Chapter Outline

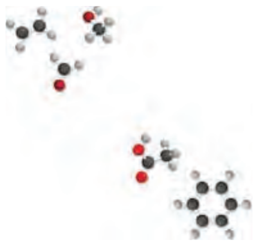
A Look Ahead

- We begin by defining the scope and nature of organic chemistry. (24.1)
- Next, we examine aliphatic hydrocarbons. First we study the nomenclature and reactions of alkanes. We examine the optical isomerism of substituted alkanes and also the properties of cycloalkanes. We then study unsaturated hydrocarbons, molecules that contain carbon-to-carbon double bonds and triple bonds. We focus on their nomenclature, properties, and geometric isomers. (24.2)
- Aromatic compounds all contain one or more benzene rings. They are in general more stable than aliphatic hydrocarbons. (24.3)
- Finally, we see that the reactivity of organic compounds can be largely accounted for by the presence of functional groups. We classify the oxygen- and nitrogen-containing functional groups in alcohols, ethers, aldehydes and ketones, carboxylic acids, esters, and amines. (24.4)

Organic chemistry is the study of carbon compounds. The word "organic" was originally used by eighteenth-century chemists to describe substances obtained from living sources—plants and animals. These chemists believed that nature possessed a certain vital force and that only living things could produce organic compounds. This romantic notion was disproved in 1828 by Friedrich Wohler, a German chemist who prepared urea, an organic compound, from the reaction between inorganic compounds lead cyanate and aqueous ammonia:

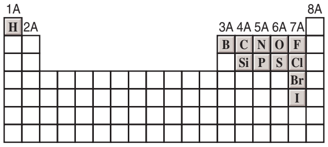
$$Pb(OCN)_2 + 2NH_3 + 2H_2O \longrightarrow \underset{\text{urea}}{2(NH_2)_2CO} + Pb(OH)_2$$

Today, well over 20 million synthetic and natural organic compounds are known. This number is significantly greater than the 100,000 or so known inorganic compounds.



24.1 Classes of Organic Compounds

Recall that the linking of like atoms is called catenation. The ability of carbon to catenate is discussed in Section 21.3.



Common elements in organic compounds.

Carbon can form more compounds than any other element because carbon atoms are able not only to form single, double, and triple carbon-carbon bonds, but also to link up with each other in chains and ring structures. *The branch of chemistry that deals with carbon compounds* is ***organic chemistry.***

Classes of organic compounds can be distinguished according to functional groups they contain. A ***functional group*** is *a group of atoms that is largely responsible for the chemical behavior of the parent molecule*. Different molecules containing the same kind of functional group or groups undergo similar reactions. Thus, by learning the characteristic properties of a few functional groups, we can study and understand the properties of many organic compounds. In the second half of this chapter, we will discuss the functional groups known as alcohols, ethers, aldehydes and ketones, carboxylic acids, and amines.

Note that the octet rule is satisfied for all hydrocarbons.

Most organic compounds are derived from a group of compounds known as ***hydrocarbons*** because they are *made up of only hydrogen and carbon*. On the basis of structure, hydrocarbons are divided into two main classes—aliphatic and aromatic. ***Aliphatic hydrocarbons*** *do not contain the benzene group, or the benzene ring,* whereas ***aromatic hydrocarbons*** *contain one or more benzene rings*.

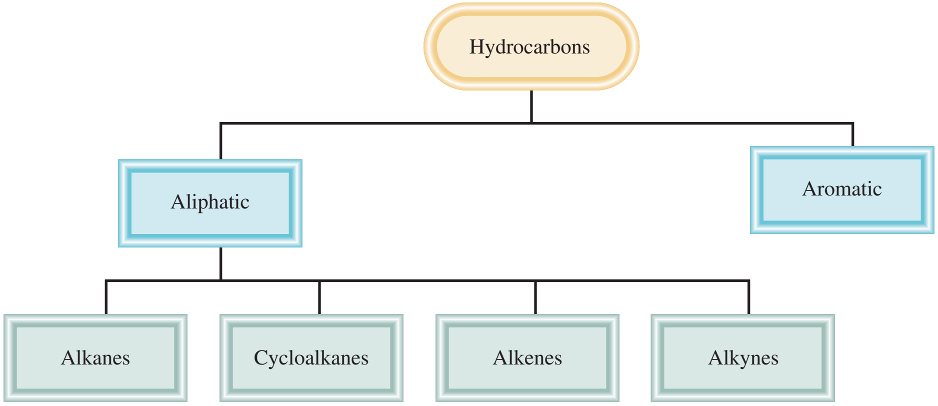
24.2 Aliphatic Hydrocarbons

Aliphatic hydrocarbons are divided into alkanes, alkenes, and alkynes, discussed next (Figure 24.1).

Alkanes

Alkanes *have the general formula* C_nH_{2n+2}, *where* $n = 1, 2, \ldots$. The essential characteristic of alkane hydrocarbon molecules is that *only single covalent bonds are present*. The alkanes are known as ***saturated hydrocarbons*** because they *contain the maximum number of hydrogen atoms that can bond with the number of carbon atoms present*.

The simplest alkane (that is, with $n = 1$) is methane CH_4, which is a natural product of the anaerobic bacterial decomposition of vegetable matter under water. Because it was first collected in marshes, methane became known as "marsh gas." A rather improbable but proven source of methane is termites. When these voracious insects consume wood, the microorganisms that inhabit their digestive system break down cellulose (the major component of wood) into methane, carbon dioxide, and other compounds. An estimated 170 million tons of methane are produced annually by termites! It is also produced in some sewage treatment processes. Commercially,



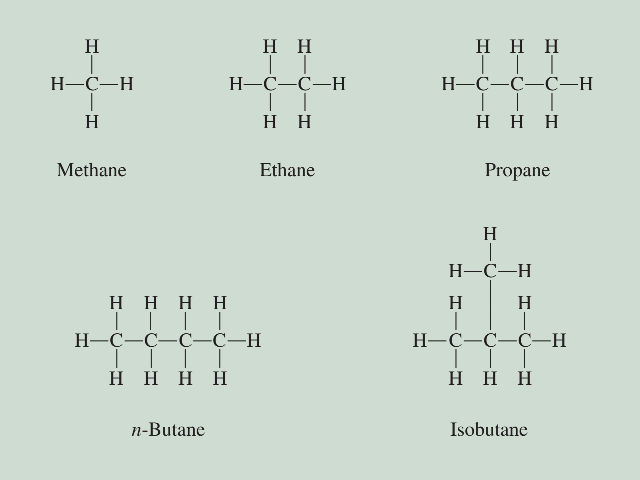


Figure 24.2 *Structures of the first four alkanes. Note that butane can exist in two structurally different forms, called structural isomers.*

methane is obtained from natural gas.

Figure 24.2 shows the structures of the first four alkanes ($n = 1$ to $n = 4$).

Natural gas is a mixture of methane, ethane, and a small amount of propane.

We discussed the bonding scheme of methane in Chapter 10. Indeed, the carbon atoms in all the **alkanes can be assumed to be *sp*^{3}-hybridized.** The structures of ethane and propane are straight-forward, for there is only one way to join the carbon atoms in these molecules. Butane, however, has two possible bonding schemes resulting in the ***structural isomers*** *n*-butane (*n* stands for normal) and isobutane, *molecules that have the same molecular formula, but different structures*. Alkanes such as the structural isomers of butane are described as having the straight chain or branched chain structures. *n*-Butane is a straight-chain alkane because the carbon atoms are joined along one line. In a branched-chain alkane like isobutane, one or more carbon atoms are bonded to at least three other carbon atoms.

In the alkane series, as the number of carbon atoms increases, the number of structural isomers increases rapidly. For example, butane, C_4H_{10}, has two isomers; decane, $C_{10}H_{22}$, has 75 isomers; and the alkane $C_{30}H_{62}$ has over 400 million, or 4×10^8, possible isomers! Obviously, most of these isomers do not exist in nature nor have they been synthesized. Nevertheless, the numbers help to explain why carbon is found in so many more compounds than any other element.

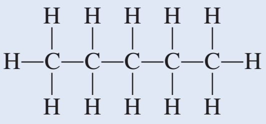
Example 24.1 deals with the number of structural isomers of an alkane.

EXAMPLE 24.1

How many structural isomers can be identified for pentane, C_5H_{12}?

Strategy For small hydrocarbon molecules (eight or fewer C atoms), it is relatively easy to determine the number of structural isomers by trial and error.

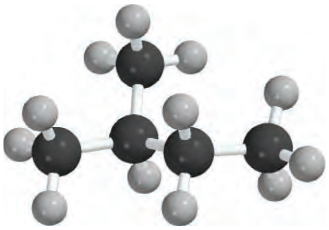
Solution The first step is to write the straight-chain structure:



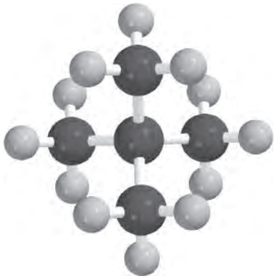
n-pentane
(b.p. 36.1°C)

(Continued)

n-pentane



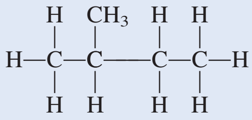
2-methylbutane



2,2-dimethylpropane

Similar problem: 24.11.

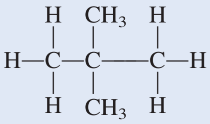
The second structure, by necessity, must be a branched chain:



$$\begin{array}{ccccccccccc}
 & & H & & CH_3 & & H & & H & & \\
 & & | & & | & & | & & | & & \\
H & - & C & - & C & - & C & - & C & - & H \\
 & & | & & | & & | & & | & & \\
 & & H & & H & & H & & H & &
\end{array}$$

2-methylbutane
(b.p. 27.9°C)

Yet another branched-chain structure is possible:



$$\begin{array}{ccccccccc}
 & & H & & CH_3 & & H & & \\
 & & | & & | & & | & & \\
H & - & C & - & C & - & C & - & H \\
 & & | & & | & & | & & \\
 & & H & & CH_3 & & H & &
\end{array}$$

2,2-dimethylpropane
(b.p. 9.5°C)

We can draw no other structure for an alkane having the molecular formula C_5H_{12}. Thus, pentane has three structural isomers, in which the numbers of carbon and hydrogen atoms remain unchanged despite the differences in structure.

Table 24.1 shows the melting and boiling points of the straight-chain isomers of the first 10 alkanes. The first four are gases at room temperature; and pentane through decane are liquids. **As molecular size increases, so does the boiling point, because of the increasing dispersion forces** .

Alkane Nomenclature

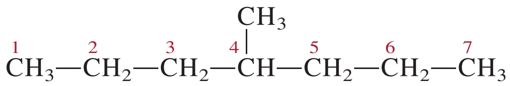
The nomenclature of alkanes and all other organic compounds is based on the rec-ommendations of the International Union of Pure and Applied Chemistry (IUPAC). The first four alkanes (methane, ethane, propane, and butane) have nonsystematic names. As Table 24.1 shows, the number of carbon atoms is reflected in the Greek

TABLE 24.1 **The First 10 Straight-Chain Alkanes**

Name of Hydrocarbon	Molecular Formula	Number of Carbon Atoms	Melting Point (°C)	Boiling Point (°C)
Methane	CH_4	1	−182.5	−161.6
Ethane	CH_3-CH_3	2	−183.3	−88.6
Propane	$CH_3-CH_2-CH_3$	3	−189.7	−42.1
Butane	$CH_3-(CH_2)_2-CH_3$	4	−138.3	−0.5
Pentane	$CH_3-(CH_2)_3-CH_3$	5	−129.8	36.1
Hexane	$CH_3-(CH_2)_4-CH_3$	6	−95.3	68.7
Heptane	$CH_3-(CH_2)_5-CH_3$	7	−90.6	98.4
Octane	$CH_3-(CH_2)_6-CH_3$	8	−56.8	125.7
Nonane	$CH_3-(CH_2)_7-CH_3$	9	−53.5	150.8
Decane	$CH_3-(CH_2)_8-CH_3$	10	−29.7	174.0

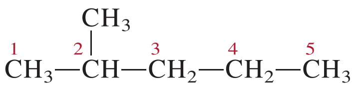
prefixes for the alkanes containing five to ten carbons. We now apply the IUPAC rules to the following examples:

1. The parent name of the hydrocarbon is that given to the longest continuous chain of carbon atoms in the molecule. Thus, the parent name of the following compound is heptane because there are seven carbon atoms in the longest chain



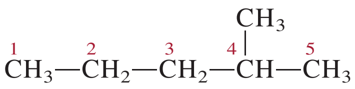
$$\overset{1}{CH_3}-\overset{2}{CH_2}-\overset{3}{CH_2}-\overset{4}{\overset{\overset{CH_3}{|}}{CH}}-\overset{5}{CH_2}-\overset{6}{CH_2}-\overset{7}{CH_3}$$

2. An alkane less one hydrogen atom is an *alkyl* group. For example, when a hydrogen atom is removed from methane, we are left with the CH_3 fragment, which is called a *methyl* group. Similarly, removing a hydrogen atom from the ethane molecule gives an *ethyl* group, or C_2H_5. Table 24.2 lists the names of several common alkyl groups. Any chain branching off the longest chain is named as an alkyl group.
3. When one or more hydrogen atoms are replaced by other groups, the name of the compound must indicate the locations of carbon atoms where replacements are made. The procedure is to number each carbon atom on the longest chain in the direction that gives the smaller numbers for the locations of all branches. Consider the two different systems for the *same* compound shown here:



$$\overset{1}{CH_3}-\overset{2}{\overset{\overset{CH_3}{|}}{CH}}-\overset{3}{CH_2}-\overset{4}{CH_2}-\overset{5}{CH_3}$$

2-methylpentane

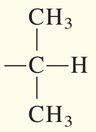
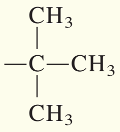


$$\overset{1}{CH_3}-\overset{2}{CH_2}-\overset{3}{CH_2}-\overset{4}{\overset{\overset{CH_3}{|}}{CH}}-\overset{5}{CH_3}$$

4-methylpentane

The compound on the left is numbered correctly because the methyl group is located at carbon 2 of the pentane chain; in the compound on the right, the methyl group is located at carbon 4. Thus, the name of the compound is 2-methylpentane, and not 4-methylpentane. Note that the branch name and the parent name are written as a single word, and a hyphen follows the number.

TABLE 24.2 Common Alkyl Groups

Name	Formula
Methyl	$-CH_3$
Ethyl	$-CH_2-CH_3$
n-Propyl	$-CH_2-CH_2-CH_3$
n-Butyl	$-CH_2-CH_2-CH_2-CH_3$
Isopropyl	 $-\underset{\underset{CH_3}{\mid}}{\overset{\overset{CH_3}{\mid}}{C}}-H$
t-Butyl*	 $-\underset{\underset{CH_3}{\mid}}{\overset{\overset{CH_3}{\mid}}{C}}-CH_3$

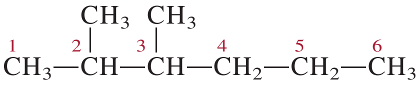
*The letter *t* stands for tertiary.

TABLE 24.3

Names of Common Substituent Groups

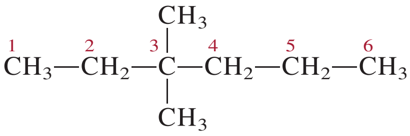
Functional Group	Name
$-NH_2$	Amino
$-F$	Fluoro
$-Cl$	Chloro
$-Br$	Bromo
$-I$	Iodo
$-NO_2$	Nitro
$-CH{=}CH_2$	Vinyl

4. When there is more than one alkyl branch of the same kind present, we use a prefix such as *di-, tri-,* or *tetra-* with the name of the alkyl group. Consider the following examples:



$$\overset{1}{\mathrm{CH_3}}-\overset{\substack{\mathrm{CH_3}\\|\\2}}{\mathrm{CH}}-\overset{\substack{\mathrm{CH_3}\\|\\3}}{\mathrm{CH}}-\overset{4}{\mathrm{CH_2}}-\overset{5}{\mathrm{CH_2}}-\overset{6}{\mathrm{CH_3}}$$

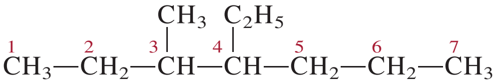
2,3-dimethylhexane



$$\overset{1}{\mathrm{CH_3}}-\overset{2}{\mathrm{CH_2}}-\underset{\substack{|\\\mathrm{CH_3}}}{\overset{\substack{\mathrm{CH_3}\\|\\3}}{\mathrm{C}}}-\overset{4}{\mathrm{CH_2}}-\overset{5}{\mathrm{CH_2}}-\overset{6}{\mathrm{CH_3}}$$

3,3-dimethylhexane

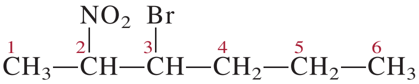
When there are two or more different alkyl groups, the names of the groups are listed alphabetically. For example,



$$\overset{1}{\mathrm{CH_3}}-\overset{2}{\mathrm{CH_2}}-\overset{\substack{\mathrm{CH_3}\\|\\3}}{\mathrm{CH}}-\overset{\substack{\mathrm{C_2H_5}\\|\\4}}{\mathrm{CH}}-\overset{5}{\mathrm{CH_2}}-\overset{6}{\mathrm{CH_2}}-\overset{7}{\mathrm{CH_3}}$$

4-ethyl-3-methylheptane

5. Of course, alkanes can have many different types of substituents. Table 24.3 lists the names of some substituents, including nitro and bromo. Thus, the compound

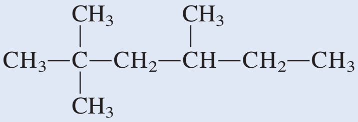


$$\overset{1}{\mathrm{CH_3}}-\overset{\substack{\mathrm{NO_2}\\|\\2}}{\mathrm{CH}}-\overset{\substack{\mathrm{Br}\\|\\3}}{\mathrm{CH}}-\overset{4}{\mathrm{CH_2}}-\overset{5}{\mathrm{CH_2}}-\overset{6}{\mathrm{CH_3}}$$

is called 3-bromo-2-nitrohexane. Note that the substituent groups are listed alphabetically in the name, and the chain is numbered in the direction that gives the lowest number to the first substituted carbon atom.

EXAMPLE 24.2

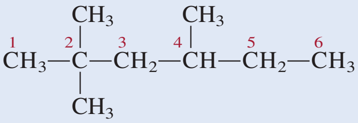
Give the IUPAC name of the following compound:



$$\mathrm{CH_3}-\underset{\substack{|\\\mathrm{CH_3}}}{\overset{\substack{\mathrm{CH_3}\\|}}{\mathrm{C}}}-\mathrm{CH_2}-\overset{\substack{\mathrm{CH_3}\\|}}{\mathrm{CH}}-\mathrm{CH_2}-\mathrm{CH_3}$$

Strategy We follow the IUPAC rules and use the information in Table 24.2 to name the compound. How many C atoms are there in the longest chain?

Solution The longest chain has six C atoms so the parent compound is called hexane. Note that there are two methyl groups attached to carbon number 2 and one methyl group attached to carbon number 4.



$$\overset{1}{\mathrm{CH_3}}-\underset{\substack{|\\\mathrm{CH_3}}}{\overset{\substack{\mathrm{CH_3}\\|\\2}}{\mathrm{C}}}-\overset{3}{\mathrm{CH_2}}-\overset{\substack{\mathrm{CH_3}\\|\\4}}{\mathrm{CH}}-\overset{5}{\mathrm{CH_2}}-\overset{6}{\mathrm{CH_3}}$$

Therefore, we call the compound 2,2,4-trimethylhexane.

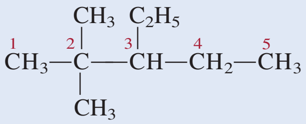
Example 24.3 shows that prefixes such as di-, tri-, and tetra- are used as needed, but are ignored when alphabetizing.

EXAMPLE 24.3

Write the structural formula of 3-ethyl-2,2-dimethylpentane.

Strategy We follow the preceding procedure and the information in Table 24.2 to write the structural formula of the compound. How many C atoms are there in the longest chain?

Solution The parent compound is pentane, so the longest chain has five C atoms. There are two methyl groups attached to carbon number 2 and one ethyl group attached to carbon number 3. Therefore, the structure of the compound is



$$\overset{1}{\mathrm{CH_3}}-\underset{\mathrm{CH_3}}{\overset{\overset{\mathrm{CH_3}}{|}\;2}{\mathrm{C}}}-\overset{\overset{\mathrm{C_2H_5}}{|}\;3}{\mathrm{CH}}-\overset{4}{\mathrm{CH_2}}-\overset{5}{\mathrm{CH_3}}$$

Reactions of Alkanes

Alkanes are generally not considered to be very reactive substances. However, under suitable conditions they do react. For example, natural gas, gasoline, and fuel oil are alkanes that undergo highly exothermic combustion reactions:

$$\mathrm{CH_4}(g) + 2\mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g) + 2\mathrm{H_2O}(l) \qquad \Delta H^\circ = -890.4\ \mathrm{kJ/mol}$$
$$2\mathrm{C_2H_6}(g) + 7\mathrm{O_2}(g) \longrightarrow 4\mathrm{CO_2}(g) + 6\mathrm{H_2O}(l) \qquad \Delta H^\circ = -3119\ \mathrm{kJ/mol}$$

These, and similar combustion reactions, have long been utilized in industrial processes and in domestic heating and cooking.

Halogenation of alkanes—that is, the replacement of one or more hydrogen atoms by halogen atoms—is another type of reaction that alkanes undergo. When a mixture of methane and chlorine is heated above 100°C or irradiated with light of a suitable wavelength, methyl chloride is produced:

$$\mathrm{CH_4}(g) + \mathrm{Cl_2}(g) \longrightarrow \underset{\text{methyl chloride}}{\mathrm{CH_3Cl}(g)} + \mathrm{HCl}(g)$$

Cycloalkanes

Alkanes whose carbon atoms are joined in rings are known as ***cycloalkanes.*** They have the general formula C_nH_{2n}, where $n = 3, 4, \ldots$. The simplest cycloalkane is cyclopropane, C_3H_6 (Figure 24.4). Many biologically significant substances such as cholesterol, testosterone, and progesterone contain one or more such ring systems. Theoretical analysis shows that cyclohexane can assume two different geometries that are relatively free of strain (Figure 24.5). By "strain" we mean that bonds are compressed, stretched, or twisted out of normal geometric shapes as predicted by sp^3 hybridization. The most stable geometry is the *chair form.*

Alkenes

The ***alkenes*** (also called *olefins*) *contain at least one carbon-carbon double bond. Alkenes have the general formula C_nH_{2n}, where $n = 2, 3, \ldots$.* The simplest alkene

Figure 24.4 *Structures of the first four cycloalkanes and their simplified forms.*

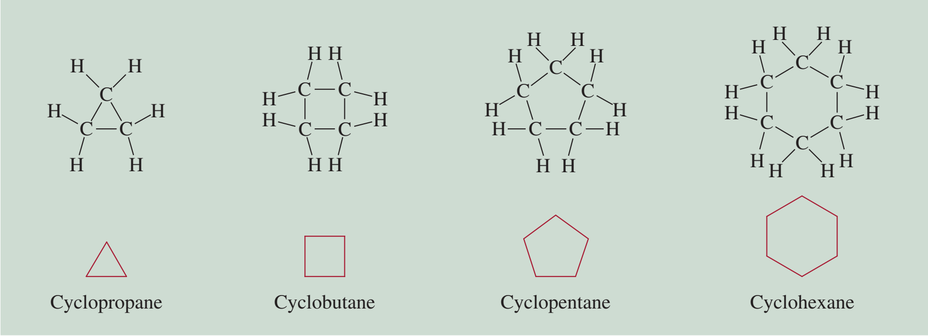
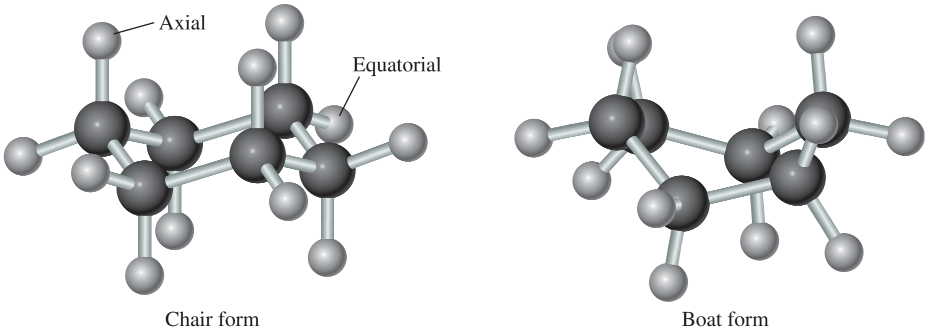


Figure 24.5 *The cyclohexane molecule can exist in various shapes. The most stable shape is the chair form and a less stable one is the boat form. Two types of H atoms are labeled axial and equatorial, respectively.*



is C_2H_4, ethylene, in which both carbon atoms are *sp*^{2}-hybridized and the double bond is made up of a sigma bond and a pi bond (see Section 10.5).

Alkene Nomenclature

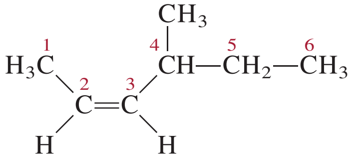
In naming alkenes we indicate the positions of the carbon-carbon double bonds. The names of compounds containing C═C bonds end with *-ene*. As with the alkanes, the name of the parent compound is determined by the number of carbon atoms in the longest chain (see Table 24.1), as shown here:

$$CH_2{=}CH{-}CH_2{-}CH_3 \qquad H_3C{-}CH{=}CH{-}CH_3$$

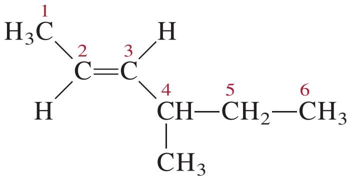
1-butene 2-butene

The numbers in the names of alkenes refer to the lowest numbered carbon atom in the chain that is part of the C═C bond of the alkene. The name "butene" means that there are four carbon atoms in the longest chain. Alkene nomenclature must specify whether a given molecule is *cis* or *trans* if it is a geometric isomer, such as

In the *cis* isomer, the two H atoms are on the same side of the C═C bond; in the *trans* isomer, the two H atoms are across from each other. Geometric isomerism was introduced in Section 22.4.



4-methyl-*cis*-2-hexene



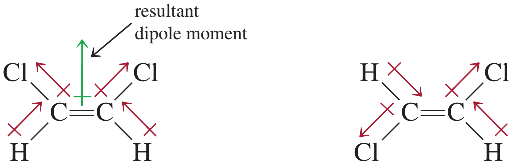
4-methyl-*trans*-2-hexene

Geometric Isomers of Alkenes

In a compound such as ethane, C_2H_6, the rotation of the two methyl groups about the carbon-carbon single bond (which is a sigma bond) is quite free. The situation is different for molecules that contain carbon-carbon double bonds, such as ethylene, C_2H_4. In addition to the sigma bond, there is a pi bond between the two carbon atoms. Rotation about the carbon-carbon linkage does not affect the sigma bond, but it does move the two $2p_z$ orbitals out of alignment for overlap and, hence, par-tially or totally destroys the pi bond (see Figure 10.16). This process requires an input of energy on the order of 270 kJ/mol. For this reason, the rotation of a carbon-carbon double bond is considerably restricted, but not impossible. Consequently, molecules containing carbon-carbon double bonds (that is, the alkenes) may have geometric isomers, which cannot be interconverted without breaking a chemical bond.

[†] Vladimir W. Markovnikov (1838–1904). Russian chemist. Markovnikov's observations of the addition reactions to alkenes were published a year after his death.

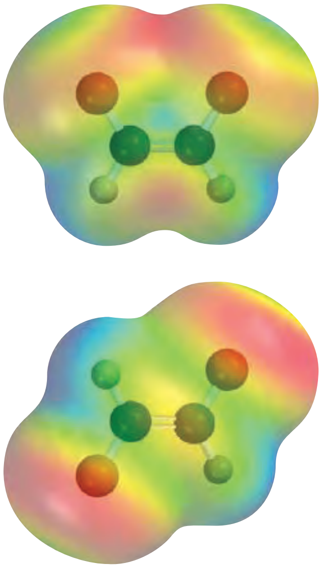
The molecule dichloroethylene, ClHC═CHCl, can exist as one of the two geometric isomers called *cis*-dichloroethylene and *trans*-dichloroethylene:



cis-dichloroethylene
$\mu = 1.89$ D
b.p. 60.3°C

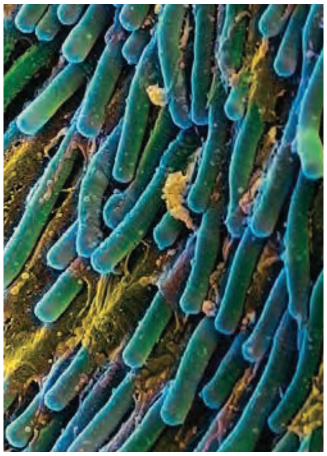
trans-dichloroethylene
$\mu = 0$
b.p. 47.5°C

where the term *cis* means that two particular atoms (or groups of atoms) are adjacent to each other, and *trans* means that the two atoms (or groups of atoms) are across from each other. Generally, *cis* and *trans* isomers have distinctly different physical and chemical properties. Heat or irradiation with light is commonly used to bring about the conversion of one geometric isomer to another, a process called *cis-trans isomerization,* or geometric isomerization. As the above data show, dipole moment measurements can be used to distinguish between geometric isomers. In general, *cis* isomers possess a dipole moment, whereas *trans* isomers do not.



In *cis*-dichloroethylene (top), the bond moments reinforce one another and the molecule is polar. The opposite holds for *trans*-dichloroethylene and the molecule is nonpolar.

***Cis-Trans* Isomerization in the Vision Process.** The molecules in the retina that respond to light are rhodopsin, which has two components called 11-*cis* retinal and opsin (Figure 24.6). Retinal is the light-sensitive component and opsin is a protein molecule. Upon receiving a photon in the visible region the 11-*cis* retinal isomerizes to the all-*trans* retinal by breaking a carbon-carbon pi bond. With the pi bond broken, the remaining carbon-carbon sigma bond is free to rotate and transforms into the all-*trans* retinal. At this point an electrical impulse is generated and transmitted to the brain, which forms a visual image. The all-*trans* retinal does not fit into the binding site on opsin and eventually separates from the protein. In time, the *trans* isomer is converted back to 11-*cis* retinal by an enzyme (in the absence of light) and rhodopsin is regenerated by the binding of the *cis* isomer to opsin and the visual cycle can begin again.



An electron micrograph of rod-shaped cells (containing rhodopsins) in the retina.

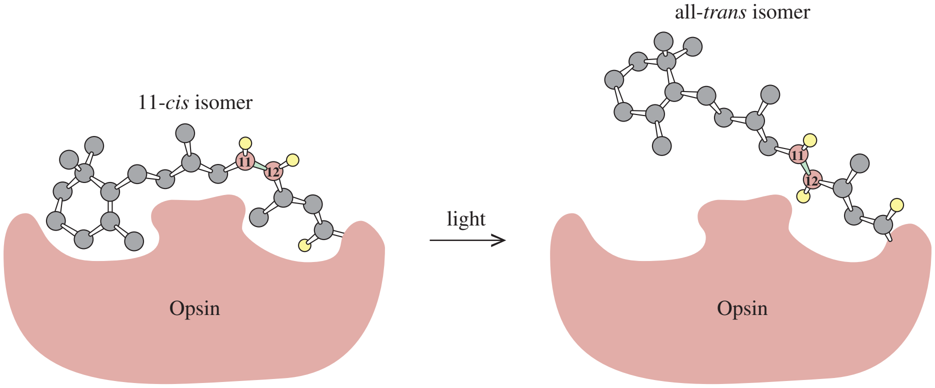


Figure 24.6 *The primary event in the vision process is the conversion of 11-cis retinal to the all-trans isomer on rhodopsin. The double bond at which the isomerization occurs is between carbon-11 and carbon-12. For simplicity, most of the H atoms are omitted. In the absence of light, this transformation takes place about once in a thousand years!*

Alkynes

***Alkynes** contain at least one carbon-carbon triple bond*. They have the *general formula* C_nH_{2n-2}, *where* $n = 2, 3, \ldots$.

Alkyne Nomenclature

Names of compounds containing $C{\equiv}C$ bonds end with *-yne*. Again, the name of the parent compound is determined by the number of carbon atoms in the longest chain (see Table 24.1 for names of alkane counterparts). As in the case of alkenes, the names of alkynes indicate the position of the carbon-carbon triple bond, as, for example, in

$$\underset{\text{1-butyne}}{HC{\equiv}C{-}CH_2{-}CH_3} \qquad \underset{\text{2-butyne}}{H_3C{-}C{\equiv}C{-}CH_3}$$

Properties and Reactions of Alkynes

The simplest alkyne is ethyne, better known as acetylene (C_2H_2). The structure and bonding of C_2H_2 were discussed in Section 10.5. Acetylene is a colorless gas (b.p. −84°C) prepared by the reaction between calcium carbide and water:

$$CaC_2(s) + 2H_2O(l) \longrightarrow C_2H_2(g) + Ca(OH)_2(aq)$$

Acetylene has many important uses in industry. Because of its high heat of combustion

$$2C_2H_2(g) + 5O_2(g) \longrightarrow 4CO_2(g) + 2H_2O(l) \qquad \Delta H^\circ = -2599.2\ \text{kJ/mol}$$

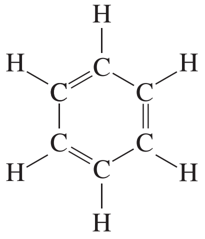
acetylene burned in an "oxyacetylene torch" gives an extremely hot flame (about 3000°C). Thus, oxyacetylene torches are used to weld metals (see p. 256).

f

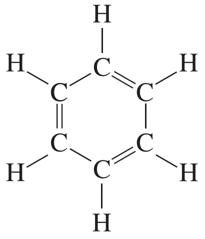

The reaction of calcium carbide with water produces acetylene, a flammable gas.

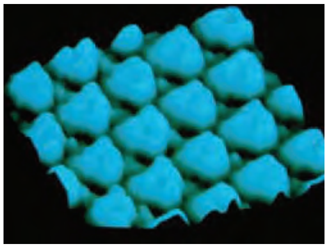
24.3 Aromatic Hydrocarbons

Benzene, the parent compound of this large family of organic substances, was discovered by Michael Faraday in 1826. Over the next 40 years, chemists were preoccupied with determining its molecular structure. Despite the small number of atoms in the molecule, there are quite a few ways to represent the structure of benzene without violating the tetravalency of carbon. However, most proposed structures were rejected because they did not explain the known properties of benzene. Finally, in 1865, August Kekulé[†] deduced that the benzene molecule could be best represented by a ring structure—a cyclic compound consisting of six carbon atoms:



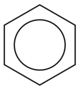
or





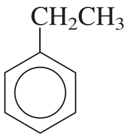
An electron micrograph of benzene molecule, which shows clearly the ring structure.

As we saw in Section 9.8, the properties of benzene are best represented by both of the above resonance structures. Alternatively, the properties of benzene can be explained in terms of delocalized molecular orbitals (see p. 448):

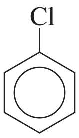


Nomenclature of Aromatic Compounds

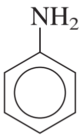
The naming of monosubstituted benzenes, that is, benzenes in which one H atom has been replaced by another atom or a group of atoms, is quite straightforward, as shown here:



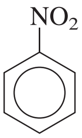
ethylbenzene



chlorobenzene

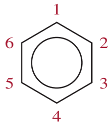


aminobenzene
(aniline)



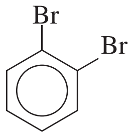
nitrobenzene

If more than one substituent is present, we must indicate the location of the second group relative to the first. The systematic way to accomplish this is to number the carbon atoms as follows:

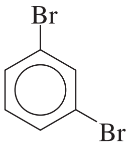


[†] August Kekulé (1829–1896). German chemist. Kekulé was a student of architecture before he became interested in chemistry. He supposedly solved the riddle of the structure of the benzene molecule after having a dream in which dancing snakes bit their own tails. Kekulé's work is regarded by many as the crowning achievement of theoretical organic chemistry of the nineteenth century.

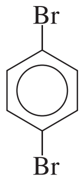
Three different dibromobenzenes are possible:



1,2-dibromobenzene
(*o*-dibromobenzene)

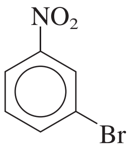


1,3-dibromobenzene
(*m*-dibromobenzene)



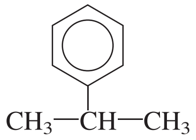
1,4-dibromobenzene
(*p*-dibromobenzene)

The prefixes *o*- (*ortho*-), *m*- (*meta*-), and *p*- (*para*-) are also used to denote the relative positions of the two substituted groups, as shown above for the dibromobenzenes. Compounds in which the two substituted groups are different are named accordingly. Thus,



is named 3-bromonitrobenzene, or *m*-bromonitrobenzene.

Finally, we note that the group containing benzene minus a hydrogen atom (C_6H_5) is called the *phenyl* group. Thus, the following molecule is called 2-phenylpropane:



$$CH_3-CH-CH_3$$

Properties and Reactions of Aromatic Compounds

Benzene is a colorless, flammable liquid obtained chiefly from petroleum and coal tar. Perhaps the most remarkable chemical property of benzene is its relative inertness. Although it has the same empirical formula as acetylene (CH) and a high degree of unsaturation, it is much less reactive than either ethylene or acetylene. The stability of benzene is the result of electron delocalization.

An enormously large number of compounds can be generated from substances in which benzene rings are fused together. Some of these *polycyclic* aromatic hydrocarbons are shown in Figure 24.7. The best known of these compounds is naphthalene, which is used in mothballs. These and many other similar compounds are present in coal tar. Some of the compounds with several rings are powerful carcinogens—they can cause cancer in humans and other animals.

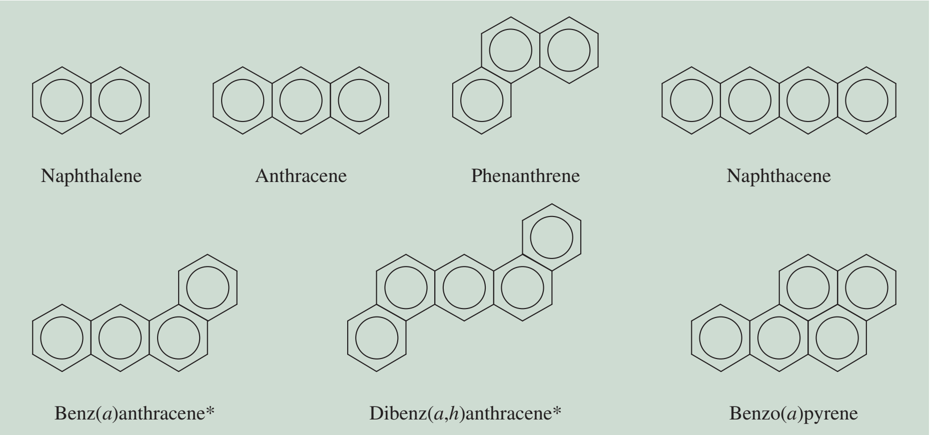
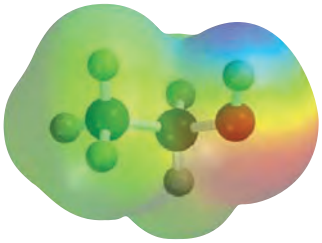

Naphthalene
Anthracene
Phenanthrene
Naphthacene
Benz(*a*)anthracene*
Dibenz(*a*,*h*)anthracene*
Benzo(*a*)pyrene

Figure 24.7 *Some polycyclic aromatic hydrocarbons. Compounds denoted by * are potent carcinogens. An enormous number of such compounds exist in nature.*

24.4 Chemistry of the Functional Groups

We now examine in greater depth some organic functional groups, groups that are responsible for most of the reactions of the parent compounds. In particular, we focus on oxygen-containing and nitrogen-containing compounds.

Alcohols



C_2H_5OH

All ***alcohols*** contain *the hydroxyl* functional *group, —OH.* Some common alcohols are shown in Figure 24.8. Ethyl alcohol, or ethanol, is by far the best known. It is produced biologically by the fermentation of sugar or starch. In the absence of oxygen, the enzymes present in bacterial cultures or yeast catalyze the reaction

$$C_6H_{12}O_6(aq) \xrightarrow{\text{enzymes}} \underset{\text{ethanol}}{2CH_3CH_2OH(aq)} + 2CO_2(g)$$

This process gives off energy, which microorganisms, in turn, use for growth and other functions.

Commercially, ethanol is prepared by an addition reaction in which water is combined with ethylene at about 280°C and 300 atm:

$$CH_2{=}CH_2(g) + H_2O(g) \xrightarrow{H_2SO_4} CH_3CH_2OH(g)$$

Ethanol has countless applications as a solvent for organic chemicals and as a starting compound for the manufacture of dyes, synthetic drugs, cosmetics, and explosives. It is also a constituent of alcoholic beverages. Ethanol is the only nontoxic (more properly, the least toxic) of the straight-chain alcohols; our bodies produce an enzyme, called *alcohol dehydrogenase,* which helps metabolize ethanol by oxidizing it to acetaldehyde:

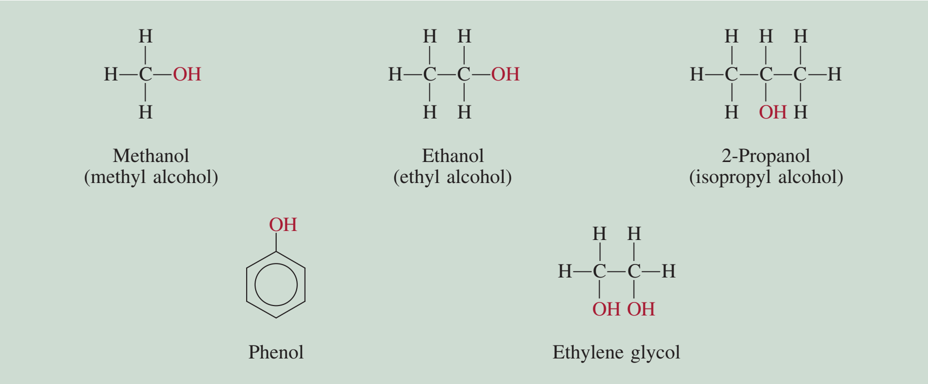


Figure 24.8 *Common alcohols. Note that all the compounds contain the OH group. The properties of phenol are quite different from those of the aliphatic alcohols.*

Methanol (methyl alcohol)

Ethanol (ethyl alcohol)

2-Propanol (isopropyl alcohol)

Phenol

Ethylene glycol

Ethanol is called an aliphatic alcohol because it is derived from an alkane (ethane). The simplest aliphatic alcohol is methanol, CH_3OH. Called *wood alcohol,* it was prepared at one time by the dry distillation of wood. It is now synthesized industrially by the reaction of carbon monoxide and molecular hydrogen at high temperatures and pressures:

$$CO(g) + 2H_2(g) \xrightarrow[\text{catalyst}]{Fe_2O_3} \underset{\text{methanol}}{CH_3OH(l)}$$

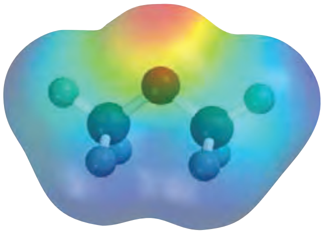
Methanol is highly toxic. Ingestion of only a few milliliters can cause nausea and blindness. Ethanol intended for industrial use is often mixed with methanol to prevent people from drinking it. Ethanol containing methanol or other toxic substances is called *denatured alcohol.*

Alcohols react more slowly with sodium metal than does water.

Two other familiar aliphatic alcohols are 2-propanol (or isopropanol), commonly known as rubbing alcohol, and ethylene glycol, which is used as an antifreeze. Note that ethylene glycol has two —OH groups and so can form hydrogen bonds with water molecules more effectively than compounds that have only one —OH group (see Figure 24.8). Most alcohols—especially those with low molar masses—are highly flammable.

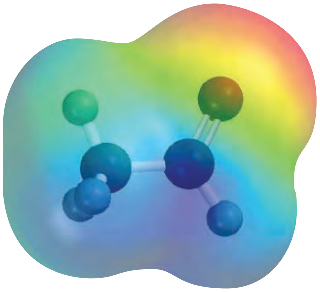
Ethers

***Ethers** contain the R—O—R′ linkage, where R and R′ are a hydrocarbon (aliphatic or aromatic) group.*



CH_3OCH_3

Peroxides contain the —O—O— linkage; the simplest peroxide is hydrogen perox-ide, H_2O_2. Diethyl ether, commonly known as "ether," was used as an anesthetic for many years. It produces unconsciousness by depressing the activity of the central nervous system. The major disadvantages of diethyl ether are its irritating effects on the respiratory system and the occurrence of postanesthetic nausea and vomiting. "Neothyl," or methyl propyl ether, $CH_3OCH_2CH_2CH_3$, is currently favored as an anes-thetic because it is relatively free of side effects.



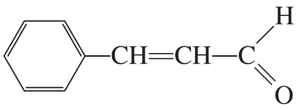
CH_3CHO

Aldehydes and Ketones

The functional group in these compounds is the *carbonyl group,* $>C{=}O$. In an ***aldehyde*** *at least one hydrogen atom is bonded to the carbon in the carbonyl group.* In a ***ketone,*** *the carbon atom in the carbonyl group is bonded to two hydrocarbon groups.*

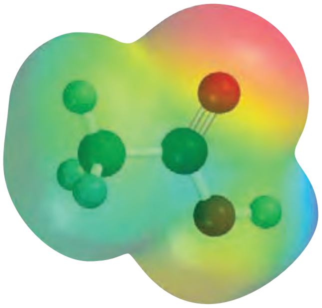
The simplest aldehyde, formaldehyde ($H_2C{=}O$). This rather disagreeable-smelling liquid is used as a starting material in the polymer industry (see Chapter 25) and in the laboratory as a preservative for animal specimens. Interestingly, the higher molar mass aldehydes, such as cinnamic aldehyde

Cinnamic aldehyde gives cinnamon its characteristic aroma.



have a pleasant odor and are used in the manufacture of perfumes.

Ketones generally are less reactive than aldehydes. The simplest ketone is acetone, a pleasant-smelling liquid that is used mainly as a solvent for organic compounds and nail polish remover.



CH_3COOH

Carboxylic Acids

Under appropriate conditions both alcohols and aldehydes can be oxidized to ***carboxylic acids,*** *acids that contain the carboxyl group, —COOH:*

$$CH_3CH_2OH + O_2 \longrightarrow CH_3COOH + H_2O$$
$$CH_3CHO + \tfrac{1}{2}O_2 \longrightarrow CH_3COOH$$

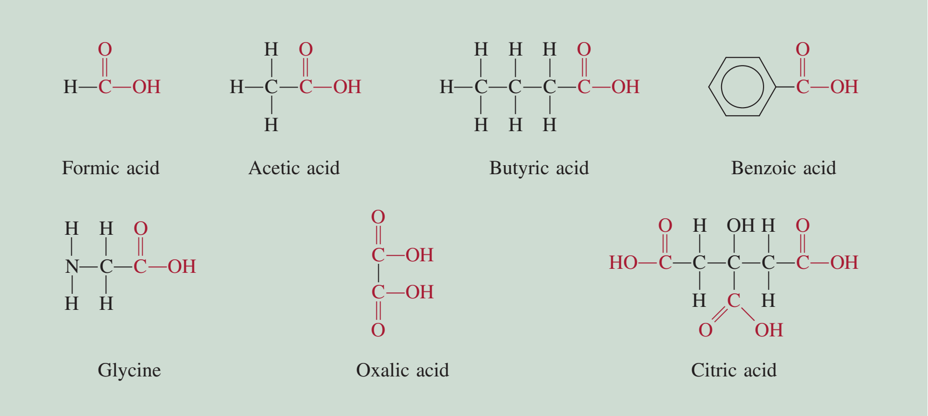


Figure 24.9 *Some common carboxylic acids. Note that they all contain the COOH group. (Glycine is one of the amino acids found in proteins.)*

These reactions occur so readily, in fact, that wine must be protected from atmospheric oxygen while in storage. Otherwise, it would soon turn to vinegar due to the formation of acetic acid. Figure 24.9 shows the structure of some of the common carboxylic acids.

The oxidization of ethanol to acetic acid in wine is catalyzed by enzymes.

Carboxylic acids are widely distributed in nature; they are found in both the plant and animal kingdoms. All protein molecules are made of amino acids, a special kind of carboxylic acid containing an amino group (—NH_2) and a carboxyl group (—COOH).

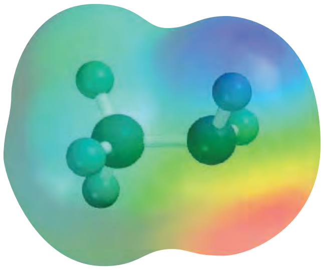
Unlike the inorganic acids HCl, HNO_3, and H_2SO_4, **carboxylic acids are usually weak.** They react with alcohols to form pleasant-smelling esters:

Esters

Esters *have the general formula R′COOR, where R′ can be H or a hydrocarbon group and R is a hydrocarbon group.* Esters are used in the manufacture of perfumes and as flavoring agents in the confectionery and soft-drink industries. Many fruits owe their characteristic smell and flavor to the presence of small quantities of esters. For example, bananas contain 3-methylbutyl acetate [$CH_3COOCH_2CH_2CH(CH_3)_2$], oranges contain octyl acetate ($CH_3COOCHCH_3C_6H_{13}$), and apples contain methyl butyrate ($CH_3CH_2CH_2COOCH_3$).

The odor of fruits is mainly due to the ester compounds they contain.

Amines


CH_3NH_2

Amines are *organic bases having the general formula R_3N, where R may be H or a hydrocarbon group.* As with ammonia, the reaction of amines with water is

$$RNH_2 + H_2O \longrightarrow RNH_3^+ + OH^-$$

where R represents a hydrocarbon group. Like all bases, the amines form salts when allowed to react with acids:

$$\underset{\text{ethylamine}}{CH_3CH_2NH_2} + HCl \longrightarrow \underset{\substack{\text{ethylammonium}\\\text{chloride}}}{CH_3CH_2NH_3^+Cl^-}$$

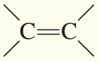
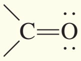
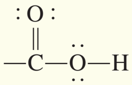
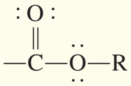
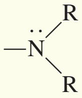
These salts are usually colorless, odorless solids.

Summary of Functional Groups

Table 24.4 summarizes the common functional groups, including the C$=$C and C$\equiv$C groups. Organic compounds commonly contain more than one functional group. Generally, the reactivity of a compound is determined by the number and types of functional groups in its makeup.

Example 24.5 shows how we can use the functional groups to predict reactions.

TABLE 24.4 Important Functional Groups and Their Reactions

Functional Group	Name
	Carbon-carbon double bond
$-C\equiv C-$	Carbon-carbon triple bond
$-\ddot{\underset{\cdot\cdot}{X}}:$ (X = F, Cl, Br, I)	Halogen
$-\ddot{\underset{\cdot\cdot}{O}}-H$	Hydroxyl
	Carbonyl
 $-\overset{\overset{:O:}{\Vert}}{C}-\ddot{\underset{\cdot\cdot}{O}}-H$	Carboxyl
 $-\overset{\overset{:O:}{\Vert}}{C}-\ddot{\underset{\cdot\cdot}{O}}-R$ (R = hydrocarbon)	Ester
 (R = H or hydrocarbon)	Amine

Summary of Facts and Concepts

1. Because carbon atoms can link up with other carbon atoms in straight and branched chains, carbon can form more compounds than any other element.
2. Organic compounds are derived from two types of hydrocarbons: aliphatic hydrocarbons and aromatic hydrocarbons.
3. Methane, CH_4, is the simplest of the alkanes, a family of hydrocarbons with the general formula C_nH_{2n+2}. Cyclopropane, C_3H_6, is the simplest of the cycloalkanes, a family of alkanes whose carbon atoms are joined in a ring. Alkanes and cycloalkanes are saturated hydrocarbons.
4. Ethylene, $CH_2{=}CH_2$, is the simplest of the olefins, or alkenes, a class of hydrocarbons containing carbon-carbon double bonds and having the general formula C_nH_{2n}.
5. Acetylene, $CH{\equiv}CH$, is the simplest of the alkynes, which are compounds that have the general formula C_nH_{2n-2} and contain carbon-carbon triple bonds.
6. Compounds that contain one or more benzene rings are called aromatic hydrocarbons. These compounds undergo substitution by halogens and alkyl groups.
7. Functional groups impart specific types of chemical reactivity to molecules. Classes of compounds characterized by their functional groups include alcohols, ethers, aldehydes and ketones, carboxylic acids and esters, and amines.

Key Words

Alcohol, p. 1042
Aldehyde, p. 1044
Aliphatic hydrocarbon, p. 1026
Alkane, p. 1026
Alkene, p. 1033
Alkyne, p. 1037
Amine, p. 1046
Aromatic hydrocarbon, p. 1026
Carboxylic acid, p. 1044
Cycloalkane, p. 1033
Ester, p. 1045
Ether, p. 1043
Functional group, p. 1026
Hydrocarbon, p. 1026
Ketone, p. 1044
Organic chemistry, p. 1026
Saturated hydrocarbon, p. 1026
Structural isomer, p. 1027
Unsaturated

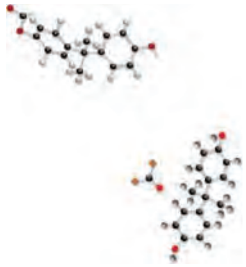
Chapter Outline

A Look Ahead

- We begin with a discussion of the general properties of organic polymers. (25.1)
- We then study the synthesis of organic polymers by addition reactions and condensation reactions. We examine both natural and synthetic rubber and other synthetic polymers. (25.2)
- Next, we learn that proteins are polymers of amino acids. We examine the structure of a protein molecule in terms of its primary, secondary, tertiary, and quaternary structures. We also study the stability of a protein molecule, the cooperativity effect, and protein denaturation. (25.3)
- The chapter ends with a brief discussion of the structure and composition of the genetic materials deoxyribonucleic acids (DNA) and ribonucleic acids (RNA). (25.4)

Polymers are very large molecules containing hundreds or thousands of atoms. People have been using polymers since prehistoric time, and chemists have been synthesizing them for the past century. Natural polymers are the basis of all life processes, and our technological society is largely dependent on synthetic polymers.

This chapter discusses some of the preparation and properties of important synthetic organic polymers in addition to two naturally occurring polymers that are vital to living systems—proteins and nucleic acids.



25.1 Properties of Polymers

A ***polymer*** is *a molecular compound distinguished by a high molar mass, ranging into thousands and millions of grams, and made up of many repeating units.* The physical properties of these so-called macromolecules differ greatly from those of small, ordinary molecules, and special techniques are required to study them.

Naturally occurring polymers include proteins, nucleic acids, cellulose (polysaccharides), and rubber (polyisoprene). Most synthetic polymers are organic compounds. Familiar examples are nylon, poly(hexamethylene adipamide); Dacron, poly(ethylene terephthalate); and Lucite or Plexiglas, poly(methyl methacrylate).

The development of polymer chemistry began in the 1920s with the investigation into a puzzling behavior of certain materials, including wood, gelatin, cotton, and rubber. For example, when rubber, with the known empirical formula of C_5H_8, was dissolved in an organic solvent, the solution displayed several unusual properties—high viscosity, low osmotic pressure, and negligible freezing-point depression. These observations strongly suggested the presence of solutes of very high molar mass, but chemists were not ready at that time to accept the idea that such giant molecules could exist. Instead, they postulated that materials such as rubber consist of aggregates of small molecular units, like C_5H_8 or $C_{10}H_{16}$, held together by intermolecular forces. This misconception persisted for a number of years, until Hermann Staudinger[†] clearly showed that these so-called aggregates are, in fact, enormously large molecules, each of which contains many thousands of atoms held together by covalent bonds.

Once the structures of these macromolecules were understood, the way was open for manufacturing polymers, which now pervade almost every aspect of our daily lives. About 90 percent of today's chemists, including biochemists, work with polymers.

25.2 Synthetic Organic Polymers

Because of their size, we might expect molecules containing thousands of carbon and hydrogen atoms to form an enormous number of structural and geometric isomers (if C═C bonds are present). However, these molecules are made up of ***monomers,*** *simple repeating units,* and this type of composition severely restricts the number of possible isomers. Synthetic polymers are created by joining monomers together, one at a time, by means of addition reactions and condensation reactions.

Addition Reactions

Addition reactions involve unsaturated compounds containing double or triple bonds, particularly C═C and C≡C. Hydrogenation and reactions of hydrogen halides and halogens with alkenes and alkynes are examples of addition reactions.

Polyethylene, a very stable polymer used in packaging wraps, is made by joining ethylene monomers via an addition-reaction mechanism. First an *initiator* molecule (R_2) is heated to produce two radicals:

$$R_2 \longrightarrow 2R\cdot$$

[†] Hermann Staudinger (1881–1963). German chemist. One of the pioneers in polymer chemistry. Staudinger was awarded the Nobel Prize in Chemistry in 1953.

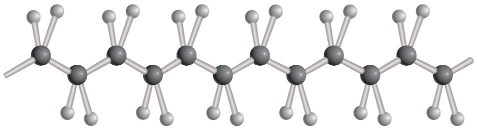


Figure 25.1 *Structure of polyethylene. Each carbon atom is* sp^3*-hybridized.*

The reactive radical attacks an ethylene molecule to generate a new radical:

$$\text{R}\cdot + \text{CH}_2{=}\text{CH}_2 \longrightarrow \text{R—CH}_2\text{—CH}_2\cdot$$

which further reacts with another ethylene molecule, and so on:

$$\text{R—CH}_2\text{—CH}_2\cdot + \text{CH}_2{=}\text{CH}_2 \longrightarrow \text{R—CH}_2\text{—CH}_2\text{—CH}_2\text{—CH}_2\cdot$$

Very quickly a long chain of CH_2 groups is built. Eventually, this process is terminated by the combination of two long-chain radicals to give the polymer called polyethylene:

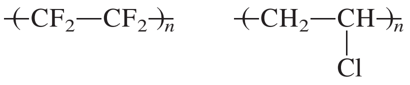
$$\text{R}\left(\text{CH}_2\text{—CH}_2\right)_n\text{CH}_2\text{CH}_2\cdot + \text{R}\left(\text{CH}_2\text{—CH}_2\right)_n\text{CH}_2\text{CH}_2\cdot \longrightarrow$$
$$\text{R}\left(\text{CH}_2\text{—CH}_2\right)_n\text{CH}_2\text{CH}_2\text{—CH}_2\text{CH}_2\left(\text{CH}_2\text{—CH}_2\right)_n\text{R}$$

where $\left(\text{CH}_2\text{—CH}_2\right)_n$ **is a convenient shorthand convention for representing the repeating unit in the polymer.** The value of n is understood to be very large, on the order of hundreds.

The individual chains of polyethylene pack together well and so account for the substance's crystalline properties (Figure 25.1). Polyethylene is mainly used in films in frozen food packaging and other product wrappings. A specially treated type of polyethylene called Tyvek is used for home insulation.

Common mailing envelopes made of Tyvek.

Polyethylene is an example of a ***homopolymer,*** which is *a polymer made up of only one type of monomer.* Other homopolymers that are synthesized by the radical mechanism are Teflon, polytetrafluoroethylene (Figure 25.2) and poly(vinyl chloride) (PVC):

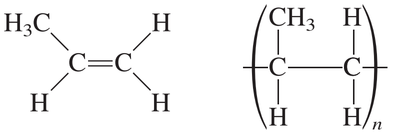


$$\left(\text{CF}_2\text{—CF}_2\right)_n \qquad \left(\text{CH}_2\text{—}\underset{\underset{\text{Cl}}{|}}{\text{CH}}\right)_n$$

Teflon PVC

Figure 25.2 *A cooking utensil coated with Silverstone, which contains polytetrafluoroethylene.*

The chemistry of polymers is more complex if the starting units are asymmetric:



propene polypropene

Several geometric isomers can result from an addition reaction of propenes (Figure 25.3). If the additions occur randomly, we obtain *atactic* polypropenes, which do not pack together well. These polymers are rubbery, amorphous, and relatively weak. Two other possibilities are an *isotactic* structure, in which the R groups are all on the same side of the asymmetric carbon atoms, and a *syndiotactic* form, in which the R groups alternate to the left and right of the asymmetric carbons. Of these, the isotactic isomer has the highest melting point and greatest crystallinity and is endowed with superior mechanical properties.

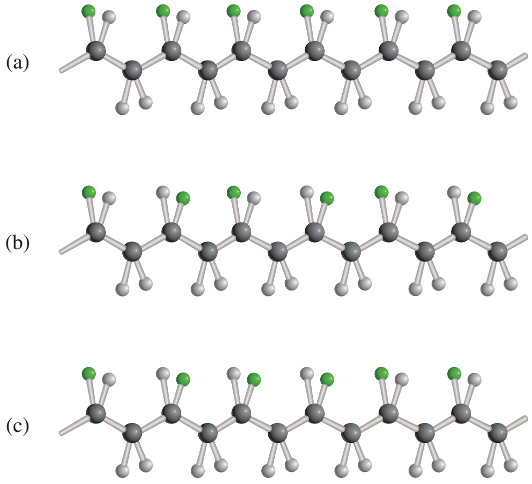
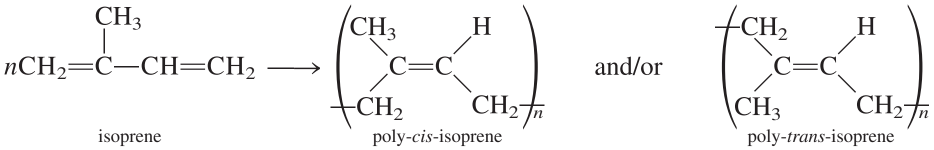


Figure 25.3 *Stereoisomers of polymers. When the R group (green sphere) is* CH_3*, the polymer is polypropene. (a) When the R groups are all on one side of the chain, the polymer is said to be isotactic. (b) When the R groups alternate from side to side, the polymer is said to be syndiotactic. (c) When the R groups are disposed at random, the polymer is atactic.*

A major problem that the polymer industry faced in the beginning was how to synthesize either the isotactic or syndiotactic polymer selectively without having it contaminated by other products.

Rubber is probably the best known organic polymer and the only true hydrocarbon polymer found in nature. It is formed by the radical addition of the monomer isoprene. Actually, polymerization can result in either poly-*cis*-isoprene or poly-*trans*-isoprene—or a mixture of both, depending on reaction conditions:



Note that in the *cis* isomer the two CH_2 groups are on the same side of the C═C bond, whereas the same groups are across from each other in the *trans* isomer. Natural rubber is poly-*cis*-isoprene, which is extracted from the tree *Hevea brasiliensis* (Figure 25.4).

An unusual and very useful property of rubber is its elasticity. Rubber will stretch up to 10 times its length and, if released, will return to its original size. In contrast, a piece of copper wire can be stretched only a small percentage of its length and still return to its original size. Unstretched rubber has no regular X-ray diffraction pattern and is therefore amorphous. Stretched rubber, however, possesses a fair amount of crystallinity and order.

Figure 25.4 *Latex (aqueous suspension of rubber particles) being collected from a rubber tree.*

The elastic property of rubber is due to the flexibility of its long-chain molecules. In the bulk state, however, rubber is a tangle of polymeric chains, and if the external force is strong enough, individual chains slip past one another, thereby causing the rubber to lose most of its elasticity. In 1839, Charles Goodyear[†] discovered that natural rubber could be cross-linked with sulfur (using zinc oxide as the catalyst) to prevent chain slippage (Figure 25.5). His process, known as *vulcanization,* paved the way for many practical and commercial uses of rubber, such as in automobile tires and dentures.

During World War II a shortage of natural rubber in the United States prompted an intensive program to produce synthetic rubber. Most synthetic rubbers (called *elastomers*) are made from petroleum products such as ethylene, propene, and butadiene.

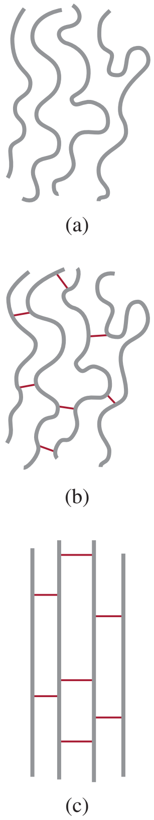
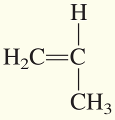
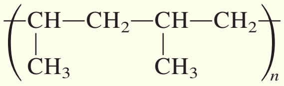
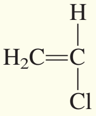
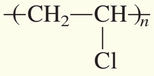
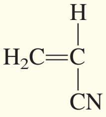
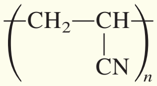
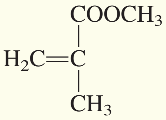
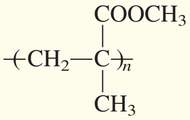
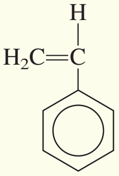
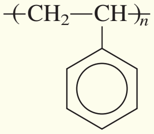
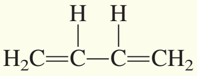
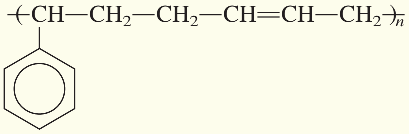


Figure 25.5 *Rubber molecules ordinarily are bent and convoluted. Parts (a) and (b) represent the long chains before and after vulcanization, respectively; (c) shows the alignment of molecules when stretched. Without vulcanization these molecules would slip past one another, and rubber's elastic properties would be gone.*

[†] Charles Goodyear (1800–1860). American chemist. Goodyear was the first person to realize the potential of natural rubber. His vulcanization process made rubber usable in countless ways and opened the way for the development of the automobile industry.

TABLE 25.1 Some Monomers and Their Common Synthetic Polymers

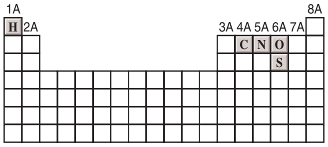
Monomer		Polymer	
Formula	**Name**	**Name and Formula**	**Uses**
$H_2C{=}CH_2$	Ethylene	Polyethylene $-\!\!(CH_2-CH_2)\!\!-_n$	Plastic piping, bottles, electrical insulation, toys
 $H_2C{=}\overset{\displaystyle H}{\underset{\displaystyle CH_3}{C}}$	Propene	Polypropene  $\left(\underset{\displaystyle CH_3}{CH}-CH_2-\underset{\displaystyle CH_3}{CH}-CH_2\right)_n$	Packaging film, carpets, crates for soft-drink bottles, lab wares, toys
 $H_2C{=}\overset{\displaystyle H}{\underset{\displaystyle Cl}{C}}$	Vinyl chloride	Poly(vinyl chloride) (PVC)  $-\!\!(CH_2-\underset{\displaystyle Cl}{CH})\!\!-_n$	Piping, siding, gutters, floor tile, clothing, toys
 $H_2C{=}\overset{\displaystyle H}{\underset{\displaystyle CN}{C}}$	Acrylonitrile	Polyacrylonitrile (PAN)  $\left(CH_2-\underset{\displaystyle CN}{CH}\right)_n$	Carpets, knitwear
$F_2C{=}CF_2$	Tetrafluoro-ethylene	Polytetrafluoroethylene (Teflon) $-\!\!(CF_2-CF_2)\!\!-_n$	Coating on cooking utensils, electrical insulation, bearings
 $H_2C{=}\overset{\displaystyle COOCH_3}{\underset{\displaystyle CH_3}{C}}$	Methyl methacrylate	Poly(methyl methacrylate) (Plexiglas)  $-\!\!(CH_2-\overset{\displaystyle COOCH_3}{\underset{\displaystyle CH_3}{C}})\!\!-_n$	Optical equipment, home furnishings
	Styrene	Polystyrene 	Containers, thermal insulation (ice buckets, water coolers), toys
 $H_2C{=}\overset{\displaystyle H}{C}-\overset{\displaystyle H}{C}{=}CH_2$	Butadiene	Polybutadiene $-\!\!(CH_2CH{=}CHCH_2)\!\!-_n$	Tire tread, coating resin
See above structures	Butadiene and styrene	Styrene-butadiene rubber (SBR) 	Synthetic rubber

Bubble gums contain synthetic styrene-butadiene rubber.

25.3 Proteins

Proteins are *polymers of amino acids;* they play a key role in nearly all biological processes. Enzymes, the catalysts of biochemical reactions, are mostly proteins. Proteins also facilitate a wide range of other functions, such as transport and storage of vital substances, coordinated motion, mechanical support, and protection against diseases. The human body contains an estimated 100,000 different kinds of proteins, each of which has a specific physiological function. As we will see in this section, the chemical composition and structure of these complex natural polymers are the basis of their specificity.

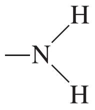
Amino Acids



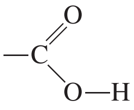
Elements in proteins.

Proteins have high molar masses, ranging from about 5000 g to 1×10^7 g, and yet the percent composition by mass of the elements in proteins is remarkably constant: carbon, 50 to 55 percent; hydrogen, 7 percent; oxygen, 23 percent; nitrogen, 16 percent; and sulfur, 1 percent.

The basic structural units of proteins are *amino acids.* An ***amino acid*** is *a compound that contains at least one amino group ($—NH_2$) and at least one carboxyl group ($—COOH$):*



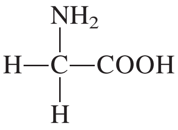
amino group



carboxyl group

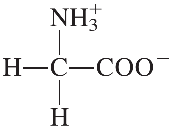
Twenty different amino acids are the building blocks of all the proteins in the human body. Table 25.2 shows the structures of these vital compounds, along with their three-letter abbreviations.

Amino acids in solution at neutral pH exist as *dipolar ions,* meaning that the proton on the carboxyl group has migrated to the amino group. Consider glycine, the simplest amino acid. The un-ionized form and the dipolar ion of glycine are shown below:



$$\mathrm{H-\overset{NH_2}{\underset{H}{C}}-COOH}$$

un-ionized form



$$\mathrm{H-\overset{NH_3^+}{\underset{H}{C}}-COO^-}$$

dipolar ion

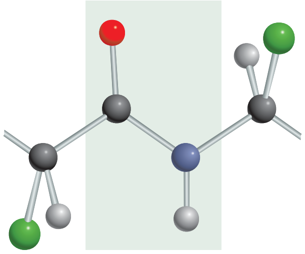


Figure 25.9 *The planar amide group in protein. Rotation about the peptide bond in the amide group is hindered by its double-bond character. The black atoms represent carbon; blue, nitrogen; red, oxygen; green, R group; and gray, hydrogen.*

Protein Structure

The type and number of amino acids in a given protein along with the sequence or order in which these amino acids are joined together determine the protein's structure.

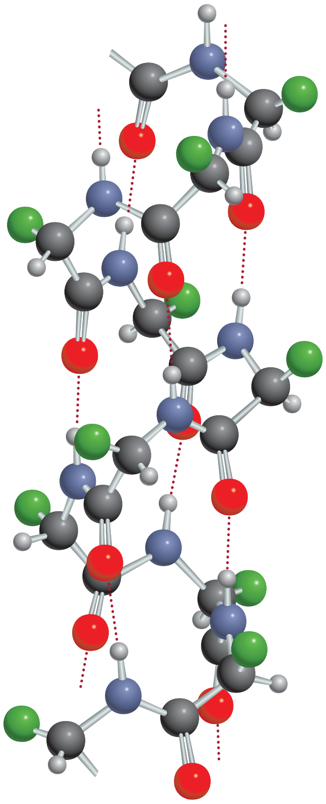
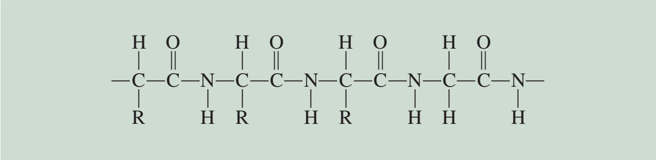


Figure 25.11 *The α-helical structure of a polypeptide chain. The gray spheres are hydrogen atoms. The structure is held in position by intramolecular hydrogen bonds, shown as dotted lines.*



$$-\underset{R}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-\underset{H}{N}-\underset{R}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-\underset{H}{N}-\underset{R}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-\underset{H}{N}-\underset{H}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-\underset{H}{N}-$$

Figure 25.10 *A polypeptide chain. Note the repeating units of the amide group. The symbol R represents part of the structure characteristic of the individual amino acids. For glycine, R is simply a H atom.*

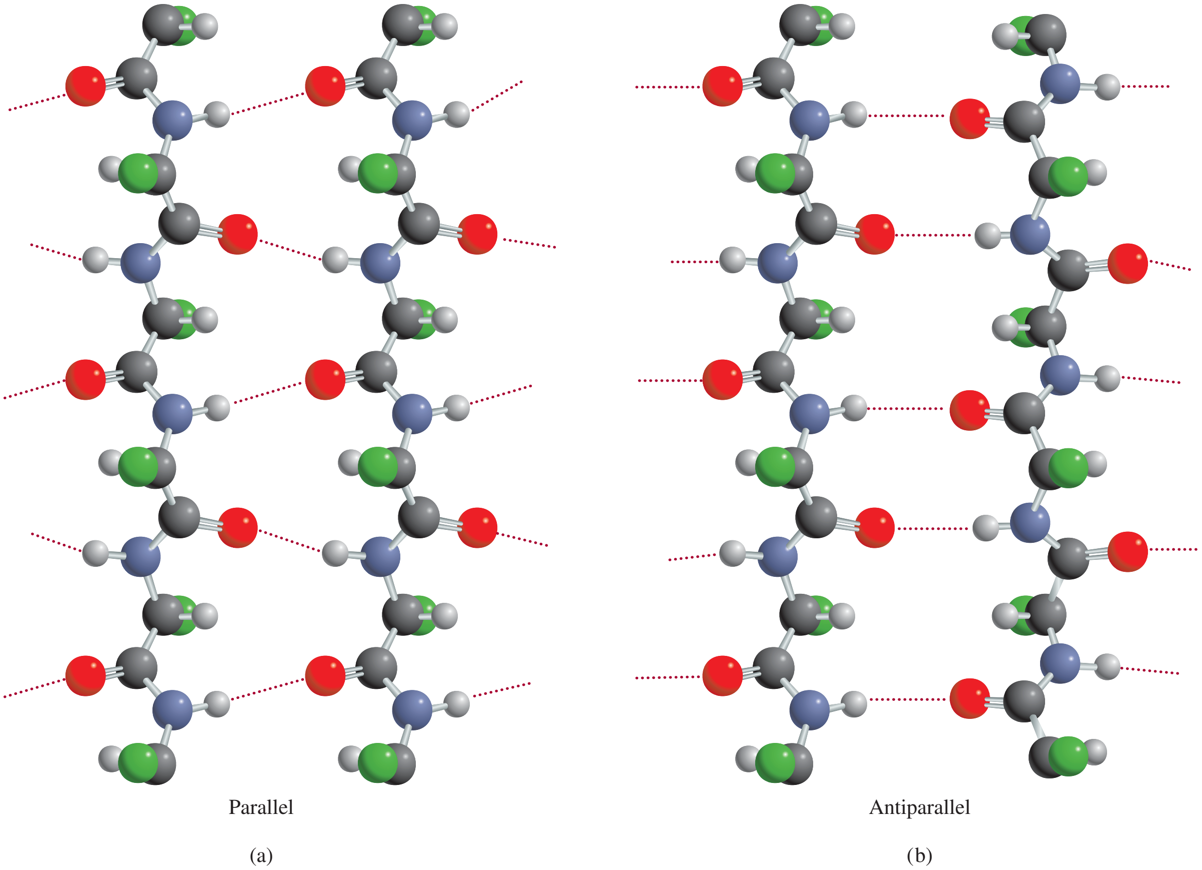


Figure 25.12 *Hydrogen bonds (a) in a parallel β-pleated sheet structure, in which all the polypeptide chains are oriented in the same direction, and (b) in an antiparallel β-pleated sheet, in which adjacent polypeptide chains run in opposite directions.*

It is customary to divide protein structure into four levels of organization. The *primary structure* refers to the unique amino acid sequence of the polypeptide chain. The *secondary structure* includes those parts of the polypeptide chain that are stabilized by a **regular pattern of hydrogen bonds between the CO and NH groups** of the backbone, for example, the α helix. The term *tertiary structure* applies to the

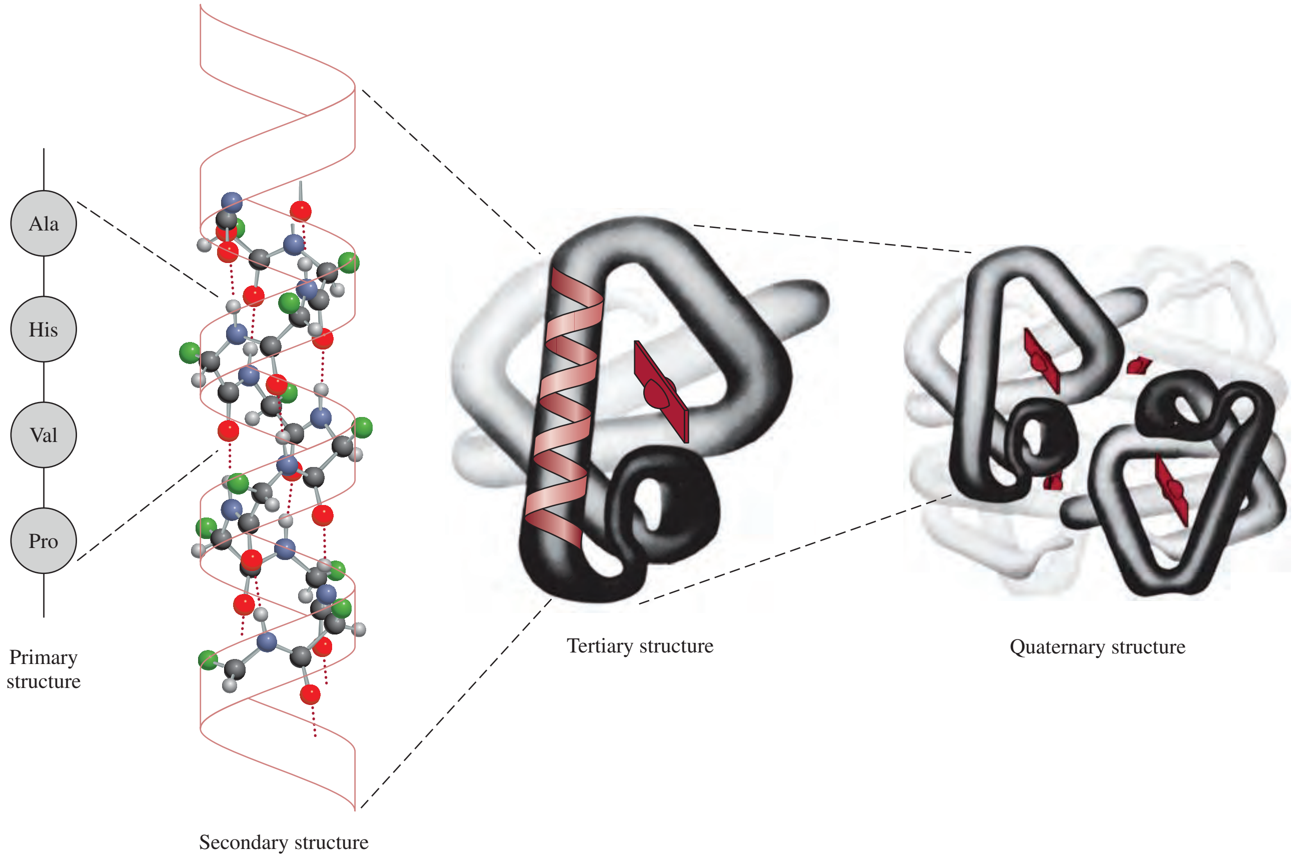


Figure 25.13 *The primary, secondary, tertiary, and quaternary structure of the hemoglobin molecule.*

three-dimensional structure stabilized by dispersion forces, hydrogen bonding, and other intermolecular forces. .

Summary of Facts and Concepts

1. Polymers are large molecules made up of small, repeating units called monomers.
2. Proteins, nucleic acids, cellulose, and rubber are natural polymers. Nylon, Dacron, and Lucite are examples of synthetic polymers.
3. Organic polymers can be synthesized via addition reactions or condensation reactions.
4. Stereoisomers of a polymer made up of asymmetric monomers have different properties, depending on how the starting units are joined together.
5. Synthetic rubbers include polychloroprene and styrene-butadiene rubber, which is a copolymer of styrene and butadiene.
6. Structure determines the function and properties of proteins. To a great extent, hydrogen bonding and other intermolecular forces determine the structure of proteins.
7. The primary structure of a protein is its amino acid sequence. Secondary structure is the shape defined by hydrogen bonds joining the CO and NH groups of the amino acid backbone. Tertiary are the three-dimensional folded arrangements of proteins that are stabilized by hydrogen bonds and other intermolecular forces.