

CHAPTER 2

ALKANES AND CYCLOALKANES

Now that we've reviewed the various bonding models, we are ready to examine organic compounds in respect to their structure, reactions, properties, and applications. Were we to list the physical and chemical properties of each of the more than 8 million organic compounds separately, it would tax the capacity of even a powerful computer. Yet someone who is trained in organic chemistry can simply look at the structure of a substance and make reasonably confident predictions about its properties, including how it will behave in a chemical reaction.

Organic chemists associate particular structural units, called **functional groups**, with characteristic patterns of reactivity; they look at large molecules as collections of functional groups attached to nonreactive frameworks. Not only does this “functional group approach” have predictive power, but time and experience have shown that it organizes the material in a way that makes learning organic chemistry easier for most students.

We'll begin the chapter with a brief survey of various kinds of hydrocarbons—compounds that contain only carbon and hydrogen—introduce some functional groups, then return to hydrocarbons to discuss alkanes in some detail. The names of alkanes may seem strange at first, but they form the foundation for the most widely accepted system of organic nomenclature. The fundamentals of this nomenclature system, the **IUPAC rules**, constitute one of the main topics of this chapter.

2.1 CLASSES OF HYDROCARBONS

Hydrocarbons are compounds that contain only carbon and hydrogen and are divided into two main classes: **aliphatic** hydrocarbons and **aromatic** hydrocarbons. This classification dates from the nineteenth century, when organic chemistry was almost

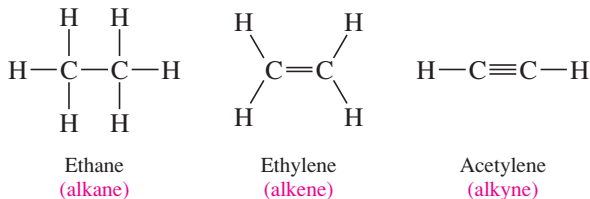
CHAPTER OUTLINE

- 2.1 Classes of Hydrocarbons
- 2.2 Reactive Sites in Hydrocarbons
- 2.3 The Key Functional Groups
- 2.4 Introduction to Alkanes: Methane, Ethane, and Propane
- 2.5 Conformations of Ethane and Propane
- Methane and the Biosphere**
- 2.6 Isomeric Alkanes: The Butanes
- 2.7 Higher Alkanes
- 2.8 IUPAC Nomenclature of Unbranched Alkanes
- 2.9 Applying the IUPAC Rules: The Names of the C₆H₁₄ Isomers
- 2.10 Alkyl Groups
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- 2.16 Conformational Analysis of Monosubstituted Cyclohexanes
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- 2.18 Polycyclic Ring Systems
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- 2.20 Chemical Properties: Combustion of Alkanes
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- Additional Problems**

exclusively devoted to the study of materials from natural sources, and terms were coined that reflected a substance's origin. Two sources were fats and oils, and the word *aliphatic* was derived from the Greek word *aleiphar* ("fat"). Aromatic hydrocarbons, irrespective of their own odor, were typically obtained by chemical treatment of pleasant-smelling plant extracts.

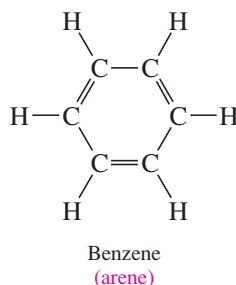
Aliphatic hydrocarbons include three major groups: alkanes, alkenes, and alkynes. **Alkanes** are hydrocarbons in which all the bonds are single bonds, **alkenes** contain one or more carbon-carbon double bonds, and **alkynes** contain one or more carbon-carbon triple bonds. Examples of the three classes of aliphatic hydrocarbons are the two-carbon compounds *ethane*, *ethylene*, and *acetylene*.

Bonding in ethane, ethylene, and acetylene was discussed in Sections 1.13–1.15.



Another name for aromatic hydrocarbons is **arenes**. Arenes have properties that are much different from alkanes, alkenes, and alkynes. The most important aromatic hydrocarbon is *benzene*.

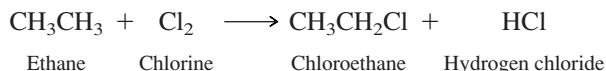
Bonding in benzene will be discussed in Section 6.1.



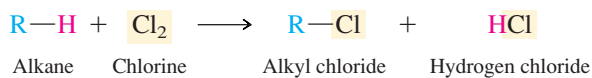
Many of the principles of organic chemistry can be developed by examining the series of hydrocarbons in the order: alkanes, alkenes, alkynes, and arenes. Alkanes are introduced in this chapter, alkenes and alkynes in Chapters 4 and 5, and arenes in Chapter 6.

2.2 REACTIVE SITES IN HYDROCARBONS

A **functional group** is the structural unit responsible for a given molecule's reactivity under a particular set of conditions. It can be as small as a single hydrogen atom, or it can encompass several atoms. The functional group of an alkane is any one of its hydrogens. A reaction that we shall discuss in Chapter 9 is one in which an alkane reacts with chlorine. For example:



One of the hydrogen atoms of ethane is replaced by chlorine. This replacement of hydrogen by chlorine is a characteristic reaction of all alkanes and can be represented by the equation:



In the general equation the functional group ($-\text{H}$) is shown explicitly, and the remainder of the alkane molecule is abbreviated as R. This is a commonly used notation that helps focus our attention on the functional group transformation without being distracted by the parts of the molecule that remain unaffected. A hydrogen atom in one alkane is very much like the hydrogen of any other alkane in its reactivity toward chlorine. Our ability to write general equations such as the one shown illustrates why the functional group approach is so useful in organic chemistry.

A hydrogen atom is a functional unit in alkenes and alkynes as well as in alkanes. These hydrocarbons, however, contain a second functional group as well. The carbon-carbon double bond is a functional group in alkenes, and the carbon-carbon triple bond is a functional group in alkynes.

A hydrogen atom is a functional group in arenes, and we represent arenes as ArH to reflect this. What will become apparent when we discuss the reactions of arenes, however, is that their chemistry is much richer than that of alkanes, and it is therefore more appropriate to consider the ring in its entirety as the functional group.

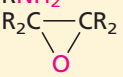
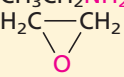
2.3 THE KEY FUNCTIONAL GROUPS

As a class, alkanes are not particularly reactive compounds, and the H in RH is not a particularly reactive functional group. Indeed, when a group other than hydrogen is present on an alkane framework, that group is almost always the functional group. Table 2.1 lists examples of some compounds of this type. All will be discussed in later chapters.

Some of the most important families of organic compounds, those that contain the carbonyl group ($\text{C}=\text{O}$), deserve separate mention and are listed in Table 2.2. Carbonyl-containing compounds rank among the most abundant and biologically significant classes of naturally occurring substances.

Carbonyl group chemistry is discussed in a block of three chapters (Chapters 11–13).

TABLE 2.1 Functional Groups in Some Important Classes of Organic Compounds

Class	Generalized Abbreviation	Representative Example	Name of Example*
Alcohol	ROH	$\text{CH}_3\text{CH}_2\text{OH}$	Ethanol
Alkyl halide	RCl	$\text{CH}_3\text{CH}_2\text{Cl}$	Chloroethane
Amine [†]	RNH_2	$\text{CH}_3\text{CH}_2\text{NH}_2$	Ethanamine
Epoxide	$\text{R}_2\text{C}-\text{CR}_2$ 	$\text{H}_2\text{C}-\text{CH}_2$ 	Oxirane
Ether	ROR	$\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$	Diethyl ether
Nitrile	$\text{RC}\equiv\text{N}$	$\text{CH}_3\text{CH}_2\text{C}\equiv\text{N}$	Propanenitrile
Nitroalkane	RNO_2	$\text{CH}_3\text{CH}_2\text{NO}_2$	Nitroethane
Thiol	RSH	$\text{CH}_3\text{CH}_2\text{SH}$	Ethanethiol

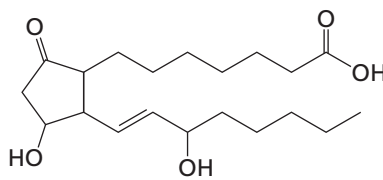
* Most compounds have more than one acceptable name.

[†] The example given is a *primary* amine (RNH_2). *Secondary* amines have the general structure R_2NH ; *tertiary* amines are R_3N .

TABLE 2.2 Classes of Compounds That Contain a Carbonyl Group

Class	Generalized Abbreviation	Representative Example	Name of Example
Aldehyde	$\text{R}\overset{\text{O}}{\parallel}\text{CH}$	$\text{CH}_3\overset{\text{O}}{\parallel}\text{CH}$	Ethanal
Ketone	$\text{R}\overset{\text{O}}{\parallel}\text{CR}$	$\text{CH}_3\overset{\text{O}}{\parallel}\text{CCH}_3$	2-Propanone
Carboxylic acid	$\text{R}\overset{\text{O}}{\parallel}\text{COH}$	$\text{CH}_3\overset{\text{O}}{\parallel}\text{COH}$	Ethanoic acid
Carboxylic acid derivatives:			
Acyl halide	$\text{R}\overset{\text{O}}{\parallel}\text{CX}$	$\text{CH}_3\overset{\text{O}}{\parallel}\text{CCl}$	Ethanoyl chloride
Acid anhydride	$\text{R}\overset{\text{O}}{\parallel}\text{CO}\overset{\text{O}}{\parallel}\text{CR}$	$\text{CH}_3\overset{\text{O}}{\parallel}\text{CO}\overset{\text{O}}{\parallel}\text{CCH}_3$	Ethanoic anhydride
Ester	$\text{R}\overset{\text{O}}{\parallel}\text{COR}$	$\text{CH}_3\overset{\text{O}}{\parallel}\text{COCH}_2\text{CH}_3$	Ethyl ethanoate
Amide	$\text{R}\overset{\text{O}}{\parallel}\text{CNR}_2$	$\text{CH}_3\overset{\text{O}}{\parallel}\text{CNH}_2$	Ethanamide

PROBLEM 2.1 Many compounds contain more than one functional group. The structure of prostaglandin E₁, a hormone that regulates the relaxation of smooth muscles, contains two different kinds of carbonyl groups. Classify each one (aldehyde, ketone, carboxylic acid, ester, amide, acyl chloride, or carboxylic acid anhydride).

Prostaglandin E₁

The reactions of the carbonyl group feature prominently in *organic synthesis*—the branch of organic chemistry that plans and carries out the preparation of compounds of prescribed structure.

2.4 INTRODUCTION TO ALKANES: METHANE, ETHANE, AND PROPANE

Alkanes have the general molecular formula $\text{C}_n\text{H}_{2n+2}$. The simplest one, **methane** (CH_4), is also the most abundant. Large amounts are present in our atmosphere, in the ground,

and in the oceans. Methane has been found on Jupiter, Saturn, Uranus, Neptune, and Pluto, and even on Halley's Comet.

Ethane (C_2H_6 , CH_3CH_3) and **propane** (C_3H_8 , $CH_3CH_2CH_3$) are second and third, respectively, to methane in many ways. Ethane is the alkane next to methane in structural simplicity, followed by propane. Ethane ($\approx 10\%$) is the second and propane ($\approx 5\%$) the third most abundant component of natural gas, which is $\approx 75\%$ methane. The characteristic odor of natural gas we use for heating our homes and cooking comes from trace amounts of unpleasant-smelling sulfur-containing compounds such as ethanethiol (see Table 2.1) that are deliberately added to it in order to warn us of potentially dangerous leaks. Natural gas is colorless and nearly odorless, as are methane, ethane, and propane.

Methane is the lowest boiling alkane, followed by ethane, then propane.

	CH_4	CH_3CH_3	$CH_3CH_2CH_3$
	Methane	Ethane	Propane
Boiling point:	$-160^\circ C$	$-89^\circ C$	$-42^\circ C$

This will generally be true as we proceed to look at other alkanes; as the number of carbon atoms increases, so does the boiling point. All the alkanes with four carbons or less are gases at room temperature and atmospheric pressure. With the highest boiling point of the three, propane is the easiest one to liquefy. We are all familiar with "propane tanks." These steel containers maintain a propane-rich mixture of hydrocarbons called liquefied petroleum gas (LPG) in a liquid state under high pressure as a convenient clean-burning fuel.

The structural features of methane, ethane, and propane are summarized in Figure 2.1. All of the carbon atoms are sp^3 -hybridized, all of the bonds are σ bonds, and the bond angles at carbon are close to tetrahedral.

PROBLEM 2.2 How many carbons are sp^3 -hybridized in propane? How many σ bonds occur in this molecule? Identify the orbital overlaps that give rise to each σ bond.

See the boxed essay: "Methane and the Biosphere" that accompanies this section.

Boiling points cited in this text are at 1 atm (760 mm of mercury) unless otherwise stated.

2.5 CONFORMATIONS OF ETHANE AND PROPANE

In addition to the constitution of ethane, another aspect of its structure commands our attention: its **conformation**.

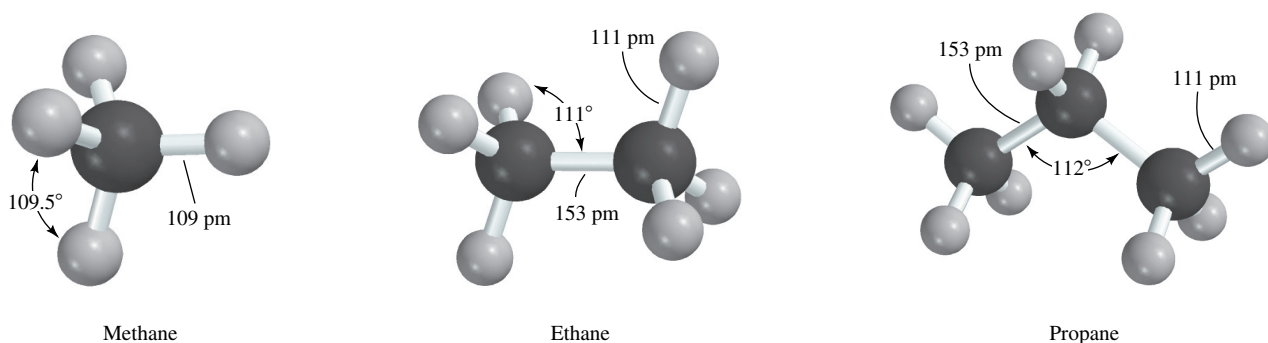
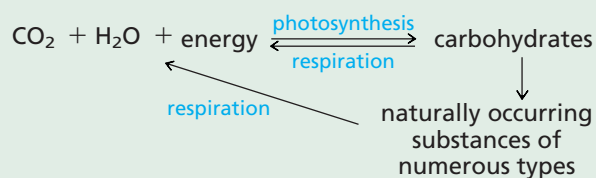


FIGURE 2.1 Structures of methane, ethane, and propane showing bond distances and bond angles.

METHANE AND THE BIOSPHERE*

One of the things that environmental scientists do is to keep track of important elements in the biosphere—in what form do these elements normally occur, to what are they transformed, and how are they returned to their normal state? Careful studies have given clear, although complicated, pictures of the “nitrogen cycle,” the “sulfur cycle,” and the “phosphorus cycle,” for example. The “carbon cycle,” begins and ends with atmospheric carbon dioxide. It can be represented in an abbreviated form as:



Methane is one of literally millions of compounds in the carbon cycle, but one of the most abundant. It is formed when carbon-containing compounds decompose in the absence of air (**anaerobic** conditions). The organisms that bring this about are called **methanoarchaea**. Cells can be divided into three types: **archaea**, **bacteria**, and **eukarya**. Methanoarchaea are one kind of archaea and may rank among the oldest living things on earth. They can convert a number of carbon-containing compounds, including carbon dioxide and acetic acid, to methane.

Virtually anywhere water contacts organic matter in the absence of air is a suitable place for methanoarchaea to thrive—at the bottom of ponds, bogs, and rice fields, for example. Marsh gas (swamp gas) is mostly methane. Methanoarchaea live inside termites and grass-eating animals. One source quotes 20 L/day as the methane output of a large cow.

The scale on which methanoarchaea churn out methane, estimated to be 10^{11} – 10^{12} lb/year, is enormous. About 10% of this amount makes its way into

the atmosphere, but most of the rest simply ends up completing the carbon cycle. It exits the anaerobic environment where it was formed and enters the aerobic world where it is eventually converted to carbon dioxide by a variety of processes.

When we consider sources of methane we have to add “old” methane, methane that was formed millions of years ago but became trapped beneath the earth’s surface, to the “new” methane just described. Firedamp, an explosion hazard to miners, occurs in layers of coal and is mostly methane. Petroleum deposits, formed by microbial decomposition of plant material under anaerobic conditions, are always accompanied by pockets of natural gas, which is mostly methane.

An interesting thing happens when trapped methane leaks from sites under the deep ocean floor. If the pressure is high enough (50 atm) and the water cold enough (4°C), the methane doesn’t simply bubble to the surface. Individual methane molecules become trapped inside clusters of 6–18 water molecules forming **methane clathrates** or **methane hydrates**. Aggregates of these clathrates stay at the bottom of the ocean in what looks like a lump of dirty ice. Ice that burns. Far from being mere curiosities, methane clathrates are potential sources of energy on a scale greater than that of all known oil reserves combined. At present, it is not economically practical to extract the methane, however.

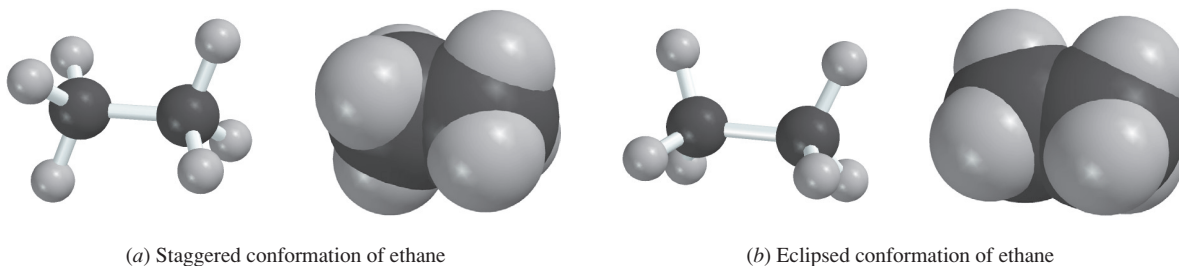
Methane clathrates have received recent attention from a different segment of the scientific community. While diving in the Gulf of Mexico in 1997, a research team of biologists and environmental scientists were surprised to find a new species of worm grazing on the mound of a methane clathrate. What were these worms feeding on? Methane? Bacteria that live on the methane? A host of questions having to do with deep-ocean ecosystems suddenly emerged. Stay tuned.

*The biosphere is the part of the earth where life is; it includes the surface, the oceans, and the lower atmosphere.

You will find it helpful at this point to construct a molecular model of ethane and view the two conformations from a variety of perspectives.

Conformations are different spatial arrangements of a molecule that are generated by rotation about single bonds.

Two of the many conformations of ethane, the **staggered conformation** and the **eclipsed conformation**, are depicted in Figure 2.2. The C—H bonds in the staggered conformation are arranged so that each one bisects the angle made by a pair of C—H bonds on



the adjacent carbon. In the eclipsed conformation each C—H bond is aligned with a C—H bond on the adjacent carbon. The staggered and eclipsed conformations interconvert by rotation around the carbon–carbon bond.

Among the various ways in which the staggered and eclipsed forms are portrayed, wedge-and-dash, sawhorse, and Newman projection drawings are especially useful. These are shown for the staggered conformation of ethane in Figure 2.3 and for the eclipsed conformation in Figure 2.4.

We used **wedge-and-dash** drawings earlier (Section 1.10) and so Figures 2.3a and 2.4a are familiar to us. A **sawhorse drawing** (Figures 2.3b and 2.4b) shows the conformation of a molecule without having to resort to different styles of bonds. In a **Newman projection** (Figures 2.3c and 2.4c), we sight down the C—C bond, and represent the front carbon by a point and the back carbon by a circle. Each carbon has three substituents that are placed symmetrically around it.

FIGURE 2.2 The staggered and eclipsed conformations of ethane shown as ball-and-stoke and space-filling models

Newman projections were devised by Professor Melvin S. Newman of Ohio State University in the 1950s.

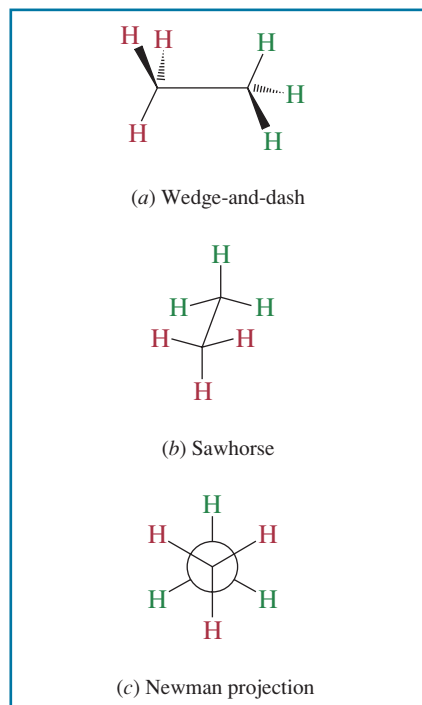


FIGURE 2.3 Some commonly used representations of the staggered conformation of ethane.

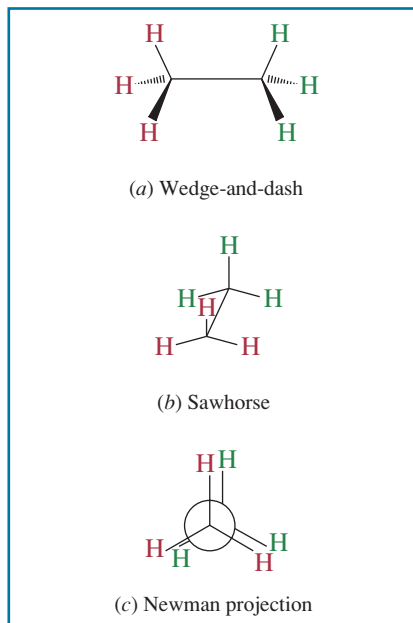


FIGURE 2.4 Some commonly used representations of the eclipsed conformation of ethane.

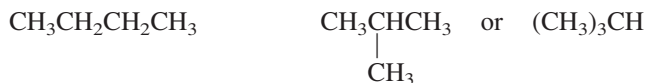
You may have noticed that, in fact, an infinite number of conformations of ethane exist that differ by only tiny increments of rotation about the carbon–carbon bond. Are all conformations possible? How fast is the process of rotation about the carbon–carbon bond? Which conformation is the most stable? Which one is the least stable? Questions of this type arise with almost all chemical substances (not just organic compounds and not just alkanes), and their study is called **conformational analysis**. In the case of ethane, the *staggered conformation is the most stable*, and the eclipsed form is the least stable of all conformations. Rotation about the carbon–carbon bond is extremely fast (several million times per second at room temperature), and conformations interconvert rapidly. At any instant, most of the ethane molecules exist in the staggered conformation. The staggered conformation is most stable because it allows for the maximum separation of electron pairs on adjacent atoms. The VSEPR model (Section 1.10) predicts molecular shapes on the basis of maximum separation of electron pairs on a single atom. In ethane the electron pairs of the C–H bonds of one carbon are farthest away from the electron pairs of the C–H bonds of the adjacent carbon when the bonds are staggered.

Because it is less stable than the staggered conformation, we say the eclipsed conformation of ethane is **strained** and identify that strain as being due to the eclipsing of bonds on adjacent atoms. This type of strain is called **torsional strain**. In the following section we will see a second type of strain that, combined with torsional strain, is an important consideration in the conformational analysis of higher alkanes.

PROBLEM 2.3 Construct a molecular model of propane and use it to draw Newman projections of the staggered and eclipsed conformations of propane. How do they differ from the conformations of ethane?

2.6 ISOMERIC ALKANES: THE BUTANES

Methane is the only alkane of molecular formula CH_4 , ethane the only one that is C_2H_6 , and propane the only one that is C_3H_8 . Beginning with C_4H_{10} , however, constitutional isomers (Section 1.8) are possible; two alkanes have this particular molecular formula. In one, called ***n*-butane**, four carbons are joined in a continuous chain. The *n* in *n*-butane stands for “normal” and means that the carbon chain is unbranched. The second isomer has a branched carbon chain and is called **isobutane**.



Boiling point:	<i>n</i> -Butane −0.4°C	Isobutane −10.2°C
Melting point:	−139°C	−160.9°C

Make molecular models of the two isomers of C_4H_{10} .

“Butane” lighters contain about 5% *n*-butane and 95% isobutane in a sealed container. The pressure produced by the two compounds (about 3 atm) is enough to keep them in the liquid state until opening a small valve emits a fine stream of the vaporized mixture across a spark which ignites it.

As noted earlier (Section 1.13), CH_3 is called a *methyl* group. In addition to having methyl groups at both ends, *n*-butane contains two CH_2 , or **methylene** groups. Isobutane contains three methyl groups bonded to a CH unit. The CH unit is called a **methine** group.

n-Butane and isobutane have the same molecular formula but differ in the order in which their atoms are connected. They are **constitutional isomers** of each other (Section 1.8). Because they are different in structure, they can have different properties. Both are gases at room temperature, but *n*-butane boils almost 10°C higher than isobutane and has a melting point that is over 20°C higher.

The bonding in *n*-butane and isobutane continues the theme begun with methane, ethane, and propane. All of the carbon atoms are sp^3 -hybridized, all of the bonds are σ

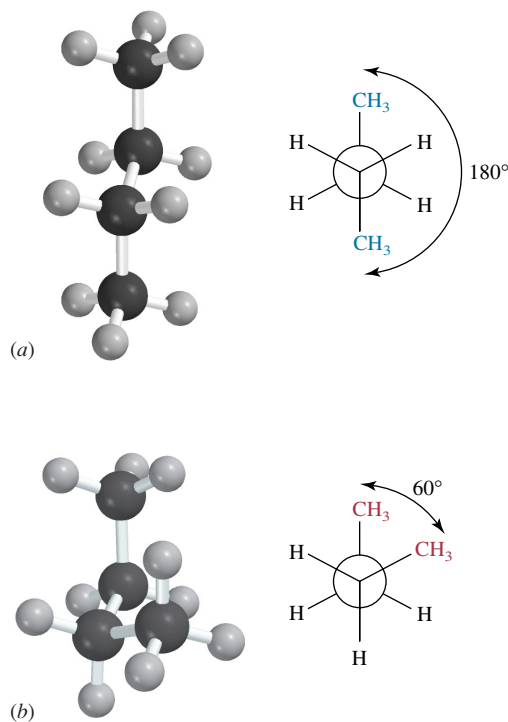


FIGURE 2.5 The (a) anti and (b) gauche conformations of butane shown as ball-and-spoke models (*left*) and as Newman projections (*right*). The gauche conformation is less stable than the anti because of the van der Waals strain between the methyl groups.

bonds, and the bond angles at carbon are close to tetrahedral. This generalization holds for all alkanes regardless of the number of carbons they have.

The most stable conformation of *n*-butane is shown in Figure 2.5(a). It has a zigzag arrangement of its carbon chain, and all the bonds are staggered. A Newman projection of this conformation, sighting down the C-2—C-3 bond, is shown at the right. As can be seen in the Newman projection, not only are the bonds to C-2 and C-3 staggered with respect to each other, but the angle between the bonds to the methyl groups is 180° . We call this the **anti** conformation.

Figure 2.5(b) depicts a second staggered conformation of *n*-butane called the **gauche** conformation. The methyl groups are much closer together in the gauche conformation, where the angle between them is only 60° , than they are in the anti, and the gauche conformation is slightly less stable than the anti. The destabilization of a molecule that results when two of its atoms are too close to each other is called **van der Waals strain** or **steric hindrance**. Because anti and gauche are both staggered conformations, they are free of torsional strain. They are rapidly interconverted at room temperature, and at any instant approximately 65% of the molecules of *n*-butane exist in the anti conformation and 35% in the gauche.

PROBLEM 2.4 Draw a Newman projection formula of the most stable conformation of isobutane.

2.7 HIGHER ALKANES

n-Alkanes are alkanes that have an unbranched carbon chain. ***n*-Pentane** and ***n*-hexane** are *n*-alkanes possessing five and six carbon atoms, respectively.

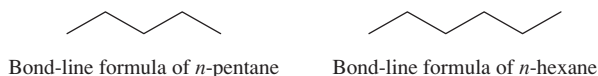


Their condensed structural formulas can be abbreviated even more by indicating within parentheses the number of methylene groups in the chain. Thus, *n*-pentane may be written as $\text{CH}_3(\text{CH}_2)_3\text{CH}_3$ and *n*-hexane as $\text{CH}_3(\text{CH}_2)_4\text{CH}_3$. This shortcut is especially convenient with longer chain alkanes. The laboratory synthesis of the “ultralong” alkane $\text{CH}_3(\text{CH}_2)_{388}\text{CH}_3$ was achieved in 1985; imagine trying to write a structural formula for this compound in anything other than an abbreviated way!

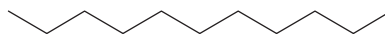
PROBLEM 2.5 An *n*-alkane of molecular formula $\text{C}_{28}\text{H}_{58}$ has been isolated from a certain fossil plant. Write a condensed structural formula for this alkane.

n-Alkanes have the general formula $\text{CH}_3(\text{CH}_2)_x\text{CH}_3$ and are said to belong to a **homologous series** of compounds, that is, one in which successive members differ by a $-\text{CH}_2-$ group.

Unbranched alkanes are sometimes referred to as “straight-chain alkanes,” but, as we saw for *n*-butane in Section 2.5, their chains are not straight but instead tend to adopt the “zigzag” shape portrayed in the bond-line formulas introduced in Section 1.7.

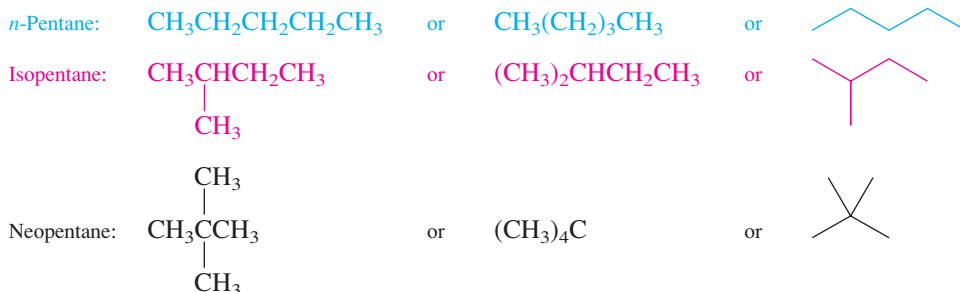


PROBLEM 2.6 Much of the communication between insects involves chemical messengers called **pheromones**. A species of cockroach secretes a substance from its mandibular glands that alerts other cockroaches to its presence and causes them to congregate. One of the principal components of this **aggregation pheromone** is the alkane shown in the bond-line formula that follows. Give the molecular formula of this substance, and represent it by a condensed formula.



Make molecular models of the three isomers of C_5H_{12} .

Three isomeric alkanes have the molecular formula C_5H_{12} . The unbranched isomer is, as we have seen, *n*-pentane. The isomer with a single methyl branch is called **isopentane**. The third isomer has a three-carbon chain with two methyl branches. It is called **neopentane**.

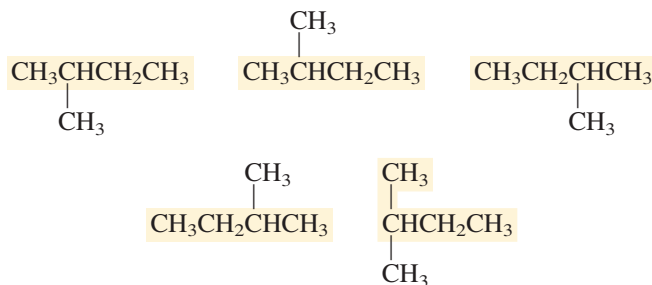


Do any additional C_5H_{12} isomers occur? Although answering that question is straightforward for an alkane with only five carbons (there are no more isomers), it is less so for alkanes with more carbons. As Table 2.3 dramatically shows, the number of isomers increases rapidly with an increasing number of carbon atoms.

TABLE 2.3 The Number of Constitutionally Isomeric Alkanes of Particular Molecular Formulas

Molecular Formula	Number of Constitutional Isomers
CH ₄	1
C ₂ H ₆	1
C ₃ H ₈	1
C ₄ H ₁₀	2
C ₅ H ₁₂	3
C ₆ H ₁₄	5
C ₇ H ₁₆	9
C ₈ H ₁₈	18
C ₉ H ₂₀	35
C ₁₀ H ₂₂	75
C ₁₅ H ₃₂	4,347
C ₂₀ H ₄₂	366,319
C ₄₀ H ₈₂	62,491,178,805,831

The best way to ensure that you have written all the isomers of a particular molecular formula is to work systematically, beginning with the unbranched chain and then shortening it while adding branches one by one. It is essential that you be able to recognize when two different-looking structural formulas are actually the same molecule written in different ways. The key point is the *connectivity* of the carbon chain. For example, the following group of structural formulas do *not* represent different compounds; they are just a portion of the many ways we could write a structural formula for isopentane. Each one has a continuous chain of four carbons with a methyl branch located one carbon from the end of the chain.

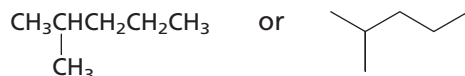


PROBLEM 2.7 Write condensed and bond-line formulas for the five isomeric C₆H₁₄ alkanes.

Sample Solution When writing isomeric alkanes, it is best to begin with the unbranched isomer.



Next, remove a carbon from the chain and use it as a one-carbon (methyl) branch at the carbon atom next to the end of the chain.



Now, write structural formulas for the remaining three isomers. Be sure that each one is a unique compound and not simply a different representation of one written previously.

A second question presents itself, namely, how can we identify alkanes so that each one has a unique name? Once again, the problem is not so difficult for C_5H_{12} with only three isomers. The same is not true for higher alkanes, however. As with writing structures, being able to name compounds in a systematic way becomes of paramount importance. By following a set of rules—presented in the following section—you will always get the same systematic name for given compound. Conversely, two different compounds will always have different names.

2.8 IUPAC NOMENCLATURE OF UNBRANCHED ALKANES

Nomenclature in organic chemistry is of two types: **common** (or “trivial”) and **systematic**. Some common names existed long before organic chemistry became an organized branch of chemical science. Methane, ethane, propane, *n*-butane, isobutane, *n*-pentane, isopentane, and neopentane are common names. One simply memorizes the name that goes with a compound in just the same way that one matches names with faces. So long as the number of names and compounds are few, the task is manageable. But millions of organic compounds are already known, and the list continues to grow! A system built on common names is not adequate to the task of communicating structural information. Beginning in 1892, chemists developed a set of rules for naming organic compounds based on their structures, which we now call the **IUPAC rules**. *IUPAC* stands for the “International Union of Pure and Applied Chemistry.”

The IUPAC rules assign names to unbranched alkanes as shown in Table 2.4. Methane, ethane, propane, and butane are retained for CH_4 , CH_3CH_3 , $CH_3CH_2CH_3$, and $CH_3CH_2CH_2CH_3$, respectively. Thereafter, the number of carbon atoms in the chain is specified by a Latin or Greek prefix preceding the suffix *-ane*, which identifies the compound as a member of the alkane family. Notice that the prefix *n*- is not part of the IUPAC system. The IUPAC name for $CH_3CH_2CH_2CH_3$ is butane, not *n*-butane.

TABLE 2.4 IUPAC Names of Unbranched Alkanes

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

* Spelled “eicosane” prior to 1979 version of IUPAC rules.

PROBLEM 2.8 What is the IUPAC name of the alkane described in Problem 2.6 as a component of the cockroach aggregation pheromone?

In Problem 2.7 you were asked to write structural formulas for the five isomeric alkanes of molecular formula C₆H₁₄. In the next section you will see how the IUPAC rules generate a unique name for each isomer.

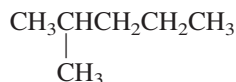
2.9 APPLYING THE IUPAC RULES: THE NAMES OF THE C₆H₁₄ ISOMERS

We can present and illustrate the most important of the IUPAC rules for alkane nomenclature by naming the five C₆H₁₄ isomers. By definition (see Table 2.4), the unbranched C₆H₁₄ isomer is hexane.



IUPAC name: **hexane**
(common name: *n*-hexane)

The IUPAC rules name branched alkanes as *substituted derivatives* of the unbranched alkanes listed in Table 2.4. Consider the C₆H₁₄ isomer represented by the structure



Step 1

Pick out the *longest continuous carbon chain*, and find the IUPAC name in Table 2.4 that corresponds to the unbranched alkane having that number of carbons. This is the parent alkane from which the IUPAC name is to be derived.

In this case, the longest continuous chain has *five* carbon atoms; the compound is named as a derivative of pentane. The key word here is *continuous*. It does not matter whether the carbon skeleton is drawn in an extended straight-chain form or in one with many bends and turns. All that matters is the number of carbons linked together in an uninterrupted sequence.

Step 2

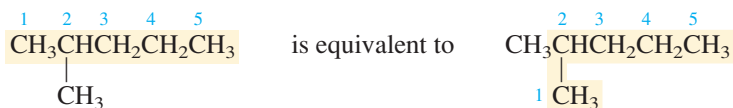
Identify the substituent groups attached to the parent chain.

The parent pentane chain bears a methyl (CH₃) group as a substituent.

Step 3

Number the longest continuous chain in the direction that gives the lowest number to the substituent at the first point of branching.

The numbering scheme



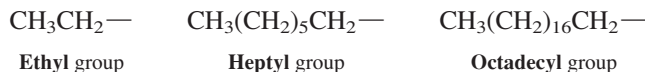
Both schemes count five carbon atoms in their longest continuous chain and bear a methyl group as a substituent at the second carbon. An alternative numbering sequence that begins at the other end of the chain is incorrect:

You might find it helpful to make molecular models of all the C₆H₁₄ isomers.

So far, the only branched alkanes that we've named have methyl groups attached to the main chain. What about groups other than CH_3 ? What do we call these groups, and how do we name alkanes that contain them?

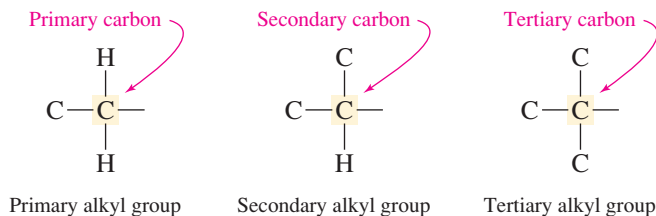
2.10 ALKYL GROUPS

An alkyl group lacks one of the hydrogens of an alkane. A methyl group (CH_3-) is an alkyl group derived from methane (CH_4). Unbranched alkyl groups in which the point of attachment is at the end of the chain are named in IUPAC nomenclature by replacing the *-ane* endings of Table 2.4 by *-yl*.



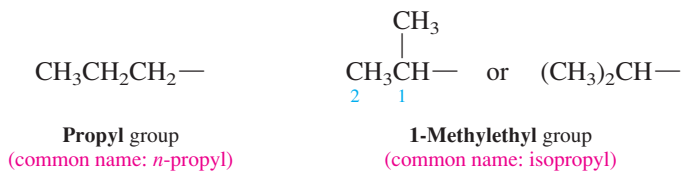
The dash at the end of the chain represents a potential point of attachment for some other atom or group.

Carbon atoms are classified according to their degree of substitution by other carbons. A **primary** carbon is *directly* attached to one other carbon. Similarly, a **secondary** carbon is directly attached to two other carbons, a **tertiary** carbon to three, and a **quaternary** carbon to four. Alkyl groups are designated as primary, secondary, or tertiary according to the degree of substitution of the carbon at the potential point of attachment.



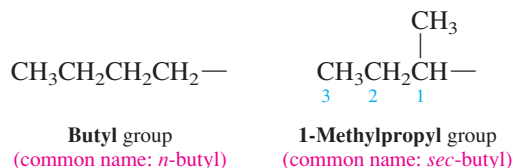
Ethyl (CH_3CH_2-), heptyl [$\text{CH}_3(\text{CH}_2)_5\text{CH}_2-$], and octadecyl [$\text{CH}_3(\text{CH}_2)_{16}\text{CH}_2-$] are examples of primary alkyl groups.

Branched alkyl groups are named by using the longest continuous chain that begins at the point of attachment as the base name. Thus, the systematic names of the two C_3H_7 alkyl groups are propyl and 1-methylethyl. Both are better known by their common names, *n*-propyl and isopropyl, respectively.

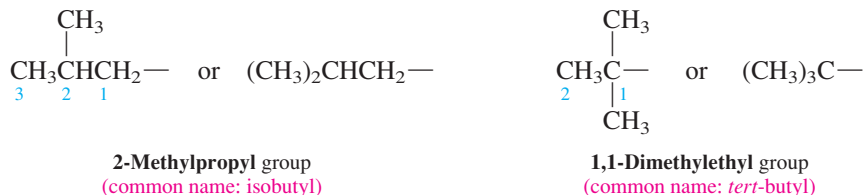


An isopropyl group is a secondary alkyl group. Its point of attachment is to a secondary carbon atom, one that is directly bonded to two other carbons.

The C_4H_9 alkyl groups may be derived either from the unbranched carbon skeleton of butane or from the branched carbon skeleton of isobutane. Those derived from butane are the butyl (*n*-butyl) group and the 1-methylpropyl (*sec*-butyl) group.



Those derived from isobutane are the 2-methylpropyl (isobutyl) group and the 1,1-dimethylethyl (*tert*-butyl) group. Isobutyl is a primary alkyl group because its potential point of attachment is to a primary carbon. *tert*-Butyl is a tertiary alkyl group because its potential point of attachment is to a tertiary carbon.

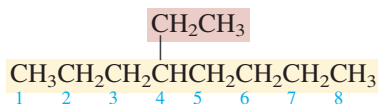


The names and structures of the most frequently encountered alkyl groups are given on the inside back cover.

In addition to methyl and ethyl groups, *n*-propyl, isopropyl, *n*-butyl, *sec*-butyl, isobutyl, and *tert*-butyl groups will appear often throughout this text. Although these are common names, they have been integrated into the IUPAC system and are an acceptable adjunct to systematic nomenclature. You should be able to recognize these groups on sight and to give their structures when needed.

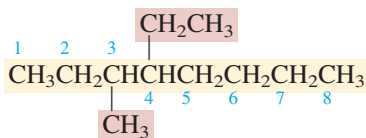
2.11 IUPAC NAMES OF HIGHLY BRANCHED ALKANES

By combining the basic principles of IUPAC notation with the names of the various alkyl groups, we can develop systematic names for highly branched alkanes. We'll start with the following alkane, name it, then increase its complexity by successively adding methyl groups at various positions.



As numbered on the structural formula, the longest continuous chain contains eight carbons, and so the compound is named as a derivative of octane. Numbering begins at the end nearest the branch, and so the ethyl substituent is located at C-4, and the name of the alkane is **4-ethyloctane**.

What happens to the IUPAC name when a methyl replaces one of the hydrogens at C-3?

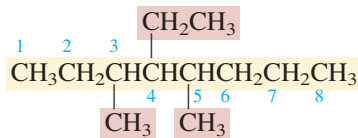


The compound becomes an octane derivative that bears a C-3 methyl group and a C-4 ethyl group.

When two or more different substituents are present, they are listed in alphabetical order in the name.

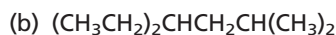
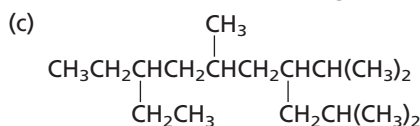
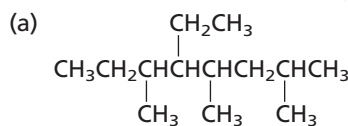
The IUPAC name for this compound is **4-ethyl-3-methyloctane**.

Replicating prefixes such as *di-*, *tri-*, and *tetra-* (see Section 2.9) are used as needed but are ignored when alphabetizing. Adding a second methyl group to the original structure, at C-5, for example, converts it to **4-ethyl-3,5-dimethyloctane**.

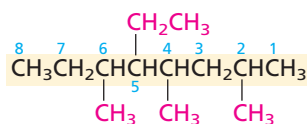


Italicized prefixes such as *sec-* and *tert-* are ignored when alphabetizing except when they are compared with each other. *tert*-Butyl precedes isobutyl, and *sec*-butyl precedes *tert*-butyl.

PROBLEM 2.11 Give an acceptable IUPAC name for each of the following alkanes:



Sample Solution (a) This problem extends the preceding discussion by adding a third methyl group to 4-ethyl-3,5-dimethyloctane, the compound just described. It is, therefore, an **ethyltrimethyloctane**. Notice, however, that the numbering sequence needs to be changed to adhere to the rule of numbering from the end of the chain nearest the first branch. When numbered properly, this compound has a methyl group at C-2 as its first-appearing substituent.



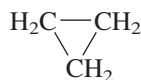
5-Ethyl-2,4,6-trimethyloctane

Finally, when equal locants are generated from two different numbering directions, choose the direction that gives the lower number to the substituent that appears first in the name. (Remember, substituents are listed alphabetically.)

The IUPAC nomenclature system is inherently logical and incorporates healthy elements of common sense into its rules. Granted, some long, funny-looking, hard-to-pronounce names are generated. Once you know the code (rules of grammar) though, it becomes a simple matter to convert those long names to unique structural formulas.

2.12 CYCLOALKANE NOMENCLATURE

Cycloalkanes are alkanes that contain a ring of three or more carbons. They are frequently encountered in organic chemistry and are characterized by the molecular formula C_nH_{2n} . Some examples include:



Cyclopropane

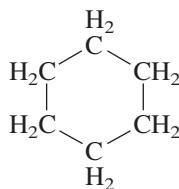
usually represented as



A tabular summary of the IUPAC rules for alkane nomenclature appears on page 62.

Cycloalkanes are one class of **alicyclic** (*aliphatic cyclic*) hydrocarbons.

If you make a molecular model of cyclohexane, you will find its shape to be very different from a planar hexagon. We'll discuss the reasons why beginning in Section 2.14.

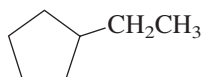


Cyclohexane

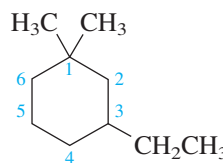
usually represented as



As you can see, cycloalkanes are named, under the IUPAC system, by adding the prefix *cyclo-* to the name of the unbranched alkane with the same number of carbons as the ring. Attached groups are identified in the usual way. Their positions are specified by numbering the carbon atoms of the ring in the direction that gives the lowest number to the substituted carbon at the first point of difference.



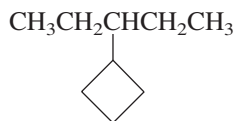
Ethylcyclopentane



3-Ethyl-1,1-dimethylcyclohexane

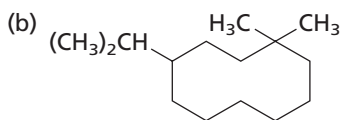
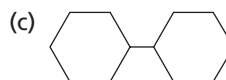
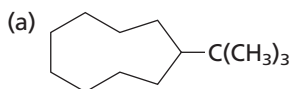
(not 1-ethyl-3,3-dimethylcyclohexane, because first point of difference rule requires 1,1,3 substitution pattern rather than 1,3,3)

When the ring contains fewer carbon atoms than an alkyl group attached to it, the compound is named as an alkane, and the ring is treated as a cycloalkyl substituent:



3-Cyclobutylpentane

PROBLEM 2.12 Name each of the following compounds:



Sample Solution (a) The molecule has a *tert*-butyl group bonded to a nine-membered cycloalkane. It is *tert*-butylcyclononane. Alternatively, the *tert*-butyl group could be named systematically as a 1,1-dimethylethyl group, and the compound would then be named (1,1-dimethylethyl)cyclononane. (Parentheses are used when necessary to avoid ambiguity. In this case the parentheses alert the reader that the locants 1,1 refer to substituents on the alkyl group and not to ring positions.)

2.13 CONFORMATIONS OF CYCLOALKANES

Conformational analysis is far simpler in cyclopropane than in any other cycloalkane. Cyclopropane's three carbons are, of geometric necessity, coplanar.



All adjacent pairs of bonds are eclipsed in cyclopropane

As can be seen in this depiction of cyclopropane, the three C—H bonds on the upper face of the ring are eclipsed, as are the three on the bottom face. Thus, cyclopropane incorporates an element of **torsional strain** (Section 2.5) into its structure. A more serious source of strain exists in cyclopropane, however. An equilateral triangle has angles of 60° , yet the bond angles at carbon when attached to four atoms or groups are ideally 109.5° . This distortion of the bond angles at carbon from the tetrahedral value is referred to as **angle strain** and makes cyclopropane less stable than other members of the alkane and cycloalkane family.

Cyclopropane is the only planar cycloalkane. Cyclobutane has less angle strain than cyclopropane and can reduce torsional strain by adopting the nonplanar “puckered” conformation shown in Figure 2.6a. Cyclopentane exists in a nonplanar conformation to relieve torsional strain; angle strain is relatively small because the 108° angles of a regular pentagon are close to the 109.5° angles of sp^3 -hybridized carbon. One of the nonplanar conformations of cyclopentane, the envelope conformation, is shown in Figure 2.6b.

The torsional strain of planar cyclopentane can be readily seen with a molecular model.

2.14 CONFORMATIONS OF CYCLOHEXANE

Six-membered rings occur more often than rings of any other size in organic compounds. Consequently, six-membered rings have been studied more extensively and their conformations are well understood. A planar conformation of cyclohexane would suffer from angle strain because the angles of a regular hexagon are 120° . It would also have a significant amount of torsional strain. The most stable conformation of cyclohexane is a nonplanar conformation known as the **chair conformation**, shown in Figure 2.7. A second, much less stable, nonplanar conformation is the **boat conformation**, shown in Figure 2.8.

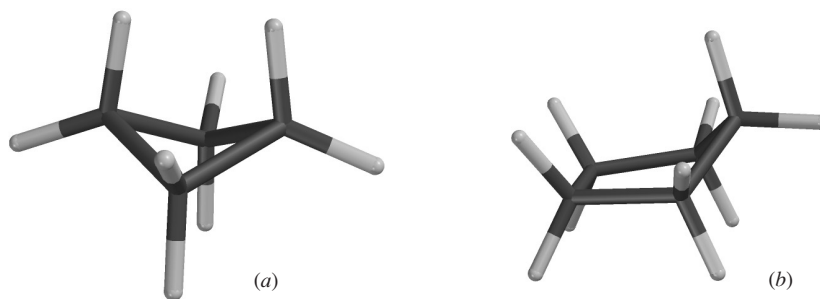


FIGURE 2.6 (a) Nonplanar (“puckered”) conformation of cyclobutane. (b) Envelope conformation of cyclopentane

FIGURE 2.7 (a) A ball-and-spoke model and (b) a space-filling model of the chair conformation of cyclohexane.

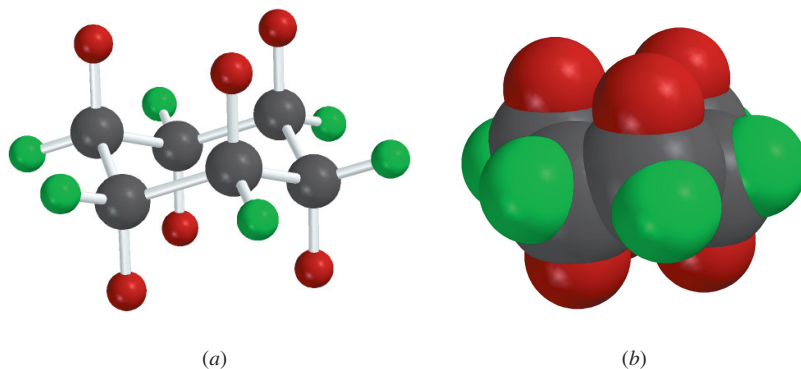
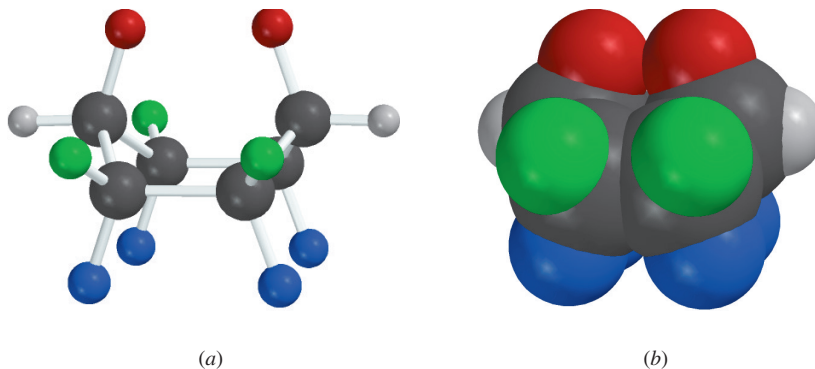
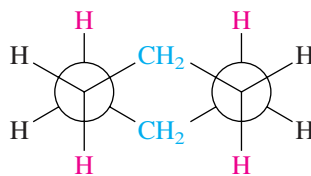


FIGURE 2.8 (a) A ball-and-spoke model and (b) a space-filling model of the boat conformation of cyclohexane. The close approach of the two uppermost hydrogens is clearly evident in the space-filling model.



While both are free of angle strain, the chair is free of torsional strain as well.

Make a molecular model of the chair conformation of cyclohexane, and turn it so that you can look down one of the C—C bonds.

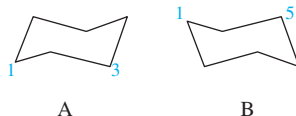


Staggered arrangement of bonds in chair conformation of cyclohexane

Considering the chair conformation in detail reveals some surprising features. The 12 hydrogen atoms are not all identical but are divided into two groups, as shown in Figure 2.9. Six of the hydrogens, called **axial** hydrogens, have their bonds parallel to a vertical axis that passes through the ring's center. These axial bonds alternately are directed up and down on adjacent carbons. The second set of six hydrogens, called **equatorial** hydrogens, are located approximately along the equator of the molecule. Notice that the four bonds to each carbon are arranged tetrahedrally, consistent with an sp^3 hybridization of carbon.

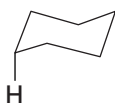
The conformational features of six-membered rings are fundamental to organic chemistry, so it is essential that you have a clear understanding of the directional properties of axial and equatorial bonds and be able to represent them accurately. Figure 2.10 on page 54 offers some guidance on the drawing of chair cyclohexane rings. Be sure to study the figure before attempting the following problem.

PROBLEM 2.13 Given the chair conformations of cyclohexane shown here, draw the indicated carbon–hydrogen bonds.



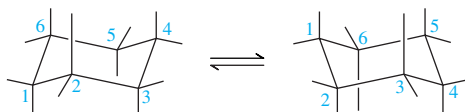
- (a) Axial C—H on C-1 of A (c) Equatorial C—H on C-1 of B
 (b) Equatorial C—H on C-3 of A (d) Axial C—H on C-5 of B

Sample Solution (a) Carbon in position 1 lies below its nearest neighbors; it is “down.” Axial bonds point alternately straight up and straight down and take their direction from the carbon atom to which they are attached. Draw the axial bond to C-1 straight down.

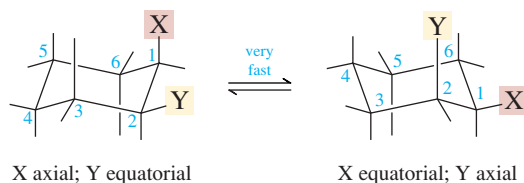


2.15 CONFORMATIONAL INVERSION (RING FLIPPING) IN CYCLOHEXANE

We have seen that alkanes are not locked into a single conformation. Rotation around the central carbon–carbon bond in butane occurs rapidly, interconverting anti and gauche conformations. Cyclohexane, too, is conformationally mobile. Through a process known as **ring inversion**, **chair–chair interconversion**, or, more simply, **ring flipping**, one chair conformation is converted to another chair.



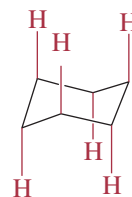
The most important result of ring inversion is that *any substituent that is axial in the original chair conformation becomes equatorial in the ring-flipped form and vice versa*.



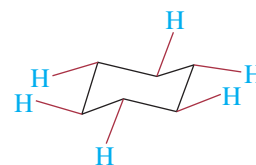
The consequences of this point are developed for a number of monosubstituted cyclohexane derivatives in the following section, beginning with methylcyclohexane.

2.16 CONFORMATIONAL ANALYSIS OF MONOSUBSTITUTED CYCLOHEXANES

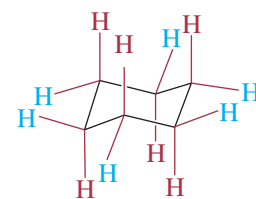
Ring inversion in methylcyclohexane differs from that of cyclohexane in that the two chair conformations are not equivalent. In one chair the methyl group is axial; in the other it is equatorial. At room temperature approximately 95% of the molecules of



Axial C—H bonds



Equatorial C—H bonds



Axial and equatorial bonds together

FIGURE 2.9 Axial and equatorial bonds in cyclohexane.

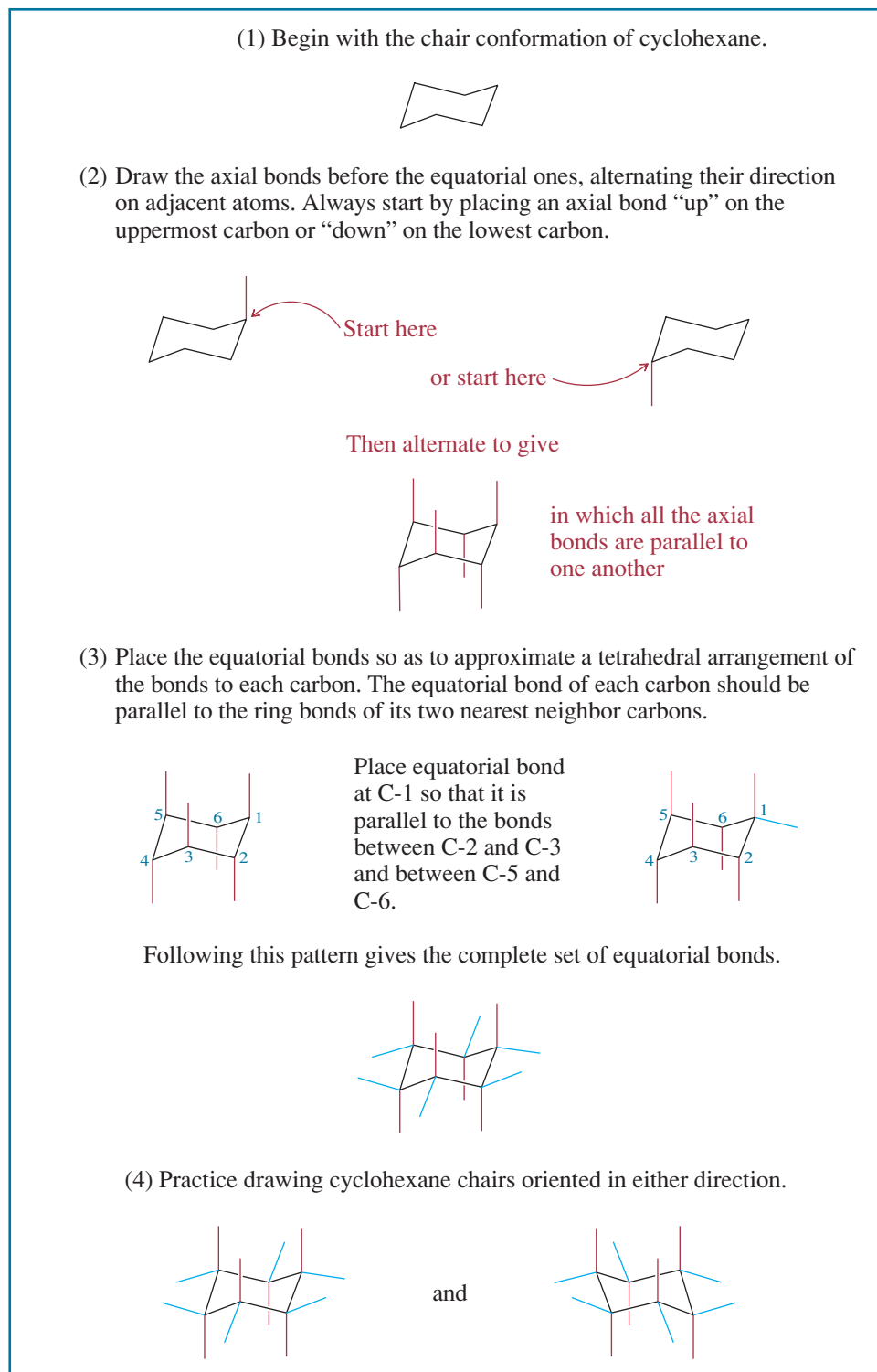
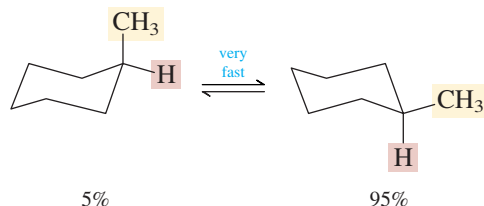


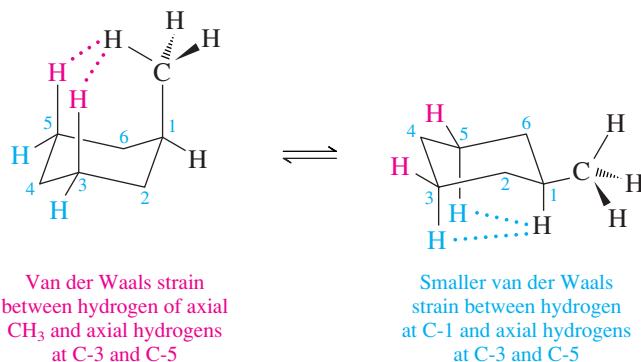
FIGURE 2.10 A guide to representing the orientations of the bonds in the chair conformation of cyclohexane.

methylcyclohexane are in the chair conformation that has an equatorial methyl group, whereas only 5% of the molecules have an axial methyl group.



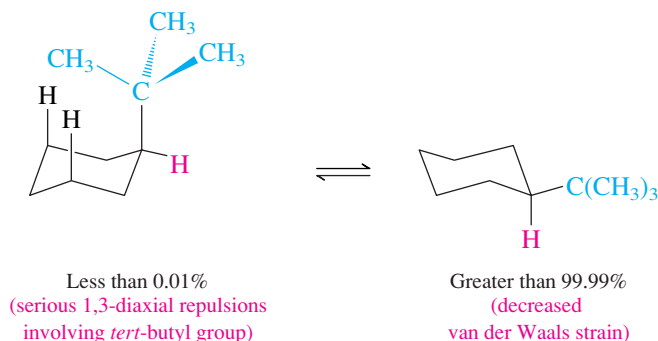
When two conformations of a molecule are in equilibrium with each other, the one with the lower free energy predominates. Why is equatorial methylcyclohexane more stable than axial methylcyclohexane?

A methyl group is less crowded when it is equatorial than when it is axial. One of the hydrogens of an axial methyl group is within 190–200 pm of the axial hydrogens at C-3 and C-5. This distance is less than the sum of the van der Waals radii of two hydrogens (240 pm) and causes van der Waals strain in the axial conformation. When the methyl group is equatorial, it experiences no significant crowding.



The greater stability of an equatorial methyl group, compared with an axial one, is another example of a **steric effect**. An axial substituent is said to be crowded because of **1,3-diaxial repulsions** between itself and the other two axial substituents located on the same side of the ring.

The same reasoning can explain the observed conformation of other substituted cyclohexanes. The larger group tends to be equatorial, and this tendency increases as the group becomes progressively “bulkier.” Although the ratio of equatorial to axial methylcyclohexane conformations is 95:5, that ratio increases to greater than 999:1 for *tert*-butylcyclohexane.



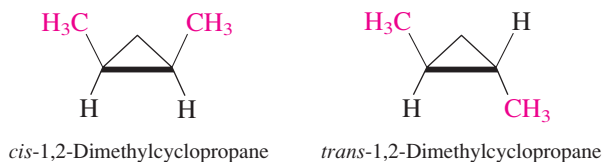
Highly branched groups such as *tert*-butyl are commonly described as “bulky.”

PROBLEM 2.14 Draw the most stable conformation of 1-*tert*-butyl-1-methylcyclohexane.

In general, a group is “bulky” in organic chemistry if it is highly branched. A very long carbon chain is no bulkier than a shorter one, but a branched alkyl group is bulkier than an unbranched one.

2.17 DISUBSTITUTED CYCLOALKANES: STEREOISOMERS

When a cycloalkane bears two substituents on different carbons—methyl groups, for example—these substituents may be on the same or on opposite sides of the ring. When substituents are on the same side, we say they are **cis** to each other; if they are on opposite sides, they are **trans** to each other. Both terms come from the Latin, in which *cis* means “on this side” and *trans* means “across.”

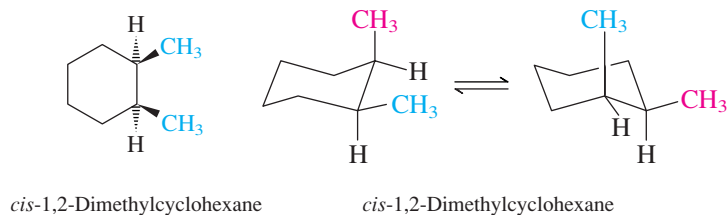


PROBLEM 2.15 Exclusive of compounds with double bonds, four hydrocarbons are constitutional isomers of *cis*- and *trans*-1,2-dimethylcyclopropane. Identify these compounds.

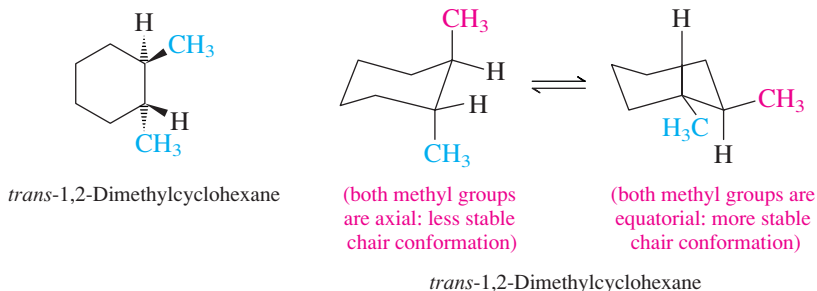
The prefix *stereo-* is derived from the Greek word *stereos*, meaning “solid.” **Stereochemistry** is the term applied to the three-dimensional aspects of molecular structure and reactivity.

The *cis* and *trans* forms of 1,2-dimethylcyclopropane are stereoisomers. **Stereoisomers** are isomers that have their atoms bonded in the same order—that is, they have the same constitution, but they differ in the arrangement of atoms in space. Stereoisomers of the *cis*–*trans* type are sometimes referred to as **geometric isomers**.

Stereoisomerism in disubstituted cyclohexanes is somewhat more complicated than in cyclopropanes because, as we have seen, the cyclohexane ring is not planar. Let us first examine *cis*-1,2-dimethylcyclohexane. Both methyl groups in the *cis* stereoisomer are on the same face of the molecule. As the following structures show, both are “up,” that is, above the hydrogen on the same carbon. Recalling that ring flipping interconverts axial and equatorial positions, we can see that the molecule can adopt either of two equivalent chair conformations. In each one, one methyl group is axial and the other equatorial.



The situation is different for *trans*-1,2-dimethylcyclohexane, however. The two chair conformations are not equivalent. In one, both methyl groups are axial; in the other, both are equatorial.



The chair conformation in which both methyl groups are equatorial is more stable than the one in which both are axial and is the predominant one at equilibrium. We can understand why by recalling that equatorial substituents are less crowded than axial ones.

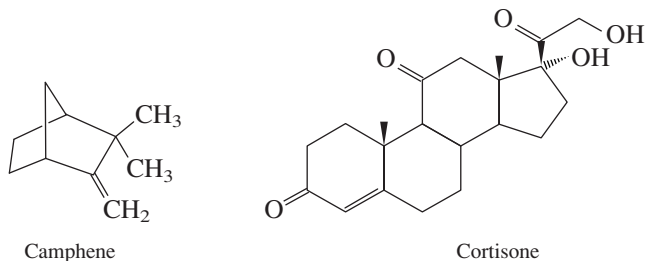
If two substituent groups are different, the preferred conformation will be the one in which the bulkier group is equatorial. Thus the most stable conformation of *cis*-1-*tert*-butyl-2-methylcyclohexane has an equatorial *tert*-butyl group and an axial methyl group.

PROBLEM 2.16 Draw the most stable conformation of *cis*- and *trans*-1-*tert*-butyl-2-methylcyclohexane.

All the properties of a molecule ultimately depend on its structure. Constitution or connectivity is an important element of molecular structure, but it is not the only one. The three-dimensional shape of a molecule—the arrangement of its atoms in space, or its **stereochemistry**—is also important. Many organic reactions and biochemical processes are known in which one stereoisomeric form of a substance reacts readily, but the other form is essentially inert under the same conditions.

2.18 POLYCYCLIC RING SYSTEMS

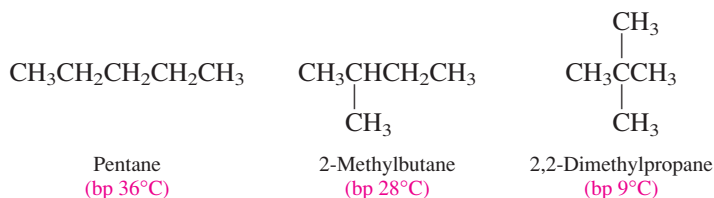
Organic compounds are not limited to a single ring, and many compounds contain two or more rings. Substances that contain two rings are referred to as **bicyclic**, those with three rings are called **tricyclic**, and so on. Camphene is a naturally occurring bicyclic hydrocarbon obtained from pine oil. Cortisone is a **steroid** that is formed in the outer layer of the adrenal gland and is commonly prescribed as an antiinflammatory drug. Steroids are a major class of tetracyclic lipids and are discussed in Chapter 16.



These are but two examples of the wide variety of compounds that contain more than one ring.

2.19 PHYSICAL PROPERTIES OF ALKANES AND CYCLOALKANES

Boiling Point As we have seen earlier in this chapter, methane, ethane, propane, and butane are gases at room temperature. The unbranched alkanes, pentane (C_5H_{12}) through heptadecane ($C_{17}H_{36}$), are liquids, whereas higher homologs are solids. As shown in Figure 2.11, the boiling points of unbranched alkanes increase with the number of carbon atoms. Figure 2.11 also shows that the boiling points for 2-methyl-branched alkanes are lower than those of the unbranched isomer. This effect of chain branching can be clearly seen by comparing the three C_5H_{12} isomers.



The most instructive way to consider the relation between boiling point and molecular structure is to ask yourself why any substance, pentane, for example, is a liquid rather than a gas. Pentane is a liquid at room temperature and atmospheric pressure because the attractive forces between molecules are greater in the liquid state than in the vapor. These **intermolecular attractive forces** must be overcome to vaporize pentane, or any other substance.

The strength of the intermolecular attractive forces is directly related to the surface area of the molecule. Branched isomers have lower boiling points than their unbranched counterparts because they are more compact and have a smaller surface area. The shapes of these isomers are clearly evident in the space-filling models depicted in Figure 2.12.

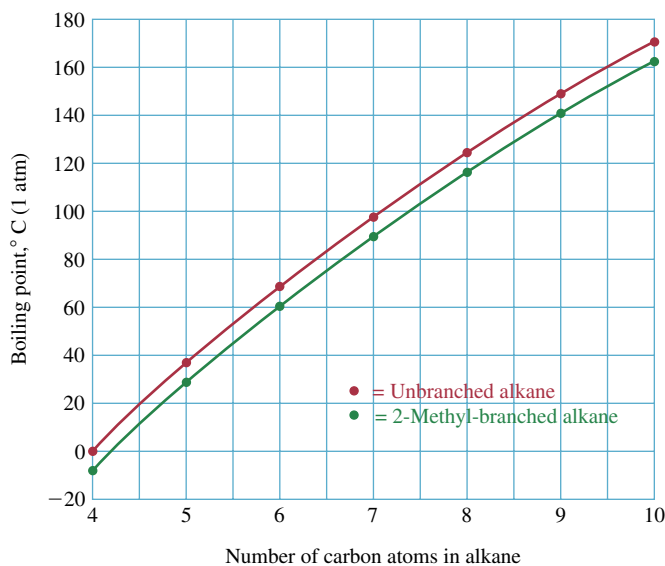


FIGURE 2.11 Boiling points of unbranched alkanes and their 2-methyl-branched isomers.

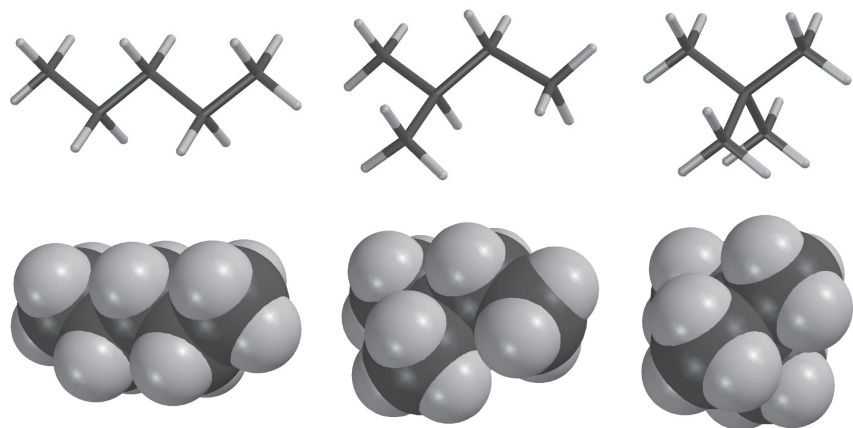
(a) Pentane: $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ (b) 2-Methylbutane:
 $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_3$ (c) 2,2-Dimethylpropane:
 $(\text{CH}_3)_4\text{C}$

FIGURE 2.12 Space-filling models of (a) pentane, (b) 2-methylbutane, and (c) 2,2-dimethylpropane. The most branched isomer, 2,2-dimethylpropane, has the most compact, most spherical, three-dimensional shape.

PROBLEM 2.17 Match the boiling points with the appropriate alkanes.

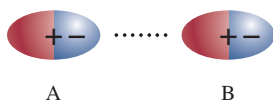
Alkanes: octane, 2-methylheptane, 2,2,3,3-tetramethylbutane

Boiling points ($^{\circ}\text{C}$, 1 atm): 106, 116, 126

Although the boiling point trends noted above clearly indicate the presence of intermolecular forces in alkanes, it might seem that two nearby molecules A and B of a nonpolar substance such as an alkane would be unaffected by each other.



The electron clouds of neighboring molecules “feel” each other’s presence, however, and a temporary distortion of the electron clouds results in an **induced-dipole/induced-dipole** attractive force.



The resulting weak attraction is one example of a **van der Waals force**. Van der Waals forces of the induced-dipole/induced-dipole type are the most important intermolecular forces present in the liquid state of an alkane. We will encounter additional attractive van der Waals forces in the next chapter.

Solubility in Water A familiar physical property of alkanes is contained in the adage “oil and water don’t mix.” Alkanes—indeed all hydrocarbons—are virtually insoluble in water. A more general statement about solubility is “like dissolves like.” That is, polar solutes tend to dissolve in polar solvents, and nonpolar solutes tend to dissolve in nonpolar solvents.

Why is it that nonpolar substances (such as alkanes) are soluble in one another, but not soluble in water? The intermolecular attractive forces in a nonpolar solvent are the same as those in a nonpolar solute: induced-dipole/induced-dipole attractions. Thus hexane, for example, can readily dissolve in decane because the solute–solvent attractions in the solution are comparable to the forces present in each component.

For an alkane to dissolve in water, however, the attractive forces between the alkane and water would have to be strong enough to replace the dipole–dipole attractive forces between water molecules. They are not. Alkanes, being nonpolar, interact only weakly with water molecules. Alkanes are less dense than water, with densities in the 0.6–0.8 g/mL range, and thus float on water as the environmental damage from oil spills demonstrates. The exclusion of nonpolar molecules, such as alkanes, from water is called the **hydrophobic effect**.

2.20 CHEMICAL PROPERTIES: COMBUSTION OF ALKANES

As a group, alkanes are relatively unreactive, but they do burn in air. Their combination with oxygen is called **combustion**. On combustion in air, alkanes are converted to carbon dioxide and water.



The combustion of alkanes is **exothermic**, meaning that it gives off heat, and is a principal source of energy in our society. Natural gas is, as we have noted, predominantly methane accompanied by smaller amounts of ethane, propane, and butane. Petroleum, from the Latin words *petra* (“rock”) and *oleum* (“oil”), is the source of many of the fuels we use every day. The complex mixture of materials present in petroleum (also called **crude oil**) can be separated into simpler mixtures by distillation. The fraction boiling in the range 30–150°C is called **straight-run gasoline** and contains, among other substances, alkanes with 5–10 carbon atoms. Kerosene is the petroleum fraction boiling at 175–325°C; it is principally C₈ through C₁₄ hydrocarbons and is used as diesel fuel. Higher boiling fractions are used as lubricating oils, greases, and asphalt.

Petroleum is much more than a source of gasoline, and refineries do much more than make automobile fuel. Petroleum is far more valuable as a source of **petrochemicals** than as a source of gasoline. Petroleum fractions can be “cracked” to give ethylene and other hydrocarbons, and these compounds lead to a host of products that we use in our everyday lives. We will describe some materials derived from ethylene and other petrochemicals in later chapters.

Straight-run gasoline is not a satisfactory fuel for automobile engines because its “octane rating” is too low. Premature ignition of the fuel gives rise to engine “knock” and robs high-compression engines of their power. A refinery process known as **reforming** is one way of enhancing the octane rating of the gasoline fraction.

LEARNING OBJECTIVES

This chapter used the family of hydrocarbons known as alkanes to introduce the concepts of structure and nomenclature in organic chemistry. The skills you have learned in this chapter should enable you to:

- Recognize the hydrocarbon families, functionally substituted derivatives of alkanes, and classes of compounds containing the carbonyl group.
- Give the IUPAC names of the unbranched alkanes having up to 20 carbon atoms.

Continued

- Given an alkane or cycloalkane, write its IUPAC name.
- Given the IUPAC name for an alkane or cycloalkane, write its structural formula.
- Recognize by common name and structure the alkyl groups that contain up to four carbon atoms.
- Recognize and represent conformations of particular molecules by wedge-and-dash, Newman projection, and sawhorse formulas.
- Draw a chair conformation for a cyclohexane derivative, clearly showing substituent(s) in axial or equatorial orientations as appropriate.
- Know the meaning of the terms *eclipsed conformation*, *staggered conformation*, *anti conformation*, and *gauche conformation*.
- Know the meaning of the terms *angle strain*, *torsional strain*, and *van der Waals strain*.
- Given the chair conformation for a cyclohexane derivative, draw a structural formula for its ring-flipped form.
- Understand the difference between constitutional isomers and stereoisomers.
- Understand how branching affects the boiling point of an alkane.

2.21 SUMMARY

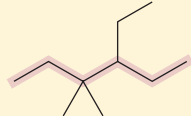
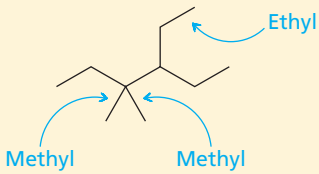
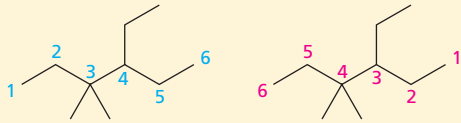
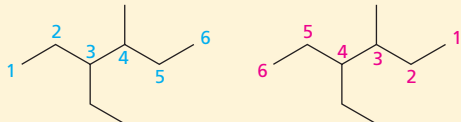
The classes of hydrocarbons are **alkanes**, **alkenes**, **alkynes**, and **arenes** (Section 2.1). Alkanes are hydrocarbons in which all of the bonds are *single* bonds and are characterized by the molecular formula C_nH_{2n+2} .

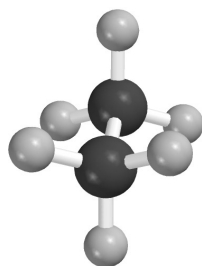
Functional groups are the structural units responsible for the characteristic reactions of a molecule. The functional groups in an alkane are its hydrogens (Section 2.2). Other families of organic compounds, listed in Table 2.1, bear more reactive functional groups, and the hydrocarbon chain to which they are attached can often be viewed as a supporting framework for the reactive function (Section 2.3). Several classes of organic compounds contain the **carbonyl group**, >C=O (Table 2.2).

The simplest alkane is **methane** CH_4 (Section 2.4); **ethane** is C_2H_6 , and **propane** is C_3H_8 . Constitutional isomers are possible for alkanes with four or more carbons (Section 2.6). A single alkane may have different names; a name may be a **common name** or it may be a **systematic name** developed by a well-defined set of rules. The system that is the most widely used in chemistry is **IUPAC nomenclature** (Sections 2.8 to 2.12). According to IUPAC nomenclature, alkanes are named as derivatives of unbranched parents. Substituents on the longest continuous chain are identified and their positions specified by number. The IUPAC rules for naming alkanes are summarized in Table 2.5.

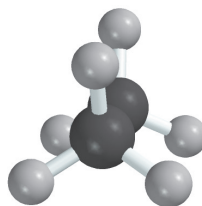
Conformations are different spatial arrangements of a molecule that are generated by rotation about single bonds. The most stable and least stable conformations of ethane are the **staggered** and the **eclipsed**, respectively (Section 2.5)

TABLE 2.5 Summary of IUPAC Nomenclature of Alkanes

Rule	Example
1. Find the longest continuous chain of carbon atoms, and assign a basis name to the compound corresponding to the IUPAC name of the unbranched alkane having the same number of carbons.	<p>The longest continuous chain in the alkane shown is six carbons.</p> 
2. List the substituents attached to the longest continuous chain in alphabetical order. Use the prefixes <i>di-</i> , <i>tri-</i> , <i>tetra-</i> , and so on, when the same substituent appears more than once. Ignore these prefixes when alphabetizing.	<p>This alkane is named as a derivative of hexane.</p> <p>The alkane bears two methyl groups and an ethyl group. It is an ethyldimethylhexane.</p> 
3. Number the chain in the direction that gives the lower locant to a substituent at the first point of difference.	<p>When numbering from left to right, the substituents appear at carbons 3, 3, and 4. When numbering from right to left the locants are 3, 4, and 4; therefore, number from left to right.</p> 
4. When two different numbering schemes give equivalent sets of locants, choose the direction that gives the lower locant to the group that appears first in the name.	<p>The correct name is 4-ethyl-3,3-dimethylhexane.</p> <p>In the following example, the substituents are located at carbons 3 and 4 regardless of the direction in which the chain is numbered.</p>  <p>Ethyl precedes methyl in the name; therefore 3-ethyl-4-methylhexane is correct.</p>



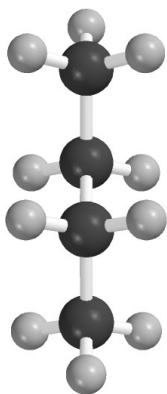
Staggered conformation of ethane
(most stable conformation)



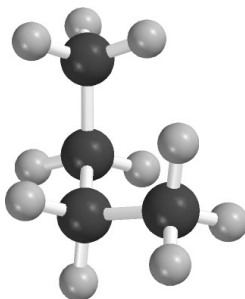
Eclipsed conformation of ethane
(least stable conformation)

Torsional strain is the destabilization that results from the eclipsing of bonds. Staggered conformations are more stable than eclipsed because they have no torsional strain.

The two staggered conformations of butane are not equivalent. The **anti** conformation is more stable than the **gauche** (Section 2.6).



Anti conformation of butane

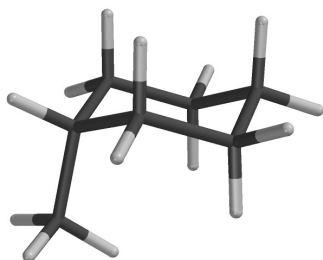


Gauche conformation of butane

Neither staggered conformation incorporates any torsional strain. The gauche conformation is less stable than the anti because of van der Waals strain involving the methyl groups.

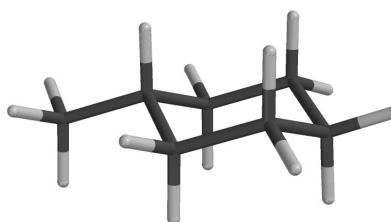
Cyclopropane is planar and strained (angle strain and torsional strain). Cyclobutane is nonplanar and less strained than cyclopropane. Cyclopentane has two nonplanar conformations, one of which is the envelope (Section 2.13).

The chair is by far the most stable conformation for cyclohexane and its derivatives (Sections 2.14 to 2.17). The chair conformation is free of angle strain, torsional strain, and van der Waals strain. The C—H bonds in cyclohexane are not all equivalent but are divided into two sets of six each, called **axial** and **equatorial**. Cyclohexane undergoes a rapid conformational change referred to as **ring inversion**, or **ring flipping**. The process of ring inversion causes all axial bonds to become equatorial, and vice versa.



Methyl group axial (less stable)

ring flipping
←



Methyl group equatorial (more stable)

Substituents on a cyclohexane ring are more stable when they occupy equatorial sites than when they are axial. Branched substituents, especially *tert*-butyl, have a pronounced preference for the equatorial position. The relative stabilities of stereoisomeric disubstituted (and more highly substituted) cyclohexanes can be assessed by analyzing chair conformations for van der Waals strain involving axial substituents.

Alkanes and cycloalkanes are essentially nonpolar. The forces of attraction between molecules are relatively weak van der Waals forces. Because of their smaller surface area (Section 2.19), branched alkanes have lower boiling points than their unbranched isomers. Being nonpolar, alkanes are insoluble in water.

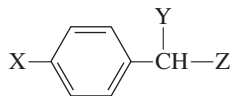
Alkanes and cycloalkanes burn in air to give carbon dioxide, water, and heat. This process is called **combustion** (Section 2.20).

ADDITIONAL PROBLEMS

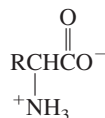
Functional Groups

2.18 The structure of the antiinflammatory drug cortisone is shown in Section 2.18 (page 57). Identify the functional groups present in this substance.

- 2.19** (a) Complete the structure of the pain-relieving drug ibuprofen on the basis of the fact that ibuprofen is a carboxylic acid that has the molecular formula $C_{13}H_{18}O_2$, X is an isobutyl group, and Y is a methyl group.



- (b) Mandelonitrile may be obtained from peach flowers. Derive its structure from the template in part (a) given that X is hydrogen, Y is the functional group that characterizes alcohols, and Z characterizes nitriles.
- 2.20** Isoamyl acetate is the common name of the substance most responsible for the characteristic odor of bananas. Write a structural formula for isoamyl acetate, given the information that it is an ester in which the carbonyl group bears a methyl substituent and there is a 3-methylbutyl group attached to one of the oxygens.
- 2.21** *n*-Butyl mercaptan is the common name of a foul-smelling substance obtained from skunk fluid. It is a thiol of the type RX, where R is an *n*-butyl group and X is the functional group that characterizes a thiol. Write a structural formula for this substance.
- 2.22** Some of the most important organic compounds in biochemistry are the α -amino acids, represented by the general formula shown.



Write structural formulas for the following α -amino acids.

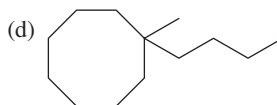
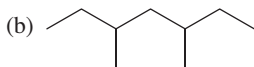
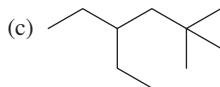
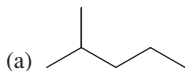
- Alanine (R = methyl)
- Valine (R = isopropyl)
- Leucine (R = isobutyl)
- Isoleucine (R = *sec*-butyl)
- Serine (R = XCH_2 , where X is the functional group that characterizes alcohols)
- Cysteine (R = XCH_2 , where X is the functional group that characterizes thiols)
- Aspartic acid (R = XCH_2 , where X is the functional group that characterizes carboxylic acids)

Structure and Nomenclature

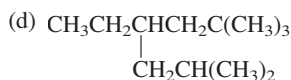
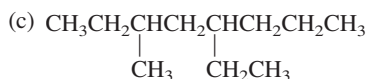
2.23 Write the structures and give the IUPAC names for all the alkanes of molecular formula C_7H_{16} that:

- Are named as methyl-substituted derivatives of hexane.
- Are named as dimethyl derivatives of pentane.
- Are named as ethyl-substituted derivatives of pentane.

2.24 Give the molecular formula and the IUPAC name for each of the following compounds:



2.25 Rewrite the following condensed structural formulas as carbon-skeleton (bond-line) formulas and give the IUPAC name for each one.



2.26 Write a structural formula for each of the following compounds:

- 3-Ethyloctane
- 6-Isopropyl-2,3-dimethylnonane
- 4-*tert*-Butyl-3-methylheptane
- 4-Isobutyl-1,1-dimethylcyclohexane
- sec*-Butylcycloheptane
- Cyclobutylcyclopentane

2.27 Which of the compounds in each of the following groups are isomers?

- Butane, cyclobutane, isobutane, 2-methylbutane
- Cyclohexane, hexane, methylcyclopentane, 1,1,2-trimethylcyclopropane
- Ethylcyclopropane, 1,1-dimethylcyclopropane, 1-cyclopropylpropane, cyclopentane
- 4-Methyltetradecane, 2,3,4,5-tetramethyldecane, pentadecane, 4-cyclobutyldecane

2.28 Write the structural formula of a compound of molecular formula $C_4H_8Cl_2$ in which

- All the carbons belong to methylene groups
- None of the carbons belong to methylene groups

2.29 Female tiger moths signify their presence to male moths by giving off a sex attractant. The sex attractant (pheromone) has been isolated and found to be a 2-methyl-branched alkane having a molecular weight of 254. What is this material?

2.30 How many σ bonds are in pentane? In cyclopentane?

2.31 Hectane is the IUPAC name for the unbranched alkane which contains 100 carbon atoms.

- What is the molecular formula of hectane?
- Write the condensed molecular formula for hectane in the form $CH_3(CH_2)_nCH_3$.
- How many σ bonds are in hectane?
- How many alkanes have names of the type X-methylhectane? (Examples include 2-methylhectane, 3-methylhectane, etc.)
- How many alkanes have names of the type 2,X-dimethylhectane?

Conformations of Alkanes and Cycloalkanes

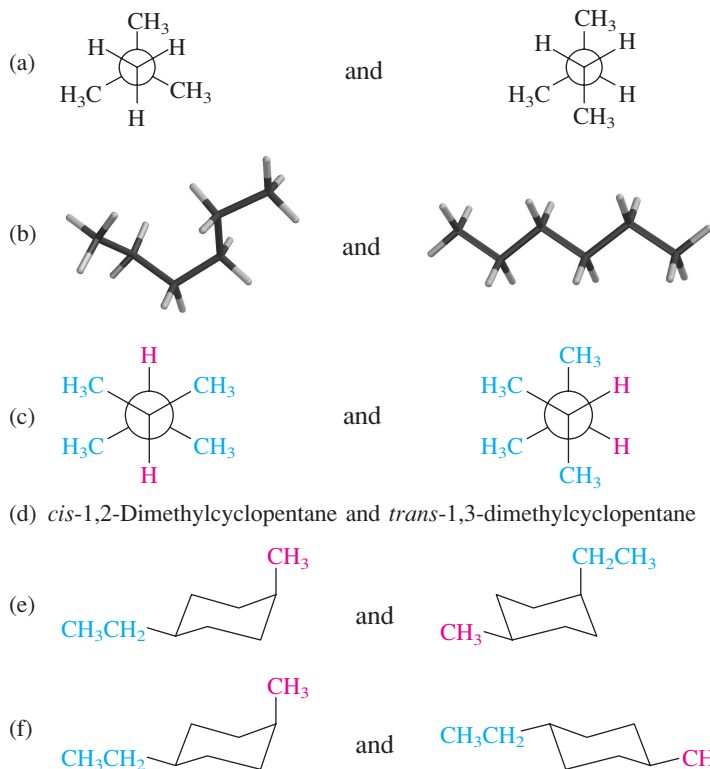
2.32 Which has more torsional strain, cyclopropane or the planar conformation of cyclopentane? Which has more angle strain?

2.33 Draw a Newman projection formula (looking down the C-1—C-2 bond) for the most stable conformation of 2,2-dimethylpropane.

2.34 Write Newman projection formulas for two different staggered conformations of 2,3-dimethylbutane (as viewed down the C-2—C-3 bond).

2.35 Draw Newman projection formulas for the three most stable conformations of 2-methylbutane (as viewed down the C-2—C-3 bond). One of these conformations is less stable than the other two. Which one? Why?

2.36 Determine whether the two structures in each of the following pairs represent **constitutional isomers**, different **conformations** of the same compound, or **stereoisomers** that cannot be interconverted by rotation about single bonds.

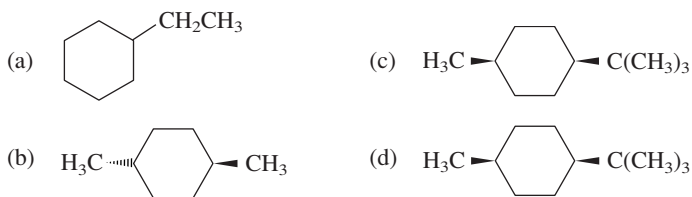
**Cyclohexane Conformations and Stereochemistry**

2.37 Draw a clear conformational depiction of the most stable conformation of:

- (a) 1,1,3-Trimethylcyclohexane (b) 1,1,4-Trimethylcyclohexane

2.38 Draw chair conformations of 1,1,3-trimethylcyclohexane and 1,1,4-trimethylcyclohexane that are less stable than those in Problem 2.37.

2.39 Draw both possible chair conformations for each of the following compounds, clearly showing the orientation of each substituent (axial or equatorial). Indicate which conformation is the more stable one.



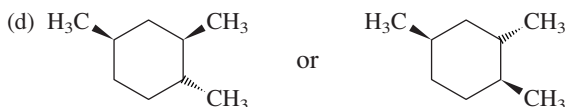
- 2.40** (a) Which stereoisomer of 1,3-dimethylcyclohexane exists in two equivalent chair conformations?
 (b) Draw the chair conformation of this stereoisomer.
 (c) Draw the 1,3-dimethylcyclohexane stereoisomer that has two nonequivalent chair conformations, and specify which conformation is more stable.

2.41 Write a structural formula for the most stable conformation of each of the following compounds:

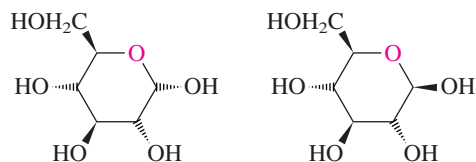
- (a) *cis*-1-Isopropyl-3-methylcyclohexane
 (b) *trans*-1-Isopropyl-3-methylcyclohexane
 (c) *cis*-1-*tert*-Butyl-4-ethylcyclohexane

2.42 Identify the more stable stereoisomer in each of the following pairs, and give the reason for your choice:

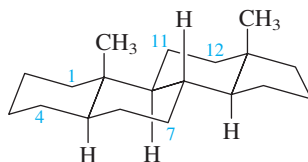
- (a) *cis*- or *trans*-1-Isopropyl-2-methylcyclohexane
 (b) *cis*- or *trans*-1-Isopropyl-3-methylcyclohexane
 (c) *cis*- or *trans*-1-Isopropyl-4-methylcyclohexane



2.43 The following are representations of two forms of glucose. The six-membered ring is known to exist in a chair conformation in each form. Draw clear representations of the most stable conformation of each. Are they two different conformations of the same molecule, or are they stereoisomers? Which substituents (if any) occupy axial sites?



2.44 A typical steroid skeleton is shown along with the numbering scheme used for this class of compounds. Specify in each case whether the designated substituent is axial or equatorial.



- (a) Substituent at C-1 *cis* to the methyl groups
 (b) Substituent at C-4 *cis* to the methyl groups
 (c) Substituent at C-7 *trans* to the methyl groups
 (d) Substituent at C-11 *trans* to the methyl groups
 (e) Substituent at C-12 *cis* to the methyl groups