}
\reactrarrow{0pt}{1cm}{}{}
\begin{tabular}{c}
\begin{XyMcompd}(1500,1450)(50,-550){}{}
\decaheterov[ej%
{b{\sixfusev[ace]{}{2==CH$_{3}$;3==CH$_{3}$}{E}}}%
]{1==N;4==N;5==N;7==HN}{6D==O;8D==O;%
4==\addbscolor{\red}{\sixheterov{}{1==(yl);4A==OH;5A==HO;6A==HO;%
3==\bluex{\ryl(3==O){4==%
\tetrahedral{2==(yl);0==P;1D==O;4==OH;3==O$^{-}$Na$^{+}$}}}%
}[ab]}}
\end{XyMcompd} \\
\compd\label{cpd:flavinFMN} \\
flavin mononucleotide (FMN) \\
\end{tabular}
\\[10pt]
```

```
\mbox{}\hfill
\rule[12pt]{0.4pt}{3cm}\reactrarrow{10pt}{1cm}{}{}
\hskip1cm
\begin{tabular}{c}
\begin{XyMcompd}(2850,1750)(50,-850){}{}
\decaheterov[ej%
{b{\sixfusev[ace]{}{2==CH$_{3}$;3==CH$_{3}$}{E}}}%
]{1==N;4==N;5==N;7==HN}{6D==O;8D==O;%
4==\addbscolor{\red}{\sixheterov{}{1==(yl);4A==OH;5A==HO;6A==HO;%
3==\bluex{\ryl(3==O){4==\tetrahedral{2==(yl);0==P;1D==O;3==O$^{-}$Na$^{+}$;%
4==\ryl(4==O){4==\tetrahedral{2==(yl);0==P;1D==O;3==O$^{-}$Na$^{+}$;%
4==\ryl(4==O\olivex{\sbond C\rlap{H\raisebox{1pt}{$_{2}$}}}){%
8==\addbscolor{\olive}{\fivesugarh{%
1s==\violetx{\put(0,300){%
\nonaheterov[begj]{1==N;3==N;5==N;7==N}{1==(yl);4==NH$_{2}$}};%
1s==\PutBondLine(0,00)(0,300){0.8pt};%
5==O;%
1s==\WedgeAsSubst(0,0)(-3,-5){120};4s==\WedgeAsSubst(0,0)(3,-5){120};%
3s==\PutBondLine(-17,0)(307,0){2.8pt}%
}{4==(yl);1Sa==H;2Sb==H;2Sa==OH;3Sb==H;3Sa==OH;4Sa==H}
}}}}}}}}[ab]}}
\end{XyMcompd} \\
\compd\label{cpd:flavinade} \\
flavin adenine dinucleotide (FAD) \\
\end{tabular}
\end{quote}
```



40-5
riboflavin (Vitamin B_2)

40-6
flavin mononucleotide (FMN)



40-7
flavin adenine dinucleotide (FAD)

The structure **40-5** of riboflavin (Vitamin B_2) is drawn as such a benzene-fused 1,3,5,8-tetrazanaphthalene nucleus, where `\sixfusev` is declared in the ⟨atomlist⟩ of `\decaheterov` according to the addition tech-

nique. The ribose unit (colored in red by using `\addbscolor`) is drawn by using `\sixhetereov`, in which two skeletal bonds are deleted by declaring its optional argument ⟨delbdlist⟩.

The structure **40-6** of flavin mononucleotide (FMN) is drawn in a similar way, where the phosphate portion is colored in blue. The command `\ryl` is used to insert an oxygen bridge between the ribose and the phosphate portion.

To draw the structure **40-7** of flavin adenine dinucleotide (FAD), the five-membered ring of ribose (colored in olive by using `\olivex`) is attached an adenine nucleus (colored in violet by using `\violetx`) and linked by means of `\ryl`. To avoid an overcrowded situation between the ring-formed ribose and the an adenine nucleus, the linking bond is elongated by a rather dirty technique based on the replacement technique (due to `\PutBondLine`). □

40.2 Coloring in the ChemEquation Environment

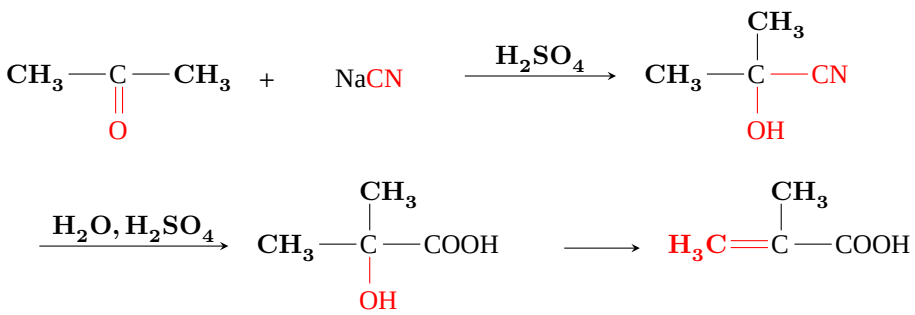
In this section, the `ChemEquation` environment is applied to draw colored reaction schemes. Other environments for printing chemical equations are also capable of involving colored structural formulas.

40.2.1 Formation of Cyanohydrins

Example 40.4. Formation of cyanohydrin is represented by using the `ChemEqnarray` environment (defined in the chemist package), as found in the following code:

```
\begin{ChemEqnarray}
&&
\tetrahedral{0==C;2==\ChemForm{CH_3};3D==\addbscolor{\red}{O};%
4==\ChemForm{CH_3}}
\qquad \raisebox{25pt}{ + \qquad Na{\red CN}} \qquad
\reactrarrow{25pt}{2cm}{\ChemForm{H_2SO_4}}{\strut} \qquad
\tetrahedral{0==C;2==\ChemForm{CH_3};3==\addbscolor{\red}{OH};%
1==\ChemForm{CH_3};4==\addbscolor{\red}{CN}} \nonumber \\
&&
\reactrarrow{25pt}{2.5cm}{\ChemForm{H_2O, H_2SO_4}}{\strut} \qquad
\tetrahedral{0==C;2==\ChemForm{CH_3};3==\addbscolor{\red}{OH};%
1==\ChemForm{CH_3};4==COOH} \qquad\qquad
\reactrarrow{25pt}{1cm}{\strut}{\strut} \qquad
\tetrahedral{0==C;2D==\addbscolor{\red}{\ChemForm{H_3C}};%
1==\ChemForm{CH_3};4==COOH} \label{eq:cyanohydrin}
\end{ChemEqnarray}
```

where the compound NaCN is printed out in upright format. Substituents and substitution bonds are colored by using the `\addbscolor` command.



(40.1)

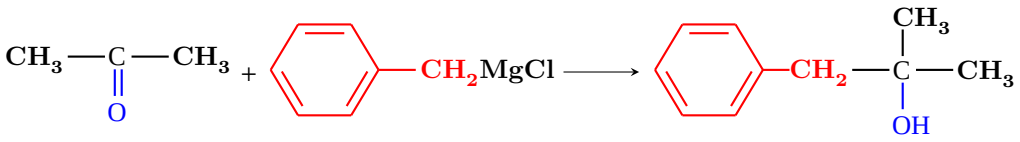
□

40.2.2 Grignard Reactions

Example 40.5. A Grignard reagent derived from benzyl chloride reacts with acetone so as to give a *tert*-alcohol, as shown in the following scheme due to the ChemEquation environment defined by the chemist package of the XeTeX system. The code:

```
\begin{ChemEquation}
\def\thinLineWidth{0.8pt}
\begin{XyMcompd}(600,300)(0,100){}{}
\tetrahedral{0==C;2==\ChemForm{CH_3};3D==\addbscolor{\blue}{O};%
4==\ChemForm{CH_3}}
\end{XyMcompd}
\quad \raisebox{0pt}{+} \quad
\begin{XyMcompd}(800,300)(350,250){}{}
{\red \bzdrh{4==\ChemForm{CH_2{\black MgCl}}}}
\end{XyMcompd}
\quad \reactrarrow{0pt}{1cm}{\strut}{\strut} \quad
\begin{XyMcompd}(1100,500)(-500,50){}{}
\tetrahedral{0==C;1==\ChemForm{CH_3};3==\addbscolor{\blue}{OH};%
2==\redx{\lyl(4==\ChemForm{CH_2}){4==\bzdrh{4==(yl)}}};%
4==\ChemForm{CH_3}}
\end{XyMcompd}
\end{ChemEquation}
```

generates the following equation containing structures with colored bonds and moieties:

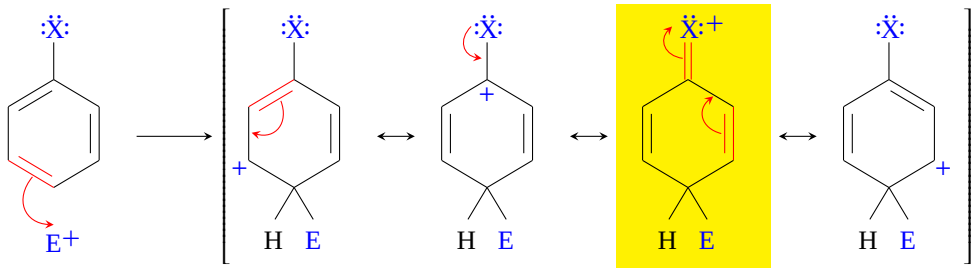


(40.2)

The declaration \def\thinLineWidth{0.8pt} just after the beginning of the ChemEquation environment indicates that the line width of each bond is changed from the standard width (0.4pt) to a thicker one (0.8pt). □

40.2.3 Electrophilic Reactions

Example 40.6. Para-attack in an electrophilic substitution of halobenzene is represented by Eq. 40.3, where curved arrows for representing electron shifts are colored in red.



(40.3)

This reaction mechanism is drawn by the following code, which is based on the ChemEquation environment.

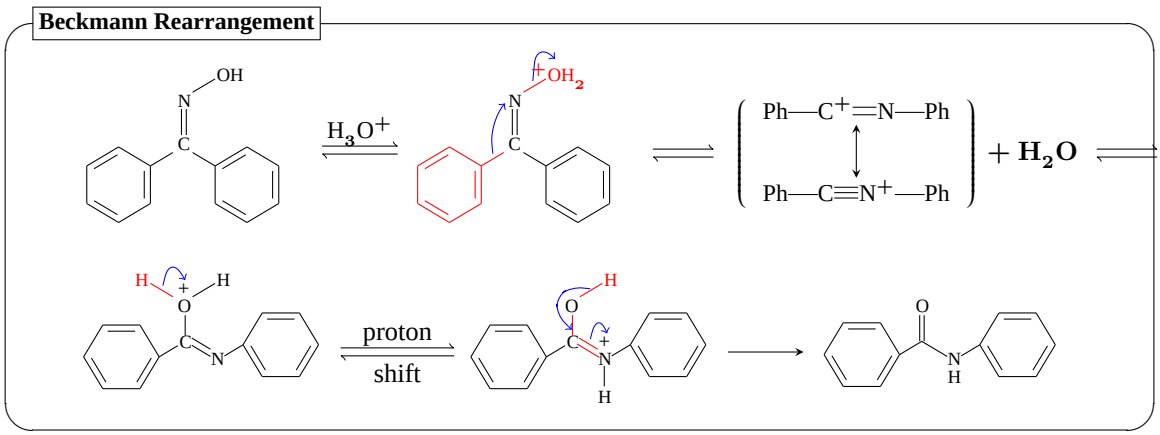
```
\begin{ChemEquation}
\begin{XyMcompd}(400,900)(220,0){}{}
\sixheterov({d{\addskbcolor{v}{\red}}})[bf{d{\adddbcolor{v}{\red}}}]{%
4s==\put(0,-160){\makebox(0,0)[t]{\bluex{E\rlap{$^{+}$}}}};%
4s==\redx{\electronrshiftarrow[1](-80,40)(0,-140)}%
}{1==\bluex{\lonepairA[124]{X}}}
\end{XyMcompd}
```

```
\reactrarrow{0pt}{1cm}{}{}
\left[%
\begin{XyMcompd}(400,900)(220,0){}{}
\sixheterov({f{\addskbcolor{v}{\red}}})[b{f{\adddbcolor{v}{\red}}}]{%
5s==\put(-30,-30){\makebox(0,0){\bluex{+}}};
1s==\red{\electronlshiftarrow[1](-160,-200)(-50,-80)}%;%
}{1==\bluex{\lonepairA[124]{X}};4Sa==\bluex{E};4Sb==H}
\end{XyMcompd}
\reactlrarrow{0pt}{0.5cm}{}{}
\begin{XyMcompd}(400,900)(220,0){}{}
\sixheterov[be]{%
1s==\put(0,-30){\makebox(0,0)[t]{\bluex{+}}};
1s==\red{\electronrshiftarrow[1](-60,200)(-20,80)}%;%
}{1==\bluex{\lonepairA[124]{X}};4Sa==\bluex{E};4Sb==H}
\end{XyMcompd}
\reactlrarrow{0pt}{0.5cm}{}{}
\colorbox{yellow}{%
\begin{XyMcompd}(400,900)(220,0){}{}
\sixheterov({b{\addskbcolor{v}{\red}}})[e{b{\adddbcolor{v}{\red}}}]{%
%1s==\put(0,-30){\makebox(0,0)[t]{\bluex{+}}};
1s==\red{\electronlshiftarrow[1](-60,200)(-20,80)};%
3s==\red{\electronlshiftarrow[1](-80,240)(-50,100)}%
}{1D==\addbscolor{\red}{\bluex{\lonepairA[12]{X}^$^{+}$}};4Sa==\bluex{E};4Sb==H}
\end{XyMcompd}}
\reactlrarrow{0pt}{0.5cm}{}{}
\begin{XyMcompd}(400,900)(220,0){}{}
\sixheterov[ae]{%
3s==\put(30,-30){\makebox(0,0){\bluex{+}}}%
}{1==\bluex{\lonepairA[124]{X}};4Sa==\bluex{E};4Sb==H}
\end{XyMcompd}
\right]
\label{eq:Electro-Subs}
\end{ChemEquation}
```

The right-hand side contains four resonance structures of a cationic intermediate, which are surrounded by a pair of brackets (`\left[...\right]`). Among them, the most preferred resonance structure is emphasized by a yellow box. For the command `\colorbox`, see the next section. □

40.2.4 Beckmann Rearrangement

Example 40.7. The following scheme concerning a Beckmann rearrangement is a color version of the reaction scheme drawn on page 656.



This scheme is drawn by the following code:

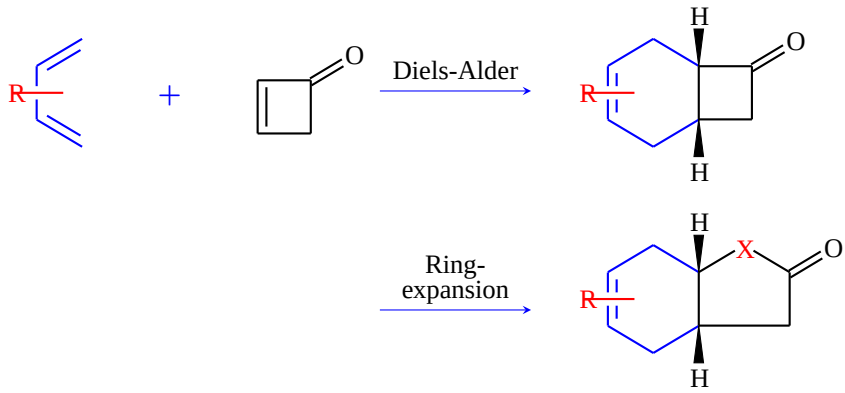
```
\begingroup
\def\tboxtitle{\bf Beckmann Rearrangement}
\begin{tboxscreen}
\changeunitlength{0.07pt}
\begin{ChemEqnarray*}
&&
\begin{XyMcompd}(1000,850)(-150,-150){}{}
\Ethylenev{1==C;2==N}{3==OH;2==\bzdrv{6==(yl)};1==\bzdrv{2==(yl)}}
\end{XyMcompd}
\mskip6mu \reacteqarrow{0pt}{1cm}{\small H$_{3}$O$^{+}$}{\strut} \mskip6mu
\begin{XyMcompd}(1000,850)(-150,-150){}{}
\Ethylenev{1==C;2==N;%
1==\bluex{\putRoundArrow{(-85,-20)(-100,150)(-20,250)}};%
2==\bluex{\putRoundArrow{(130,140)(150,350)(250,260)}}%
%%%PostScript Mode only%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%1==\pscurve[unit=\unitlength,linewidth=0.4pt]{->}%
%(-85,-20)(-100,150)(-20,250);%                    %
%2==\pscurve[unit=\unitlength,linewidth=0.4pt]{->}%
%(130,140)(150,350)(250,280)%                      %
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
}{3==\addbscolor{\red}{\llap{$^{+}$}OH$_{2}$};%
2==\bzdrv{6==(yl)};1==\addbscolor{\red}{\bzdrv{2==(yl)}}}
\end{XyMcompd}
\mskip6mu \reacteqarrow{0pt}{0.8cm}{}{} \mskip6mu
\left\lgroup
\begin{tabular}{c}
\small Ph\sbond C$^{+}$\dbond N\sbond Ph \\[-8pt]
\reactduarrow{0pt}{20pt}{}{} \\
\small Ph\sbond C\tbond N$^{+}$\sbond Ph \\
\end{tabular}
\right\rgroup
+ H_{2}O
\mskip6mu \reacteqarrow{0pt}{0.8cm}{}{}
\\ \noalign{\vskip20pt}
& &
\begin{XyMcompd}(1100,500)(-400,0){}{}
\dimethylenei[a]{1==C;2==N}{2W==\bzdrh{1==(yl)};1W==\bzdrh{4==(yl)};%
1==\Utrigonal{1==(yl);0==\upnobond{O}{+};2==H;3==\addbscolor{\red}{H};%
0=={\blue \putRoundArrow{(-80,140)(-40,300)(40,170)}
}}}
\end{XyMcompd}
\mskip6mu \reacteqarrow{0pt}{1.5cm}{proton}{shift} \mskip6mu
\begin{XyMcompd}(1100,500)(-400,0){}{}
\dimethylenei[%
{a{\replaceSKbond(25,-15)(5,-3){120}{\red}}}%
{a{\adddbcolor{i}{\red}}}%
]{1==C;2==\upnobond{N}{+};%
1==\bluex{\putRoundArrow[<-]{(-40,100)(-120,180)(-120,280)(-40,330)(60,320)}};%
1==\bluex{\putRoundArrow{(60,50)(100,200)(150,80)}}%
%%%PostScript Mode only%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%1==\pscurve[unit=\unitlength,linewidth=0.4pt]{<-}%
%(-40,100)(-120,180)(-120,280)(-40,330)(60,320);% %
%1==\pscurve[unit=\unitlength,linewidth=0.4pt]{->}%
%(60,50)(100,200)(150,80)%                         %
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
}%
{2==H;2W==\bzdrh{1==(yl)};1W==\bzdrh{4==(yl)};%
```

```
1==\addbscolor{\red}{\Utrigonal{0==\blackx{O};2==H;1==(yl)}}}
\end{XyMcompd}
\mskip6mu \reactrarrow{0pt}{1cm}{}{} \mskip6mu
\begin{XyMcompd}(1100,500)(-400,0){}{}
\dimethylenei{2==\downnobond{N}{H}}{2W==\bzdrh{1==(yl)};1W==\bzdrh{4==(yl)};1D==O}
\end{XyMcompd}
\end{ChemEqnarray*}
\end{tboxscreen}
\endgroup
```

Skeletal and double bonds participating in the Beckman reaction are colored by using `\replaceSKbond` (skeletal bonds) and `\adddbcolor` (double bonds). Although round arrows have been drawn by using `\psline` (defined in the PSTricks package) in Section 4.5 of the online-manual (xymtx405406.pdf), they are now drawn by using the newly-defined command `\putRoundArrow`, which is compatible to the PDF mode as well as to the PostScript mode of the XeLaTeX system. Because the old designations due to `\psline` are commented out, the comparison between `\putRoundArrow` and `\psline` shows their correspondence.[a] □

40.2.5 A New Diels-Alder Building Block

Example 40.8. The following scheme (Eq. 40.4) is cited from a short article "Diels-Alder Building Block Debuts" published in *Chem. & Eng. News*, August 9 (2010) pages 30–31.



(40.4)

R = various group; X = $\mathbf{CH_2}$, O, or NH

This scheme is drawn by writing the following code:

```
\def\markashR(#1,#2){%
\ifPSmode
{\put(#1,#2){\tetrahedral{4==(yl);%
2==\addbscolor{\psset{linecolor=white}\def\thinLineWidth{5pt}}{\null};%
2==R\kern-5pt}}%
\else
{\put(#1,#2){\tetrahedral{4==(yl);%
2==\addbscolor{\white\def\thinLineWidth{5pt}}{\null};%
2==R\kern-5pt}}\fi%
}
{\blue \def\thinLineWidth{0.8pt}
\begin{ChemEqnarray}
\begin{XyMcompd}(300,600)(100,150){}{}
```

[a] The mechanism of drawing curves by the pgf package (used in the PDF-compatible mode of the XeLaTeX system is different from the corresponding mechanism by the PSTricks package (used in the PostScript-compatible mode). Hence, the same argument of `\putRoundArrow` of the two modes results in different outputs.

```
{\blue \sixheterov[df{e{\red\markashR(100,100)}}]{}{}[abc]}
\end{XyMcompd}
\qquad + \qquad
\begin{XyMcompd}(300,400)(400,200){}{}\black
\fourhetero[d]{}{3D==O}
\end{XyMcompd}
& \reactrarrow{0pt}{2cm}{\black Diels-Alder}{\strut}
&
\begin{XyMcompd}(900,600)(100,150){}{}
\sixheterov({b{\addskbcolor{v}{\black}}})
[e{e{\red\markashR(100,100)}}%
{b{\black \fourfuse{}{3D==O;1FB==H;4GB==H}{d}}}]{}{}
\end{XyMcompd}
\nonumber \\
\noalign{\vskip10pt}
& \reactrarrow{0pt}{2cm}{\black Ring-expansion}{\strut}
&
\begin{XyMcompd}(900,600)(100,150){}{}
\sixheterov({b{\addskbcolor{v}{\black}}})
[e{e{\red\markashR(100,100)}}%
{b{\black \fivefusevi{1=={\red X}}{2D==O;4FB==H;5GB==H}{D}}}%
]{}{}
\end{XyMcompd}
\label{eq:Diels-Alder} \\
\noalign{\black\centering {\red R} = various group;
{\red X} = \ChemForm{CH_2}, O, or NH} \nonumber
\end{ChemEqnarray}
}
```

The newly-defined command \markashR is to put a Markash-type substituent on a specific bond of a structural formula. The white line due to the code,
2==\addbscolor{\white\def\thinLineWidth{5pt}}{\null},
erases a part of the single bond to be substituted in a Markash way. By declaring the code, \blue \def\thinLineWidth{0.8pt}, just before \begin{ChemEqnarray}, the whole domain derived by the ChemEqnarray environment is colored in blue and typeset with using bold-lined bonds. □

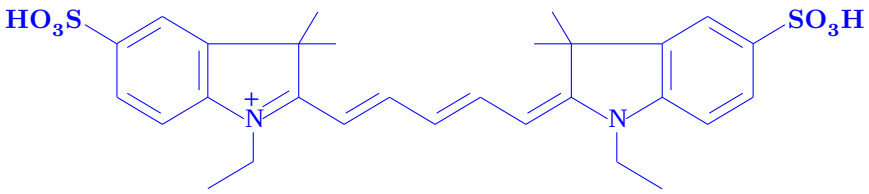
40.2.6 Thiols and Cyanine Dyes

The scheme shown in Example 40.9 is cited from a short article “How Thiols Photoswitch Cyanine Dyes” published in *Chem. & Eng. News*, December 14 (2009) page 34.

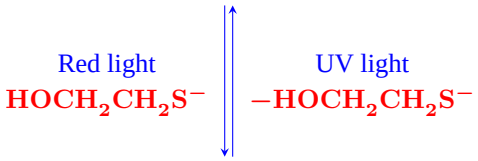
Example 40.9. Photoswitching of cyanine dyes is a key to super-resolution fluorescence microscopy techniques used for biological imaging. Red laser light switches a dye from a fluorescent to a dark state, where a thiol attacks the polymethine unit to give an adduct. Inversely, ultraviolet illumination stimulates the release of the thiol unit from the adduct so as to turn the fluorescence back on.

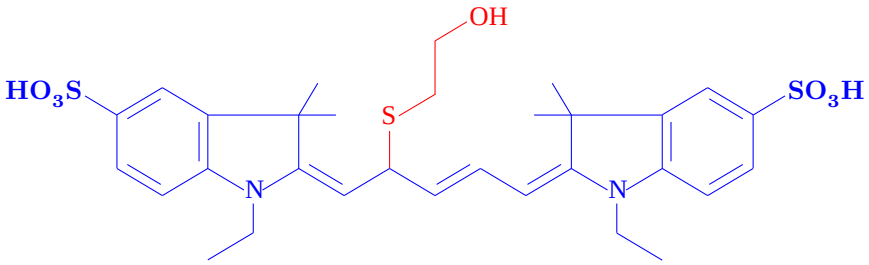
```
{\blue
\begin{ChemEqnarray*}
&
\begin{XyMcompd}(3000,700)(-800,-50){}{}
\heptamethylenei[bdf]{%
1s==\nonaheterov[aegj{1+}]{1==N}{2==(yl);1==\dimethylene{}{2==(yl)};%
3Sa==\null;3Sb==\null;5==\ChemForm{HO_{3}S}};%
7s==\fiveheterov[{b{\sixfusev[ace]{}{2==\ChemForm{SO_{3}H}}{e}}}]%
{1==N}{5==(yl);1==\dimethylenei{}{1==(yl)};4Sa==\null;4Sb==\null}}{}
\end{XyMcompd}
& \nonumber \\
\noalign{\centering\black Fluorecent} \\ \noalign{\vskip10pt}
```

```
&
\reactVEqarrow{0pt}{2cm}%
{\shortstack{Red light \\ \red \ChemForm{HOCH_2CH_2S^-}}}
{\shortstack{UV light \\ \red \ChemForm{- HOCH_2CH_2S^-}}}
& \nonumber \\
&
\begin{XyMcompd}(3000,1000)(-800,-50){}{}
\heptamethylenei[adf]{%
1s==\nonaheterov[egj]{1==N}{2==(yl);1==\dimethylene{}{2==(yl)};%
3Sa==\null;3Sb==\null;5==\ChemForm{HO_{3}S}};%
7s==\fiveheterov[{b{\sixfusev[ace]{}{2==\ChemForm{SO_{3}H}}{e}}}]%
{1==N}{5==(yl);1==\dimethylenei{}{1==(yl)};4Sa==\null;4Sb==\null}}%
{3==\addbscolor{\red}{\fiveheterov{1==S}{1==(yl);3==OH}[cde]}}
\end{XyMcompd}
& \\ \noalign{\centering\black Dark}
\end{ChemEqnarray*}}
```



Fluorescent

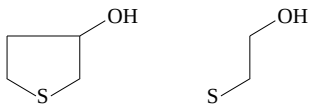




Dark

The left indole (benzopyrrole) moiety is drawn by using a ready-made command `\nonaheterov`, while the right indole (benzopyrrole) moiety is drawn by a ring-fusion technique of the `\fiveheterov` and `\sixfusev` commands. It should be noted that the $\mathbf{SCH_2CH_2OH}$ unit of the adduct is drawn by using the `\fiveheterov` command, where an optional deletion list `[cde]` is used to designate skeletal bonds to be erased. Compare the following two structures drawn by using the `\fiveheterov` command.

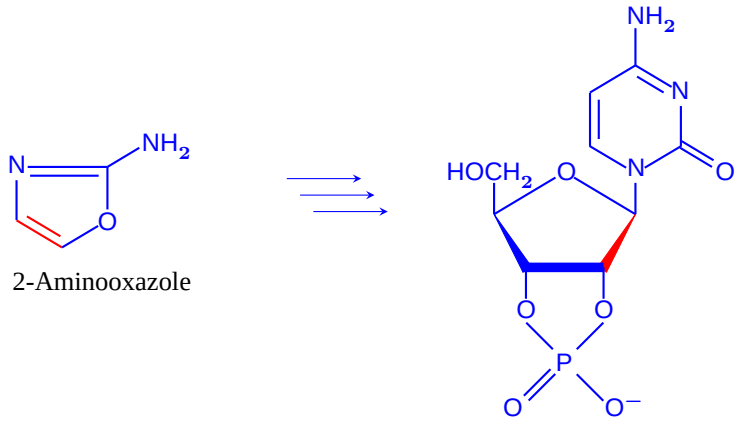
```
\fiveheterov{1==S}{3==OH}
\fiveheterov{1==S}{3==OH}[cde]
```



□

40.2.7 RNA Derived by a Counterintuitive Start

Example 40.10. The following scheme (Eq. 40.5) is cited from "Chemical Year in Review 2009" published in *Chem. & Eng. News*, December219 (2009) page 37 (entitled "DNA May Have Had a Counterintuitive Start").



(40.5)

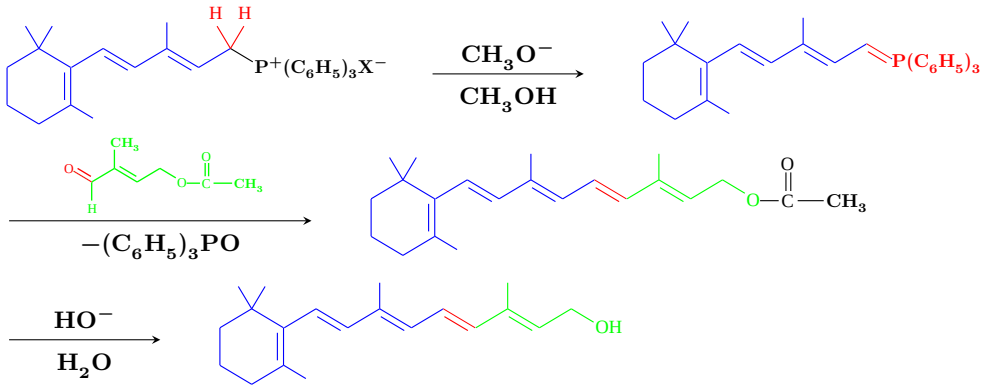
This scheme is drawn by writing the following code:

```
{\blue \def\thinLineWidth{0.8pt}
\let\substfont=\sffamily
\begin{ChemEquation}
\begin{tabular}{c}
\begin{XyMcompd}(500,500)(300,200){}{}
\fiveheterov({e{\addskbcolor{v}{\red}}})%
[c{e{\adddbcolor{i}{\red}}}]{2==O;4==N}{3==NH$_{2}$}
\end{XyMcompd}\\
\black 2-Aminooxazole
\end{tabular}
\qquad
\shortstack{$\llongrightarrow$ \\
\kern10pt$\llongrightarrow$ \\
\kern20pt$\llongrightarrow$}
\qquad
\begin{XyMcompd}(1000,1550)(100,-350){}{}
\fivesugarh{5==O;1s=={\red \WedgeAsSubst(0,0)(-3,-5){125}};%
4s==\WedgeAsSubst(0,0)(3,-5){125};%
3s==\PutBondLine(-15,0)(292,0){3.6pt}%
}{2Sa==O\put(-171,-190){\squareplanar{1==(yl);0==P;2==O$^{-}$;3D==O;1==;4==}};
%OH;
3Sa==O;4Sb==HOC\rlap{H$_{2}$};
1Sb==\sixheterov[ae]{2==N;4==N}{4==(yl);3D==O;1==NH$_{2}$}%
}[abc]
\end{XyMcompd}
\label{eq:DNA}
\end{ChemEquation}
}
```

For drawing furanose derivatives having bold skeletal bonds, see Section 18.2. The cyclic phosphate group is drawn by using the `\squareplanar` command. The declaration `\let\substfont=\sffamily` changes the font for printing substituents. □

40.2.8 Vitamin A_1

Example 40.11. Vitamin A_1 is synthesized industrially by using a Wittig reaction, as shown in the following scheme (Eq. 40.6), where a phosphorus ylide is an important intermediate.



Vitamin A_1 (40.6)

This scheme (Eq. 40.6) is obtained by the following code due to the `ChemEqnarray` environment of the chemist package (or the chmst-pdf or chmst-ps package):

```
{\def\thinLineWidth{0.6pt}
\begin{ChemEqnarray}
&&
\scalebox{0.7}{\VitaminAiIntA}\qquad
\reactrarrow{-5pt}{2cm}{\small \ChemForm{CH_3O^{-}}}{\small \ChemForm{CH_3OH}}
\qquad
\scalebox{0.7}{\VitaminAiIntB} \nonumber \\
&&
\reactrarrow{0pt}{4cm}{\def\thinLineWidth{1pt}
\scalebox{0.5}{\VitaminAiIntC}\\[5pt]}{\small \ChemForm{-(C_6H_5)_3PO}}\qquad
\scalebox{0.7}{\VitaminAiEster} \nonumber \\
&&
\reactrarrow{25pt}{2cm}{\small \ChemForm{HO^{-}}}{\small \ChemForm{H_2O}}\qquad
\shortstack{\scalebox{0.7}{\VitaminAi} \\ Vitamin A$_{1}$}
\end{ChemEqnarray}}
```

where respective intermediates (A–C and a Vitamin A_1 ester) and the final product (Vitamin A_1) are drawn after defining commands, `\VitaminAiIntA`, `\VitaminAiIntB`, `\VitaminAiIntC`, `\VitaminAiEster`, and `\VitaminAi`. The top declaration `\def\thinLineWidth{0.6pt}` is placed to make bonds thicker, so that the narrowing effects of size reduction (`\scalebox`) are cancelled out.

The intermediate A (the right intermediate in the first row of Eq. 40.6 is drawn by the command `\VitaminAiIntA`, which is defined as follows:

```
\def\VitaminAiIntA{%
\begin{XyMcompd}(1800,650)(300,250){}{}\blue
\sixheterov[b]{%
2s==\hexamethylene[bd]{}{1==(yl);4==\null;%
6W==\addbscolor{\black}{\ChemForm{P^{+}(C_6H_5)_3X^{-}}};%
6Sa==\addbscolor{\red}{H};6Sb==\addbscolor{\red}{H}}}
{1Sa==\null;1Sb==\null;3==\null}
\end{XyMcompd}
}
```

where `\addbscolor` commands are used to color substituents and substitution bonds. Although the whole structure of `\VitaminAiIntA` is colored blue by declaring `\blue` globally, the local declarations of `\red` and `\black` overwrite respective colored objects over the blue backbone of the structure.

The intermediate B (the left intermediate in the first row of Eq. 40.6) is a Wittig reagent (a phosphorus ylide), which is drawn by the macro `\VitaminAiIntB`. The macro is defined as follows:

```
\def\VitaminAiIntB{%
```

```
\begin{XyMcompd}(1800,600)(300,250){}{}\blue
\sixheterov[b]{%
2s==\heptamethylene[bd
{f{\adddbcolor{}{\red}}}%
{f{\replaceSKbond(0,0)(5,-3){130}{\red}}}%
]{7==\redx{\ChemForm{P(C_6H_5)_3}}
}{1==(yl);4==\null}}
{1Sa==\null;1Sb==\null;3==\null}
\end{XyMcompd}
}
```

where the \adddbcolor command is used to color a double bond and the \replaceSKbond command is used to color a skeletal bond.

The intermediate C above the reaction arrow in the second row of Eq. 40.6 is an aldehyde intermediate, which is drawn by the command \VitaminAiIntC. The macro for drawing the intermediate C is defined as follows:

```
\def\VitaminAiIntC{%
\begin{XyMcompd}(1300,500)(250,0){}{}\green
\pentamethylenei[c%
{a{\adddbcolor{i}{\red}}}%
{a{\replaceSKbond(171,-103)(-5,3){135}{\red}}}%
]{1==\redx{O}}%
{2==H;3==\ChemForm{CH_3};%
5W==\ryl(2==O){4==\tetrahedral{2==(yl);0==C;1D==O;4==\ChemForm{CH_3}}}}
\end{XyMcompd}
}
```

where the \adddbcolor command is used to color a double bond and the \replaceSKbond command is used to color a skeletal bond. Note that the local declaration of \red partially cancels the global coloring of the intermediate C by \green.

The right intermediate in the second row of Eq. 40.6 is a Vitamin A_1 ester, which is drawn by the macro \VitaminAiEster defined as follows:

```
\def\VitaminAiEster{%
\begin{XyMcompd}(2500,600)(300,250){}{}\blue
\sixheterov[b]{%
2s==\heptamethylene[bd
{f{\adddbcolor{}{\red}}}%
{f{\replaceSKbond(0,0)(5,-3){171}{\red}}}%
]{%
7s==\greenx{\tetramethylene[b]{}%
{1==(yl);2==\null;%
4W==\blackx{\ryl(2==\greenx{O}){%
4==\tetrahedral{2==(yl);0==C;1D==O;4==\ChemForm{CH_3}}}}}}
}{1==(yl);4==\null}}
{1Sa==\null;1Sb==\null;3==\null}
\end{XyMcompd}
```

where the left moiety (due to the Wittig reagent) and the right moiety (due to the aldehyde intermediate) are differentiated by colors (blue and green). Moreover, the resulting olefinic function is emphasized by drawing in red. The terminal acetyl group is differentiated from other portions by drawing in black, because it participates in a subsequent hydrolysis.

The final product, Vitamin A_1, in the third row of Eq. 40.6 is drawn by the following code:

```
\def\VitaminAi{%
\begin{XyMcompd}(2000,600)(300,250){}{}\blue
\sixheterov[b]{%
2s==\heptamethylene[bd%
{f{\adddbcolor{}{\red}}}%
```

```
{f{\replaceSKbond(0,0)(5,-3){171}{\red}}}]
{7s==\greenx{\tetramethylene[b]{}%
{1==(yl);2==\null;4W==OH}}%
{1==(yl);4==\null}}%
{1Sa==\null;1Sb==\null;3==\null}
\end{XyMcompd}
}
```

where a newly introduced double bond is differentiated by red color. □

40.3 Coloring in the `tabular` Environment

40.3.1 Vitamin D_2

This is a color version of the reaction scheme drawn in Section 2.5 of the on-line manual of XyMTEX version 4.04 (xymtx404.pdf), where skeletal and double bonds participating photochemical and thermochemical reactions are colored by using `\replaceSKbond` (skeletal bonds) and `\adddbcolor` (double bonds).

Example 40.12. Irradiation of ergosterol (and lumisterol) causes the opening of the B ring to produce previtamin D_2 having a conjugated triene, which is a precursor of vitamin D_2 (ergocalciferol), as shown in Fig. 40.1. The double bonds of each intermediate are colored by the present technique of coloring double bonds.

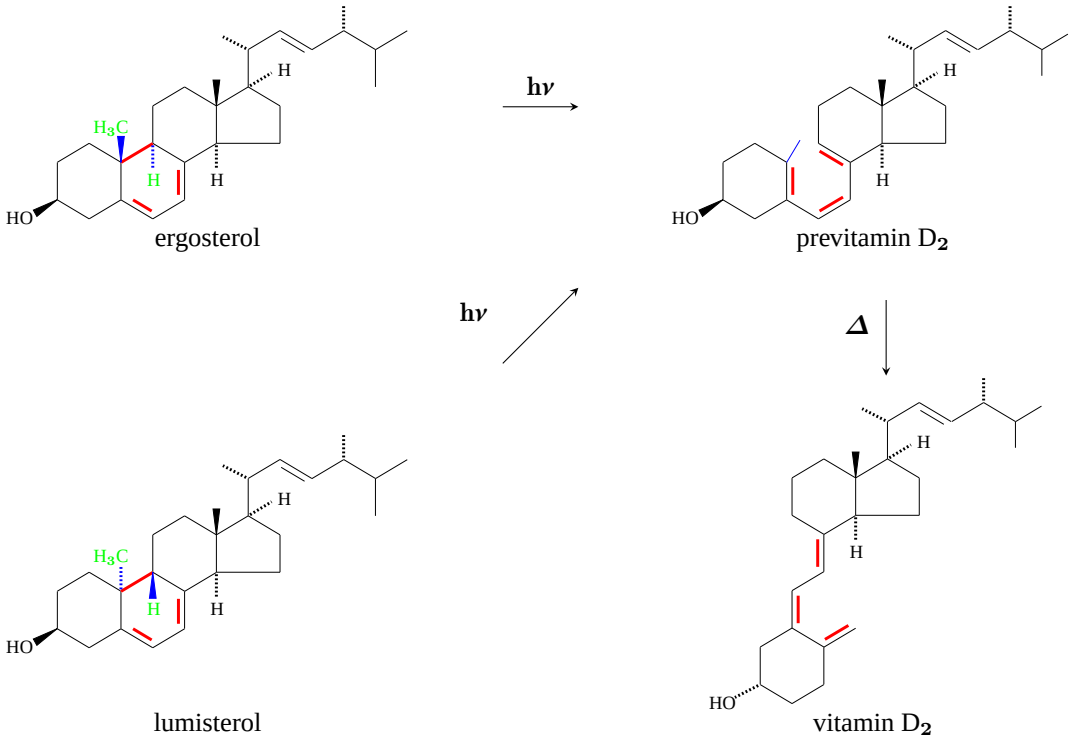


Figure 40.1. Photochemistry of ergosterol and lumisterol

To draw the intermediates contained in Fig. 40.1, macros for drawing them are defined by applying the systematic way of coloring double bonds, i.e., `\lumisterol` for drawing lumisterol, `\ergosterol` for drawing ergosterol, `\previtaminD` for drawing previtamin D, and `\vitaminDii` for drawing vitamin D_2.

```
%lumisterol
\def\lumisterol{%
\begin{XyMcompd}(2050,1150)(0,250){}{}
\steroidChain[{Zc}%
{i{\replaceSKbond[1.6pt](0,0)(5,3){171}{\red}}}%
```

```
{e{\adddbcolor{v}{\red\def\thinLineWidth{1.6pt}}}}%
{g{\adddbcolor{v}{\red\def\thinLineWidth{1.6pt}}}}%
]%
{3B==HO;9B==\addbscolor{\blue}{\greenx{H}};%
{10}A==\addbscolor{\blue}{\greenx{\lmoiety{H$_{3}$C}}};%
{13}B==\null;{14}A==H;{17}GA==H;%
{20}A==\null;{24}A==\null}
\end{XyMcompd}
}

%ergosterol
\def\ergosterol{%
\begin{XyMcompd}(2050,1150)(0,250){}{}
\steroidChain[{Zc}%
{i{\replaceSKbond[1.6pt](0,0)(5,3){171}{\red}}}%
{e{\adddbcolor{v}{\red\def\thinLineWidth{1.6pt}}}}%
{g{\adddbcolor{v}{\red\def\thinLineWidth{1.6pt}}}}%
]%
{3B==HO;9A==\addbscolor{\blue}{\greenx{H}};%
{10}B==\addbscolor{\blue}{\greenx{\lmoiety{H$_{3}$C}}};%
{13}B==\null;{14}A==H;{17}GA==H;%
{20}A==\null;{24}A==\null}
\end{XyMcompd}
}

%previtamin D
\def\previtaminD{%
\begin{XyMcompd}(2050,1150)(0,250){}{}
\sixheterov[%
{b{\sixfusev[%
{a{\adddbcolor{v}{\red\def\thinLineWidth{1.6pt}}}}%
{c{\adddbcolor{v}{\red\def\thinLineWidth{1.6pt}}}}%
{e{\adddbcolor{v}{\red\def\thinLineWidth{1.6pt}}}}%
{a{\sixfusev[%
{b{\fivefusevi[%
{a{\sixfusev[a]{%
2s==\trimethylene{}{1==(yl);2A==\null;3==\null;3W==\null}
}{6A==\null}{D}[bc]}}
]{}{1GA==H}{D}}}
]{}{2FB==\null;3GA==H}{D}}}
]{}{}{E}[f]}}]
{}{2Sb==\addbscolor{\blue}{\null};5B==HO}
\end{XyMcompd}
}

%vitamin D$_{2}$ (ergocalciferol)
\def\vitaminDii{%
\begin{XyMcompd}(1650,1750)(0,250){}{}
\sixheterov[%
{a{\sixfusev[%
{c{\adddbcolor{v}{\red\def\thinLineWidth{1.6pt}}}}%
{e{\adddbcolor{v}{\red\def\thinLineWidth{1.6pt}}}}%
{f{\sixfusev[%b%
{b{\adddbcolor{v}{\red\def\thinLineWidth{1.6pt}}}}%
{a{\sixfusev[%
{b{\fivefusevi[
{a{\sixfusev[a]{%
2s==\trimethylene{}{1==(yl);2A==\null;3==\null;3W==\null}
```

```
}{6A==\null}{D}[bc]}}
]{}{1GA==H}{D}}}
]{}{2FB==\null;3GA==H}{D}%
}}]{}{}{C}[def]}}]{}{}{D}[ab]}}]{}{5A==HO}
\end{XyMcompd}
}
```

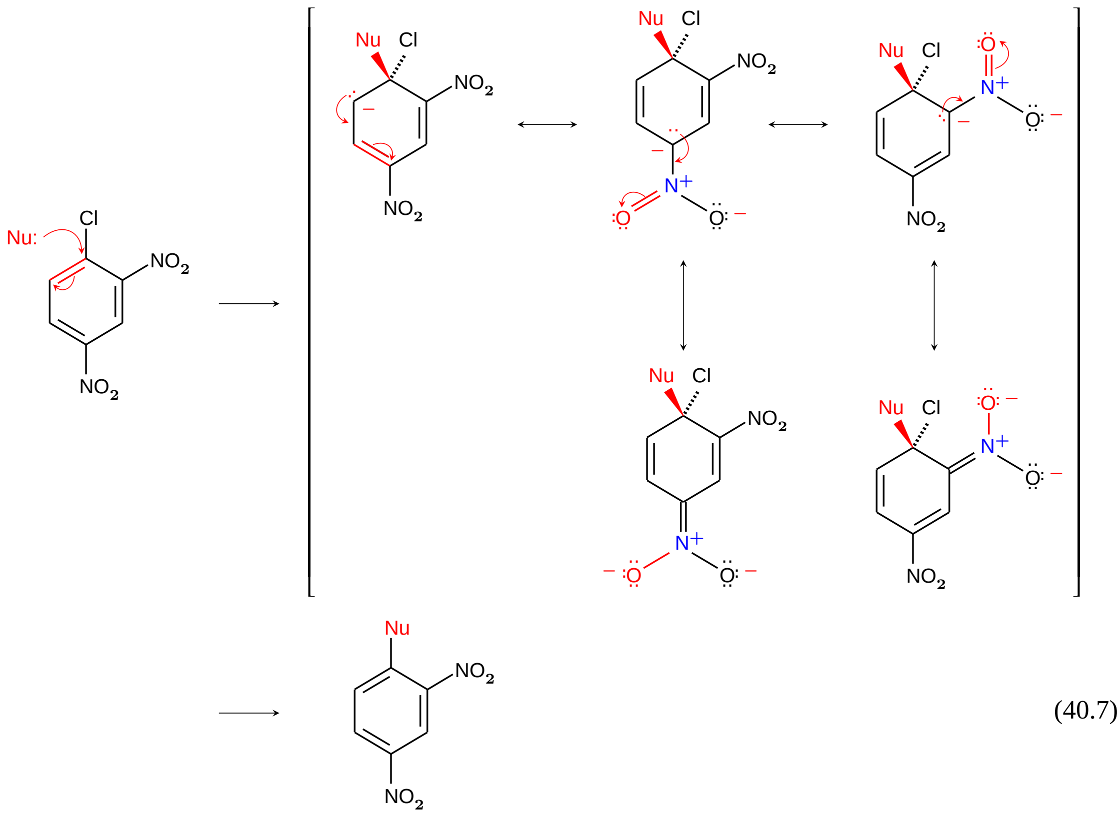
By using these macros, Fig. 40.1 is drawn by the following code:

```
\begin{figure}[h]
\begin{center}
\begin{tabular}{ccc}
\scalebox{0.7}{\ergosterol} &
\reactrarrow{0pt}{1cm}{$h\nu$}{\strut} & \scalebox{0.7}{\previtaminD} \\
ergosterol & & previtamin D$_{2}$ \\[10pt]
& \reactnearrow{0pt}{1cm}{\raisebox{10pt}{\rlap{$h\nu$}}}{\strut} &
\reactdarrow{0pt}{1cm}{$\Delta$}{\strut}  \\
\scalebox{0.7}{\lumisterol} && \scalebox{0.7}{\vitaminDii} \\
lumisterol & & vitamin D$_{2}$
\end{tabular}
\end{center}
\caption{Photochemistry of ergosterol and lumisterol}
\label{ff:PEL}
\end{figure}
```

□

40.3.2 Nucleophilic Reactions

Example 40.13. A nucleophilic substitution of 1-chloro-2,4-dinitrobenzene is represented by Eq. 40.7, where curved arrows for representing electron shifts are colored in red.



(40.7)

This reaction mechanism is drawn by the following code, in which the tabular environment is used in the ChemEqnarray environment. The bond thickness is changed by declaring \def\thinLineWidth{0.8pt} and the font is changed by declaring \let\substfont=\sffamily.

```
{\def\thinLineWidth{0.8pt}
\let\substfont=\sffamily
\tabcolsep=5pt
\begin{ChemEqnarray}
\scalebox{0.8}{%
\begin{XyMcompd}(800,900)(50,0){}{}
\sixheterov({f{\addskbcolor{v}{\red}}})[bd{f{\adddbcolor{v}{\red}}}]{%
1s==\red \electronrshiftarrow(-200,100)(-20,20)};%
1s==\put(-200,100){\makebox(0,0)[rc]{\red Nu:~}};%
6s==\red \electronlshiftarrow[1](20,-20)(120,20)}%
}{1==Cl;2==NO$_{2}$;4==NO$_{2}$}
\end{XyMcompd}}
& \mathrel{\scalebox{0.8}{\reactrarrow{0pt}{1cm}{}{}}} &
\left[%
\scalebox{0.8}{%
\begin{tabular}{ccccc}
\begin{XyMcompd}(700,900)(150,0){}{}
\sixheterov({d{\addskbcolor{v}{\red}}})[bd{d{\adddbcolor{v}{\red}}}]{%
6==\red \lonepairB[4]{\phantom{c}\rlap{$_{-}$}}};%
6s==\red \electronrshiftarrow[1](-30,30)(-20,-100)};%
4s==\red \electronrshiftarrow(-80,100)(5,25)}%
}{1SA==Cl;1SB==\addbscolor{\red}{Nu};2==NO$_{2}$;4==NO$_{2}$}
\end{XyMcompd}
& $\llongleftrightarrow$ &
\begin{XyMcompd}(700,1100)(150,-200){}{}
\sixheterov[be]{%
4==\lower0.5em\hbox{\red \lonepairA[1]{\llap{$_{-}$}\phantom{C}}};%
4s==\red \electronrshiftarrow[1](35,50)(10,-80)}%
}{1SA==Cl;1SB==\addbscolor{\red}{Nu};2==NO$_{2}$;
4==\Dtrigonal{1==(yl);0=={\blue N\rlap{$^{+}$}};%
0=={\red \electronlshiftarrow(-200,-70)(-90,-20)};%
2==\lonepairA[123]{O\rlap{\red $\,\,^{-}$}};%
3D==\addbscolor{\red}{\lonepairA[34]{O}}}}
\end{XyMcompd}
& \kern-20pt$\llongleftrightarrow$\kern10pt &
\begin{XyMcompd}(800,1000)(250,0){}{}
\sixheterov[ce]{%
2==\lower0.1em\hbox{\red \lonepairB[3]{\phantom{C}\rlap{$_{-}$}}};%
2s==\red \electronrshiftarrow(-35,0)(60,50)}%
}{1SA==Cl;1SB==\addbscolor{\red}{Nu};
4==NO$_{2}$;%
2==\Dtrigonal{3==(yl);0=={\blue N\rlap{$^{+}$}};%
0=={\red \electronrshiftarrow[1](70,120)(90,250)};%
2==\lonepairA[123]{O\rlap{\red $\,\,^{-}$}};%
1D==\addbscolor{\red}{\lonepairA[14]{O}}}}
\end{XyMcompd}
\\
& & \reactduarrow{0pt}{1.5cm}{}{}\kern10pt & &
\reactduarrow{0pt}{1.5cm}{}{}\kern30pt \\
\noalign{\vskip5pt}
&&
\begin{XyMcompd}(800,1100)(50,-200){}{}
\sixheterov[be]{%
```

```
}{1SA==Cl;1SB==\addbscolor{\red}{Nu};2==NO$_{2}$;
4D==\Dtrigonal{1==(yl);0=={\blue N\rlap{$^{+}$}};%
%0=={\red \electronlshiftarrow(-200,-70)(-90,-20)};%
2==\lonepairA[123]{O\rlap{\red $\,\,^{-}$}};%
3==\addbscolor{\red}{\lonepairA[134]{\llap{$^{-}\,\,$}O}}}
\end{XyMcompd}
& &
\begin{XyMcompd}(800,1000)(250,0){}{}
\sixheterov[ce]{%
}{1SA==Cl;1SB==\addbscolor{\red}{Nu};
4==NO$_{2}$;%
2D==\Dtrigonal{3==(yl);0=={\blue N\rlap{$^{+}$}};%
2==\lonepairA[123]{O\rlap{\red $\,\,^{-}$}};%
1==\addbscolor{\red}{\lonepairA[124]{O\rlap{$\,\,^{-}$}}}}}
\end{XyMcompd}
\\
\end{tabular}}
\right] \nonumber \\
& \mathrel{\scalebox{0.8}{\reactrarrow{0pt}{1cm}{}{}}} &
\scalebox{0.8}{%
\begin{XyMcompd}(800,900)(50,0){}{}
\sixheterov[bdf]{%
}{1==\redx{Nu};2==NO$_{2}$;4==NO$_{2}$}
\end{XyMcompd}}
\label{eq:Nucl-Subs}
\end{ChemEqnarray}
}
```

The left single structure in the first row is drawn in a `tabular` environment, while the left scheme involving five structures is drawn in another `tabular` environment surrounded by a pair of brackets (`\left[...\right]`). Each scale of them is reduced by using the `\scalebox` command supported by the graphicx package, which is automatically loaded by any modes of the XeLaTeX system. □

40.4 Reaction Schemes in Color Boxes

40.4.1 Drawing by the `\colorbox` Command

The command `\colorbox` of the xcolor package takes the following syntax:

```
\colorbox[⟨model⟩]{⟨backcolor⟩}{⟨text⟩}
```

where the optional argument ⟨model⟩ denotes a color model (e.g., cmyk, gray, etc.), the argument ⟨color⟩ denotes a color or a color specification due to ⟨model⟩, and the argument ⟨text⟩ indicates any text. The text due to ⟨text⟩ is surrounded by a tight box, the background of which is colored according to ⟨color⟩. A color for ⟨color⟩ is selected from the left-hand columns of Tables 38.1 and 38.2 after the symbol \ is omitted.

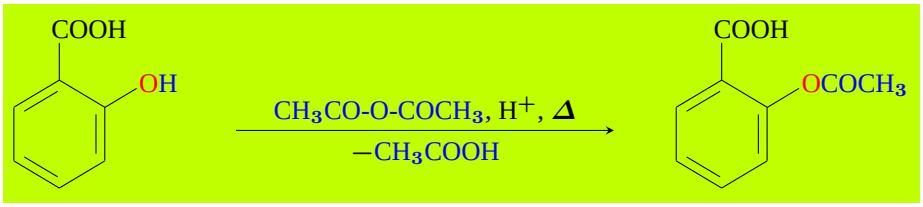
Reaction schemes drawn by the XeLaTeX system are regarded as a kind of texts, which are acceptable as the ⟨text⟩ of `\colorbox`.

Example 40.14. For example, the following code:

```
\begin{center}
\colorbox{lime}{%
\begin{XyMcompd}(500,650)(280,250){}{}
\benzenev{1==COOH;2==\redx{O}\bluex{H}}
\end{XyMcompd}
\qquad
```

```
\reactrarrow{-10pt}{5cm}{\bluex{CH$_{3}$CO-O-COCH$_{3}$}, H$^{+}$, $\Delta$}%
{$-$\bluex{CH$_{3}$COOH}}
\qquad
\begin{XyMcompd}(750,650)(280,250){}{}
\benzenev{1==COOH;2==\redx{O}\bluex{COCH$_{3}$}}
\end{XyMcompd}}
\end{center}
```

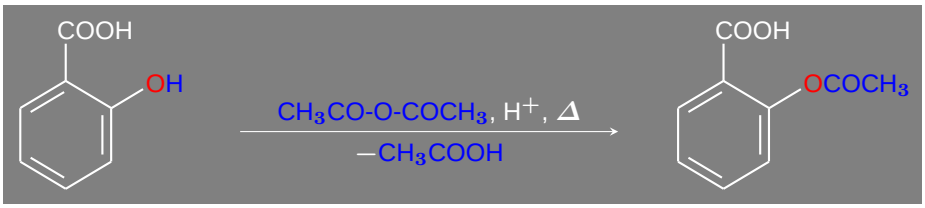
generates a colored box involving a reaction scheme:



□

Example 40.15. The default color of the ⟨text⟩ of `\colorbox` is black, unless other colors are specified, as found in the preceding output. The color of ⟨text⟩ can be changed freely. If the background color is selected to be dark, even `\white` can be declared to print ⟨text⟩. The following output is a typical example:

```
\begin{center}
\colorbox{gray}{\white%
\def\thinLineWidth{0.8pt}
\let\substfont=\sffamily
\sffamily
\begin{XyMcompd}(500,650)(280,250){}{}
\benzenev{1==COOH;2==\redx{O}\bluex{H}}
\end{XyMcompd}
\qquad
\reactrarrow{-10pt}{5cm}{\bluex{CH$_{3}$CO-O-COCH$_{3}$}, H$^{+}$, $\Delta$}%
{$-$\bluex{CH$_{3}$COOH}}
\qquad
\begin{XyMcompd}(750,650)(280,250){}{}
\benzenev{1==COOH;2==\redx{O}\bluex{COCH$_{3}$}}
\end{XyMcompd}}
\end{center}
```

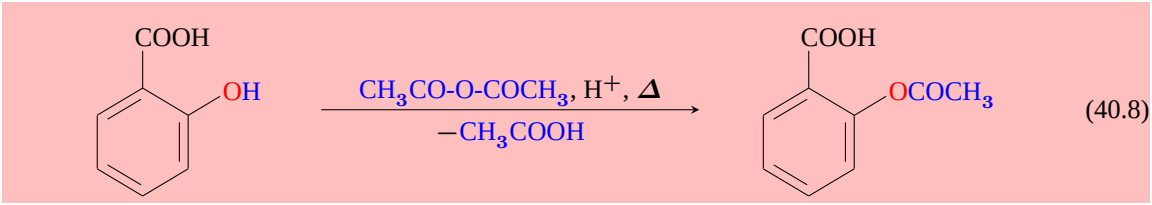


□

Example 40.16. A reaction scheme in the `ChemEquation` environment is surrounded by the `minipage` environment, the width of which is selected to be equal to the text width of your document. The `\colorbox` puts a space around the text of ⟨text⟩, where the space is adopted to be equal to `\fboxsep` (default value 3pt) of the LaTeX-command `\fbox`. Hence, you should declare `\fboxsep=0pt` to avoid the overfull warning.

```
\noindent
{\fboxsep=0pt
\colorbox{pink}{%
\begin{minipage}{\textwidth}
\begin{ChemEquation}
\begin{XyMcompd}(500,650)(280,250){}{}
\benzenev{1==COOH;2==\redx{O}\bluex{H}}
```

```
\end{XyMcompd}
\qquad
\reactrarrow{0pt}{5cm}{\bluex{CH$_{3}$CO-O-COCH$_{3}$}, H$^{+}$, $\Delta$}%
{$-$\bluex{CH$_{3}$COOH}}
\qquad
\begin{XyMcompd}(750,650)(280,250){}{}
\benzenev{1==COOH;2==\redx{O}\bluex{COCH$_{3}$}}
\end{XyMcompd}
\end{ChemEquation}%
\end{minipage}%
}}
```



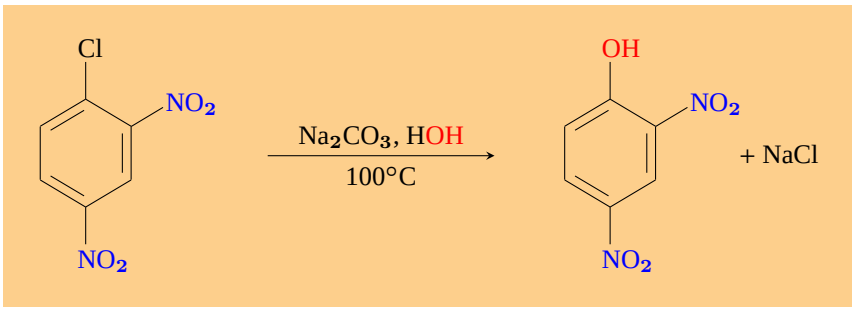
(40.8)

□

Example 40.17. The `cmyk` or `rgb` model assigned to the optional argument ⟨model⟩ is capable of selecting any color for coloring the background of a color box. When the `cmyk` model is adopted, the color specifications of cyan, magenta, yellow, and black are respectively selected to be 0 to 1, as shown in the following example:

```
\begin{center}
\fboxsep=10pt
\colorbox[cmyk]{0,0.2,0.5,0}{%
\begin{XyMcompd}(550,900)(250,0){}{}
\benzenev{1==Cl;2==\bluex{NO$_{2}$};4==\bluex{NO$_{2}$}}
\end{XyMcompd}
\qquad
\reactrarrow{0pt}{3cm}{Na$_{2}$CO$_{3}$, H\redx{OH}}{100$^{\circ}$C}
\qquad
\begin{XyMcompd}(550,900)(250,0){}{}
\benzenev{1==\redx{OH};2==\bluex{NO$_{2}$};4==\bluex{NO$_{2}$}}
\end{XyMcompd}
+ NaCl }
\end{center}
```

Note that the space surrounding the text is set to be 10pt by declaring `\fboxsep=10pt`, where this declaration is restricted to be local by putting it in the `center` environment. The above code generates the following reaction scheme in a color box, for which the magenta value and the yellow value are selected to be 0.2 and 0.5.

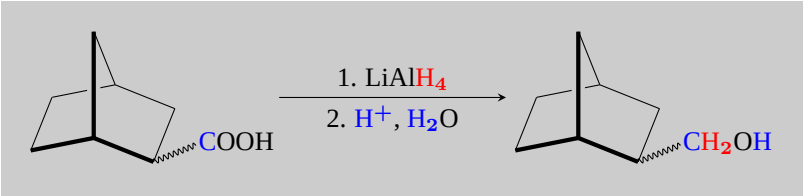


□

Example 40.18. When the `gray` model is adopted, the specification of gray is selected to be 0 to 1, as shown in the following example. Note that a smaller value corresponds to a darker gray background (0: black; and

1: white). Because the default color of a background is selected to be white during drawing bond crossing, it should be changed into the new background color by defining `\BackGroundColor`. This changing is switched according to the PDF-compatible or the PostScript-compatible mode.

```
\begin{center}
\fboxsep=10pt
\colorbox[gray]{0.8}{%
\ifPDFmode
\def\BackGroundColor{\color[gray]{0.8}}%
\else\ifPSmode
\def\BackGroundColor{%
\definecolor{TempColor}{gray}{0.8}%
\psset{linecolor=TempColor}}
\fi\fi
\begin{XyMcompd}(800,500)(250,200){}{}
\bornane{3U==\bluex{C}OOH}
\end{XyMcompd}
%}
\reactrarrow{0pt}{3cm}{1. LiAl\redx{H$_{4}$}}
{2. \bluex{H$^{+}$}, \bluex{H$_{2}$}O}
\begin{XyMcompd}(850,500)(250,200){}{}
\bornane{3U==\bluex{C}\redx{H$_{2}$}O\bluex{H}}
\end{XyMcompd}
}
\end{center}
```



□

40.4.2 Drawing by the `\fcolorbox` Command

The command `\fcolorbox` of the xcolor package takes the following syntax:

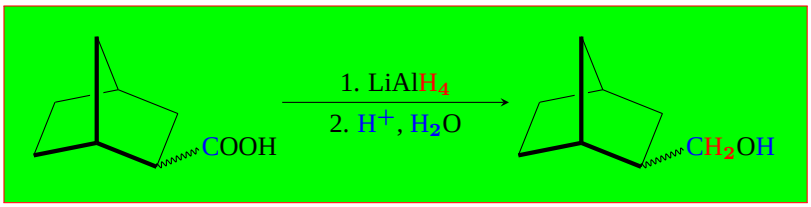
```
\fcolorbox[⟨famemodel⟩]{⟨framecolor⟩}[⟨backmodel⟩]{⟨backcolor⟩}{⟨text⟩}
```

where the optional argument ⟨framemodel⟩ and ⟨backmodel⟩ denote a color models (e.g., cmyk, gray, etc.) for the frame and the background, the argument ⟨framecolor⟩ and ⟨backcolor⟩ denotes colors or color specifications due to ⟨framemodel⟩ and ⟨backmodel⟩, and the argument ⟨text⟩ indicates any text. The text due to ⟨text⟩ is surrounded by a frame box, the background of which is colored according to ⟨backcolor⟩. A color for ⟨framecolor⟩ or ⟨backcolor⟩ is selected from the left-hand columns of Tables 38.1 and 38.2 after the symbol \ is omitted.

Example 40.19. Let us examine a case in which the color of a frame is red (⟨framecolor⟩: red) and the color of a background is green (⟨backcolor⟩: green). Because the default color of a background is selected to be white during drawing bond crossing, it should be changed into green by declaring `\let\BackGroundColor=\green`. The color of a text is black as default.

```
\begin{center}
\fboxsep=10pt
\fcolorbox{red}{green}{\let\BackGroundColor=\green%
\begin{XyMcompd}(800,500)(250,200){}{}
\bornane{3U==\bluex{C}OOH}
\end{XyMcompd}
```

```
\reactrarrow{0pt}{3cm}{1. LiAl\redx{H$_{4}$}}
{2. \bluex{H$^{+}$}, \bluex{H$_{2}$}O}
\begin{XyMcompd}(850,500)(250,200){}{}
\bornane{3U==\bluex{C}\redx{H$_{2}$}O\bluex{H}}
\end{XyMcompd}
}
\end{center}
```

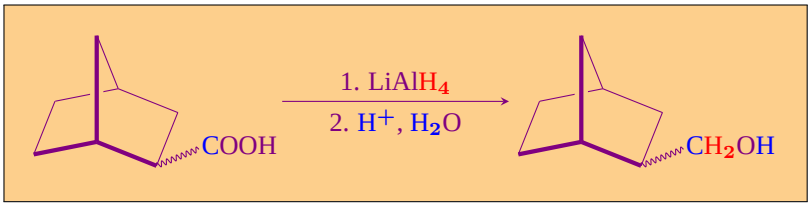


□

The color of a text can be changed by using a command selected from the left-hand columns of Tables 38.1 and 38.2 (`\red` etc.), by the command `\color` of the xcolor package (`\color{red}` etc.), or by the command `\textcolor` of the xcolor package (`\textcolor{red}{...}` etc.).

Example 40.20. The following example selects black for the color of a frame, a specified color `[cmyk]{0,0.2,0.5,0}` for the color of a background, and violet for the color of a text. Because the default color of a background is selected to be white during drawing bond crossing, it should be changed into the new background color by defining `\BackGroundColor`.

```
\fboxsep=10pt
\fcolorbox{black}[cmyk]{0,0.2,0.5,0}{\textcolor{violet}{%
\ifPDFmode
\def\BackGroundColor{\color[cmyk]{0,0.2,0.5,0}}%
\else\ifPSmode
\def\BackGroundColor{%
\definecolor{TempColor}{cmyk}{0,0.2,0.5,0}%
\psset{linecolor=TempColor}}
\fi\fi
\begin{XyMcompd}(800,500)(250,200){}{}
\bornane{3U==\bluex{C}OOH}
\end{XyMcompd}
%}
\reactrarrow{0pt}{3cm}{1. LiAl\redx{H$_{4}$}}
{2. \bluex{H$^{+}$}, \bluex{H$_{2}$}O}
\begin{XyMcompd}(850,500)(250,200){}{}
\bornane{3U==\bluex{C}\redx{H$_{2}$}O\bluex{H}}
\end{XyMcompd}
}}
\end{center}
```



□

References

[1] K. P. C. Vollhardt and N. E. Schore, “Organic Chemistry. Structure and Function,” 4th ed., Freeman, New York (2003).

Part X

Appendices

Chapter 41

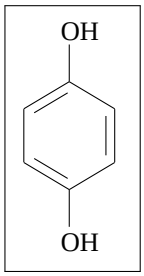
EPS Files Containing XyMTeX Formulas

41.1 LaTeX Documents with XyMTeX Codes

As shown in Section 1.3.3, a LaTeX document with XyMTeX codes can be directly processed by the PDF-compatible mode. For example, XyMTeX codes are placed in a LaTeX document as a tex file.

```
\documentclass{article}
\usepackage{xymtexpdf}%PDF-compatible mode
%\usepackage{xymtexps}%PS-compatible mode
%%\usepackage{xymtex}%TeX/LaTeX-compatible mode

\begin{document}
\fbox{%
\begin{XyMcompd}(300,900)(250,0){}{}
\bzdrv{1==OH;4==OH}
\end{XyMcompd}
}
\end{document}
```

This file produces the following structural formula:



where the bounding box of the formula is specified by using the `XyMcompd` environment defined in the chemist package, which is automatically loaded by any mode of the XyMTeX system. This situation holds true for the PostScript-compatible mode or the TeX/LaTeX-compatible mode.

On the other hand, another route for incorporating XyMTeX formulas is to use LaTeX documents with EPS files of XyMTeX structures, which are produced by separate procedures. The present chapter is devoted to describe the know-how of making and manipulating EPS files according to Fig. 41.1.

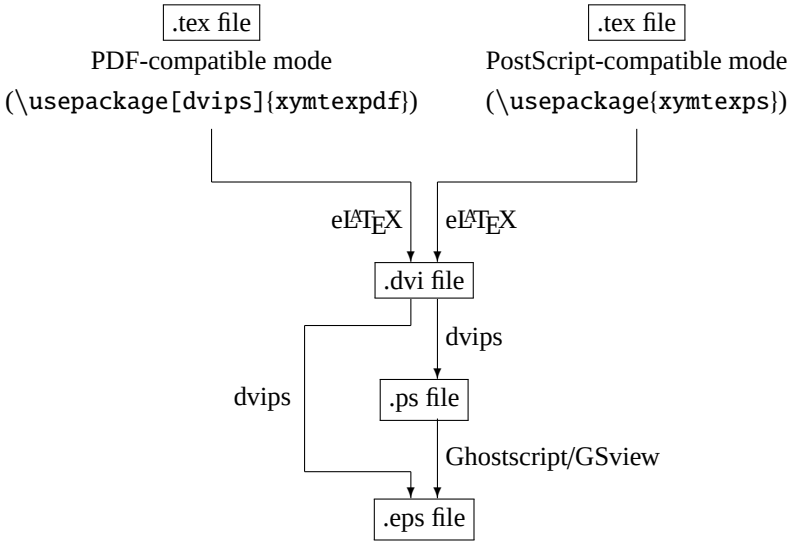


Figure 41.1. Generation of EPS files under the PDF-compatible mode and under the PostScript-compatible mode.

41.2 Making a Single-Page PostScript File with XyMTEX Formulas

41.2.1 Under the PDF-Compatible Mode of the XyMTEX System

The default setting in the PDF-compatible mode of the XyMTEX system (`\usepackage{xymtexpdf}`) provides a dvi file suitable for the processing of dvipdfmx, which produces a PDF file (.pdf). As shown in Subsection 1.3.3, however, the PDF-compatible mode is also capable of outputting a dvi file suitable for the processing of dvips, when the option "dvips" of the xymtexpdf package (`\usepackage[dvips]{xymtexpdf}`) is declared (the left branch of Fig. 41.1). Thus, the resulting dvi file can be converted into a PostScript file (.ps) under the processing of dvips. Such a PostScript file is necessary to obtain the corresponding EPS file (.eps).

For the purpose of accomplishing smooth conversion, a dvi file (as well as the resulting PostScript file) should be of a single page, which contains a set of XyMTEX structures to be bundled. For example, the following tex file (named eps-test1.tex) shows a typical format for producing a single-page PostScript file. Note that the declaration `\pagestyle{empty}` is important to obtain a correct bounding box.

```
%eps-test1.tex
\documentclass{article}
\usepackage[dvips]{xymtexpdf}%PDF-compatible mode, dvips option
\pagestyle{empty}%This command is important!
\begin{document}

\begin{XyMcompd}(300,900)(250,0){}{}
\bzdrv{1==OH;4==OH}
\end{XyMcompd}

\end{document}
```

According to the procedures of Subsection 1.3.3, the eLaTeX processing of the tex file (eps-test1.tex):

```
elatex eps-test1
```

produces a dvi file (eps-test1.dvi). The subsequent processing of the dvi file by dvips:

```
dvips eps-test1
```

produces the corresponding PostScript file (eps-test1.ps), which can be browsed by GSview coupled with Ghostscript.

41.2.2 Under the PostScript-Compatible Mode of the XƎMTEX System

As shown in Subsection 1.3.2, the PostScript-compatible mode generates a dvi file (.dvi), which is suitable for generating a PostScript file under the action of the dvips converter. The dvi or PostScript file can be converted into the corresponding EPS file.

For the purpose of obtaining a EPS file, a PostScript file should be of a single page. For example, the following tex file (named eps-test1.tex) shows a typical format for producing a single-page PostScript file. Note that the declaration `\pagestyle{empty}` is important to obtain a correct bounding box.

```
%eps-test1a.tex
\documentclass{article}
\usepackage{xymtexps}%PostScript-compatible mode
\pagestyle{empty}%This command is important!
\begin{document}

\begin{XyMcompd}(300,900)(250,0){}{}
\bzdrv{1==OH;4==OH}
\end{XyMcompd}

\end{document}
```

According to the procedures of Subsection 1.3.2, the LaTeX or eLaTeX processing of the tex file (eps-test1a.tex):

```
elatex eps-test1a
```

produces a dvi file (eps-test1a.dvi). The subsequent processing of the dvi file by dvips:

```
dvips eps-test1a
```

produces the corresponding PostScript file (eps-test1a.ps), which can be browsed by GSview coupled with Ghostscript.

41.3 EPS Files with Correct Bounding Boxes

41.3.1 Conversion of PostScript Files to EPS Files

The PostScript file (eps-test1.ps) due to the PDF-compatible mode (the 'dvips' option) as well as the PostScript file (eps-test1a.ps) due to the PostScript-compatible mode is browsed by GSview (coupled with Ghostscript), where the button "File" is clicked to show its menu (Fig. 41.2). The button "PS to EPS" in the menu (Fig. 41.2) is selected to result in the appearance of a confirmation box (Fig. 41.3), in which the button "yes" is clicked after checking "automatically calculated Bounding Box".

Thereby, there appears an input box (Fig. 41.4), from which the resulting eps file is stored after inputting an appropriate name (here "eps-test1Figr.eps"). Note that the "保存" button in Japanese means "store". The resulting file (eps-test1Figr.eps) can be browsed by GSview as shown in Fig. 41.5, where the XƎMTEX structure is surrounded by a dotted frame showing the corresponding bounding box.

41.3.2 Conversion of DVI Files to EPS Files

The dvips converter can produce EPS files directly from dvi files when the option -E is added to the command line, e.g.,

```
dvipsk -E -D2400 -Pdl -p1 -n1 eps-test1.dvi -o eps-test1FigA.eps
```

However, the resulting EPS files sometimes exhibit incorrect bounding boxes.

To calculate correct bounding boxes, the resulting EPS files (e.g., eps-test1FigA.eps) are opened by GSview and processed according to Figs. 41.2 to 41.5. Thereby, new EPS files with a recalculated bounding box are generated.

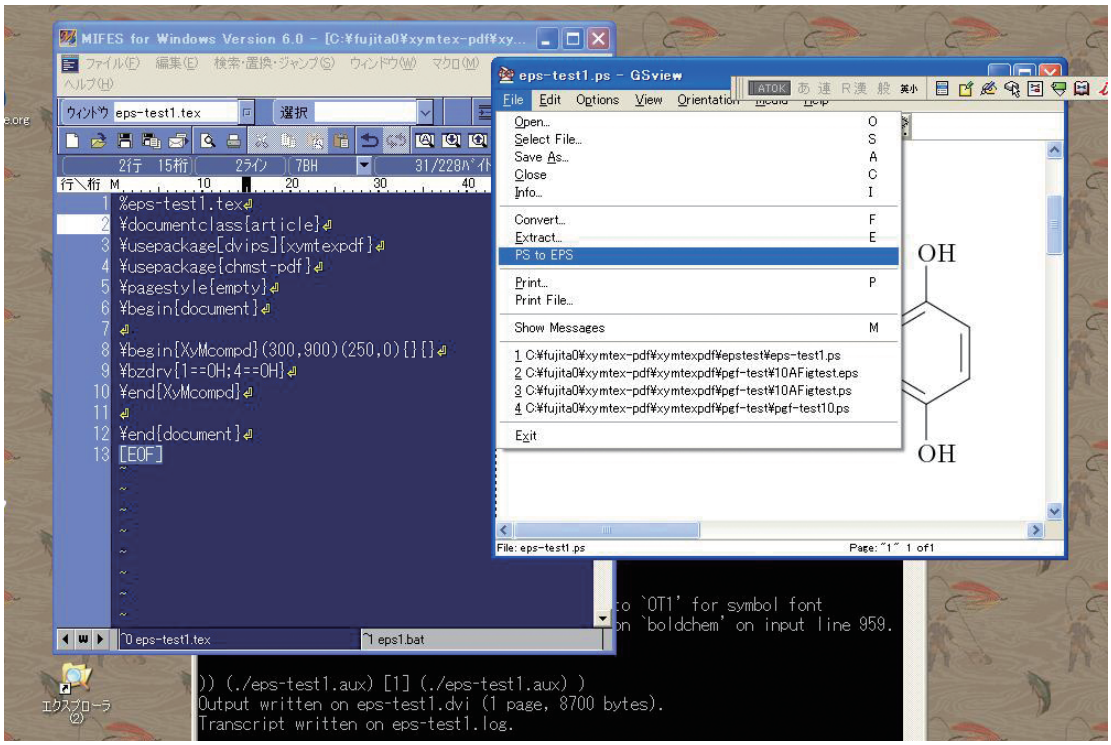


Figure 41.2. Making EPS files of structural formulas. “EP to EPS” button

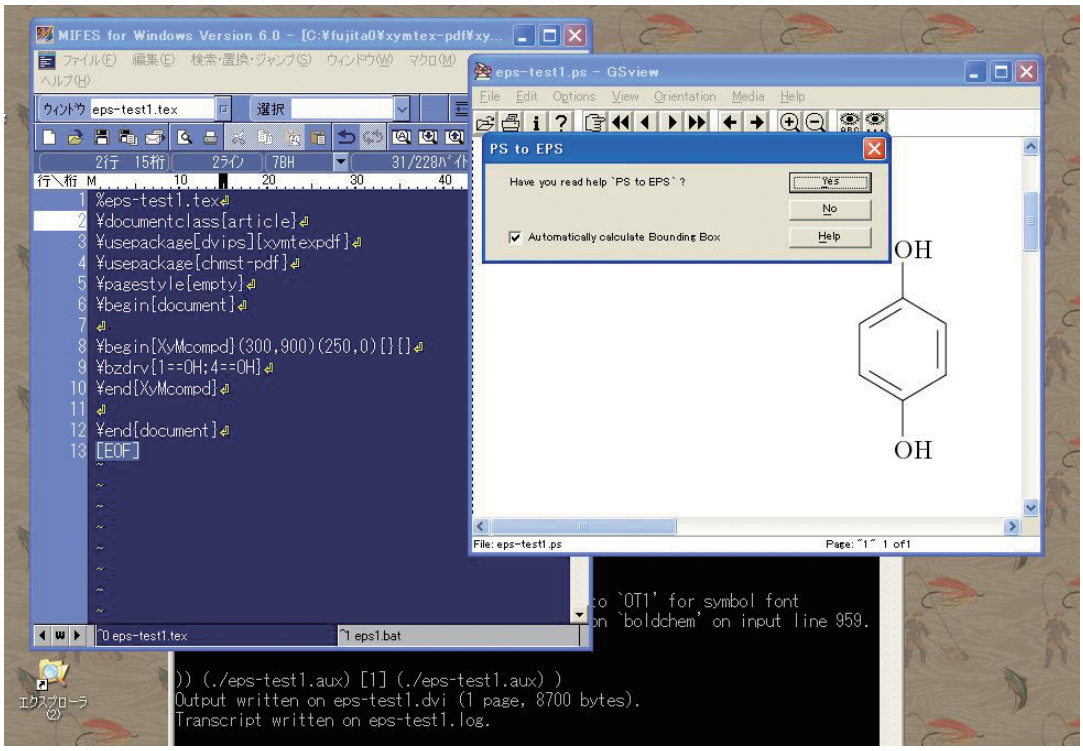


Figure 41.3. Making EPS files of structural formulas. Confirmation box

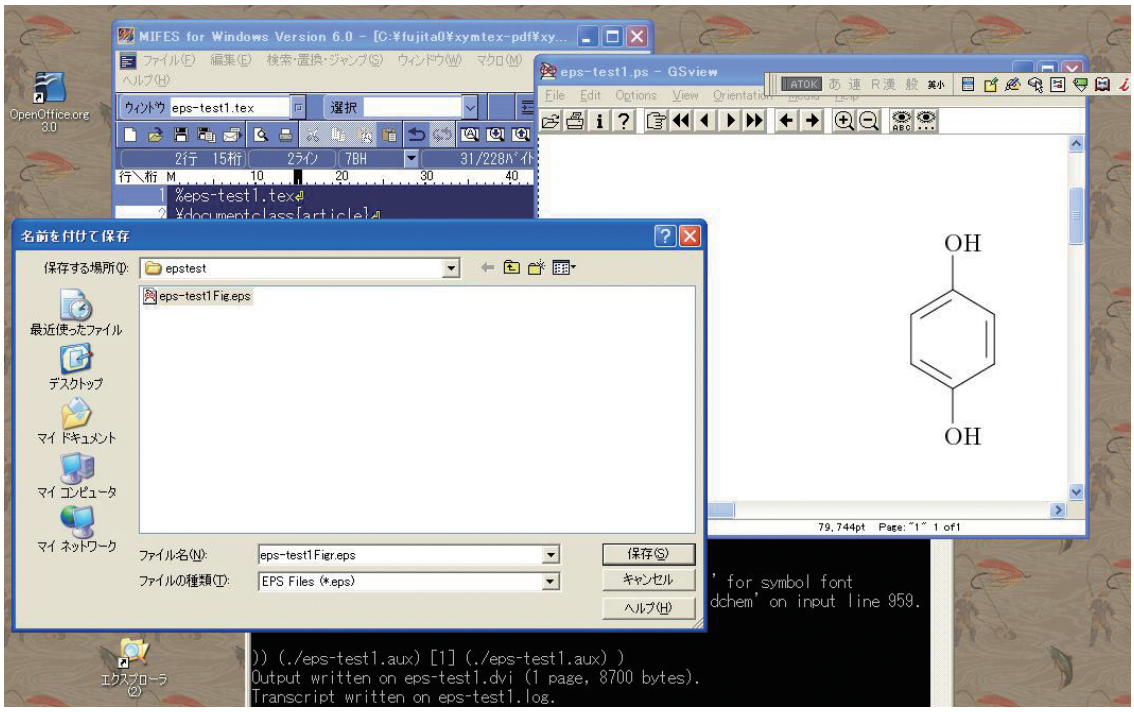


Figure 41.4. Making EPS files of structural formulas. Naming and storing an EPS file

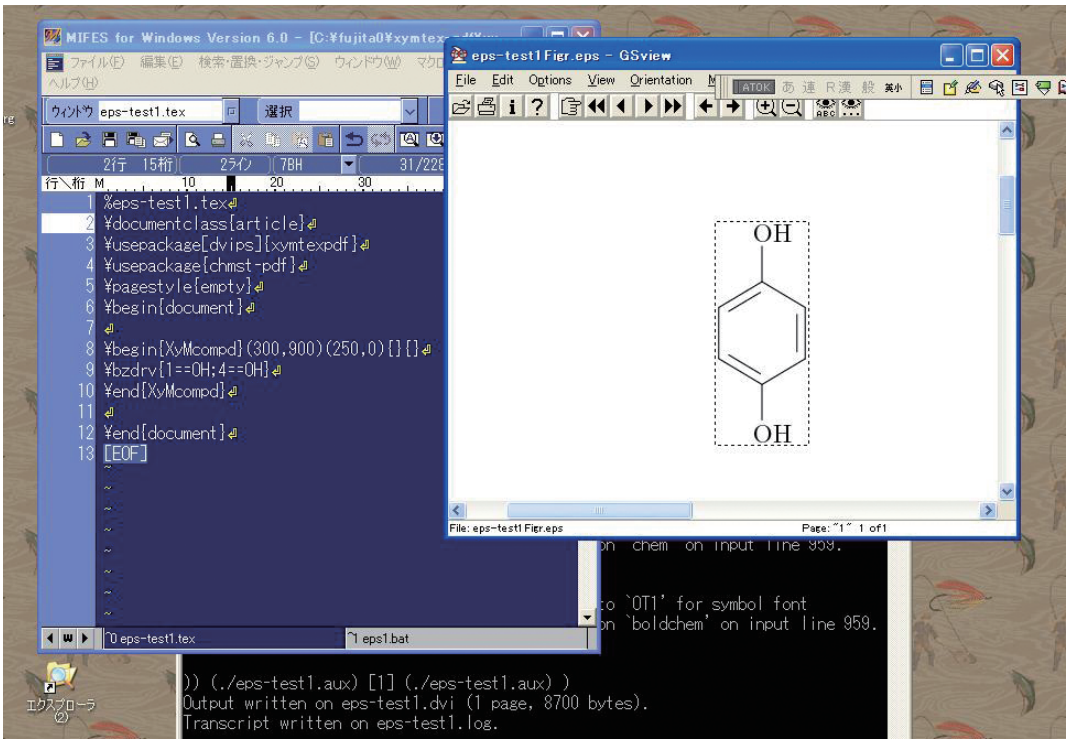


Figure 41.5. Making EPS files of structural formulas. EPS file with a bounding box

41.4 Incorporation of EPS Files in LaTeX Documents

The following tex file (eps-test2.tex) is prepared to use the file (eps-test1Figr.eps) described above. The command `\usepackage{xymtexpdf}` has no optional argument, the resulting dvi file is processed by the dvipdfm(x) converter so as to generate the corresponding PDF file (eps-test2.pdf) directly. The command

\includegraphics is supported by the graphicx package. Note that the xymtexpdf package automatically loads the pgf package, which in turn loads the graphicx package automatically.

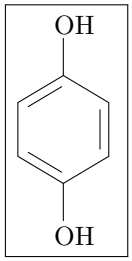
```
%eps-test2.tex
\documentclass{article}
\usepackage{xymtexpdf}%PDF-compatible mode
%\usepackage{xymtexps}%PostScript-compatible mode
\begin{document}

\fbox{%
\includegraphics{eps-test1Figr.eps}
}

\end{document}
```

If the \usepackage{xymtexps} command is made effective and the \usepackage{xymtexpdf} command is commented out, the above tex file generates a dvi file. This file can be converted into a PostScript file, which is finally converted into the corresponding PDF file by using an appropriate converter such as Adobe Distiller.

To simulate the processing of eps-test2.tex, the same code for the XMTEX structure is written here in the present document:

```
\fbox{%
\includegraphics{eps-test1Figr.eps}
}
```

which generates the following structural formula:

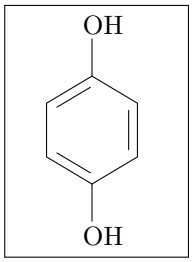


The bounding box of the EPS file (eps-test1Figr.eps) can be checked by an appropriate editor, where it contains the following line:

```
%%BoundingBox: 151 627 188 715
```

The bounding box can be changed by replacing these four integers by others. The bounding box can alternatively be changed as follows:

```
\fbox{%
\includegraphics[bb=140 627 200 715]{eps-test1Figr.eps}
}
```



Chapter 42

PDF Files Containing XyMTEX Formulas

For the purpose of including the PDF file (the PDF-compatible mode only!) in a LaTeX document, it is necessary to obtain a bounding box of a net object contain in the PDF file. This chapter mainly deals with cases in which such a net object is a diagram drawn by the XyMTEX system.

42.1 PDF Files Containing a Single Figure

42.1.1 Generation of a PDF File Containing a Single Figure

First we should obtain a PDF file containing a single figure drawn by the XyMTEX system. For example, a tex file "pdfcrop-test1.tex" written on the basis of the PDF-compatible mode of the XyMTEX system in a directory (folder) named `c:\pdfcroptest`.

```
%pdfcrop-test1.tex
\documentclass{article}
\usepackage{xymtexpdf}%PDF-compatible mode
\pagestyle{empty}%This command is important!
\begin{document}
\begin{XyMcompd}(300,900)(250,0){}{}
\bzdrv{1==OH;4==OH}
\end{XyMcompd}
\end{document}
```

According to the procedures of Subsection 1.3.3, the eLaTeX processing of the tex file (pdfcrop-test1.tex) is conducted by inputting the following command:

```
c:\pdfcroptest> elatex pdfcrop-test1
```

in a DOS command prompt line of Windows. As a result, a dvi file (pdfcrop-test1.dvi) is generated. The subsequent processing of the dvi file by dvipdfmx:

```
c:\pdfcroptest> dvipdfmx pdfcrop-test1
```

produces the corresponding PDF file (pdfcrop-test1.pdf), which can be browsed by GSview coupled with Ghostscript (Fig. 42.1) or by Adobe Reader.

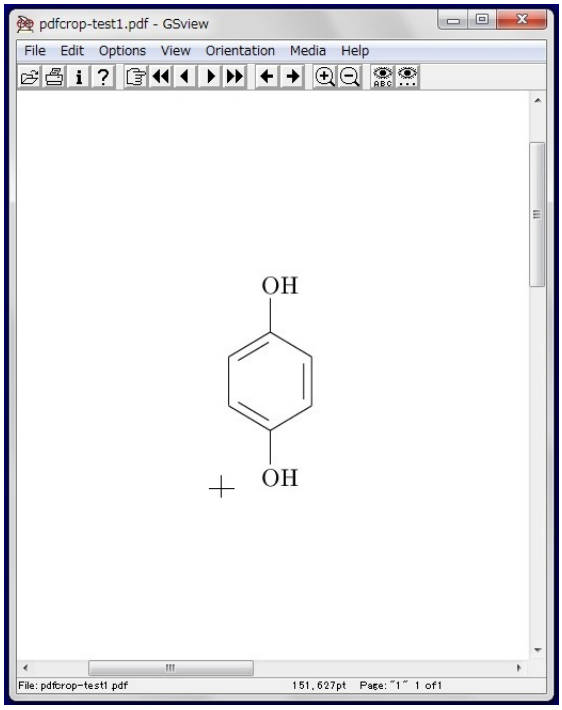


Figure 42.1. GSview display for the $(\mathbf{x}, \mathbf{y})$-coordinates of a cursor position, which indicates the bottom-left corner of the bonding box, $(\mathbf{151}, \mathbf{627})$.

42.1.2 Acquisition of Bounding Boxes

To include the PDF file (pdfcrop-test1.pdf), the bounding box (the net domain) of the object (the diagram of hydroquinone in this case) should be obtained. Hence, the second task is to acquire the bounding box from the data contained in the PDF file.

Manual Acquisition of Bounding Boxes

One of the methods for acquiring a bounding box is a manual one using the display of the GSview. As found in Fig. 42.1, the display of GSview contains the $(\mathbf{x}, \mathbf{y})$-coordinates of a cursor position in the bottom row. From the data of Fig. 42.1, we are able to obtain $(\mathbf{151}, \mathbf{627})$, which shows the bottom-left corner of the bounding box. Similarly we are able to obtain $(\mathbf{188}, \mathbf{715})$, which shows the upper-right corner of the bounding box. Thereby, the bounding box at issue is summarized to give a data array `151 627 188 715`.

Batch Acquisition of Bounding Boxes

The bounding box of the object can be alternatively obtained by using a device `bbx` of Ghostscript. For this purpose, a batch file named “bboxget.bat” is defined as follows:

(bboxget.bat)

```
:bboxget <file name>
@echo off
c:\gs\gs9.02\bin\gswin32c ^
-dBATCH -dNOPAUSE -sDEVICE=bbox %1.pdf >%1.ybb 2>&1
type %1.ybb
```

This batch file presumes that the executable file of Ghostscript (`gswin32c.exe`) is stored in the `c:\gs\gs9.02\bin` directory, which may be changed according to the setting of your computer.

To gain the bounding box of the PDF file (pdfcrop-test1.pdf), the following command is input in a DOS prompt line of Windows.

```
c:\pdfcroptest> bboxget pdfcrop-test1
```

Thereby, the PDF File (pdfcrop-test1.pdf) is read by Ghostscript and the data of its bounding box is printed out in the display and in the file “pdfcrop-test1.ybb”:

```
GPL Ghostscript 9.02 (2011-03-30)
Copyright (C) 2010 Artifex Software, Inc.  All rights reserved.
This software comes with NO WARRANTY: see the file PUBLIC for details.
Processing pages 1 through 1.
Page 1
%%BoundingBox: 152 628 187 715
%%HiResBoundingBox: 152.395800 628.307981 186.868190 714.563978
```

The data obtained by the batch process is almost equal to (shows a slightly narrower area than) the data array `151 627 188 715` obtained manually.

(Remarks): The ebb utility cannot be used to obtain a bounding box in the above case. The resulting bb file contains the data `%%BoundingBox: 0 0 595 842`, which shows the bounding box of the whole area of the PDF file (pdfcrop-test1.pdf).

42.1.3 Including PDF Files in Chemical Documents

By referring to the data of the bounding box as the optional argument of the command `\includegraphics`, the following tex file (pdfinclude-test0.tex) is prepared to include the file (pdfcrop-test1.pdf) described above. The command `\includegraphics` is supported by the graphicx package.

```
%pdfinclude-test0.tex
\documentclass{article}
\usepackage{xymtexpdf}%PDF-compatible mode
\begin{document}
\fbox{%
\includegraphics[bb=151 627 188 715]{pdfcrop-test1.pdf}%
}
\end{document}
```

The command `\usepackage{xymtexpdf}` has no optional argument, the resulting dvi file is processed by the dvipdfm(x) converter so as to generate the corresponding PDF file (pdfinclude-test0.pdf) directly.

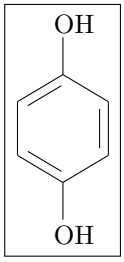
```
c:\pdfcroptest> elatex pdfinclude-test0
c:\pdfcroptest> dvipdfmx pdfinclude-test0
```

Note that the xymtexpdf package automatically loads the pgf package, which in turn loads the graphicx package automatically.

To simulate the processing of pdfinclude-test0.tex, the same code for the X$\mathfrak{y}$MTEX structure is written here in the present document:

```
\fbox{%
\includegraphics[bb=151 627 188 715]{pdfcrop-test1.pdf}%
}
```

which generates the following structural formula:



42.2 Net Figures of XƎMTEX Formulas

Another way is to covert the original PDF file into a cropped PDF file, which contains a net figure drawn by the XƎMTEX system. This task is accomplished by using the pdfcrop converter, which is distributed by TeX Live or W32TeX.

42.2.1 Cropped PDF Files and Their Bounding Boxes

For example, a cropped PDF file corresponding to the above-mentioned PDF file (pdfcrop-test1.pdf) is obtained by inputting the following command in the DOS command prompt of Windows.

```
c:\pdfcroptest> pdfcrop pdfcrop-test1.pdf
```

Thereby, the corresponding cropped PDF file (pdfcrop-test1-crop.pdf) is obtained, where the name is automatically given by adding the suffix "-crop". The cropped PDF file can be browsed by GSview coupled with Ghostscript or by Adobe Reader.

To gain the bounding box of the cropped PDF file (pdfcrop-test1-crop.pdf), the following command is input in a DOS prompt line of Windows.

```
c:\pdfcroptest> ebb pdfcrop-test1-crop.pdf
```

This input produces the corresponding bb file (pdfcrop-test1-crop.bb), although it output a warning:

```
** Warning ** Garbage in xref stream
```

on the display.

The bb file (pdfcrop-test1-crop.bb) is a text file, which contains the following content:

```
%%Title: ./pdfcrop-test1-crop.pdf
%%Creator: extractbb Version 0.2
%%BoundingBox: 0 0 35 87
%%CreationDate: Mon Aug 12 08:26:43 2013
```

The statement `%%BoundingBox: 0 0 35 87` shows the net domain of the figure.

42.2.2 Inclusion of Cropped PDF File in Chemical Documents

To include the cropped file (pdfcrop-test1-crop.pdf) described above, the data of the bounding box are declared in the optional argument of the command `\includegraphics`, as found in the following tex file (pdfinclude-test1.tex). The command `\includegraphics` is supported by the graphicx package.

```
%pdfinclude-test1.tex
\documentclass{article}
\usepackage{xymtexpdf}%PDF-compatible mode
\begin{document}
\fbox{%
\includegraphics[bb=0 0 35 87]{pdfcrop-test1-crop.pdf}%
}
\end{document}
```

The command `\usepackage{xymtexpdf}` has no optional argument, the resulting dvi file is processed by the dvipdfm(x) converter so as to generate the corresponding PDF file (pdfinclude-test1.pdf) directly.

```
c:\pdfcroptest> elatex pdfinclude-test1
c:\pdfcroptest> dvipdfmx pdfinclude-test1
```

During the process of executing dvipdfmx, there appears the following warning on the display:

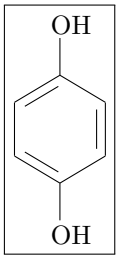
```
** Warning ** Garbage in xref stream
```

which can be ignored in practice.

To simulate the processing of pdfinclude-test1.tex, the same code for the XƎMTEX structure is written here in the present document:

```
\fbox{%
\includegraphics[bb=0 0 35 87]{pdfcrop-test1-crop.pdf}%
}
```

which generates the following structural formula:



42.3 Conversion of PDF Files into EPS Files

42.3.1 Conversion Using the pdftops Converter

Semi-Manual Conversion

For the purpose of converting PDF files into EPS files, we use the pdftops converter with the option `-eps`.

```
c:\pdfcroptest> pdftops -eps pdfcrop-test1.pdf pdfcrop-test1.ps
```

Note that the resulting file “pdfcrop-test1.ps” is not a full eps file, because it has no bounding box.

To convert the resulting semi-eps file (.ps as an extension) into a full eps file, it is browsed by the GSview. After clicking the “PS to EPS” button appearing in the “File” menu, check “Automatically calculated Bounding Box” and click the “Yes” button. The resulting file is stored after naming it “pdfcrop-test1.eps”, which can be incorporated in chemical documents.

Batch Conversion

The step of clicking the “PS to EPS” button described above is replaced by the use of the ps2eps converter. For the purpose of executing pdftops and ps2eps in a single batch process, a batch file named “pdftops2eps.bat” is defined as follows:

(pdftops2eps.bat)

```
:pdftops2eps <filename>
:<filename>.pdf into <filename>.eps
@echo off
pdftops -eps %1.pdf %1.ps | ps2eps -f %1.ps
del %1.ps
```

To obtain the EPS file (pdfcrop-test1.eps), the following command is input in a DOS prompt line of Windows.

```
c:\pdfcroptest> pdftops2eps pdfcrop-test1
```

Thereby, the PDF file (pdfcrop-test1.pdf) is converted into the corresponding EPS file (pdfcrop-test1.eps).

42.3.2 Conversion Using Adobe Acrobat

Converting a PDF file into an EPS file is conducted simply by Adobe Acrobat Professional. For the purpose of treating PDF files containing structural formulas, however, this method is applicable to a cropped PDF file such pdfcrop-test1-crop.pdf.

1. Open the PDF file (pdfcrop-test1-crop.pdf) by Adobe Acrobat.
2. Click File ¿ Export. Thereby, there appear a check box.

3. Select “EPS (Encapsulated PostScript) (*.eps)” in a check box. Thereby, the name is assigned automatically to be “pdfcrop-test1-crop.eps”.
4. . Click the “Save” button. There appears the EPS file named “pdfcrop-test1-crop.eps”.

42.3.3 Including PDF Files in Chemical Documents

The following tex file (pdfinclude-test2.tex) is prepared to include the file (pdfcrop-test1.eps) described above.

```
%pdfinclude-test2.tex
\documentclass{article}
\usepackage{xymtexpdf}%PDF-compatible mode
\begin{document}
\fbox{%
\includegraphics{pdfcrop-test1.eps}%
}
\end{document}
```

The command `\usepackage{xymtexpdf}` has no optional argument, the resulting dvi file is processed by the dvipdfm(x) converter so as to generate the corresponding PDF file (pdfinclude-test2.pdf) directly.

```
c:\pdfcroptest> elatex pdfinclude-test2
c:\pdfcroptest> dvipdfmx pdfinclude-test2
```

To simulate the processing of pdfinclude-test0.tex, the same code for the XƎMTEX structure is written here in the present document:

```
\fbox{%
\includegraphics{pdfcrop-test1.eps}%
}
```

which generates the following structural formula: