

CHAPTER

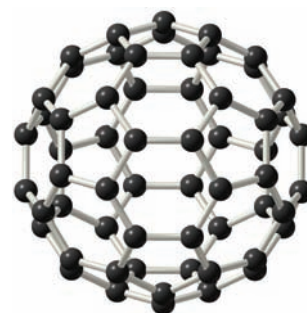
4



Nomenclature and Conformations of Alkanes and Cycloalkanes

Diamond is an exceptionally hard material. One reason diamond is so strong is that it contains a rigid network of carbon-carbon bonds. Muscle, on the other hand, which also contains many carbon-carbon bonds, is strong yet has great flexibility. This remarkable contrast in properties, from the rigidity of diamond to the flexibility of muscles, depends on whether rotation is possible about individual carbon-carbon bonds. In this chapter we shall consider changes in molecular structure and energy that result from rotation about carbon-carbon bonds, using a process called conformational analysis.

We learned in Chapter 2 that our study of organic chemistry can be organized around functional groups. Now we consider the hydrocarbon framework to which functional groups are attached—the framework that consists of only carbon and hydrogen atoms. From the standpoint of an architect, hydrocarbon frameworks present a dream of limitless possibilities, which is part of what makes organic chemistry such a fascinating discipline. Buckminsterfullerene, named after the visionary architect Buckminster Fuller, is just one example of a carbon-based molecule with an intriguing molecular architecture.



Buckminsterfullerene

IN THIS CHAPTER WE WILL CONSIDER:

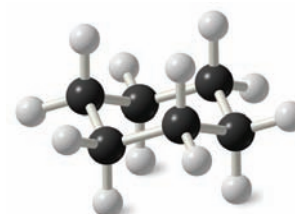
- how to name many simple organic molecules
- the flexible, three-dimensional nature of organic molecules
- an organic reaction that can convert alkenes and alkynes to alkanes

[WHY DO THESE TOPICS MATTER?] At the end of the chapter, we will show how, using the same set of rules, both chemists and nature have created some unique arrangements of carbon and hydrogen atoms. Some of these structural arrangements were not expected to exist, one structural arrangement lets you write, and others are fueling advances in the area of materials research and nanotechnology.

4.1 INTRODUCTION TO ALKANES AND CYCLOALKANES

We noted earlier that the family of organic compounds called hydrocarbons can be divided into several groups on the basis of the type of bond that exists between the individual carbon atoms. Those hydrocarbons in which all of the carbon–carbon bonds are single bonds are called **alkanes**, those hydrocarbons that contain a carbon–carbon double bond are called **alkenes**, and those with a carbon–carbon triple bond are called **alkynes**.

Cycloalkanes are alkanes in which all or some of the carbon atoms are arranged in a ring. Alkanes have the general formula C_nH_{2n+2} ; cycloalkanes containing a single ring have two fewer hydrogen atoms and thus have the general formula C_nH_{2n} .



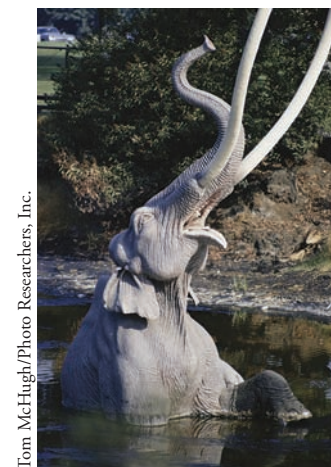
Cyclohexane

4.1A Sources of Alkanes: Petroleum

The primary source of alkanes is petroleum. Petroleum is a complex mixture of organic compounds, most of which are alkanes and aromatic compounds (cf. Chapter 14). It also contains small amounts of oxygen-, nitrogen-, and sulfur-containing compounds.

Some of the molecules in petroleum are clearly of biological origin. Most scientists believe that petroleum originated with accumulation of dead microorganisms that settled to the bottom of the sea and that were entombed in sedimentary rock. These microbial remains eventually were transformed into oil by the heat radiating from Earth's core.

Hydrocarbons are also found in outer space. Asteroids and comets contain a variety of organic compounds. Methane and other hydrocarbons are found in the atmospheres of Jupiter, Saturn, and Uranus. Saturn's moon Titan has a solid form of methane–water ice at its surface and an atmosphere rich in methane. Whether of terrestrial or celestial origin, we need to understand the properties of alkanes. We begin with a consideration of their shapes and how we name them.



Tom McHugh/Photo Researchers, Inc.

Petroleum is a finite resource that likely originated with decay of primordial microbes. At the La Brea Tar Pits in Los Angeles, many prehistoric animals perished in a natural vat containing hydrocarbons.

THE CHEMISTRY OF... Petroleum Refining

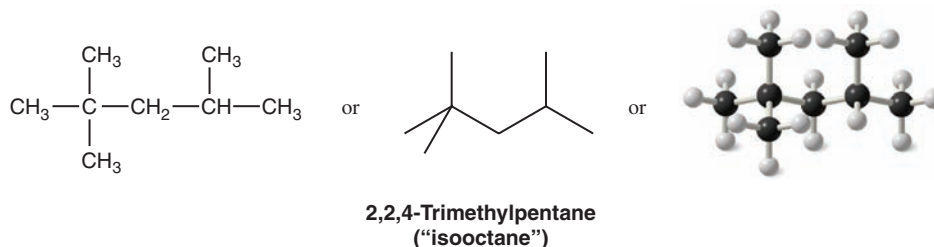
The first step in refining petroleum is distillation; the object here is to separate the petroleum into fractions based on the volatility of its components. Complete separation into fractions containing individual compounds is economically impractical and virtually impossible technically. More than 500 different compounds are contained in the petroleum distillates boiling below 200 °C, and many have almost the same boiling points. Thus the fractions taken contain mixtures of alkanes of similar boiling points (see the table below). Mixtures of alkanes, fortunately, are perfectly suitable for uses as fuels, solvents, and lubricants, the primary uses of petroleum.

The demand for gasoline is much greater than that supplied by the gasoline fraction of petroleum. Important processes in the petroleum industry, therefore, are concerned with converting hydrocarbons from other fractions into gasoline. When a mixture of alkanes from the gas oil fraction (C_{12} and higher) is heated at very high temperatures (~500 °C) in the presence of a variety of catalysts, the molecules break apart and rearrange to smaller, more highly branched hydrocarbons containing 5–10 carbon atoms. This process is called *catalytic cracking*. **Cracking** can also be done in the absence of a catalyst—called **thermal**

(continues on next page)

cracking—but in this process the products tend to have unbranched chains, and alkanes with unbranched chains have a very low “octane rating.”

The highly branched compound 2,2,4-trimethylpentane (called isooctane in the petroleum industry) burns very smoothly (without knocking) in internal combustion engines and is used as one of the standards by which the octane rating of gasolines is established. According to this scale, 2,2,4-trimethylpentane has an octane rating of 100. Heptane, $\text{CH}_3(\text{CH}_2)_5\text{CH}_3$, a compound that produces much knocking when it is burned in an internal combustion engine, is given an octane rating of 0. Mixtures of 2,2,4-trimethylpentane and heptane are used as standards for octane ratings between 0 and 100. A gasoline, for example, that has the same characteristics in an engine as a mixture of 87% 2,2,4-trimethylpentane and 13% heptane would be rated as 87-octane gasoline.



TYPICAL FRACTIONS OBTAINED BY DISTILLATION OF PETROLEUM

Boiling Range of Fraction (°C)	Number of Carbon Atoms per Molecule	Use
Below 20	$\text{C}_1\text{--}\text{C}_4$	Natural gas, bottled gas, petrochemicals
20–60	$\text{C}_5\text{--}\text{C}_6$	Petroleum ether, solvents
60–100	$\text{C}_6\text{--}\text{C}_7$	Ligroin, solvents
40–200	$\text{C}_8\text{--}\text{C}_{10}$	Gasoline (straight-run gasoline)
175–325	$\text{C}_{12}\text{--}\text{C}_{18}$	Kerosene and jet fuel
250–400	C_{12} and higher	Gas oil, fuel oil, and diesel oil
Nonvolatile liquids	C_{20} and higher	Refined mineral oil, lubricating oil, and grease
Nonvolatile solids	C_{20} and higher	Paraffin wax, asphalt, and tar

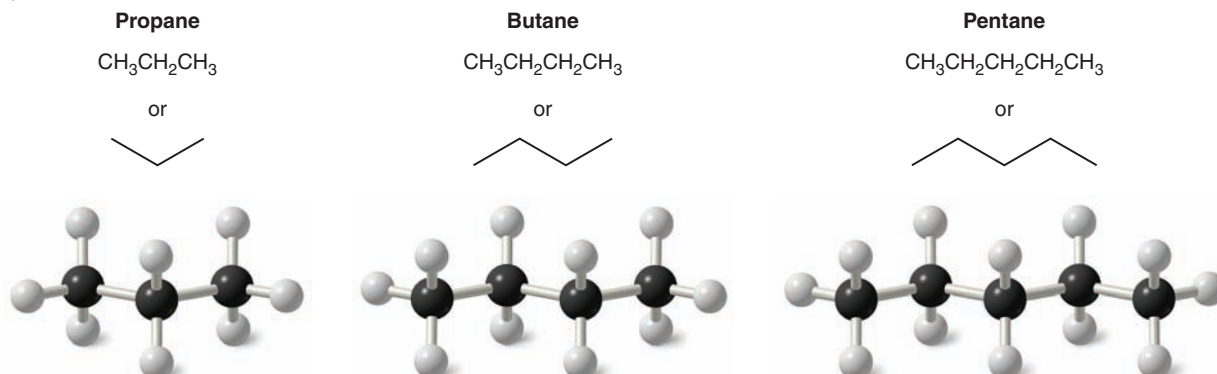
Adapted with permission of John Wiley & Sons, Inc., from Holm, J. R., *General, Organic, and Biological Chemistry*, Ninth Edition, p. 213. Copyright 1995.

4.2 SHAPES OF ALKANES

A general tetrahedral orientation of groups—and thus sp^3 hybridization—is the rule for the carbon atoms of all alkanes and cycloalkanes. We can represent the shapes of **alkanes** as shown in Fig. 4.1.

Butane and pentane are examples of alkanes that are sometimes called “straight-chain” alkanes. One glance at three-dimensional models, however, shows that because of their tetrahedral carbon atoms the chains are zigzagged and not at all straight. Indeed,

FIGURE 4.1 Ball-and-stick models for three simple alkanes.



the structures that we have depicted in Fig. 4.1 are the straightest possible arrangements of the chains because rotations about the carbon–carbon single bonds produce arrangements that are even less straight. A better description is **unbranched**. This means that each carbon atom within the chain is bonded to no more than two other carbon atoms and that unbranched alkanes contain only primary and secondary carbon atoms. Primary, secondary, and tertiary carbon atoms were defined in Section 2.5.

Isobutane, isopentane, and neopentane (Fig. 4.2) are examples of branched-chain alkanes. In neopentane the central carbon atom is bonded to four carbon atoms.

Helpful Hint

You should build your own molecular models of the compounds in Figs. 4.1 and 4.2. View them from different perspectives and experiment with how their shapes change when you twist various bonds. Make drawings of your structures.

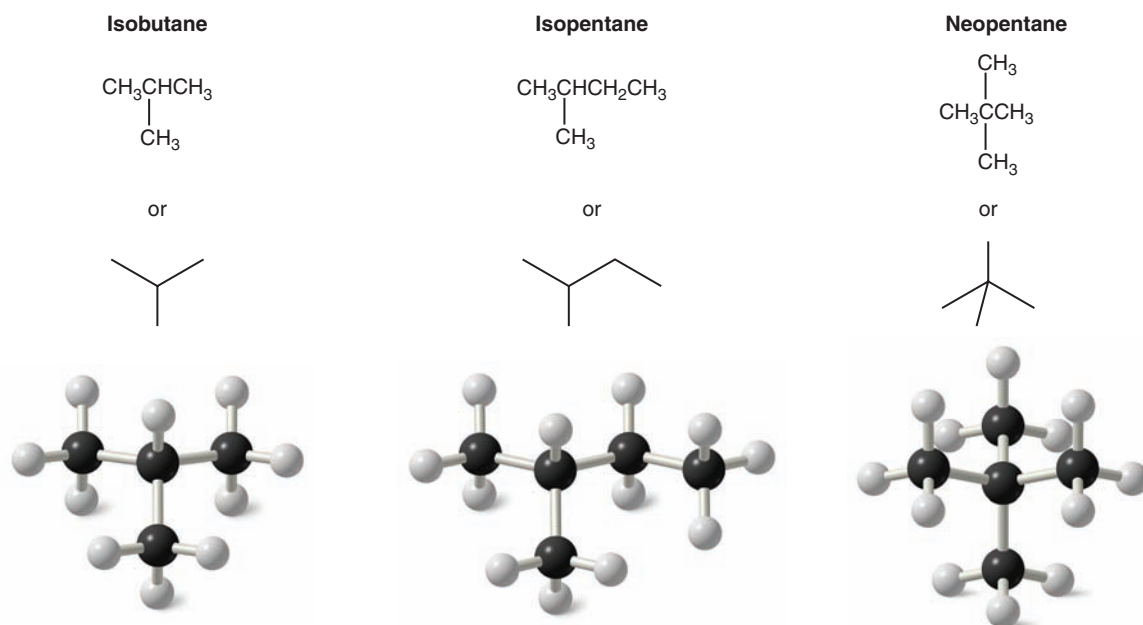


FIGURE 4.2 Ball-and-stick models for three branched-chain alkanes. In each of the compounds one carbon atom is attached to more than two other carbon atoms.

Butane and isobutane have the same molecular formula: C_4H_{10} . The two compounds have their atoms connected in a different order and are, therefore, **constitutional isomers** (Section 1.3). Pentane, isopentane, and neopentane are also constitutional isomers. They, too, have the same molecular formula (C_5H_{12}) but have different structures.

Write condensed and bond-line structural formulas for all of the constitutional isomers with the molecular formula C_7H_{16} . (There are a total of nine constitutional isomers.)

PRACTICE PROBLEM 4.1

Constitutional isomers, as stated earlier, have different physical properties. The differences may not always be large, but constitutional isomers are always found to have different melting points, boiling points, densities, indexes of refraction, and so forth. Table 4.1 gives some of the physical properties of the C_6H_{14} isomers, of which there are only five. Note that the number of constitutional isomers that is possible increases dramatically as the number of carbon atoms in the alkane increases.

Prior to the development near the end of the nineteenth century of a formal system for naming organic compounds, many organic compounds had already been discovered or synthesized. Early chemists named these compounds, often on the basis of the source of the compound. Acetic acid (systematically called ethanoic acid) is an example; it was obtained by distilling vinegar, and it got its name from the Latin word for vinegar, *acetum*. Formic acid (systematically called methanoic acid) had been obtained by the distillation of the bodies of ants, so it got the name from the Latin word for ants, *formicae*. Many of these older names for compounds, called common or trivial names, are still in wide use today.

Today, chemists use a systematic nomenclature developed and updated by the International Union of Pure and Applied Chemistry (IUPAC). Underlying the IUPAC

TABLE 4.1 PHYSICAL CONSTANTS OF THE HEXANE ISOMERS

Molecular Formula	Condensed Structural Formula	Bond-Line Formula	mp (°C)	bp (°C) ^a (1 atm)	Density (g mL ⁻¹) at 20 °C	Index of Refraction ^b (n _D 20 °C)
C ₆ H ₁₄	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃		-95	68.7	0.6594	1.3748
C ₆ H ₁₄	CH ₃ CH(CH ₃)CH ₂ CH ₂ CH ₃		-153.7	60.3	0.6532	1.3714
C ₆ H ₁₄	CH ₃ CH ₂ CH(CH ₃)CH ₂ CH ₃		-118	63.3	0.6643	1.3765
C ₆ H ₁₄	CH ₃ CH(CH ₃)CH(CH ₃)CH ₃		-128.8	58	0.6616	1.3750
C ₆ H ₁₄	CH ₃ C(CH ₃) ₂ CH ₂ CH ₃		-98	49.7	0.6492	1.3688

^aUnless otherwise indicated, all boiling points given in this book are at 1 atm or 760 torr.

^bThe index of refraction is a measure of the ability of the alkane to bend (refract) light rays. The values reported are for light of the D line of the sodium spectrum (n_D).

system is a fundamental principle: **each different compound should have a different and unambiguous name.***

4.3 HOW TO NAME ALKANES, ALKYL HALIDES, AND ALCOHOLS: THE IUPAC SYSTEM

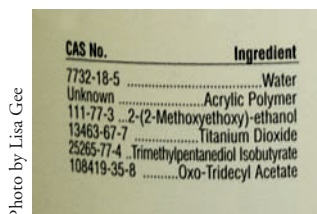
The **IUPAC system** for naming **alkanes** is not difficult to learn, and the principles involved are used in naming compounds in other families as well. For these reasons we begin our study of the IUPAC system with the rules for naming alkanes and then study the rules for alkyl halides and alcohols.

The names for several of the unbranched alkanes are listed in Table 4.2. The ending for all of the names of alkanes is *-ane*. The stems of the names of most of the alkanes (above C₄) are of Greek and Latin origin. Learning the stems is like learning to count in organic chemistry. Thus, one, two, three, four, and five become meth-, eth-, prop-, but-, and pent-.

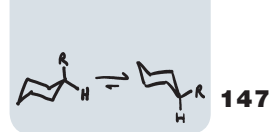
TABLE 4.2 THE UNBRANCHED ALKANES

Name	Number of Carbon Atoms	Structure	Name	Number of Carbon Atoms	Structure
Methane	1	CH ₄	Undecane	11	CH ₃ (CH ₂) ₉ CH ₃
Ethane	2	CH ₃ CH ₃	Dodecane	12	CH ₃ (CH ₂) ₁₀ CH ₃
Propane	3	CH ₃ CH ₂ CH ₃	Tridecane	13	CH ₃ (CH ₂) ₁₁ CH ₃
Butane	4	CH ₃ (CH ₂) ₂ CH ₃	Tetradecane	14	CH ₃ (CH ₂) ₁₂ CH ₃
Pentane	5	CH ₃ (CH ₂) ₃ CH ₃	Pentadecane	15	CH ₃ (CH ₂) ₁₃ CH ₃
Hexane	6	CH ₃ (CH ₂) ₄ CH ₃	Hexadecane	16	CH ₃ (CH ₂) ₁₄ CH ₃
Heptane	7	CH ₃ (CH ₂) ₅ CH ₃	Heptadecane	17	CH ₃ (CH ₂) ₁₅ CH ₃
Octane	8	CH ₃ (CH ₂) ₆ CH ₃	Octadecane	18	CH ₃ (CH ₂) ₁₆ CH ₃
Nonane	9	CH ₃ (CH ₂) ₇ CH ₃	Nonadecane	19	CH ₃ (CH ₂) ₁₇ CH ₃
Decane	10	CH ₃ (CH ₂) ₈ CH ₃	Eicosane	20	CH ₃ (CH ₂) ₁₈ CH ₃

*The complete IUPAC rules for nomenclature can be found through links at the IUPAC website.

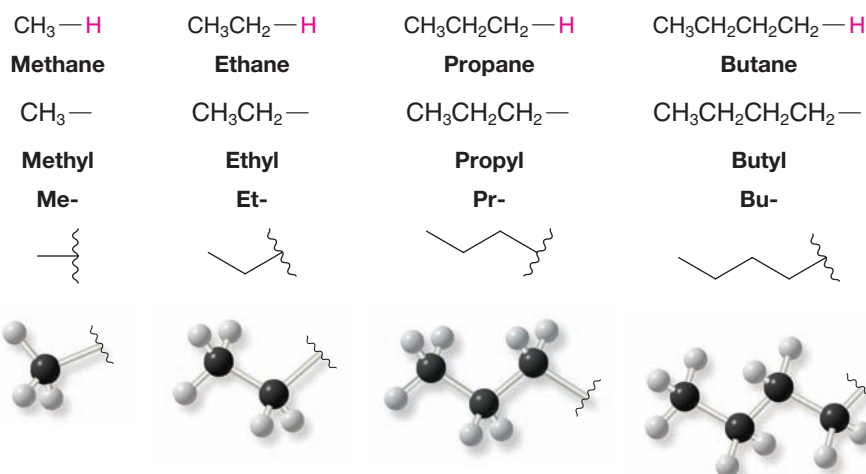


The Chemical Abstracts Service assigns a CAS Registry Number to every compound. CAS numbers make it easy to find information about a compound in the chemical literature. The CAS numbers for ingredients in a can of latex paint are shown here.



4.3A HOW TO Name Unbranched Alkyl Groups

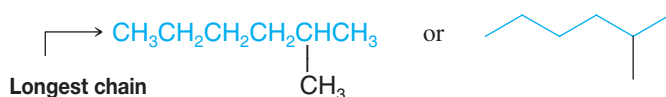
If we remove one hydrogen atom from an alkane, we obtain what is called an **alkyl group**. These alkyl groups have names that end in **-yl**. When the alkane is **unbranched**, and the hydrogen atom that is removed is a **terminal** hydrogen atom, the names are straightforward:



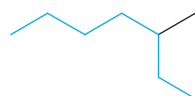
4.3B HOW TO Name Branched-Chain Alkanes

Branched-chain alkanes are named according to the following rules:

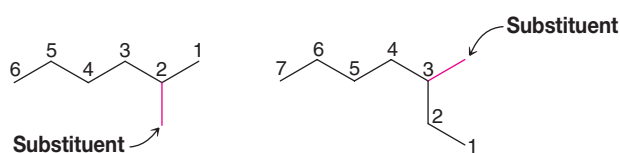
- 1. Locate the longest continuous chain of carbon atoms; this chain determines the parent name for the alkane.** We designate the following compound, for example, as a *hexane* because the longest continuous chain contains six carbon atoms:



The longest continuous chain may not always be obvious from the way the formula is written. Notice, for example, that the following alkane is designated as a *heptane* because the longest chain contains seven carbon atoms:

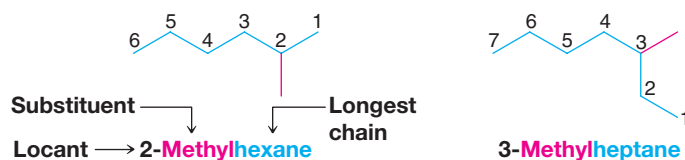


- 2. Number the longest chain beginning with the end of the chain nearer the substituent.** Applying this rule, we number the two alkanes that we illustrated previously in the following way:

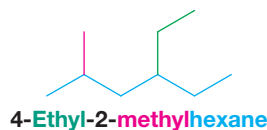


- 3. Use the numbers obtained by application of rule 2 to designate the location of the substituent group.** The parent name is placed last, and the substituent group, preceded by the number designating its location on the chain, is placed first. Numbers

are separated from words by a hyphen. Our two examples are 2-methylhexane and 3-methylheptane, respectively:



4. When two or more substituents are present, give each substituent a number corresponding to its location on the longest chain. For example, we designate the following compound as 4-ethyl-2-methylhexane:



The substituent groups should be listed *alphabetically* (i.e., ethyl before methyl).^{*} In deciding on alphabetical order, disregard multiplying prefixes such as “di” and “tri.”

5. When two substituents are present on the same carbon atom, use that number twice:

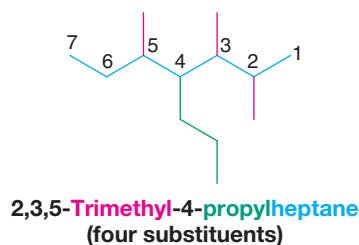


6. When two or more substituents are identical, indicate this by the use of the prefixes *di-*, *tri-*, *tetra-*, and so on. Then make certain that each and every substituent has a number. Commas are used to separate numbers from each other:

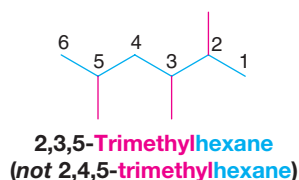


Application of these six rules allows us to name most of the alkanes that we shall encounter. Two other rules, however, may be required occasionally:

7. When two chains of equal length compete for selection as the parent chain, choose the chain with the greater number of substituents:



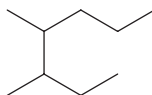
8. When branching first occurs at an equal distance from either end of the longest chain, choose the name that gives the lower number at the first point of difference:



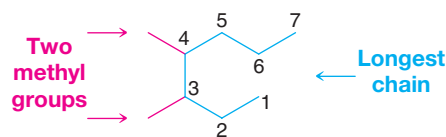
^{*}Some handbooks also list the groups in order of increasing size or complexity (i.e., methyl before ethyl). An alphabetical listing, however, is now by far the most widely used system.


 SOLVED PROBLEM 4.1

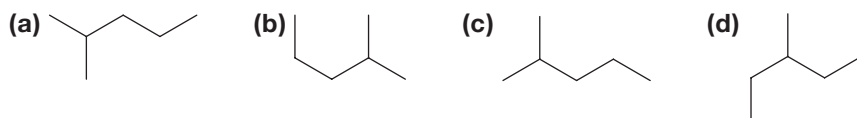
Provide an IUPAC name for the following alkane.



STRATEGY AND SOLUTION: We find the longest chain (shown in blue) to be seven carbons; therefore the parent name is heptane. There are two methyl substituents (shown in red). We number the chain so as to give the first methyl group the lower number. The correct name, therefore, is **3,4-dimethylheptane**. Numbering the chain from the other end to give 4,5-dimethylheptane would have been incorrect.



Which structure does not represent 2-methylpentane?



 PRACTICE PROBLEM 4.2

Write the structure and give the IUPAC name for an alkane with formula C_6H_{14} that has only primary and secondary carbon atoms.


 PRACTICE PROBLEM 4.3

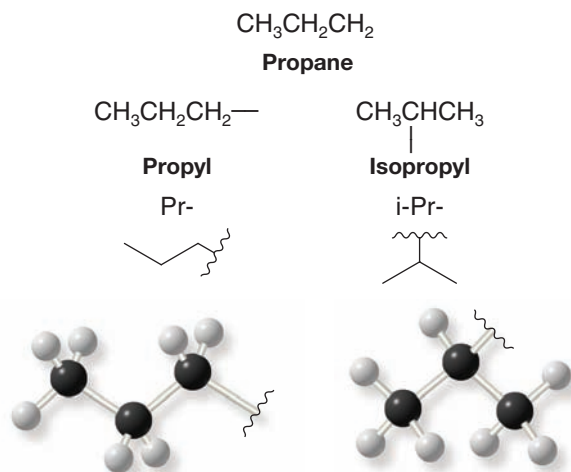
Draw bond-line formulas for all of the isomers of C_8H_{18} that have (a) methyl substituents, and (b) ethyl substituents.


 PRACTICE PROBLEM 4.4

4.3C HOW TO Name Branched Alkyl Groups

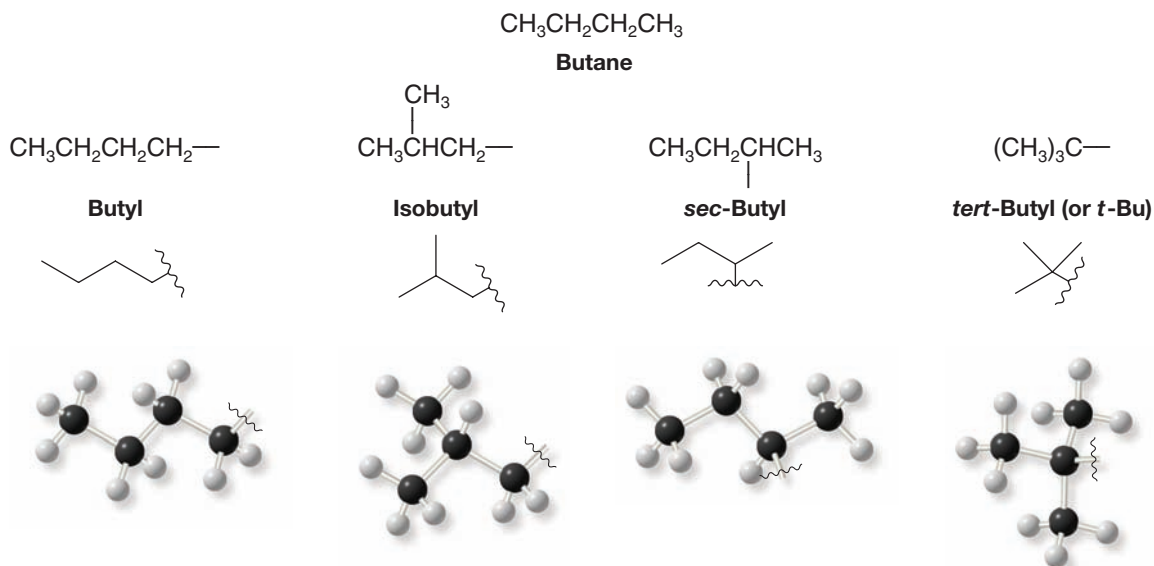
In Section 4.3A you learned the names for the unbranched alkyl groups such as methyl, ethyl, propyl, and butyl, groups derived by removing a terminal hydrogen from an alkane. For alkanes with more than two carbon atoms, more than one derived group is possible. Two groups can be derived from propane, for example; the **propyl group** is derived by removal of a terminal hydrogen, and the **1-methylethyl** or **isopropyl group** is derived by removal of a hydrogen from the central carbon:

Three-Carbon Groups

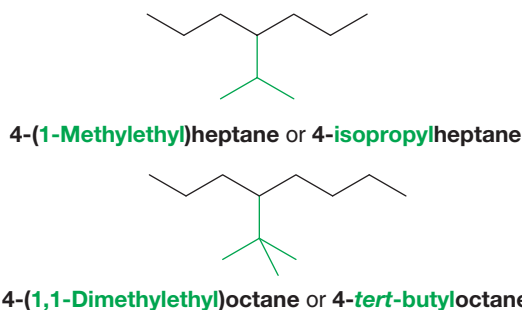


1-Methylethyl is the systematic name for this group; isopropyl is a common name. Systematic nomenclature for alkyl groups is similar to that for branched-chain alkanes, with the provision that *numbering always begins at the point where the group is attached to the main chain*. There are four C_4 groups.

Four-Carbon Groups

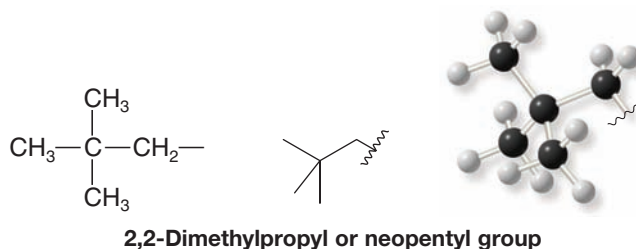


The following examples show how the names of these groups are employed:



The common names **isopropyl**, **isobutyl**, **sec-butyl**, and **tert-butyl** are approved by the IUPAC for the unsubstituted groups, and they are still very frequently used. You should learn these groups so well that you can recognize them any way they are written. In deciding on alphabetical order for these groups you should disregard structure-defining prefixes that are written in italics and separated from the name by a hyphen. Thus *tert*-butyl precedes ethyl, but ethyl precedes isobutyl.*

There is one five-carbon group with an IUPAC approved common name that you should also know: the 2,2-dimethylpropyl group, commonly called the **neopentyl group**.

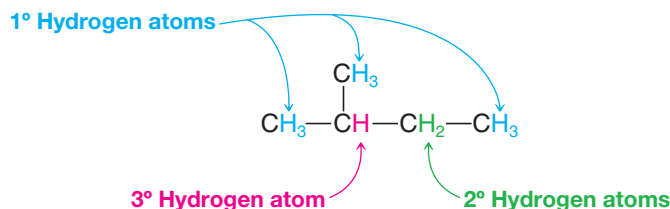
**PRACTICE PROBLEM 4.5**

(a) In addition to the 2,2-dimethylpropyl (or neopentyl) group just given, there are seven other five-carbon groups. Draw bond-line formulas for their structures and give each structure its systematic name. **(b)** Draw bond-line formulas and provide IUPAC names for all of the isomers of C_7H_{16} .

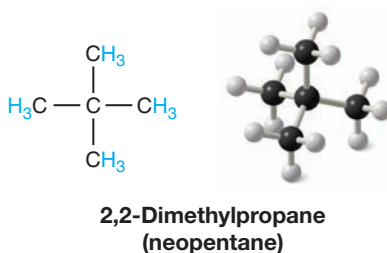
*The abbreviations *i*-, *s*-, and *t*- are sometimes used for *iso*-, *sec*-, and *tert*-, respectively.

4.3D HOW TO Classify Hydrogen Atoms

The hydrogen atoms of an alkane are classified on the basis of the carbon atom to which they are attached. A hydrogen atom attached to a primary carbon atom is a primary (1°) hydrogen atom, and so forth. The following compound, 2-methylbutane, has primary, secondary (2°), and tertiary (3°) hydrogen atoms:

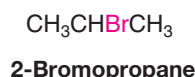
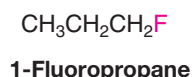
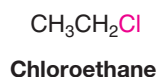


On the other hand, 2,2-dimethylpropane, a compound that is often called **neopentane**, has only primary hydrogen atoms:



4.3E HOW TO Name Alkyl Halides

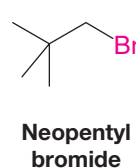
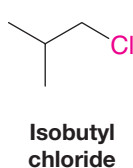
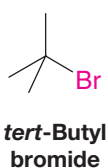
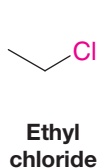
Alkanes bearing halogen substituents are named in the IUPAC substitutive system as haloalkanes:



- When the parent chain has both a halo and an alkyl substituent attached to it, number the chain from the end nearer the first substituent, regardless of whether it is halo or alkyl. If two substituents are at equal distance from the end of the chain, then number the chain from the end nearer the substituent that has alphabetical precedence:



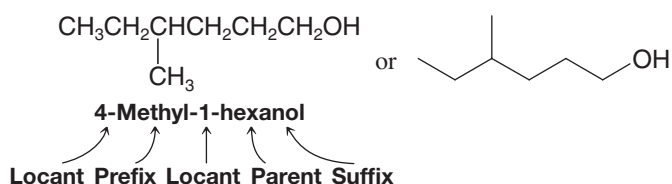
Common names for many simple haloalkanes are still widely used, however. In this common nomenclature system, called **functional class nomenclature**, haloalkanes are named as alkyl halides. (The following names are also accepted by the IUPAC.)



PRACTICE PROBLEM 4.6 Draw bond-line formulas and give IUPAC substitutive names for all of the isomers of (a) C_4H_9Cl and (b) $C_5H_{11}Br$.

4.3F HOW TO Name Alcohols

In what is called IUPAC **substitutive nomenclature**, a name may have as many as four features: **locants**, **prefixes**, **parent compound**, and **suffixes**. Consider the following compound as an illustration without, for the moment, being concerned as to how the name arises:



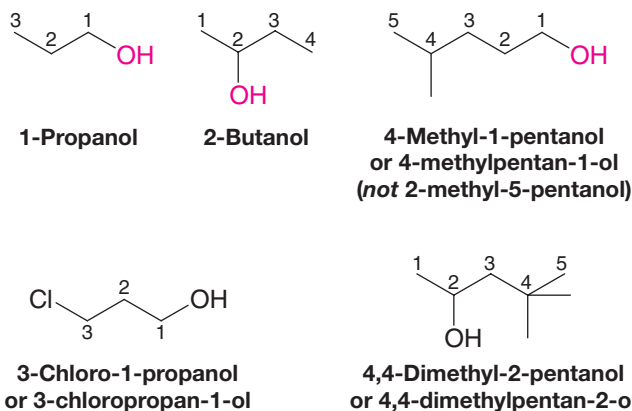
The *locant* **4-** tells that the substituent **methyl** group, named as a *prefix*, is attached to the *parent compound* at C4. The parent compound contains six carbon atoms and no multiple bonds, hence the parent name **hexane**, and it is an alcohol; therefore it has the *suffix* **-ol**. The locant **1-** tells that C1 bears the hydroxyl group. **In general, numbering of the chain always begins at the end nearer the group named as a suffix.**

The locant for a suffix (whether it is for an alcohol or another functional group) may be placed before the parent name as in the above example or, according to a 1993 IUPAC revision of the rules, immediately before the suffix. Both methods are IUPAC approved. Therefore, the above compound could also be named **4-methylhexan-1-ol**.

The following procedure should be followed in giving alcohols IUPAC substitutive names:

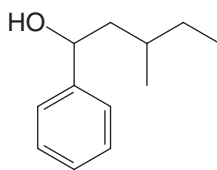
1. Select the longest continuous carbon chain *to which the hydroxyl is directly attached*. Change the name of the alkane corresponding to this chain by dropping the final *-e* and adding the suffix *-ol*.
2. Number the longest continuous carbon chain so as to give the carbon atom bearing the hydroxyl group the lower number. Indicate the position of the hydroxyl group by using this number as a locant; indicate the positions of other substituents (as prefixes) by using the numbers corresponding to their positions along the carbon chain as locants.

The following examples show how these rules are applied:

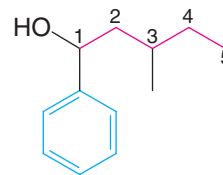



 SOLVED PROBLEM 4.2

Give an IUPAC name for the compound shown.



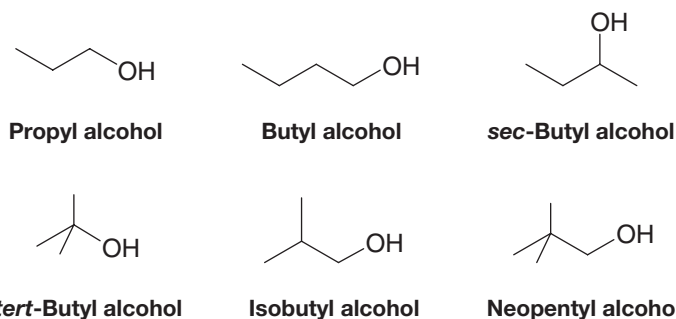
STRATEGY AND ANSWER: We find that the longest carbon chain (in red at right) has five carbons and it bears a hydroxyl group on the first carbon. So we name this part of the molecule as a 1-pentanol. There is a phenyl group on carbon-1 and a methyl group on carbon-3, so the full name is 3-methyl-1-phenyl-1-pentanol.



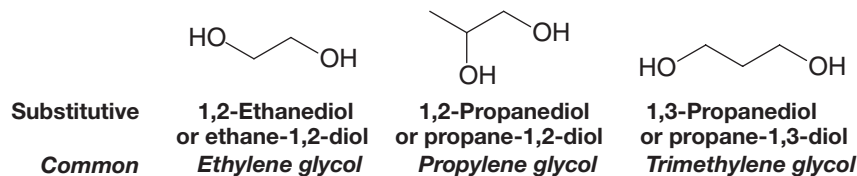
Draw bond-line formulas and give IUPAC substitutive names for all of the isomeric alcohols with the formulas (a) $C_4H_{10}O$ and (b) $C_5H_{12}O$.


 PRACTICE PROBLEM 4.7

Simple alcohols are often called by *common* functional class names that are also approved by the IUPAC. We have seen several examples already (Section 2.6). In addition to *methyl alcohol*, *ethyl alcohol*, and *isopropyl alcohol*, there are several others, including the following:



Alcohols containing two hydroxyl groups are commonly called **glycols**. In the IUPAC substitutive system they are named as **diols**:

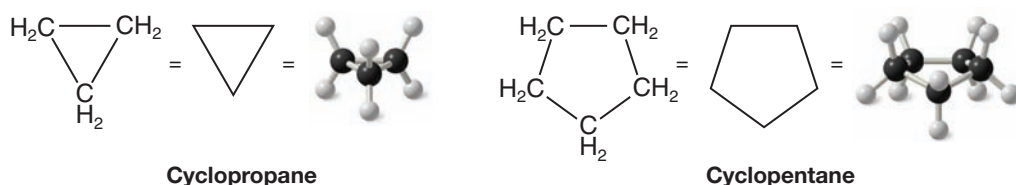


4.4 HOW TO NAME CYCLOALKANES

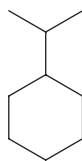
4.4A HOW TO Name Monocyclic Cycloalkanes

Cycloalkanes are named by adding “cyclo” before the parent name.

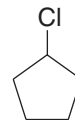
- Cycloalkanes with one ring and no substituents:* Count the number of carbon atoms in the ring, then add “cyclo” to the beginning of the name of the alkane with that number of carbons. For example, cyclopropane has three carbons and cyclopentane has five carbons.



2. *Cycloalkanes with one ring and one substituent:* Add the name of the substituent to the beginning of the parent name. For example, cyclohexane with an attached isopropyl group is isopropylcyclohexane. For compounds with only one substituent, it is not necessary to specify a number (locant) for the carbon bearing the substituent.

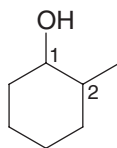


Isopropylcyclohexane

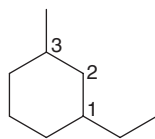
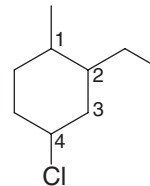


Chlorocyclopentane

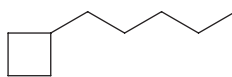
3. *Cycloalkanes with one ring and two or more substituents:* For a ring with two substituents, begin by numbering the carbons in the ring, starting at the carbon with the substituent that is first in the alphabet and number in the direction that gives the next substituent the lower number possible. When there are three or more substituents, begin at the substituent that leads to the lowest set of numbers (locants). The substituents are listed in alphabetical order, not according to the number of their carbon atom.



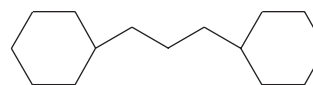
2-Methylcyclohexanol

1-Ethyl-3-methylcyclohexane
(not 1-ethyl-5-methylcyclohexane)4-Chloro-2-ethyl-1-methylcyclohexane
(not 1-chloro-3-ethyl-4-methylcyclohexane)

4. When a single ring system is attached to a single chain with a greater number of carbon atoms, or when more than one ring system is attached to a single chain, then it is appropriate to name the compounds as *cycloalkylalkanes*. For example.



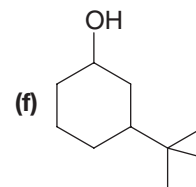
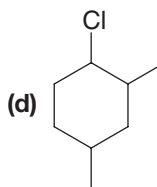
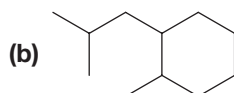
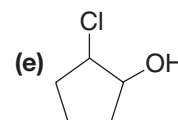
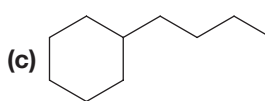
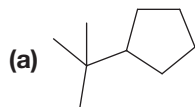
1-Cyclobutylpentane



1,3-Dicyclohexylpropane

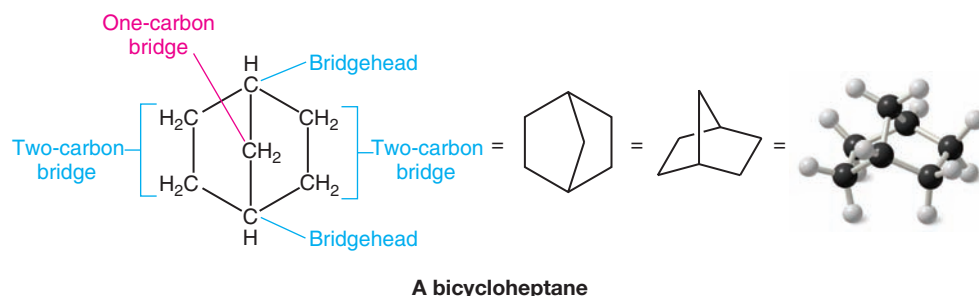
PRACTICE PROBLEM 4.8

Give names for the following substituted alkanes:



4.4B HOW TO Name Bicyclic Cycloalkanes

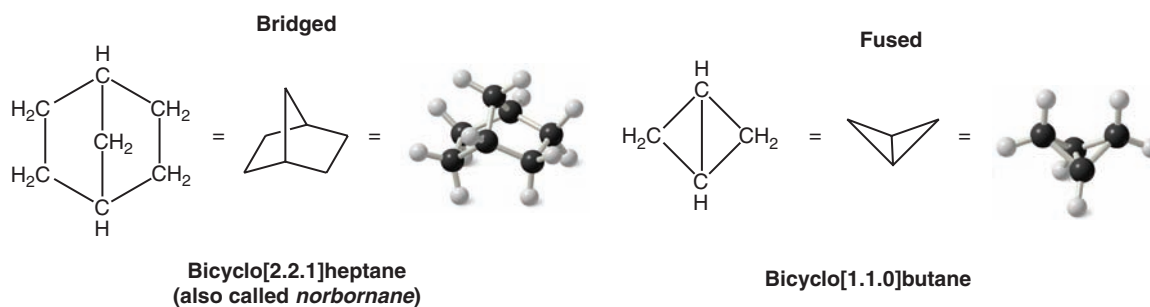
- We name compounds containing two fused or bridged rings as bicycloalkanes and we use the name of the alkane corresponding to the total number of carbon atoms in the rings as the parent name. The following compound, for example, contains seven carbon atoms and is, therefore, a bicycloheptane. The carbon atoms common to both rings are called bridgeheads, and each bond, or each chain of atoms connecting the bridgehead atoms, is called a bridge.



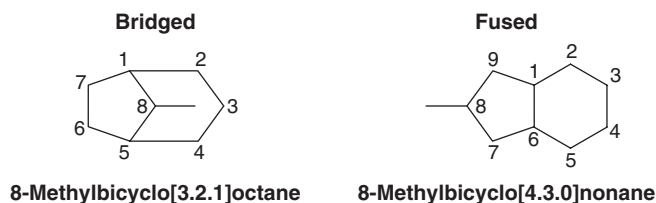
Helpful Hint

Explore the structures of these **bicyclic compounds** by building handheld molecular models.

- We then interpose an expression in brackets within the name that denotes the number of carbon atoms in each bridge (in order of decreasing length). Fused rings have zero carbons in their bridge. For example,



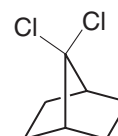
- In bicycloalkanes with substituents, we number the bridged ring system beginning at one bridgehead, proceeding first along the longest bridge to the other bridgehead, then along the next longest bridge back to the first bridgehead; the shortest bridge is numbered last.



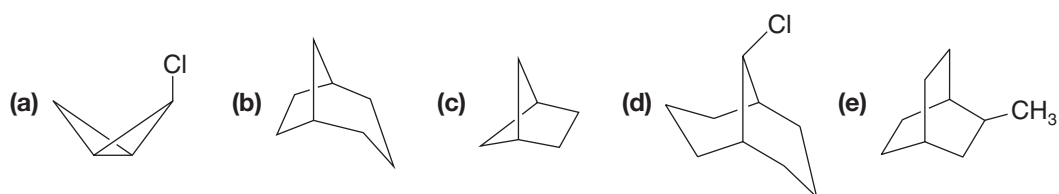
SOLVED PROBLEM 4.3

Write a structural formula for 7,7-dichlorobicyclo[2.2.1]heptane.

STRATEGY AND ANSWER: First we write a bicyclo[2.2.1]heptane ring and number it. Then we add the substituents (two chlorine atoms) to the proper carbon.



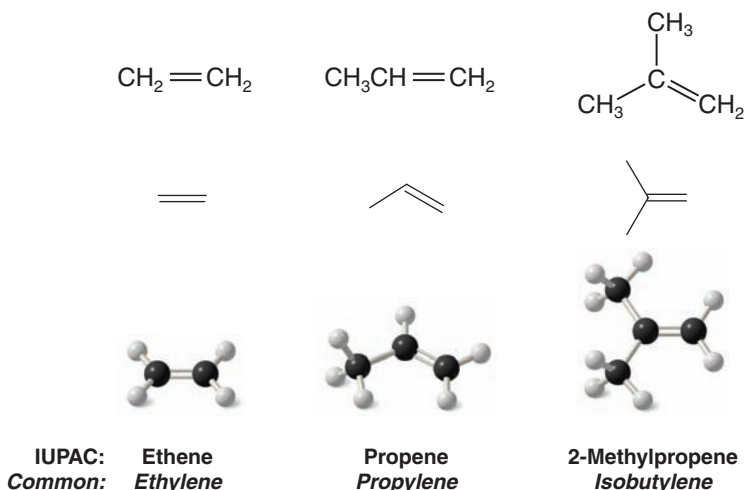
PRACTICE PROBLEM 4.9 Give names for each of the following bicyclic alkanes:



(f) Write the structure of a bicyclic compound that is a constitutional isomer of bicyclo[2.2.0]hexane and give its name.

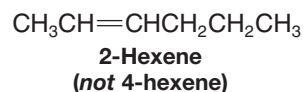
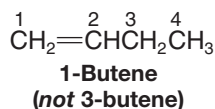
4.5 HOW TO NAME ALKENES AND CYCLOALKENES

Many older names for **alkenes** are still in common use. Propene is often called propylene, and 2-methylpropene frequently bears the name isobutylene:

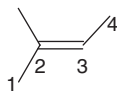


The IUPAC rules for naming alkenes are similar in many respects to those for naming alkanes:

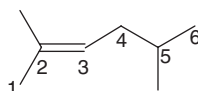
- Determine the parent name by selecting the longest chain that contains the double bond and change the ending of the name of the alkane of identical length from -ane to -ene.** Thus, if the longest chain contains five carbon atoms, the parent name for the alkene is *pentene*; if it contains six carbon atoms, the parent name is *hexene*, and so on.
- Number the chain so as to include both carbon atoms of the double bond, and begin numbering at the end of the chain nearer the double bond. Designate the location of the double bond by using the number of the first atom of the double bond as a prefix. The locant for the alkene suffix may precede the parent name or be placed immediately before the suffix.** We will show examples of both styles:



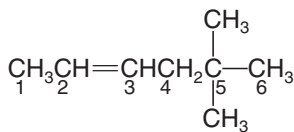
3. Indicate the locations of the substituent groups by the numbers of the carbon atoms to which they are attached:



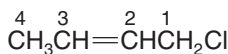
2-Methyl-2-butene
or 2-methylbut-2-ene



2,5-Dimethyl-2-hexene
or 2,5-dimethylhex-2-ene

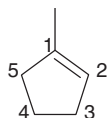


5,5-Dimethyl-2-hexene
or 5,5-dimethylhex-2-ene

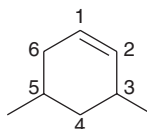


1-Chloro-2-butene
or 1-chlorobut-2-ene

4. Number substituted cycloalkenes in the way that gives the carbon atoms of the double bond the 1 and 2 positions and that also gives the substituent groups the lower numbers at the first point of difference. With substituted cycloalkenes it is not necessary to specify the position of the double bond since it will always begin with C1 and C2. The two examples shown here illustrate the application of these rules:

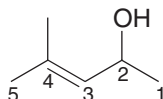


1-Methylcyclopentene
(not 2-methylcyclopentene)

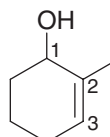


3,5-Dimethylcyclohexene
(not 4,6-dimethylcyclohexene)

5. Name compounds containing a double bond and an alcohol group as alkenols (or cycloalkenols) and give the alcohol carbon the lower number:



4-Methyl-3-penten-2-ol
or 4-methylpent-3-en-2-ol

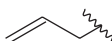


2-Methyl-2-cyclohexen-1-ol
or 2-methylcyclohex-2-en-1-ol

6. Two frequently encountered alkenyl groups are the **vinyl group** and the **allyl group**:

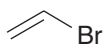


The vinyl group



The allyl group

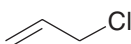
Using substitutive nomenclature, the vinyl and allyl groups are called *ethenyl* and *prop-2-en-1-yl*, respectively. The following examples illustrate how these names are employed:



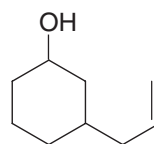
Bromoethene
or
vinyl bromide
(common)



Ethenylcyclopropane
or
vinylcyclopropane



3-Chloropropene
or
allyl chloride
(common)



3-(Prop-2-en-1-yl)cyclohexan-1-ol
or
3-allylcyclohexanol

7. If two identical or substantial groups are on the same side of the double bond, the compound can be designated *cis*; if they are on opposite sides it can be designated *trans*:

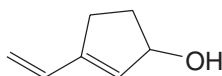


cis-1,2-Dichloroethene **trans-1,2-Dichloroethene**

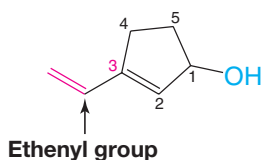
(In Section 7.2 we shall see another method for designating the geometry of the double bond.)

SOLVED PROBLEM 4.4

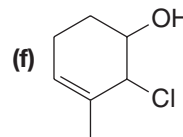
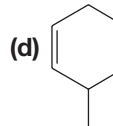
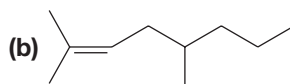
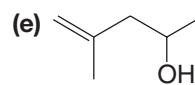
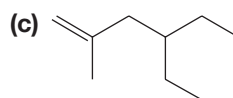
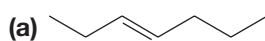
Give an IUPAC name for the molecule shown.



STRATEGY AND ANSWER: We number the ring as shown below starting with the hydroxyl group so as to give the double bond the lower possible number. We include in the name the substituent (an ethenyl group) and the double bond (*-ene-*), and the hydroxyl group (*-ol*) with numbers for their respective positions. Hence the IUPAC name is 3-ethenyl-2-cyclopenten-1-ol.



PRACTICE PROBLEM 4.10 Give IUPAC names for the following alkenes:



PRACTICE PROBLEM 4.11 Write bond-line formulas for the following:

(a) *cis*-3-Octene

(f) 1-Bromo-2-methyl-1-(prop-2-en-1-yl)cyclopentane

(b) *trans*-2-Hexene

(g) 3,4-Dimethylcyclopentene

(c) 2,4-Dimethyl-2-pentene

(h) Vinylcyclopentane

(d) *trans*-1-Chlorobut-2-ene

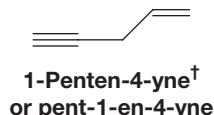
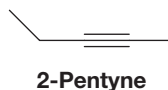
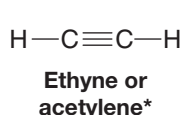
(i) 1,2-Dichlorocyclohexene

(e) 4,5-Dibromo-1-pentene

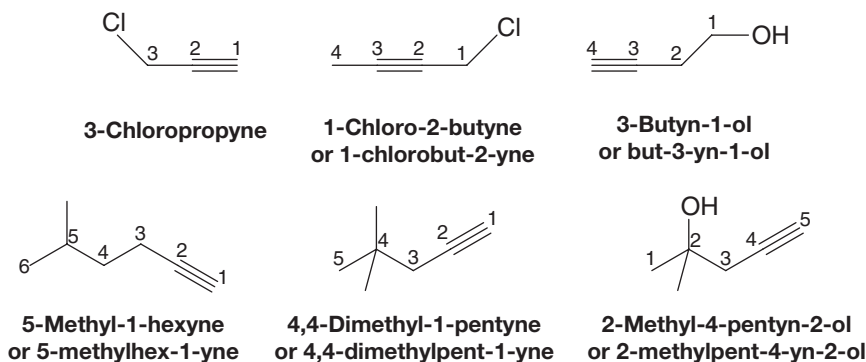
(j) *trans*-1,4-Dichloro-2-pentene

4.6 HOW TO NAME ALKYNES

Alkynes are named in much the same way as alkenes. Unbranched alkynes, for example, are named by replacing the **-ane** of the name of the corresponding alkane with the ending **-yne**. The chain is numbered to give the carbon atoms of the triple bond the lower possible numbers. The lower number of the two carbon atoms of the triple bond is used to designate the location of the triple bond. The IUPAC names of three unbranched alkynes are shown here:



The locations of substituent groups of branched alkynes and substituted alkynes are also indicated with numbers. An —OH group has priority over the triple bond when numbering the chain of an alkyne:



Give the structures and IUPAC names for all the alkynes with the formula C_6H_{10} .

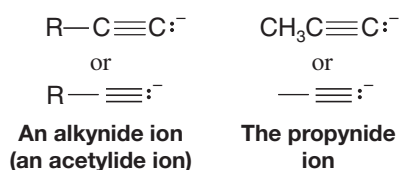
PRACTICE PROBLEM 4.12

Monosubstituted acetylenes or 1-alkynes are called **terminal alkynes**, and the hydrogen attached to the carbon of the triple bond is called the **acetylenic hydrogen atom**:



When named as a substituent, the $HC \equiv C-$ group is called the ethynyl group.

The anion obtained when the acetylenic hydrogen is removed is known as an *alkynide ion* or an acetylide ion. As we shall see in Section 7.11, these ions are useful in synthesis:



4.7 PHYSICAL PROPERTIES OF ALKANES AND CYCLOALKANES

If we examine the unbranched **alkanes** in Table 4.2, we notice that each alkane differs from the preceding alkane by one $-CH_2-$ group. Butane, for example, is $CH_3(CH_2)_2CH_3$ and pentane is $CH_3(CH_2)_3CH_3$. A series of compounds like this, where each member differs from the next member by a constant unit, is called a **homologous series**. Members of a homologous series are called **homologues**.

At room temperature (25 °C) and 1 atm pressure the first four members of the homologous series of unbranched alkanes are gases (Fig. 4.3), the C_5-C_{17} unbranched alkanes (pentane to heptadecane) are liquids, and the unbranched alkanes with 18 and more carbon atoms are solids.

*The name acetylene is retained by the IUPAC system for the compound $HC \equiv CH$ and is used frequently.

†When double and triple bonds are present, the direction of numbering is chosen so as to give the lowest overall set of locants. In the face of equivalent options, then preference is given to assigning lowest numbers to the double bonds.

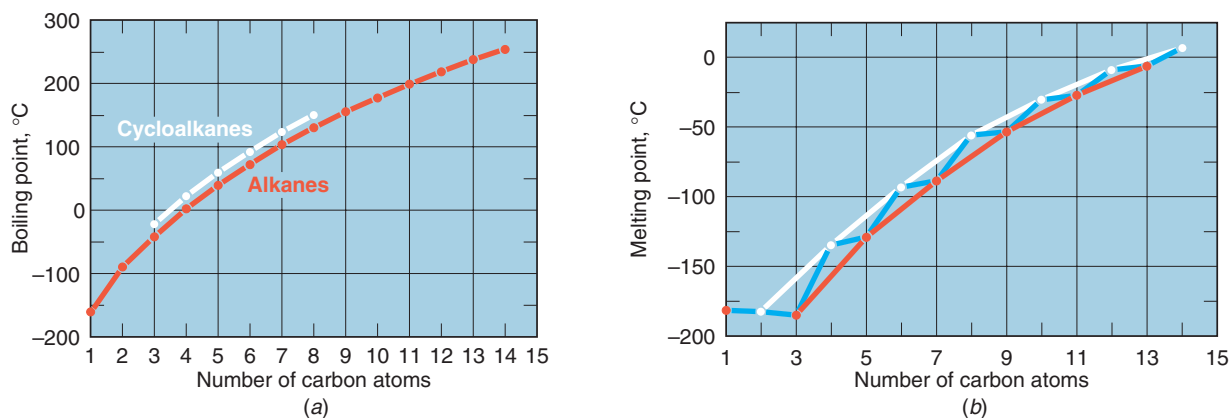
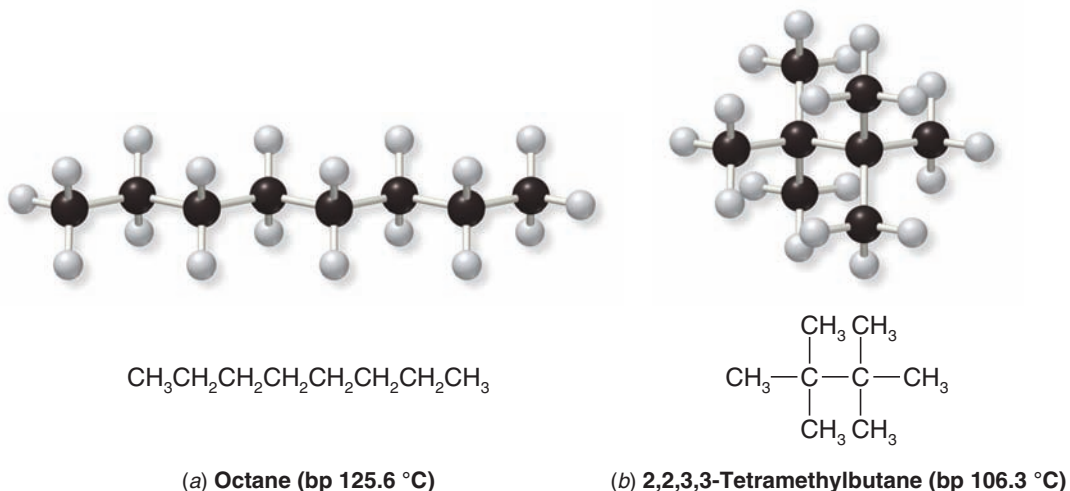


FIGURE 4.3 (a) Boiling points of unbranched alkanes (in red) and cycloalkanes (in white). (b) Melting points of unbranched alkanes.

Boiling Points The boiling points of the unbranched alkanes show a regular increase with increasing molecular weight (Fig. 4.3a) in the homologous series of straight-chain alkanes. Branching of the alkane chain, however, lowers the boiling point. The hexane isomers in Table 4.1 exemplify this trend.

Part of the explanation for these effects lies in the dispersion forces that we studied in Section 2.13B. With unbranched alkanes, as molecular weight increases, so too do molecular size and, even more importantly, molecular surface area. With increasing surface area, the dispersion forces between molecules increase; therefore, more energy (a higher temperature) is required to separate molecules from one another and produce boiling. Chain branching, on the other hand, makes a molecule more compact, reducing its surface area and with it the strength of the dispersion forces operating between it and adjacent molecules; this has the effect of lowering the boiling point. Figure 4.4 illustrates this for two C₈ isomers.

FIGURE 4.4 Chain-branching decreases the contact surface area between molecules, as for the branched C₈ isomer in (b), lessening the dispersion forces between them and leading to a lower boiling point than for the unbranched C₈ isomer (a).



Melting Points The unbranched alkanes do not show the same smooth increase in melting points with increasing molecular weight (blue line in Fig. 4.3b) that they show in their boiling points. There is an alternation as one progresses from an unbranched alkane with an even number of carbon atoms to the next one with an odd number of carbon atoms. If, however, the even- and odd-numbered alkanes are plotted on *separate* curves (white and red lines in Fig. 4.3b), there *is* a smooth increase in melting point with increasing molecular weight.

X-ray diffraction studies, which provide information about molecular structure, have revealed the reason for this apparent anomaly. Alkane chains with an even number of carbon atoms pack more closely in the crystalline state. As a result, attractive forces between individual chains are greater and melting points are higher.

Cycloalkanes also have much higher melting points than their open-chain counterparts (Table 4.3).

TABLE 4.3 PHYSICAL CONSTANTS OF CYCLOALKANES

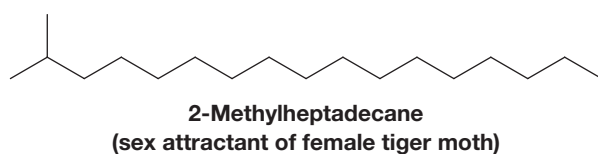
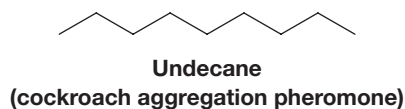
Number of Carbon Atoms	Name	bp (°C) (1 atm)	mp (°C)	Density at 20 °C (g mL ⁻¹)	Refractive Index (n _D ²⁰)
3	Cyclopropane	-33	-126.6	—	—
4	Cyclobutane	13	-90	—	1.4260
5	Cyclopentane	49	-94	0.751	1.4064
6	Cyclohexane	81	6.5	0.779	1.4266
7	Cycloheptane	118.5	-12	0.811	1.4449
8	Cyclooctane	149	13.5	0.834	—

Density As a class, the alkanes and cycloalkanes are the least dense of all groups of organic compounds. All alkanes and cycloalkanes have densities considerably less than 1.00 g mL⁻¹ (the density of water at 4 °C). As a result, petroleum (a mixture of hydrocarbons rich in alkanes) floats on water.

Solubility Alkanes and cycloalkanes are almost totally insoluble in water because of their very low polarity and their inability to form hydrogen bonds. Liquid alkanes and cycloalkanes are soluble in one another, and they generally dissolve in solvents of low polarity. Good solvents for them are benzene, carbon tetrachloride, chloroform, and other hydrocarbons.

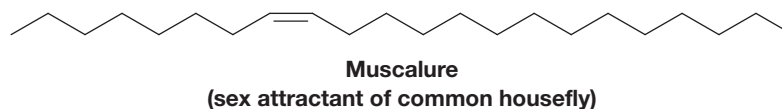
THE CHEMISTRY OF ... Pheromones: Communication by Means of Chemicals

Many animals communicate with other members of their species using a language based not on sounds or even visual signals but on the odors of chemicals called **pheromones** that these animals release. For insects, this appears to be the chief method of communication. Although pheromones are secreted by insects in extremely small amounts, they can cause profound and varied biological effects. Some insects use pheromones in courtship as sex attractants. Others use pheromones as warning substances, and still others secrete chemicals called “aggregation compounds” to cause members of their species to congregate. Often these pheromones are relatively simple compounds, and some are hydrocarbons. For example, a species of cockroach uses undecane as an aggregation pheromone:



When a female tiger moth wants to mate, she secretes 2-methylheptadecane, a perfume that the male tiger moth apparently finds irresistible.

The sex attractant of the common housefly (*Musca domestica*) is a 23-carbon alkene with a cis double bond between atoms 9 and 10 called muscalure:

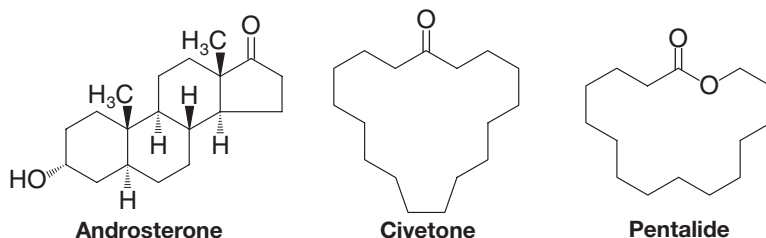


Danilo Donadoni/Photoshor Holdings Ltd.

(continues on next page)

Many insect sex attractants have been synthesized and are used to lure insects into traps as a means of insect control, a much more environmentally sensitive method than the use of insecticides.

Research suggests there are roles for pheromones in the lives of humans as well. For example, studies have shown that the phenomenon of menstrual synchronization among women who live or work with each other is likely caused by pheromones. Olfactory sensitivity to musk, which includes steroids such as androsterone, large cyclic ketones, and lactones (cyclic esters), also varies cyclically in women, differs between the sexes, and may influence our behavior. Some of these compounds are used in perfumes, including civetone, a natural product isolated from glands of the civet cat, and pentalide, a synthetic musk.



4.8 SIGMA BONDS AND BOND ROTATION

Two groups bonded by only a single bond can undergo rotation about that bond with respect to each other.

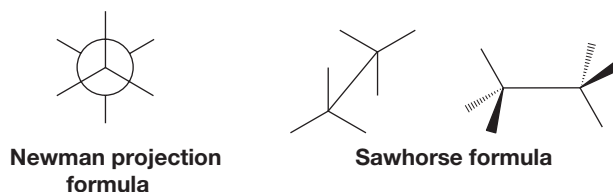
- The temporary molecular shapes that result from such a rotation are called **conformations** of the molecule.
- Each possible structure is called a **conformer**.
- An analysis of the energy changes that occur as a molecule undergoes rotations about single bonds is called a **conformational analysis**.

4.8A Newman Projections and HOW TO Draw Them

When we do conformational analysis, we will find that certain types of structural formulas are especially convenient to use. One of these types is called a **Newman projection formula** and another type is a **sawhorse formula**. Sawhorse formulas are much like dash-wedge three-dimensional formulas we have used so far. In conformational analyses, we will make substantial use of Newman projections.

Helpful Hint

Learn to draw Newman projections and sawhorse formulas. Build handheld molecular models and compare them with your drawings.



To write a Newman projection formula:

- We imagine ourselves taking a view from one atom (usually a carbon) directly along a selected bond axis to the next atom (also usually a carbon atom).
- The front carbon and its other bonds are represented as .
- The back carbon and its bonds are represented as .

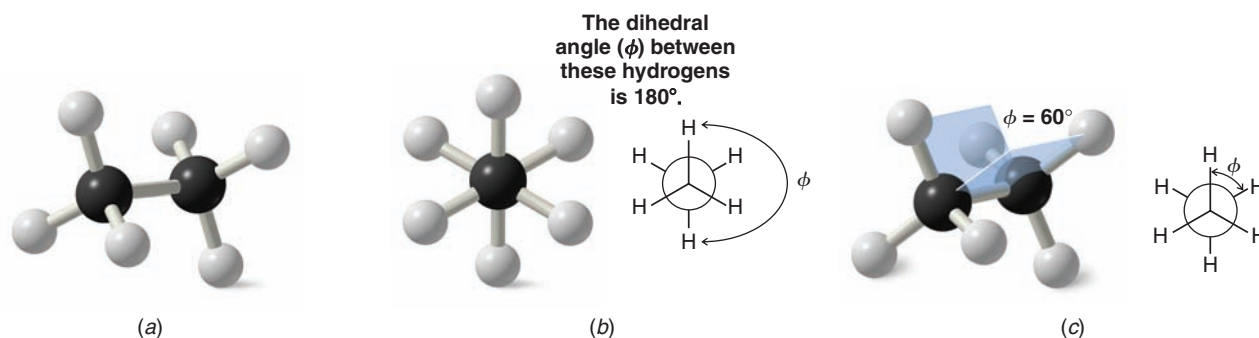


FIGURE 4.5 (a) The staggered conformation of ethane. (b) The Newman projection formula for the staggered conformation. (c) The dihedral angle between these hydrogen atoms is 60° .

In Figs. 4.5*a,b* we show ball-and-stick models and a Newman projection formula for the staggered conformation of ethane. The **staggered conformation** of a molecule is that conformation where the **dihedral angle** between the bonds at each of the carbon–carbon bonds is 180° and where atoms or groups bonded to carbons at each end of a carbon–carbon bond are as far apart as possible. The 180° dihedral angle in the staggered conformation of ethane is indicated in Fig. 4.5*b*.

The eclipsed conformation of ethane is shown in Fig. 4.6 using ball-and-stick models and a Newman projection. In an **eclipsed conformation** the atoms bonded to carbons at each end of a carbon–carbon bond are directly opposed to one another. The dihedral angle between them is 0° .

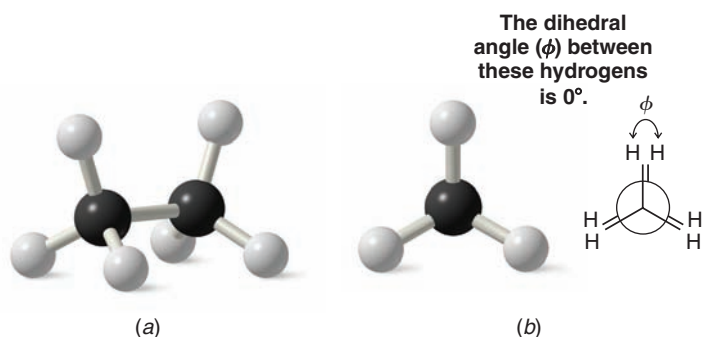


FIGURE 4.6 (a) The eclipsed conformation of ethane. (b) The Newman projection formula for the eclipsed conformation.

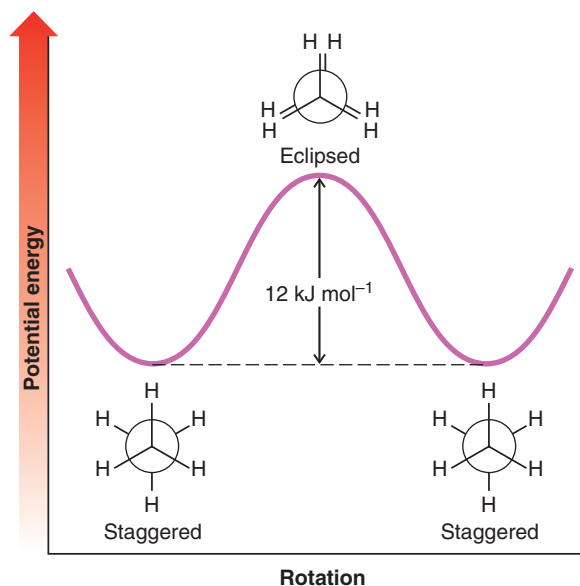
4.8B HOW TO Do a Conformational Analysis

Now let us consider a conformational analysis of ethane. Clearly, infinitesimally small changes in the dihedral angle between C–H bonds at each end of ethane could lead to an infinite number of conformations, including, of course, the staggered and eclipsed conformations. These different conformations are not all of equal stability, however, and it is known that the staggered conformation of ethane is the most stable conformation (i.e., it is the conformation of lowest potential energy). The explanation for greater stability of the staggered conformation relates mainly to steric repulsion between bonding pairs of electrons. In the eclipsed conformation electron clouds from the C–H bonds are closer and repel one another. The staggered conformation allows the maximum possible separation of the electron pairs in the C–H bonds. In addition, there is a phenomenon called **hyperconjugation** that involves favorable overlap between filled and unfilled sigma orbitals in the staggered conformation. Hyperconjugation helps to stabilize the staggered conformation. The more important factor, however, is the minimization of steric repulsions in the staggered form. In later chapters we shall explain hyperconjugation further and the role it plays in relative stability of reactive species called carbocations.

- The energy difference between the conformations of ethane can be represented graphically in a **potential energy diagram**, as shown in Figure 4.7.

In ethane the energy difference between the staggered and eclipsed conformations is about 12 kJ mol^{-1} . This small barrier to rotation is called the **torsional barrier** of the single bond. Because of this barrier, some molecules will wag back and forth with their atoms in staggered or nearly staggered conformations, while others with slightly more energy will rotate through an eclipsed conformation to another staggered conformation. At any given moment, unless the temperature is extremely low ($-250 \text{ }^\circ\text{C}$), most ethane molecules will have enough energy to undergo bond rotation from one conformation to another.

FIGURE 4.7 Potential energy changes that accompany rotation of groups about the carbon–carbon bond of ethane.



The idea that certain conformations of molecules are favored originates from the work of J.H. van't Hoff. He was also winner of the first Nobel Prize in Chemistry (1901) for his work in chemical kinetics.

What does all this mean about ethane? We can answer this question in two different ways. If we consider a single molecule of ethane, we can say, for example, that it will spend most of its time in the lowest energy, staggered conformation, or in a conformation very close to being staggered. Many times every second, however, it will acquire enough energy through collisions with other molecules to surmount the torsional barrier and it will rotate through an eclipsed conformation. If we speak in terms of a large number of ethane molecules (a more realistic situation), we can say that at any given moment most of the molecules will be in staggered or nearly staggered conformations.

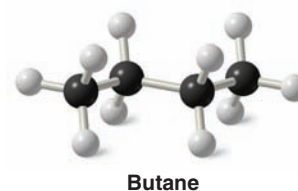
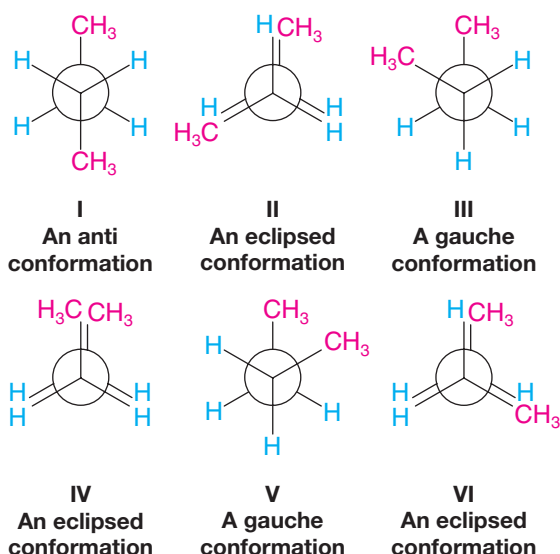
4.9 CONFORMATIONAL ANALYSIS OF BUTANE

Now let us consider rotation about the C2—C3 bond of butane. The barriers to rotation about the C2—C3 bond in butane are larger than for rotation about the C—C bond in ethane, but still not large enough to prevent the rotations that lead to all possible butane conformers.

- The factors involved in barriers to bond rotation are together called **torsional strain** and include the repulsive interactions called **steric hindrance** between electron clouds of the bonded groups.

In butane, torsional strain results from steric hindrance between the terminal methyl groups and hydrogen atoms at C-2 and C-3 and from steric hindrance directly between

the two methyl groups. These interactions result in six important conformers of butane, shown as **I–VI** below.



Helpful Hint

You should build a molecular model of butane and examine its various conformations as we discuss their relative potential energies.

The **anti conformation** (**I**) does not have torsional strain from steric hindrance because the groups are staggered and the methyl groups are far apart. The anti conformation is the most stable. The methyl groups in the **gauche conformations** **III** and **V** are close enough to each other that the dispersion forces between them are *repulsive*; the electron clouds of the two groups are so close that they repel each other. This repulsion causes the gauche conformations to have approximately 3.8 kJ mol^{-1} more energy than the anti conformation.

The eclipsed conformations (**II**, **IV**, and **VI**) represent energy maxima in the potential energy diagram (Fig. 4.8). Eclipsed conformations **II** and **VI** have repulsive dispersion forces arising from the eclipsed methyl groups and hydrogen atoms. Eclipsed conformation **IV** has the greatest energy of all because of the added large repulsive dispersion forces between the eclipsed methyl groups as compared to **II** and **VI**.

Although the barriers to rotation in a butane molecule are larger than those of an ethane molecule (Section 4.8), they are still far too small to permit isolation of the gauche and anti conformations at normal temperatures. Only at extremely low temperatures would the molecules have insufficient energies to surmount these barriers.

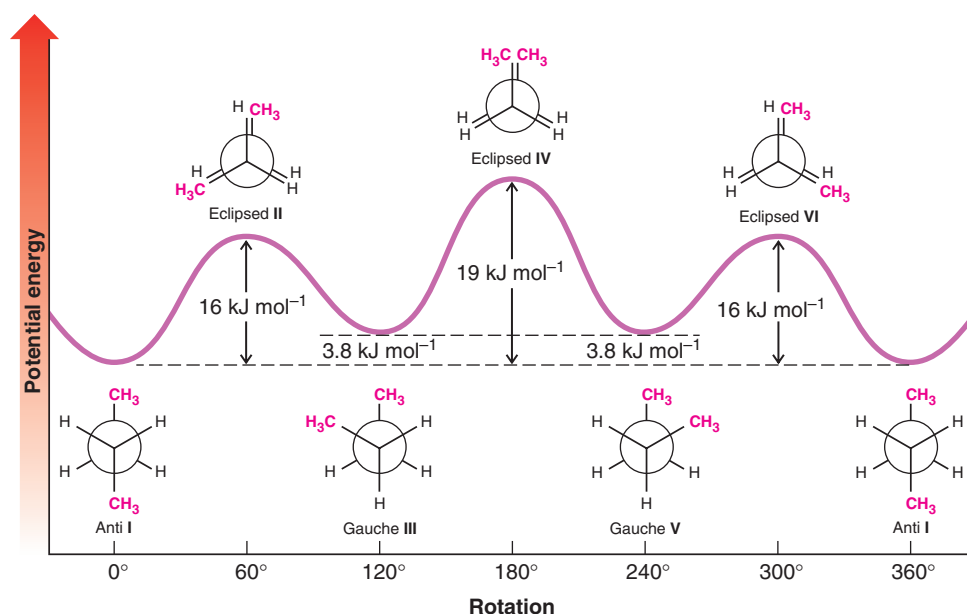


FIGURE 4.8 Energy changes that arise from rotation about the C2—C3 bond of butane.

We saw earlier (Section 2.16C) that dispersion forces can be *attractive*. Here, however, we find that they can also be *repulsive*, leading to steric hindrance. Whether dispersion interactions lead to attraction or to repulsion depends on the distance that separates the two groups. As two nonpolar groups are brought closer and closer together, the first effect is one in which a momentarily unsymmetrical distribution of electrons in one group induces an opposite polarity in the other. The opposite charges induced in those portions of the two groups that are in closest proximity lead to attraction between them. This attraction increases to a maximum as the internuclear distance of the two groups decreases. The internuclear distance at which the attractive force is at a maximum is equal to the sum of what are called the *van der Waals radii* of the two groups. The van der Waals radius of a group is, in effect, a measure of its size. If the two groups are brought still closer—closer than the sum of their van der Waals radii—their electron clouds begin to penetrate each other, and strong electron–electron repulsion occurs.

4.9A Stereoisomers and Conformational Stereoisomers

Gauche conformers **III** and **V** of butane are examples of stereoisomers.

- **Stereoisomers** have the same molecular formula and connectivity but different arrangements of atoms in three-dimensional space.
- **Conformational stereoisomers** are related to one another by bond rotations.

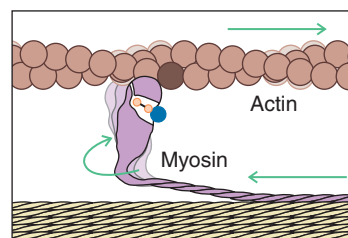
Conformational analysis is but one of the ways in which we will consider the three-dimensional shapes and stereochemistry of molecules. We shall see that there are other types of stereoisomers that cannot be interconverted simply by rotations about single bonds. Among these are *cis–trans* cycloalkane isomers (Section 4.13) and others that we shall consider in Chapter 5.

PRACTICE PROBLEM 4.13

Sketch a curve similar to that in Fig. 4.8 showing in general terms the energy changes that arise from rotation about the C2—C3 bond of 2-methylbutane. You need not concern yourself with the actual numerical values of the energy changes, but you should label all maxima and minima with the appropriate conformations.

THE CHEMISTRY OF ... Muscle Action

Muscle proteins are essentially very long linear molecules (folded into a compact shape) whose atoms are connected by single bonds in a chainlike fashion. Relatively free rotation is possible about atoms joined by single bonds, as we have seen. When your muscles contract to do work, like they are for the person shown exercising here, the cumulative effect of rotations about many single bonds is to move the tail of each myosin molecule 60 Å along the adjacent protein (called actin) in a step called the “power stroke.” This process occurs over and over again as part of a ratcheting mechanism between many myosin and actin molecules for each muscle movement.



Power stroke in muscle

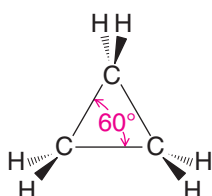
4.10 THE RELATIVE STABILITIES OF CYCLOALKANES: RING STRAIN

Cycloalkanes do not all have the same relative stability. Experiments have shown that cyclohexane is the most stable cycloalkane and that, in comparison, cyclopropane and cyclobutane are much less stable. This difference in relative stability is due to **ring strain**, which comprises **angle strain** and **torsional strain**.

- **Angle strain** is the result of deviation from ideal bond angles caused by inherent structural constraints (such as ring size).
- **Torsional strain** is the result of repulsive dispersion forces that cannot be relieved due to restricted conformational mobility.

4.10A Cyclopropane

The carbon atoms of alkanes are sp^3 hybridized. The normal tetrahedral bond angle of an sp^3 -hybridized atom is 109.5° . In cyclopropane (a molecule with the shape of a regular triangle), the internal angles must be 60° and therefore they must depart from this ideal value by a very large amount—by 49.5° :



Angle strain exists in a cyclopropane ring because the sp^3 orbitals comprising the carbon–carbon σ bonds cannot overlap as effectively (Fig. 4.9*a*) as they do in alkanes (where perfect end-on overlap is possible). The carbon–carbon bonds of cyclopropane are often described as being “bent.” Orbital overlap is less effective. (The orbitals used for these bonds are not purely sp^3 ; they contain more p character.) The carbon–carbon bonds of cyclopropane are weaker, and as a result the molecule has greater potential energy.

While angle strain accounts for most of the ring strain in cyclopropane, it does not account for it all. Because the ring is (of necessity) planar, the C—H bonds of the ring are all *eclipsed* (Figs. 4.9*b,c*), and the molecule has torsional strain from repulsive dispersion forces as well.

4.10B Cyclobutane

Cyclobutane also has considerable angle strain. The internal angles are 88° —a departure of more than 21° from the normal tetrahedral bond angle. The cyclobutane ring is not planar but is slightly “folded” (Fig. 4.10*a*). If the cyclobutane ring were planar, the angle strain would be somewhat less (the internal angles would be 90° instead of 88°), but torsional strain would be considerably larger because all eight C—H bonds would be eclipsed. By folding or bending slightly the cyclobutane ring relieves more of its torsional strain than it gains in the slight increase in its angle strain.

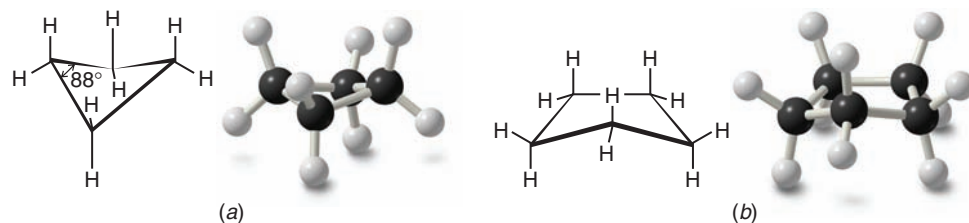


FIGURE 4.10 (a) The “folded” or “bent” conformation of cyclobutane. (b) The “bent” or “envelope” form of cyclopentane. In this structure the front carbon atom is bent upward. In actuality, the molecule is flexible and shifts conformations constantly.

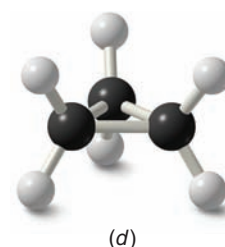
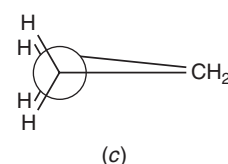
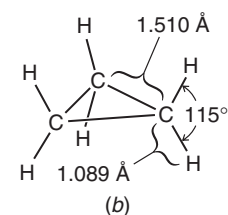
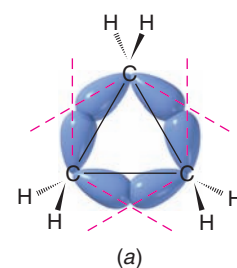


FIGURE 4.9 (a) Orbital overlap in the carbon–carbon bonds of cyclopropane cannot occur perfectly end-on. This leads to weaker “bent” bonds and to angle strain. (b) Bond distances and angles in cyclopropane. (c) A Newman projection formula as viewed along one carbon–carbon bond shows the eclipsed hydrogens. (Viewing along either of the other two bonds would show the same picture.) (d) Ball-and-stick model of cyclopropane.

Helpful Hint

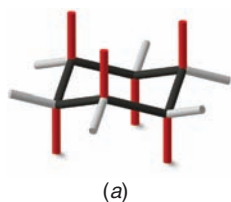
An understanding of this and subsequent discussions of conformational analysis can be aided immeasurably through the use of molecular models. We suggest you “follow along” with models as you read Sections 4.11–4.13.

4.10C Cyclopentane

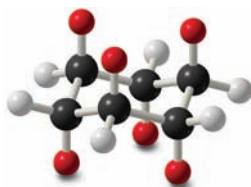
The internal angles of a regular pentagon are 108° , a value very close to the normal tetrahedral bond angles of 109.5° . Therefore, if cyclopentane molecules were planar, they would have very little angle strain. Planarity, however, would introduce considerable torsional strain because all ten C—H bonds would be eclipsed. Consequently, like cyclobutane, cyclopentane assumes a slightly bent conformation in which one or two of the atoms of the ring are out of the plane of the others (Fig. 4.10*b*). This relieves some of the torsional strain. Slight twisting of carbon–carbon bonds can occur with little change in energy and causes the out-of-plane atoms to move into plane and causes others to move out. Therefore, the molecule is flexible and shifts rapidly from one conformation to another. With little torsional strain and angle strain, cyclopentane is almost as stable as cyclohexane.

4.11 CONFORMATIONS OF CYCLOHEXANE: THE CHAIR AND THE BOAT

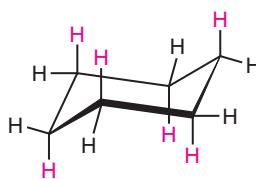
FIGURE 4.11 Representations of the chair conformation of cyclohexane: (a) tube format; (b) ball-and-stick format; (c) line drawing; (d) space-filling model of cyclohexane. Notice that there are two orientations for the hydrogen substituents—those that project obviously up or down (shown in red) and those that lie around the perimeter of the ring in more subtle up or down orientations (shown in black or gray). We shall discuss this further in Section 4.12.



(a)



(b)



(c)



(d)

Cyclohexane is more stable than the other **cycloalkanes** we have discussed, and it has several conformations that are important for us to consider.

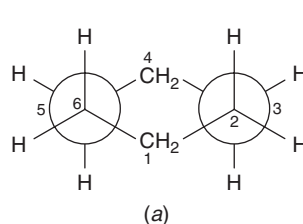
- The most stable **conformation of cyclohexane** is the **chair conformation**.
- There is no angle or torsional strain in the chair form of cyclohexane.

In a chair conformation (Fig. 4.11), all of the carbon–carbon bond angles are 109.5° , and are thereby free of angle strain. The chair conformation is free of torsional strain, as well. When viewed along any carbon–carbon bond (viewing the structure from an end, Fig. 4.12), the bonds are seen to be perfectly staggered. Moreover, the hydrogen atoms at opposite corners of the cyclohexane ring are maximally separated.

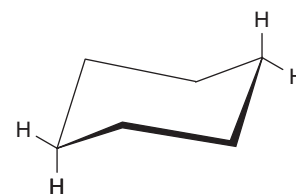
- By partial rotations about the carbon–carbon single bonds of the ring, the chair conformation can assume another shape called the **boat conformation** (Fig. 4.13).
- The boat conformation has no angle strain, but it does have torsional strain.

When a model of the boat conformation is viewed down carbon–carbon bond axes along either side (Fig. 4.14*a*), the C—H bonds at those carbon atoms are found to be eclipsed, causing torsional strain. Additionally, two of the hydrogen atoms on C1 and C4 are close enough to each other to cause van der Waals repulsion (Fig. 4.14*b*). This latter effect has been called the “flagpole” interaction of the boat conformation. Torsional strain and flagpole interactions cause the boat conformation to have considerably higher energy than the chair conformation.

FIGURE 4.12 (a) A Newman projection of the chair conformation of cyclohexane. (Comparisons with an actual molecular model will make this formulation clearer and will show that similar staggered arrangements are seen when other carbon–carbon bonds are chosen for sighting.) (b) Illustration of large separation between hydrogen atoms at opposite corners of the ring (designated C1 and C4) when the ring is in the chair conformation.



(a)



(b)

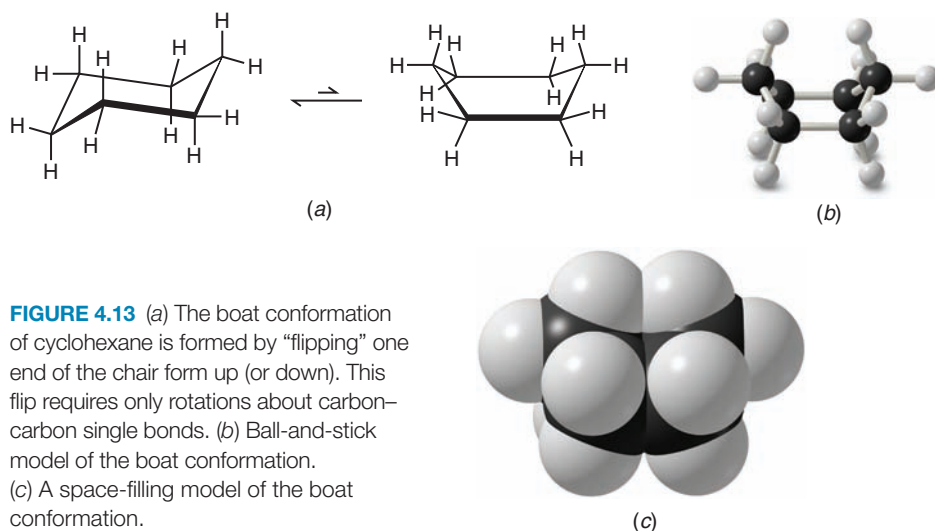


FIGURE 4.13 (a) The boat conformation of cyclohexane is formed by “flipping” one end of the chair form up (or down). This flip requires only rotations about carbon–carbon single bonds. (b) Ball-and-stick model of the boat conformation. (c) A space-filling model of the boat conformation.

Although it is more stable, the chair conformation is much more rigid than the boat conformation. The boat conformation is quite flexible. By flexing to a new form—the twist conformation (Fig. 4.15)—the boat conformation can relieve some of its torsional strain and, at the same time, reduce the flagpole interactions.

- The twist boat conformation of cyclohexane has a lower energy than the pure boat conformation, but is not as stable as the chair conformation.

The stability gained by flexing is insufficient, however, to cause the twist conformation to be more stable than the chair conformation. The chair conformation is estimated to be lower in energy than the twist conformation by approximately 23 kJ mol^{-1} .

The energy barriers between the chair, boat, and twist conformations of cyclohexane are low enough (Fig. 4.16) to make separation of the conformers impossible at room temperature. At room temperature the thermal energies of the molecules are great enough to cause approximately 1 million interconversions to occur each second.

- Because of the greater stability of the chair, more than 99% of the molecules are estimated to be in a chair conformation at any given moment.

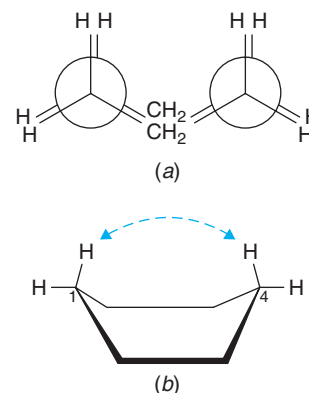


FIGURE 4.14 (a) Illustration of the eclipsed conformation of the boat conformation of cyclohexane. (b) Flagpole interaction of the C1 and C4 hydrogen atoms of the boat conformation. The C1–C4 flagpole interaction is also readily apparent in Fig. 4.13c.

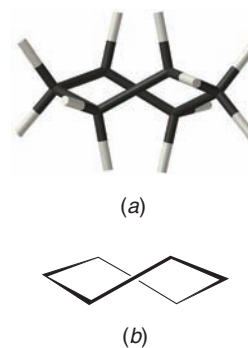


FIGURE 4.15 (a) Tube model and (b) line drawing of the twist conformation of cyclohexane.

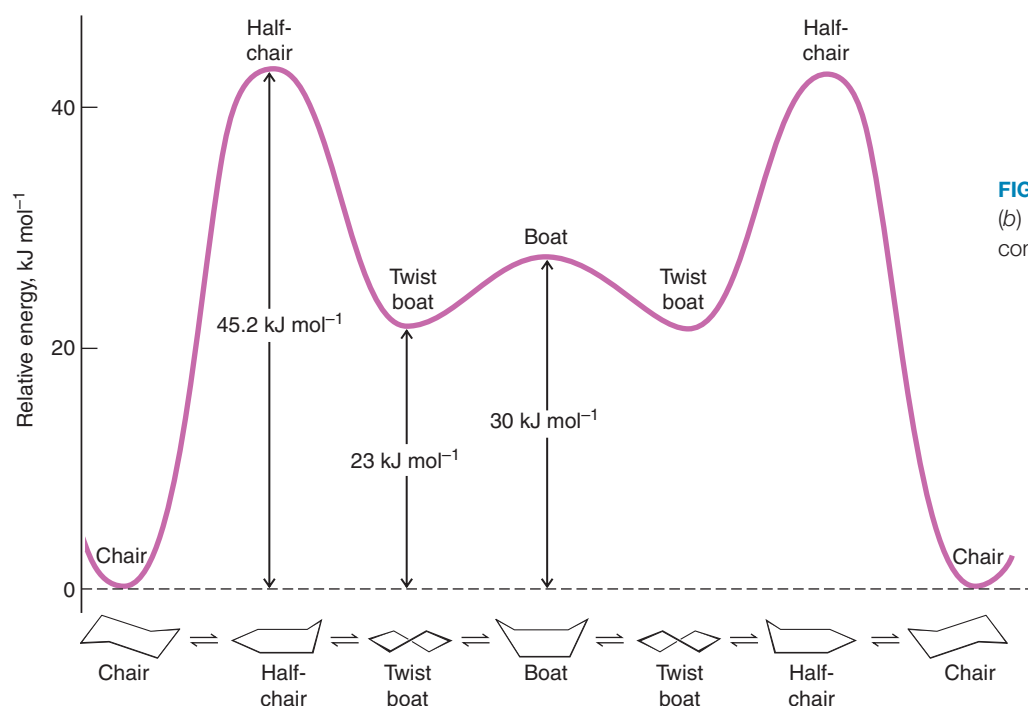
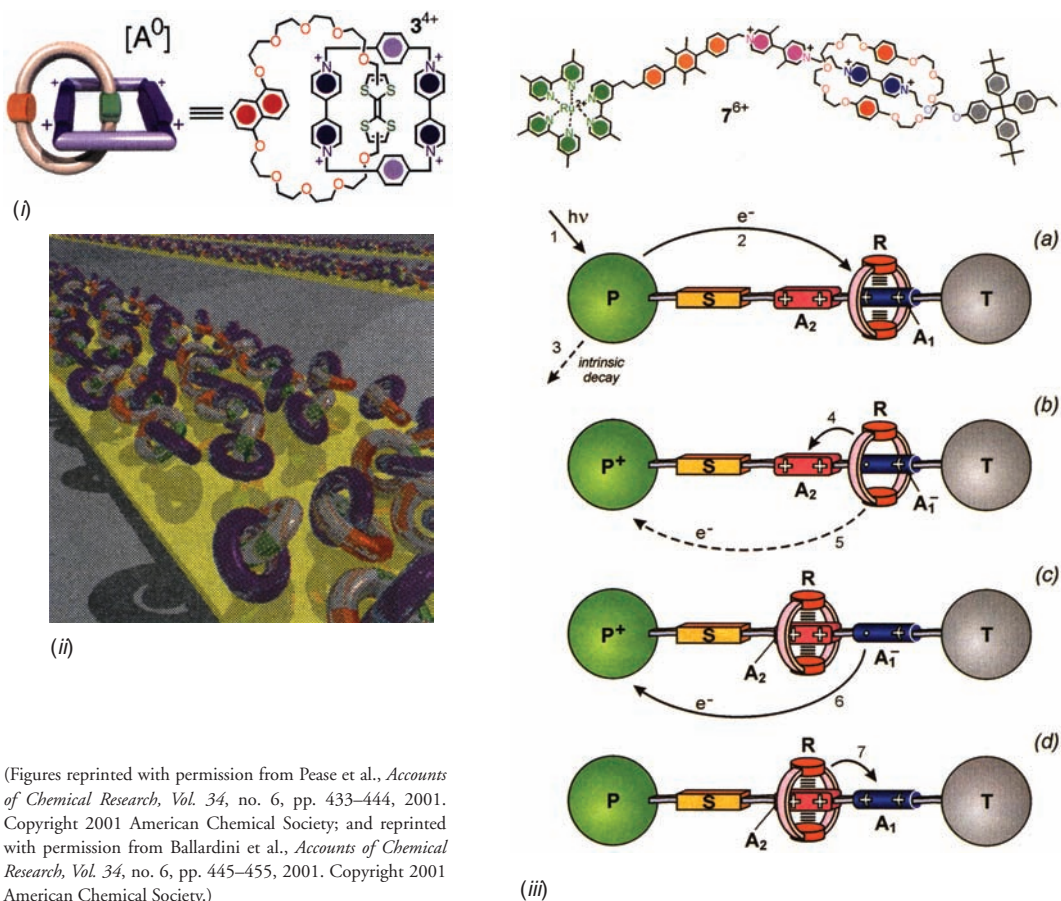


FIGURE 4.16 The relative energies of the various conformations of cyclohexane. The positions of maximum energy are conformations called half-chair conformations, in which the carbon atoms of one end of the ring have become coplanar.

THE CHEMISTRY OF ... Nanoscale Motors and Molecular Switches

Molecular rings that interlock with one another and compounds that are linear molecules threaded through rings are proving to have fascinating potential for the creation of molecular switches and motors. Molecules consisting of interlocking rings, like a chain, are called **catenanes**. The first catenanes were synthesized in the 1960s and have come to include examples such as olympiadane, as mentioned in Section 4.11A. Further research by J. F. Stoddart (UCLA) and collaborators on interlocking molecules has led to examples such as the catenane molecular switch shown here in (i). In an application that could be useful in design of binary logic circuits, one ring of this molecule can be made to circumrotate in controlled fashion about the other, such that it switches between two defined states. As a demonstration of its potential for application in electronics fabrication, a monolayer of these molecules has been “tiled” on a surface (ii) and shown to have characteristics like a conventional magnetic memory bit.

Molecules where a linear molecule is threaded through a ring are called **rotaxanes**. One captivating example of a rotaxane system is the one shown here in (iii), under development by V. Balzani (University of Bologna) and collaborators. By conversion of light energy to mechanical energy at the molecular level, this rotaxane behaves like a “four-stroke” shuttle engine. In step (a) light excitation of an electron in the **P** group leads to transfer of the electron to the initially +2 **A₁** group, at which point **A₁** is reduced to the +1 state. Ring **R**, which was attracted to **A₁** when it was in the +2 state, now slides over to **A₂** in step (b), which remains +2. Back transfer of the electron from **A₁** to **P⁺** in step (c) restores the +2 state of **A₁**, causing ring **R** to return to its original location in step (d). Modifications envisioned for this system include attaching binding sites to **R** such that some other molecular species could be transported from one location to another as **R** slides along the linear molecule, or linking **R** by a springlike tether to one end of the “piston rod” such that additional potential and mechanical energy can be incorporated in the system.



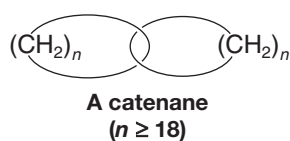
(Figures reprinted with permission from Pease et al., *Accounts of Chemical Research*, Vol. 34, no. 6, pp. 433–444, 2001. Copyright 2001 American Chemical Society; and reprinted with permission from Ballardini et al., *Accounts of Chemical Research*, Vol. 34, no. 6, pp. 445–455, 2001. Copyright 2001 American Chemical Society.)

4.11A Conformations of Higher Cycloalkanes

Cycloheptane, cyclooctane, and cyclononane and other higher cycloalkanes also exist in nonplanar conformations. The small instabilities of these higher cycloalkanes appear to be caused primarily by torsional strain and repulsive dispersion forces between hydrogen atoms across rings, called *transannular strain*. The nonplanar conformations of these rings, however, are essentially free of angle strain.

X-ray crystallographic studies of cyclodecane reveal that the most stable conformation has carbon–carbon–carbon bond angles of 117° . This indicates some angle strain. The wide bond angles apparently allow the molecules to expand and thereby minimize unfavorable repulsions between hydrogen atoms across the ring.

There is very little free space in the center of a cycloalkane unless the ring is quite large. Calculations indicate that cyclooctadecane, for example, is the smallest ring through which a $-\text{CH}_2\text{CH}_2\text{CH}_2-$ chain can be threaded. Molecules have been synthesized, however, that have large rings threaded on chains and that have large rings that are interlocked like links in a chain. These latter molecules are called **catenanes**:



In 1994 J. F. Stoddart and co-workers, then at the University of Birmingham (England), achieved a remarkable synthesis of a catenane containing a linear array of five interlocked rings. Because the rings are interlocked in the same way as those of the olympic symbol, they named the compound **olympiadane**.

4.12 SUBSTITUTED CYCLOHEXANES: AXIAL AND EQUATORIAL HYDROGEN GROUPS

The six-membered ring is the most common ring found among nature's organic molecules. For this reason, we shall give it special attention. We have already seen that the chair conformation of cyclohexane is the most stable one and that it is the predominant conformation of the molecules in a sample of cyclohexane.

The chair conformation of a cyclohexane ring has two distinct orientations for the bonds that project from the ring. These positions are called axial and equatorial, as shown for cyclohexane in Fig. 4.17.

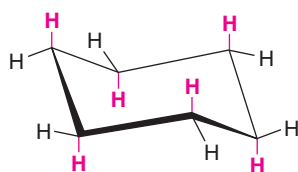


FIGURE 4.17 The chair conformation of cyclohexane. Axial hydrogen atoms are shown in red, equatorial hydrogens are shown in black.

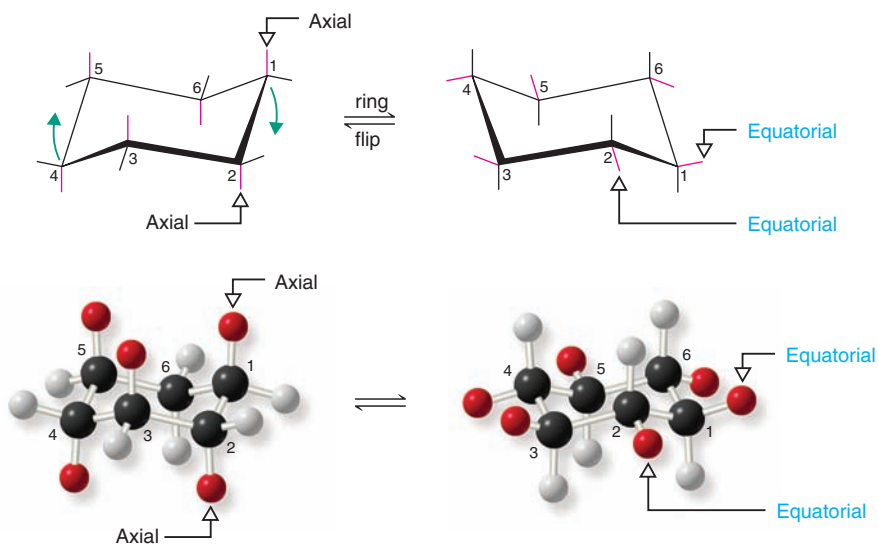
- The **axial bonds** of cyclohexane are those that are perpendicular to the average plane of the ring. There are three axial bonds on each face of the cyclohexane ring, and their orientation (up or down) alternates from one carbon to the next.
- The **equatorial bonds** of cyclohexane are those that extend from the perimeter of the ring. The equatorial bonds alternate from slightly up to slightly down in their orientation from one carbon to the next.



DEREK H. R. BARTON

(1918–1998) and ODD HASSEL (1897–1981) shared the Nobel Prize in 1969 “for developing and applying the principles of conformation in chemistry.” Their work led to fundamental understanding of not only the conformations of cyclohexane rings but also the structures of steroids (Section 23.4) and other compounds containing cyclohexane rings.

- When a cyclohexane ring undergoes a chair–chair conformational change (a **ring flip**), all of the bonds that were axial become equatorial, and all bonds that were equatorial become axial.



4.12A HOW TO Draw Chair Conformational Structures

A set of guidelines will help you draw chair conformational structures that are clear and that have unambiguous axial and equatorial bonds.

- Notice in Fig. 4.18a that sets of parallel lines define opposite sides of the chair. Notice, too, that equatorial bonds are parallel to ring bonds that are one bond away from them in either direction. When you draw chair conformational structures, try to make the corresponding bonds parallel in your drawings.
- When a chair formula is drawn as shown in Fig. 4.18, the axial bonds are all either up or down, in a vertical orientation (Fig. 4.18b). When a vertex of bonds in the ring points up, the axial bond at that position is also up, and the equatorial bond at the same carbon is angled slightly down. When a vertex of ring bonds is down, the axial bond at that position is also down, and the equatorial bond is angled slightly upward.

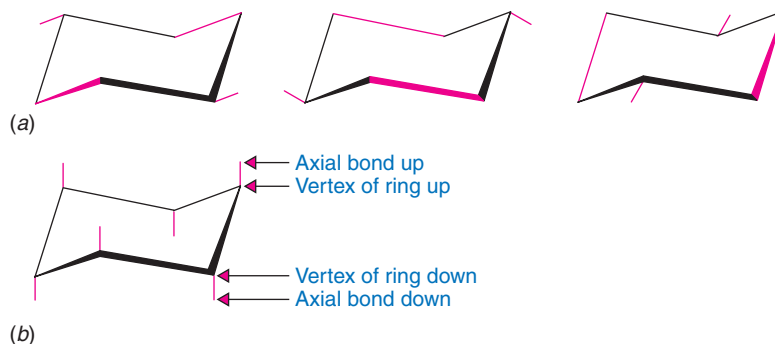


FIGURE 4.18 (a) Sets of parallel lines that constitute the ring and equatorial C—H bonds of the chair conformation. (b) The axial bonds are all vertical. When the vertex of the ring points up, the axial bond is up and vice versa.

Now, try to draw some chair conformational structures for yourself that include the axial and equatorial bonds. Then, compare your drawings with those here and with actual models. You will see that with a little practice your chair conformational structures can be perfect.

4.12B A Conformational Analysis of Methylcyclohexane

Now let us consider methylcyclohexane. Methylcyclohexane has two possible chair conformations (Fig. 4.19, **I** and **II**), and these are interconvertible through the bond rotations that constitute a ring flip. In conformation (Fig. 4.19a) the methyl group (with yellow hydrogens in the space-filling model) occupies an *axial* position, and in conformation **II** the methyl group occupies an *equatorial* position.

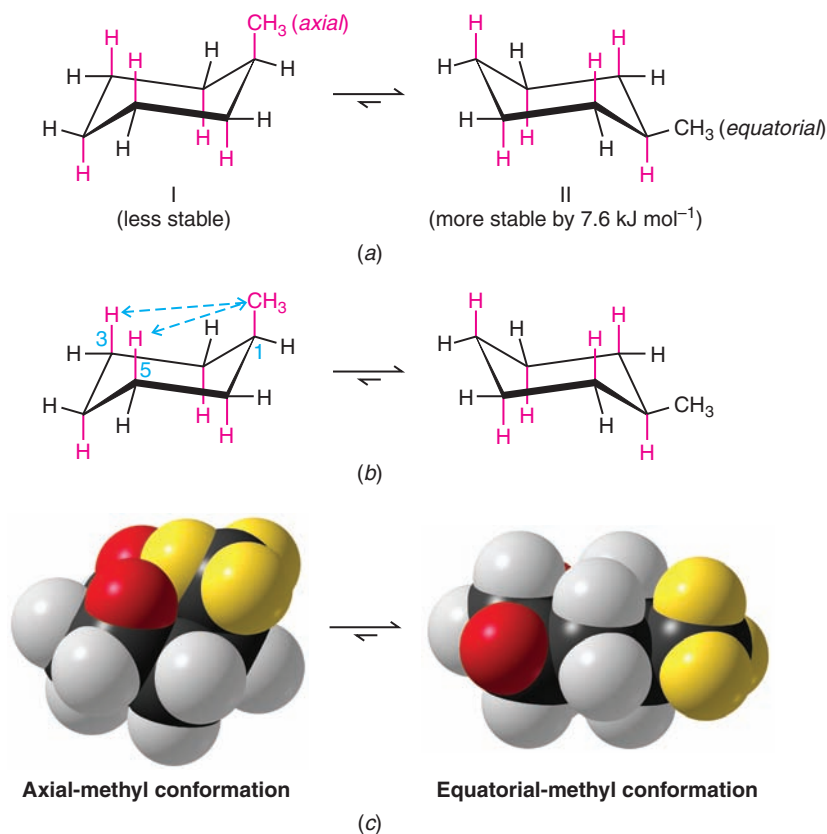


FIGURE 4.19 (a) The conformations of methylcyclohexane with the methyl group axial (**I**) and equatorial (**II**). (b) 1,3-Diaxial interactions between the two axial hydrogen atoms and the axial methyl group in the axial conformation of methylcyclohexane are shown with dashed arrows. Less crowding occurs in the equatorial conformation. (c) Space-filling molecular models for the axial-methyl and equatorial-methyl conformers of methylcyclohexane. In the axial-methyl conformer the methyl group (shown with yellow hydrogen atoms) is crowded by the 1,3-diaxial hydrogen atoms (red), as compared to the equatorial-methyl conformer, which has no 1,3-diaxial interactions with the methyl group.

- The most stable conformation for a monosubstituted cyclohexane ring (a cyclohexane ring where one carbon atom bears a group other than hydrogen) is the conformation where the substituent is equatorial.

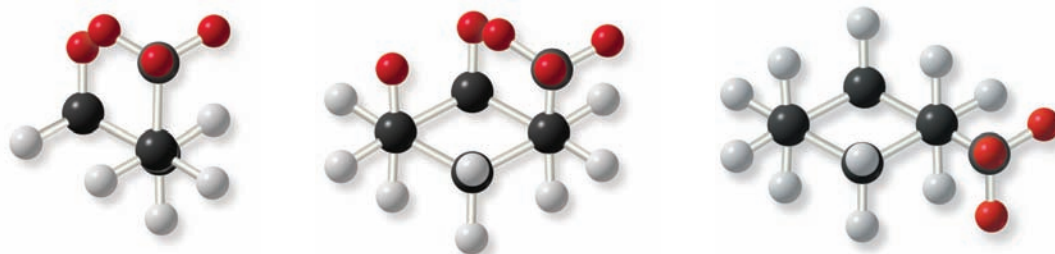
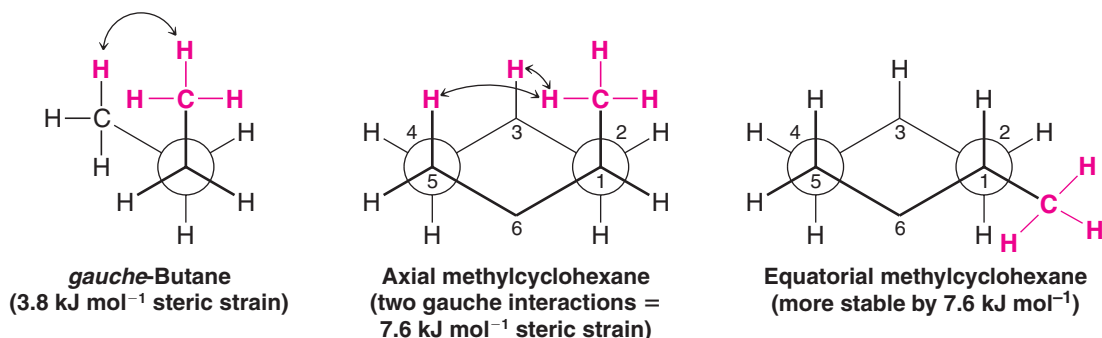
Studies indicate that conformation **II** with the equatorial methyl group is more stable than conformation **I** with the axial methyl group by about 7.6 kJ mol^{-1} . Thus, in the equilibrium mixture, the conformation with the methyl group in the equatorial position is the predominant one, constituting about 95% of the equilibrium mixture.

The greater stability of methylcyclohexane with an equatorial methyl group can be understood through an inspection of the two forms as they are shown in Figs. 4.19a–c.

- Studies done with models of the two conformations show that when the methyl group is axial, it is so close to the two axial hydrogens on the same side of the ring (attached to the C3 and C5 atoms) that **the dispersion forces between them are repulsive**.
- This type of steric strain, because it arises from an interaction between an axial group on carbon atom 1 and an axial hydrogen on carbon atom 3 (or 5), is called a **1,3-diaxial interaction**.
- Studies with other substituents show that **there is generally less repulsion when any group larger than hydrogen is equatorial rather than axial**.

The strain caused by a 1,3-diaxial interaction in methylcyclohexane is the same as the strain caused by the close proximity of the hydrogen atoms of methyl groups in the *gauche* form of butane (Section 4.9). Recall that the interaction in *gauche*-butane (called,

for convenience, a *gauche* interaction) causes *gauche*-butane to be less stable than *anti*-butane by 3.8 kJ mol^{-1} . The following Newman projections will help you to see that the two steric interactions are the same. In the second projection we view axial methylcyclohexane along the C1—C2 bond and see that what we call a 1,3-diaxial interaction is simply a *gauche* interaction between the hydrogen atoms of the methyl group and the hydrogen atom at C3:



Viewing methylcyclohexane along the C1—C6 bond (do this with a model) shows that it has a second identical *gauche* interaction between the hydrogen atoms of the methyl group and the hydrogen atom at C5. The methyl group of axial methylcyclohexane, therefore, has two *gauche* interactions and, consequently, it has 7.6 kJ mol^{-1} of strain. The methyl group of equatorial methylcyclohexane does not have a *gauche* interaction because it is *anti* to C3 and C5.

PRACTICE PROBLEM 4.14 Show by a calculation (using the formula $\Delta G^\circ = -RT \ln K_{\text{eq}}$) that a free-energy difference of 7.6 kJ mol^{-1} between the axial and equatorial forms of methylcyclohexane at 25°C (with the equatorial form being more stable) does correlate with an equilibrium mixture in which the concentration of the equatorial form is approximately 95%.

4.12C 1,3-Diaxial Interactions of a *tert*-Butyl Group

In cyclohexane derivatives with larger alkyl substituents, the strain caused by 1,3-diaxial interactions is even more pronounced. The conformation of *tert*-butylcyclohexane with the *tert*-butyl group equatorial is estimated to be approximately 21 kJ mol^{-1} more stable than the axial form (Fig. 4.20). This large energy difference between the two conformations means that, at room temperature, 99.99% of the molecules of *tert*-butylcyclohexane have the *tert*-butyl group in the equatorial position. (The molecule is not conformationally “locked,” however; it still flips from one chair conformation to the other.)

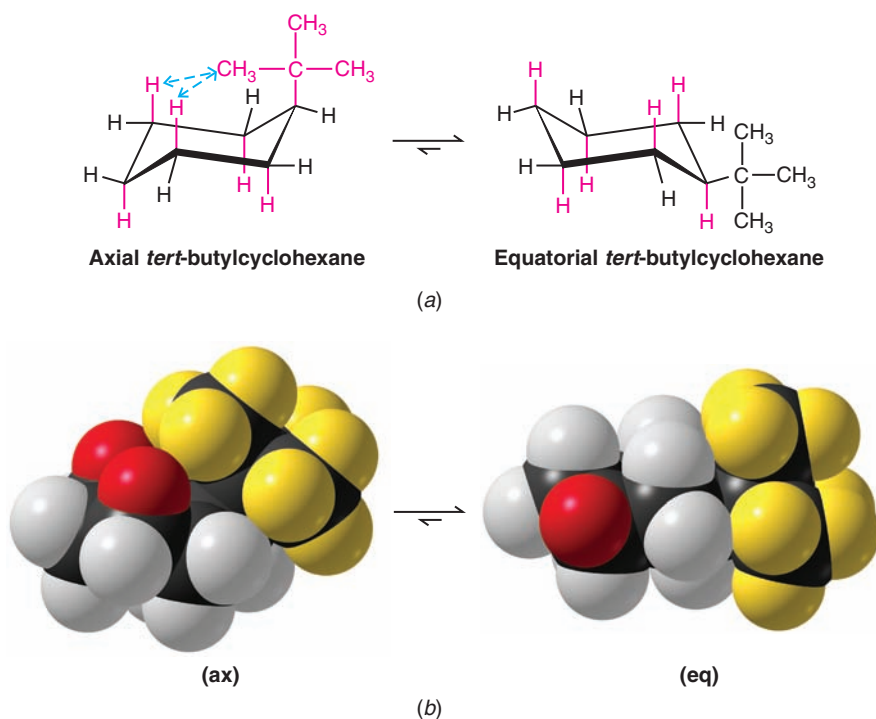


FIGURE 4.20 (a) Diaxial interactions with the large *tert*-butyl group axial cause the conformation with the *tert*-butyl group equatorial to be the predominant one to the extent of 99.99%. (b) Space-filling molecular models of *tert*-butylcyclohexane in the axial (ax) and equatorial (eq) conformations, highlighting the position of the 1,3-hydrogens (red) and the *tert*-butyl group (shown with yellow hydrogen atoms).

4.13 DISUBSTITUTED CYCLOALKANES: CIS-TRANS ISOMERISM

The presence of two substituents on different carbons of a cycloalkane allows for the possibility of **cis–trans isomerism** similar to the kind we saw for alkenes in Section 1.14B. These cis–trans isomers are also **stereoisomers** because they differ from each other only in the arrangement of their atoms in space. Consider 1,2-dimethylcyclopropane (Fig. 4.21) as an example.

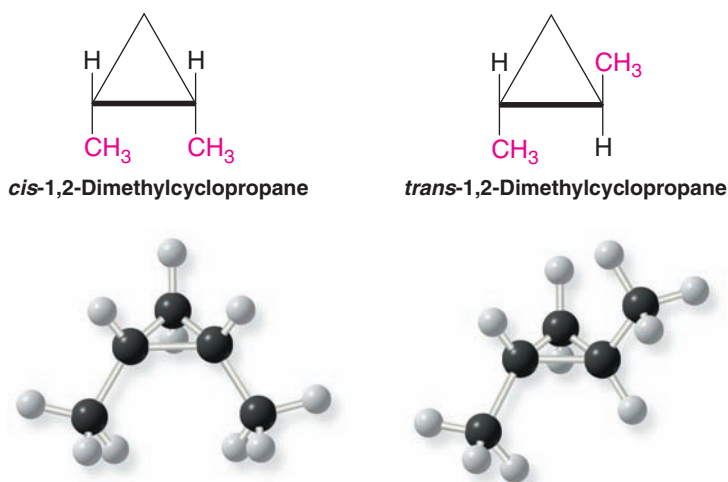


FIGURE 4.21 The *cis*- and *trans*-1,2-dimethylcyclopropane isomers.

The planarity of the cyclopropane ring makes the cis–trans isomerism obvious. In the first structure the methyl groups are on the same side of the ring; therefore, they are *cis*. In the second structure, they are on opposite sides of the ring; they are *trans*.

Cis and *trans* isomers such as these cannot be interconverted without breaking carbon–carbon bonds. They will have different physical properties (boiling points, melting points, and so on). As a result, they can be separated, placed in separate bottles, and kept indefinitely.

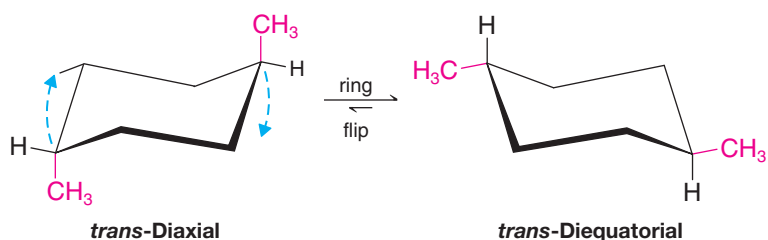


PRACTICE PROBLEM 4.15 Write structures for the cis and trans isomers of (a) 1,2-dichlorocyclopentane and (b) 1,3-dibromocyclobutane. (c) Are cis–trans isomers possible for 1,1-dibromocyclobutane?

4.13A Cis–Trans Isomerism and Conformational Structures of Cyclohexanes

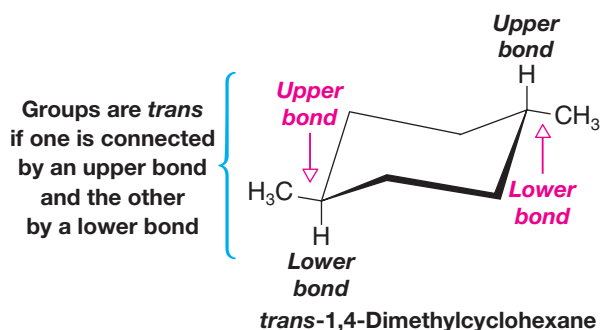
Trans 1,4-Disubstituted Cyclohexanes If we consider dimethylcyclohexanes, the structures are somewhat more complex because the cyclohexane ring is not planar. Beginning with *trans*-1,4-dimethylcyclohexane, because it is easiest to visualize, we find there are two possible chair conformations (Fig. 4.22). In one conformation both methyl groups are axial; in the other both are equatorial. The diequatorial conformation is, as we would expect it to be, the more stable conformation, and it represents the structure of at least 99% of the molecules at equilibrium.

FIGURE 4.22 The two chair conformations of *trans*-1,4-dimethylcyclohexane: *trans*-diequatorial and *trans*-diaxial. The *trans*-diequatorial form is more stable by 15.2 kJ mol^{-1} .

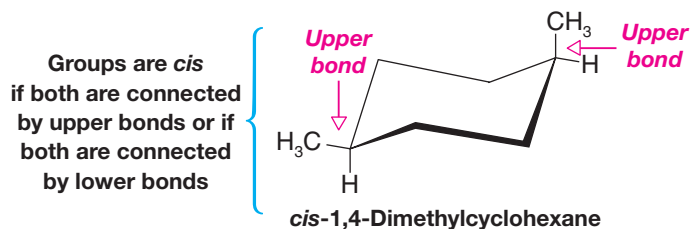


That the diaxial form of *trans*-1,4-dimethylcyclohexane is a *trans* isomer is easy to see; the two methyl groups are clearly on opposite sides of the ring. The *trans* relationship of the methyl groups in the diequatorial form is not as obvious, however.

How do we know two groups are *cis* or *trans*? A general way to recognize a *trans*-disubstituted cyclohexane is to notice that one group is attached by the *upper* bond (of the two to its carbon) and one by the *lower* bond:



In a *cis* 1,4-disubstituted cyclohexane both groups are attached by an upper bond or both by a lower bond. For example,



Cis 1,4-Disubstituted Cyclohexanes *cis*-1,4-Dimethylcyclohexane exists in two *equivalent* chair conformations (Fig. 4.23). In a *cis* 1,4-disubstituted cyclohexane, one group is axial and the other is equatorial in both of the possible chair conformations.

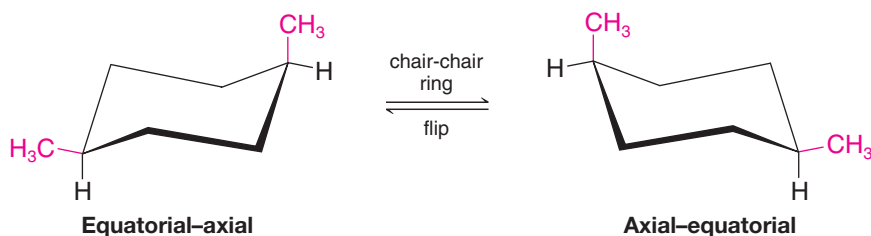
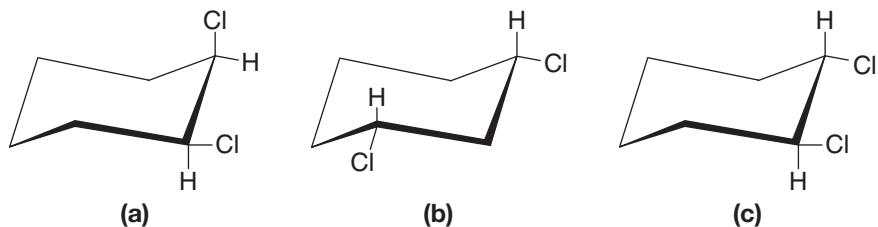


FIGURE 4.23 Equivalent conformations of *cis*-1,4-dimethylcyclohexane.

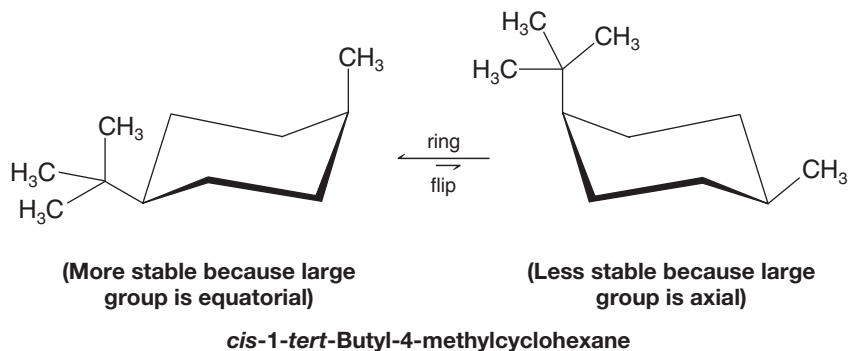
SOLVED PROBLEM 4.5

Consider each of the following conformational structures and tell whether each is *cis* or *trans*:



ANSWER: (a) Each chlorine is attached by the upper bond at its carbon; therefore, both chlorine atoms are on the same side of the molecule and this is a *cis* isomer. This is a *cis*-1,2-dichlorocyclohexane. (b) Here both chlorine atoms are attached by a lower bond; therefore, in this example, too, both chlorine atoms are on the same side of the molecule and this, too, is a *cis* isomer. It is *cis*-1,3-dichlorocyclohexane. (c) Here one chlorine atom is attached by a lower bond and one by an upper bond. The two chlorine atoms, therefore, are on opposite sides of the molecule, and this is a *trans* isomer. It is *trans*-1,2-dichlorocyclohexane. Verify these facts by building models.

The two conformations of *cis* 1,4-disubstituted cyclohexanes *are not equivalent* if one group is larger than the other. Consider *cis*-1-*tert*-butyl-4-methylcyclohexane:



Here the more stable conformation is the one with the larger group equatorial. This is a general principle:

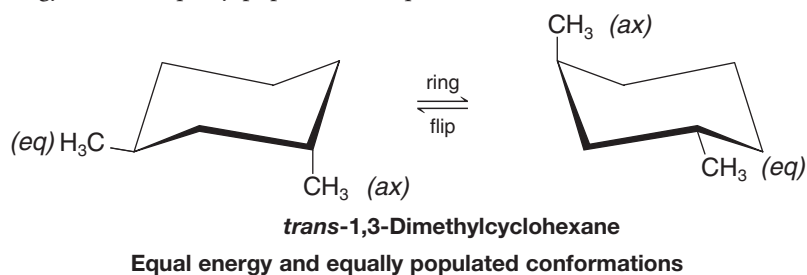
- When one ring substituent group is larger than the other and they cannot both be equatorial, the conformation with the larger group equatorial will be more stable.

(a) Write structural formulas for the two chair conformations of *cis*-1-isopropyl-4-methylcyclohexane. (b) Are these two conformations equivalent? (c) If not, which would be more stable? (d) Which would be the preferred conformation at equilibrium?

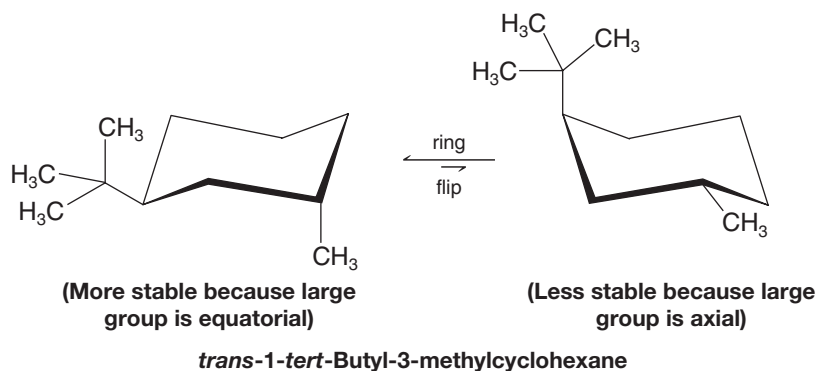
PRACTICE PROBLEM 4.16

Trans 1,3-Disubstituted Cyclohexanes *trans*-1,3-Dimethylcyclohexane is like the *cis* 1,4 compound in that each conformation has one methyl group in an axial position

and one methyl group in an equatorial position. The following two conformations are of equal energy and are equally populated at equilibrium:

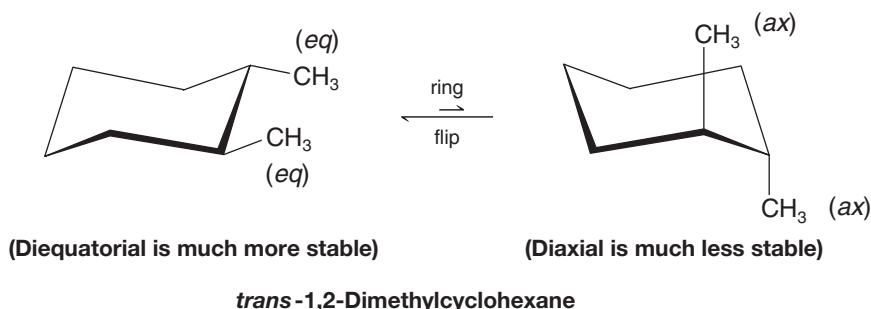


The situation is different for *trans-1-tert-butyl-3-methylcyclohexane* (shown below) because the two ring substituents are not the same. Again, we find that the lower energy conformation is that with the largest group equatorial.

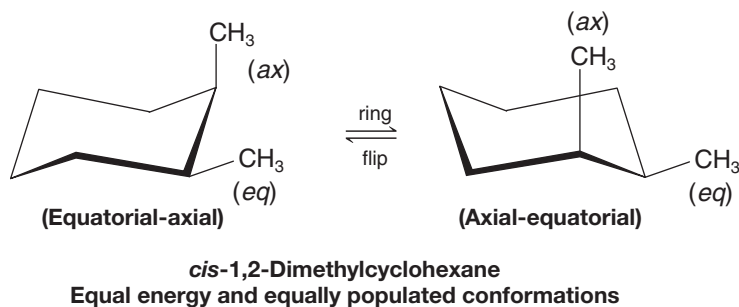


Cis 1,3-Disubstituted Cyclohexanes *cis*-1,3-Dimethylcyclohexane has a conformation in which both methyl groups are equatorial and one in which both methyl groups are axial. As we would expect, the conformation with both methyl groups equatorial is the more stable one.

Trans 1,2-Disubstituted Cyclohexanes *trans*-1,2-Dimethylcyclohexane has a conformation in which both methyl groups are equatorial and one in which both methyl groups are axial. As we would expect, the conformation with both methyl groups equatorial is the more stable one.



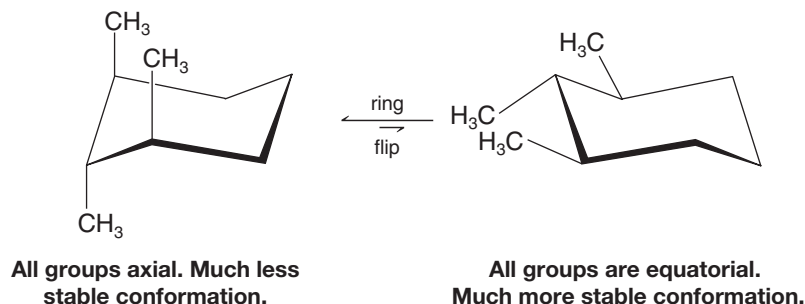
Cis 1,2-Disubstituted Cyclohexanes *cis*-1,2-Dimethylcyclohexane has one methyl group that is axial and one methyl group that is equatorial in each of its chair conformations, thus its two conformations are of equal stability.




SOLVED PROBLEM 4.6

Write a conformational structure for 1,2,3-trimethylcyclohexane in which all the methyl groups are axial and then show its more stable conformation.

ANSWER: A ring flip gives a conformation in which all the groups are equatorial and, therefore, much more stable.



Write a conformational structure for 1-bromo-3-chloro-5-fluorocyclohexane in which all the substituents are equatorial. Then write its structure after a ring flip.

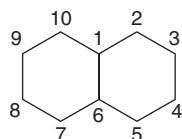

PRACTICE PROBLEM 4.17

(a) Write the two conformations of *cis*-1-*tert*-butyl-2-methylcyclohexane. **(b)** Which conformer has the lowest potential energy?


PRACTICE PROBLEM 4.18

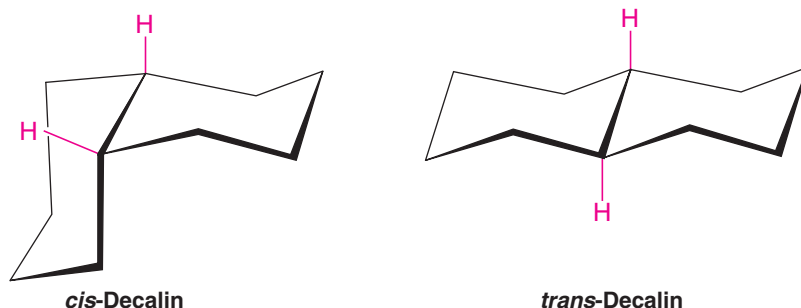
4.14 BICYCLIC AND POLYCYCLIC ALKANES

Many of the molecules that we encounter in our study of organic chemistry contain more than one ring (Section 4.4B). One of the most important bicyclic systems is bicyclo[4.4.0]decane, a compound that is usually called by its common name, *decalin*:



Decalin (bicyclo[4.4.0]decane)
(carbon atoms 1 and 6 are bridgehead carbon atoms)

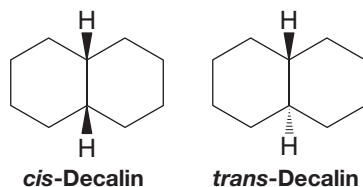
Decalin shows *cis*–*trans* isomerism:



Helpful Hint

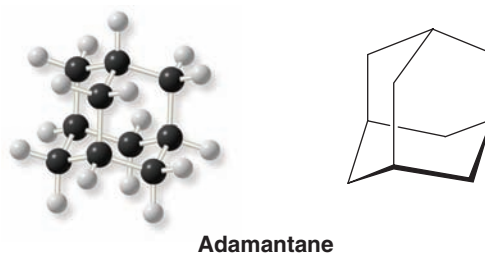
Chemical Abstracts Service (CAS) determines the number of rings by the formula $S - A + 1 = N$, where S is the number of single bonds in the ring system, A is the number of atoms in the ring system, and N is the calculated number of rings (see Problem 4.30).

In *cis*-decalin the two hydrogen atoms attached to the bridgehead atoms lie on the same side of the ring; in *trans*-decalin they are on opposite sides. We often indicate this by writing their structures in the following way:



Simple rotations of groups about carbon–carbon bonds do not interconvert *cis*- and *trans*-decalins. They are stereoisomers and they have different physical properties.

Adamantane is a tricyclic system that contains a three-dimensional array of cyclohexane rings, all of which are in the chair form.



In the chapter closer we shall see several examples of other unusual and highly strained, cyclic hydrocarbons.

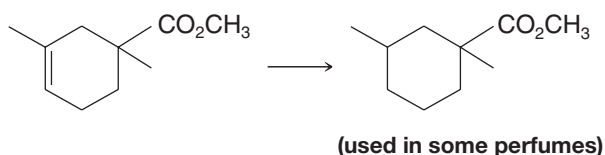
4.15 CHEMICAL REACTIONS OF ALKANES

Alkanes, as a class, are characterized by a general inertness to many chemical reagents. Carbon–carbon and carbon–hydrogen bonds are quite strong; they do not break unless alkanes are heated to very high temperatures. Because carbon and hydrogen atoms have nearly the same electronegativity, the carbon–hydrogen bonds of alkanes are only slightly polarized. As a consequence, they are generally unaffected by most bases. Molecules of alkanes have no unshared electrons to offer as sites for attack by acids. This low reactivity of alkanes toward many reagents accounts for the fact that alkanes were originally called **paraffins** (*parum affinis*, Latin: little affinity).

The term paraffin, however, was probably not an appropriate one. We all know that alkanes react vigorously with oxygen when an appropriate mixture is ignited. This combustion occurs, for example, in the cylinders of automobiles, in furnaces, and, more gently, with paraffin candles. When heated, alkanes also react with chlorine and bromine, and they react explosively with fluorine. We shall study these reactions in Chapter 10.

4.16 SYNTHESIS OF ALKANES AND CYCLOALKANES

A chemical synthesis may require, at some point, the conversion of a carbon–carbon double or triple bond to a single bond. Synthesis of the following compound, used as an ingredient in some perfumes, is an example.



This conversion is easily accomplished by a reaction called **hydrogenation**. There are several reaction conditions that can be used to carry out hydrogenation, but among the common ways is use of hydrogen gas and a solid metal catalyst such as platinum, palladium, or nickel. Equations in the following section represent general examples for the hydrogenation of alkenes and alkynes.

4.16A Hydrogenation of Alkenes and Alkynes

- Alkenes and alkynes react with hydrogen in the presence of metal catalysts such as nickel, palladium, and platinum to produce **alkanes**.

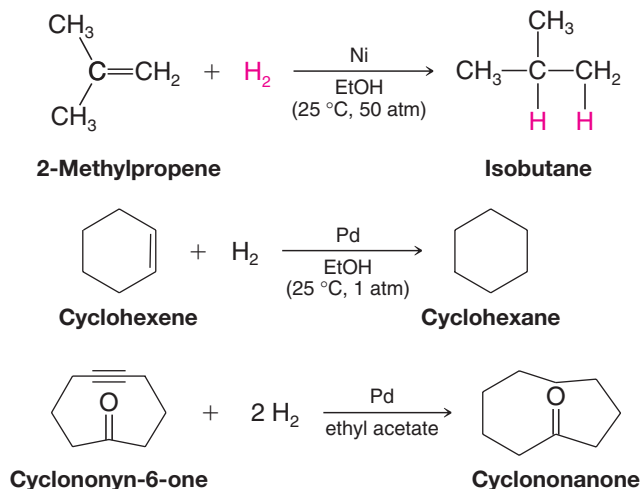
The general reaction is one in which the atoms of the hydrogen molecule add to each atom of the carbon–carbon double or triple bond of the alkene or alkyne. This converts the alkene or alkyne to an alkane:

General Reaction



The reaction is usually carried out by dissolving the alkene or alkyne in a solvent such as ethyl alcohol (C₂H₅OH), adding the metal catalyst, and then exposing the mixture to hydrogen gas under pressure in a special apparatus. One molar equivalent of hydrogen is required to reduce an alkene to an alkane. Two molar equivalents are required to reduce an alkyne. (We shall discuss the mechanism of this reaction in Chapter 7.)

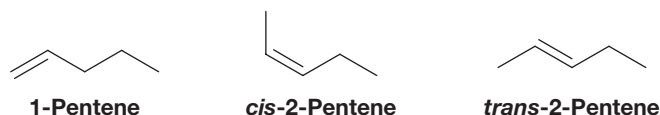
Specific Examples



SOLVED PROBLEM 4.7

Write the structures of three pentenes that would all yield pentane on hydrogenation.

ANSWER:



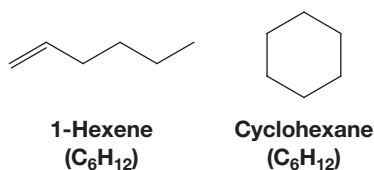
PRACTICE PROBLEM 4.19 Show the reactions involved for hydrogenation of all the alkenes and alkynes that would yield 2-methylbutane.

4.17 HOW TO GAIN STRUCTURAL INFORMATION FROM MOLECULAR FORMULAS AND THE INDEX OF HYDROGEN DEFICIENCY

A chemist working with an unknown compound can obtain considerable information about its structure from the compound's molecular formula and its **index of hydrogen deficiency (IHD)**.

- The **index of hydrogen deficiency (IHD)*** is defined as the difference in the *number of pairs* of hydrogen atoms between the compound under study and an acyclic alkane having the same number of carbons.

Saturated acyclic hydrocarbons have the general molecular formula C_nH_{2n+2} . Each double bond or ring reduces the number of hydrogen atoms by two as compared with the formula for a saturated compound. Thus each ring or double bond provides one unit of hydrogen deficiency. For example, 1-hexene and cyclohexane have the same molecular formula (C_6H_{12}) and they are constitutional isomers.



Both 1-hexene and cyclohexane (C_6H_{12}) have an index of hydrogen deficiency equal to 1 (meaning one pair of hydrogen atoms), because the corresponding acyclic alkane is hexane (C_6H_{14}).

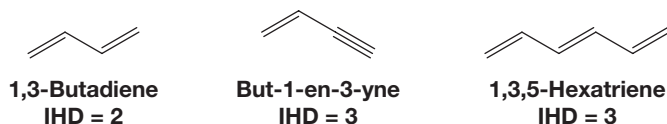
$$C_6H_{14} = \text{formula of corresponding alkane (hexane)}$$

$$\frac{C_6H_{12}}{H_2} = \text{formula of compound (1-hexene or cyclohexane)}$$

$$H_2 = \text{difference} = 1 \text{ pair of hydrogen atoms}$$

$$\text{Index of hydrogen deficiency} = 1$$

Alkynes and alkenadienes (alkenes with two double bonds) have the general formula C_nH_{2n-2} . Alkenynes (hydrocarbons with one double bond and one triple bond) and alkatrienes (alkenes with three double bonds) have the general formula C_nH_{2n-4} , and so forth.

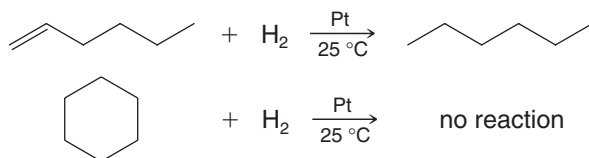


The index of hydrogen deficiency is easily determined by comparing the molecular formula of a given compound with the formula for its hydrogenation product.

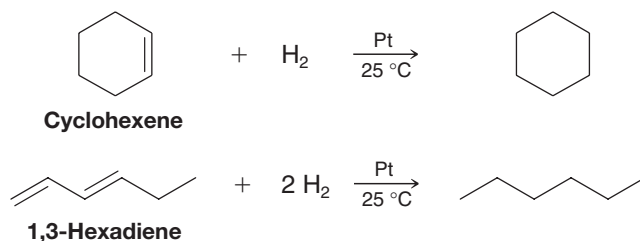
- Each double bond consumes one molar equivalent of hydrogen and counts for one unit of hydrogen deficiency.
- Each triple bond consumes two molar equivalents of hydrogen and counts for two units of hydrogen deficiency.
- Rings are not affected by hydrogenation, but each ring still counts for one unit of hydrogen deficiency.

*Some organic chemists refer to the index of hydrogen deficiency as the “degree of unsaturation” or “the number of double-bond equivalencies.”

Hydrogenation, therefore, allows us to distinguish between rings and double or triple bonds. Consider again two compounds with the molecular formula C_6H_{12} : 1-hexene and cyclohexane. 1-Hexene reacts with one molar equivalent of hydrogen to yield hexane; under the same conditions cyclohexane does not react:



Or consider another example. Cyclohexene and 1,3-hexadiene have the same molecular formula (C_6H_{10}). Both compounds react with hydrogen in the presence of a catalyst, but cyclohexene, because it has a ring and only one double bond, reacts with only one molar equivalent. 1,3-Hexadiene adds two molar equivalents:



- (a) What is the index of hydrogen deficiency of 2-hexene? (b) Of methylcyclopentane? (c) Does the index of hydrogen deficiency reveal anything about the location of the double bond in the chain? (d) About the size of the ring? (e) What is the index of hydrogen deficiency of 2-hexyne? (f) In general terms, what structural possibilities exist for a compound with the molecular formula $C_{10}H_{16}$?

PRACTICE PROBLEM 4.20

Zingiberene, a fragrant compound isolated from ginger, has the molecular formula $C_{15}H_{24}$ and is known not to contain any triple bonds. (a) What is the index of hydrogen deficiency of zingiberene? (b) When zingiberene is subjected to catalytic hydrogenation using an excess of hydrogen, 1 mol of zingiberene absorbs 3 mol of hydrogen and produces a compound with the formula $C_{15}H_{30}$. How many double bonds does a molecule of zingiberene have? (c) How many rings?

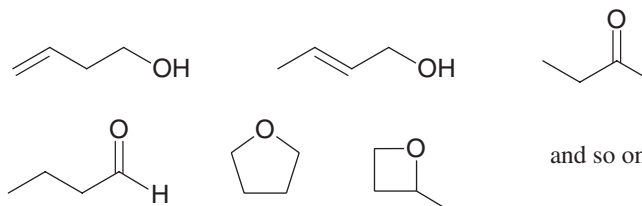
PRACTICE PROBLEM 4.21

4.17A Compounds Containing Halogens, Oxygen, or Nitrogen

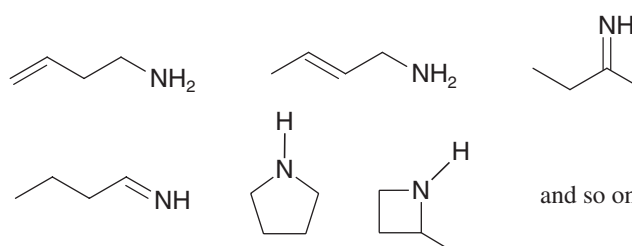
Calculating the index of hydrogen deficiency (IHD) for compounds other than hydrocarbons is relatively easy.

For compounds containing halogen atoms, we simply count the halogen atoms as though they were hydrogen atoms. Consider a compound with the formula $C_4H_6Cl_2$. To calculate the IHD, we change the two chlorine atoms to hydrogen atoms, considering the formula as though it were C_4H_8 . This formula has two hydrogen atoms fewer than the formula for a saturated alkane (C_4H_{10}), and this tells us that the compound has $IHD = 1$. It could, therefore, have either one ring or one double bond. [We can tell which it has from a hydrogenation experiment: If the compound adds one molar equivalent of hydrogen (H_2) on catalytic hydrogenation at room temperature, then it must have a double bond; if it does not add hydrogen, then it must have a ring.]

For compounds containing oxygen, we simply ignore the oxygen atoms and calculate the IHD from the remainder of the formula. Consider as an example a compound with the formula C_4H_8O . For the purposes of our calculation we consider the compound to be simply C_4H_8 and we calculate $IHD = 1$. Again, this means that the compound contains either a ring or a double bond. Some structural possibilities for this compound are shown next. Notice that the double bond may be present as a carbon–oxygen double bond:



For compounds containing nitrogen atoms we subtract one hydrogen for each nitrogen atom, and then we ignore the nitrogen atoms. For example, we treat a compound with the formula C_4H_9N as though it were C_4H_8 , and again we get $IHD = 1$. Some structural possibilities are the following:



PRACTICE PROBLEM 4.22

Carbonyl groups also count for a unit of hydrogen deficiency. What are the indices of hydrogen deficiency for the reactant and for the product in the equation shown at the beginning of Section 4.16 for synthesis of a perfume ingredient?

4.18 APPLICATIONS OF BASIC PRINCIPLES

In this chapter we have seen repeated applications of one basic principle in particular:

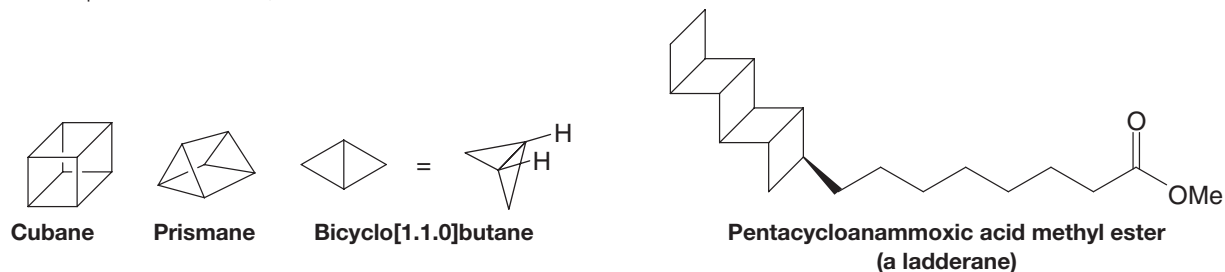
Nature Prefers States of Lower Potential Energy This principle underlies our explanations of conformational analysis in Sections 4.8–4.13. The staggered conformation of ethane (Section 4.8) is preferred (more populated) in a sample of ethane because its potential energy is lowest. In the same way, the anti conformation of butane (Section 4.9) and the chair conformation of cyclohexane (Section 4.11) are the preferred conformations of these molecules because these conformations are of lowest potential energy. Methylcyclohexane (Section 4.12) exists mainly in the chair conformation with its methyl group equatorial for the same reason. Disubstituted cycloalkanes (Section 4.13) prefer a conformation with both substituents equatorial if this is possible, and, if not, they prefer a conformation with the larger group equatorial. The preferred conformation in each instance is the one of lowest potential energy.

Another effect that we encounter in this chapter, and one we shall see again and again, is how **steric factors** (spatial factors) can affect the stability and reactivity of molecules. Unfavorable spatial interactions between groups are central to explaining why certain conformations are higher in energy than others. But fundamentally this effect is derived itself from another familiar principle: **like charges repel**. Repulsive interactions between the electrons of groups that are in close proximity cause certain conformations to have higher potential energy than others. We call this kind of effect *steric hindrance*.

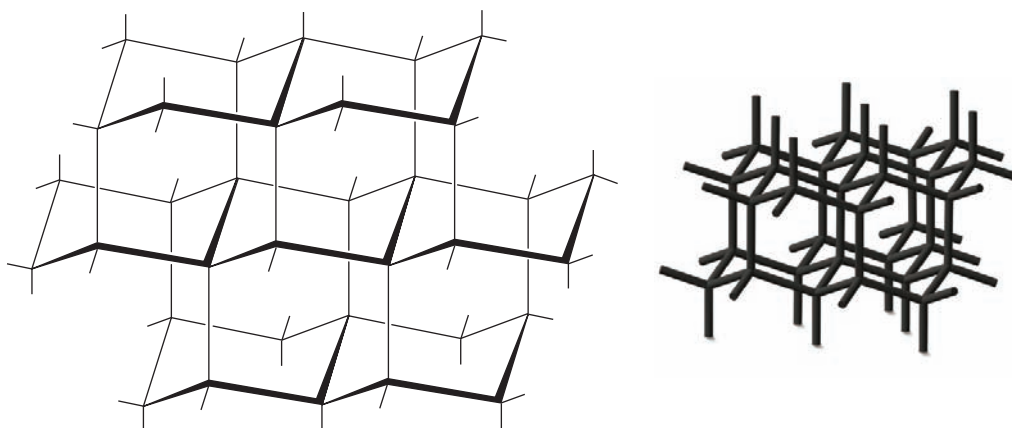
[WHY Do These Topics Matter?

PUSHING THE BOUNDARIES OF BONDING, ALL WITHIN THE RULES

In this chapter we have learned many of the rules of bond formation and of conformation. Although there are only a few kinds of bonds in organic molecules, they can be combined in an infinite number of ways, sometimes leading to molecules whose existence defies our expectations. For example, using just C—C and C—H bonds, chemists have been able to synthesize structures such as cubane, prismane, and bicyclo[1.1.0]butane, materials that have incredible strain built into their structures. Strained compounds are also found in nature, with one recent discovery being pentacycloanammoxic acid, a material isolated from a particular bacterial strain. This compound is also known as a ladderane because it has a connected set of five 4-membered rings that exist in three-dimensional space like a ladder, or staircase.



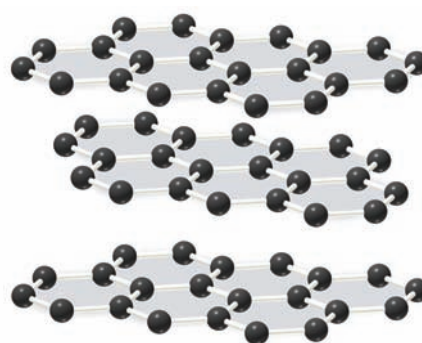
An important thing to note is that these different bond combinations and resultant three-dimensional shapes lead to completely distinct physical properties that can be harnessed for unique practical applications. Perhaps one of the best illustrations of this concept is found in materials comprised only of carbon, materials also known as allotropes since they are formed solely from a single, pure element. For example, when carbon is bonded with itself through single bonds with sp^3 hybridization, the result is diamond, the hardest of all materials found in nature and a popular component of jewelry. When carbon is bonded with itself with sp^2 hybridization through a series of interconnecting C—C and C=C bonds, it forms flat, interconnected sheets of benzene-like rings. These sheets can stack with one another, forming graphite. This material is much softer than diamond and is the material that constitutes the “lead” of pencils. Graphene, which is just one of these sheets, can be wrapped through new bonds into tubes (also called nanotubes) that have impressive properties as thermal and electrical conductors.



Charles D. Winters/Photo
Researchers, Inc.



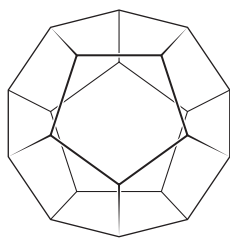
Carbon is shown here in its diamond and graphite forms



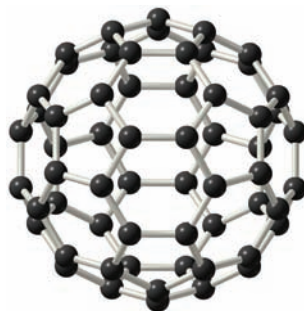
A portion of the structure of graphite

(continues on next page)

If the rings of graphite and graphene are combined together into discrete balls possessing a finite number of carbon atoms, then materials such as buckminsterfullerene (also known as buckyballs) result. The name of this material derives from its resemblance to the geodesic dome first designed by architect Buckminster Fuller. This particular compound, which is comprised of 60 carbon atoms, has bonds that look exactly like the seams of a soccer ball through its possession of 32 interlocking rings of which 20 are hexagons and 12 are pentagons. The center is large enough, in fact, to hold an atom of argon (such a compound has been made). Another variant of this type of structure is dodecahedrane, a compound composed of 20 carbon atoms and first synthesized in 1982 by scientists at the Ohio State University. Materials of this type collectively are believed to have potential in applications as diverse as armor, drug delivery, and superconductivity.



Dodecahedrane



Buckminsterfullerene

The key point is that the molecular variations are nearly endless, increasing exponentially as more and more atoms are added. This fact is one of the most beautiful elements of organic chemistry, because it means that we are largely limited in terms of possible structures by just two factors: our ability to imagine a molecule and having the tools necessary to forge it in the form of appropriate chemical reactions. This outcome is because the rules, the language, of organic chemistry are consistent.

To learn more about these topics, see:

Hopf, H. *Classics in Hydrocarbon Chemistry*. Wiley-VCH: Weinheim, 2000, p. 560.

SUMMARY AND REVIEW TOOLS

One of the reasons we organic chemists love our discipline is that, besides knowing each molecule has a family, we also know that each one has its own architecture, “personality,” and unique name. You have already learned in Chapters 1–3 about molecular personalities with regard to charge distribution, polarity, and relative acidity or basicity. In this chapter you have now learned how to give unique names to simple molecules using the IUPAC system. You also learned more about the overall shapes of organic molecules, how their shapes can change through bond rotations, and how we can compare the relative energies of those changes using conformational analysis. You now know that the extent of flexibility or rigidity in a molecule has to do with the types of bonds present (single, double, triple), and whether there are rings or bulky groups that inhibit bond rotation. Some organic molecules are very flexible members of the family, such as the molecules in our muscle fibers, while others are very rigid, like the carbon lattice of diamond. Most molecules, however, have both flexible and rigid aspects to their structures. With the knowledge from this chapter, added to other fundamentals you have already learned, you are on your way to developing an understanding of organic chemistry that we hope will be as strong as diamonds, and that you can flex like a muscle when you approach a problem. When you are finished with this chapter’s homework, maybe you can even take a break by resting your mind on the chair conformation of cyclohexane.

PROBLEMS

Note to Instructors: Many of the homework problems are available for assignment via *WileyPLUS*, an online teaching and learning solution program.

NOMENCLATURE AND ISOMERISM

4.23 Write a bond-line formula for each of the following compounds:

(a) 1,4-Dichloropentane

(c) 4-Isopropylheptane

(e) 3-Ethyl-2-methylhexane

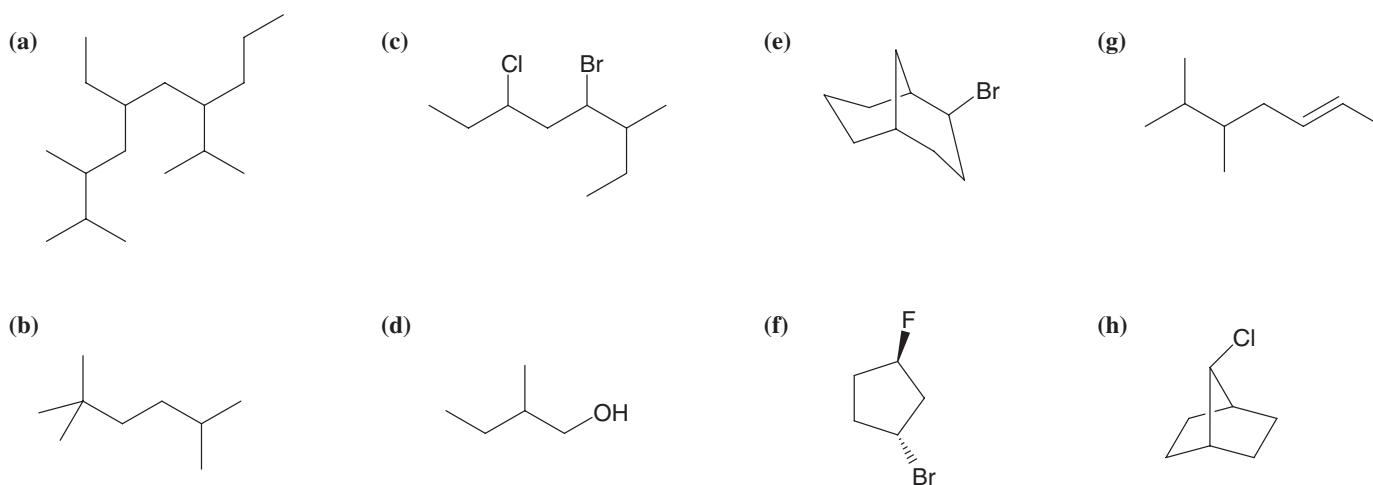
(b) *sec*-Butyl bromide

(d) 2,2,3-Trimethylpentane

(f) 1,1-Dichlorocyclopentane

- (g) *cis*-1,2-Dimethylcyclopropane (j) *trans*-4-Isobutylcyclohexanol (m) Bicyclo[2.2.2]octane
 (h) *trans*-1,2-Dimethylcyclopropane (k) 1,4-Dicyclopropylhexane (n) Bicyclo[3.1.1]heptane
 (i) 4-Methyl-2-pentanol (l) Neopentyl alcohol (o) Cyclopentylcyclopentane

4.24 Give systematic IUPAC names for each of the following:



4.25 The name *sec*-butyl alcohol defines a specific structure but the name *sec*-pentyl alcohol is ambiguous. Explain.

4.26 Write the structure and give the IUPAC systematic name of an alkane or cycloalkane with the formulas (a) C_8H_{18} that has only primary hydrogen atoms, (b) C_6H_{12} that has only secondary hydrogen atoms, (c) C_6H_{12} that has only primary and secondary hydrogen atoms, and (d) C_8H_{14} that has 12 secondary and 2 tertiary hydrogen atoms.

4.27 Write the structure(s) of the simplest alkane(s), i.e., one(s) with the fewest number of carbon atoms, wherein each possesses primary, secondary, tertiary, and quaternary carbon atoms. (A quaternary carbon is one that is bonded to four other carbon atoms.) Assign an IUPAC name to each structure.

4.28 Ignoring compounds with double bonds, write structural formulas and give names for all of the isomers with the formula C_5H_{10} .

4.29 Write structures for the following bicyclic alkanes:

- (a) Bicyclo[1.1.0]butane (c) 2-Chlorobicyclo[3.2.0]heptane
 (b) Bicyclo[2.1.0]pentane (d) 7-Methylbicyclo[2.2.1]heptane

4.30 Use the $S - A + 1 = N$ method (Helpful Hint, Section 4.14) to determine the number of rings in cubane (Section 4.14).

4.31 A spiro ring junction is one where two rings that share no bonds originate from a single carbon atom. Alkanes containing such a ring junction are called spiranes.

- (a) For the case of bicyclic spiranes of formula C_7H_{12} , write structures for all possibilities where all carbons are incorporated into rings.
 (b) Write structures for other bicyclic molecules that fit this formula.

4.32 Tell what is meant by a homologous series and illustrate your answer by writing structures for a homologous series of alkyl halides.

HYDROGENATION

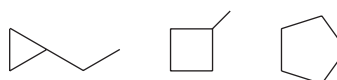
4.33 Four different cycloalkenes will all yield methylcyclopentane when subjected to catalytic hydrogenation. What are their structures? Show the reactions.

4.34 (a) Three different alkenes yield 2-methylbutane when they are hydrogenated in the presence of a metal catalyst. Give their structural formulas and write equations for the reactions involved. (b) One of these alkene isomers has characteristic absorptions at approximately 998 and 914 cm^{-1} in its IR spectrum. Which one is it?

4.35 An alkane with the formula C_6H_{14} can be prepared by hydrogenation of either of only two precursor alkenes having the formula C_6H_{12} . Write the structure of this alkane, give its IUPAC name, and show the reactions.

CONFORMATIONS AND STABILITY

4.36 Rank the following compounds in order of increasing stability based on



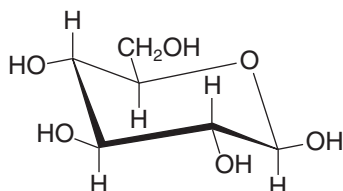
relative ring strain.

4.50 Open the 3D Molecular Models on the book's website for cyclopentane and vitamin B₁₂. Compare cyclopentane with the nitrogen-containing five-membered rings in vitamin B₁₂. Is the conformation of cyclopentane represented in the specified rings of vitamin B₁₂? What factor(s) account for any differences you observe?

4.51 Open the 3D Molecular Model on the book's website for buckminsterfullerene. What molecule has its type of ring represented 16 times in the surface of buckminsterfullerene?

LEARNING GROUP PROBLEMS

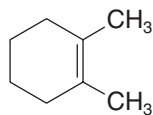
1. This is the predominant conformation for D-glucose:



Why is it not surprising that D-glucose is the most commonly found sugar in nature? (*Hint*: Look up structures for sugars such as D-galactose and D-mannose, and compare these with D-glucose.)

2. Using Newman projections, depict the relative positions of the substituents on the bridgehead atoms of *cis*- and *trans*-decalin. Which of these isomers would be expected to be more stable, and why?

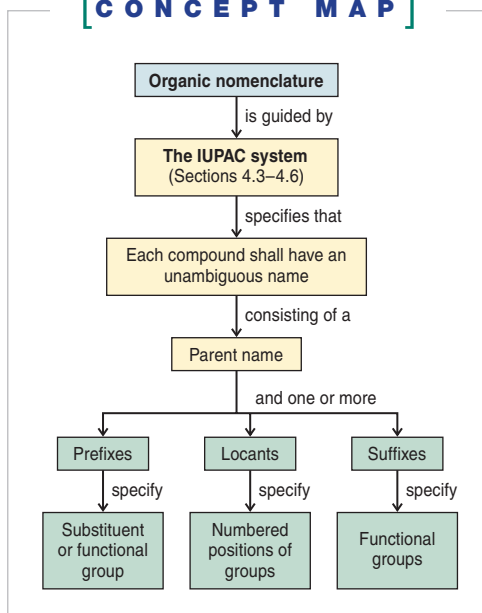
3. When 1,2-dimethylcyclohexene (below) is allowed to react with hydrogen in the presence of a platinum catalyst, the product of the reaction is a cycloalkane that has a melting point of $-50\text{ }^{\circ}\text{C}$ and a boiling point of $130\text{ }^{\circ}\text{C}$ (at 760 torr). (a) What is the structure of the product of this reaction? (b) Consult an appropriate resource (such as the web or a CRC handbook) and tell which stereoisomer it is. (c) What does this experiment suggest about the mode of addition of hydrogen to the double bond?



1,2-Dimethylcyclohexene

4. When cyclohexene is dissolved in an appropriate solvent and allowed to react with chlorine, the product of the reaction, C₆H₁₀Cl₂, has a melting point of $-7\text{ }^{\circ}\text{C}$ and a boiling point (at 16 torr) of $74\text{ }^{\circ}\text{C}$. (a) Which stereoisomer is this? (b) What does this experiment suggest about the mode of addition of chlorine to the double bond?

[CONCEPT MAP]



[CONCEPT MAP]

