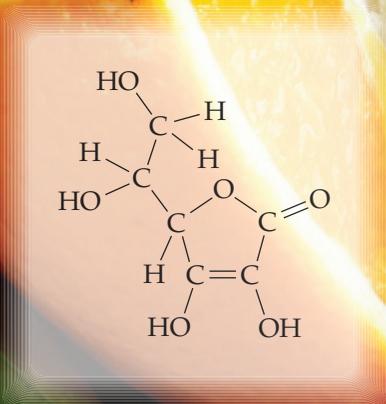


# Organic and Biological Chemistry



Ascorbic acid, also known as vitamin C, is an *essential* nutrient in the human diet because it is not synthesized in our body. We can eat citrus fruits or take pills that contain vitamin C to maintain health.



Which Is Better, Natural or Synthetic?

The answer to this question can be found in the **INQUIRY** >>> on page 1021.

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- 23.1 ▶ Organic Molecules and Their Structures: Alkanes
- 23.2 ▶ Families of Organic Compounds: Functional Groups
- 23.3 ▶ Naming Organic Compounds
- 23.4 ▶ Carbohydrates: A Biological Example of Isomers
- 23.5 ▶ Valence Bond Theory and Orbital Overlap Pictures
- 23.6 ▶ Lipids: A Biological Example of Cis-Trans Isomerism
- 23.7 ▶ Formal Charge and Resonance in Organic Compounds
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- 23.10 ▶ Aromatic Compounds and Molecular Orbital Theory
- 23.11 ▶ Nucleic Acids: A Biological Example of Aromaticity

## STUDY GUIDE

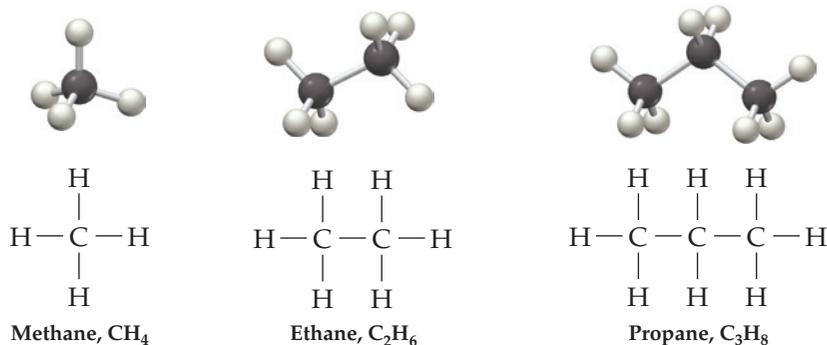
If the ultimate goal of chemistry is to understand the world around us on a molecular level, then a knowledge of **biochemistry**—the chemistry of living organisms—is a central part of that goal. Biochemistry, in turn, is a branch of *organic chemistry*, a term originally used to mean the study of compounds from living organisms while *inorganic chemistry* was used for the study of compounds from nonliving sources. Today, however, we know that there are no fundamental differences between organic and inorganic compounds; the same principles apply to both. The only common characteristic of compounds from living sources is that all contain the element carbon. Thus, **organic chemistry** is now defined as the study of carbon compounds.

But why is carbon special, and why do chemists still treat organic chemistry as a separate branch of science? The answers to these questions involve the ability of carbon atoms to bond together, forming long chains and rings. Of all the elements, only carbon is able to form such an immense array of compounds, from methane, with one carbon atom, to deoxyribonucleic acid (DNA), with tens of billions of carbon atoms. In fact, more than 67 million organic compounds have been made in laboratories around the world, and living organisms contain additional millions.

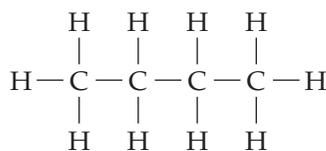
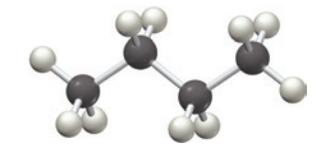
In this chapter, we will review key concepts of structure and bonding from Chapters 7 and 8 and apply them to organic compounds. We'll show how key features of molecular structure play an important role in the function of the major classes of biological molecules: carbohydrates, lipids, proteins, and nucleic acids.

## 23.1 ► ORGANIC MOLECULES AND THEIR STRUCTURES: ALKANES

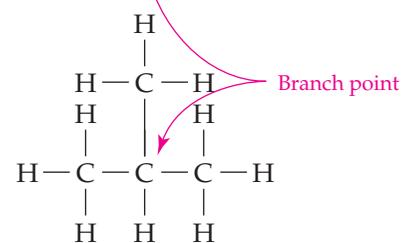
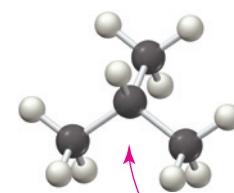
Why are there so many organic compounds? The answer is that a relatively small number of atoms can bond together in a great many ways. Take molecules that contain only carbon and hydrogen—**hydrocarbons**—and have only single bonds. Such compounds belong to the family of organic molecules called **alkanes**. Because carbon atoms have four outer-shell electrons and form four covalent bonds (Section 7.5), the only possible one-carbon alkane is methane,  $\text{CH}_4$ . Similarly, the only possible two-carbon alkane is ethane,  $\text{C}_2\text{H}_6$ , and the only possible three-carbon alkane is propane,  $\text{C}_3\text{H}_8$ .



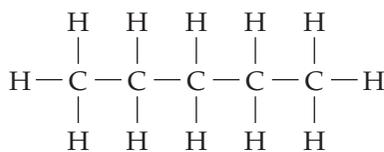
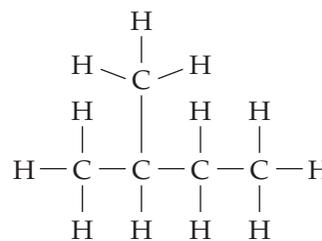
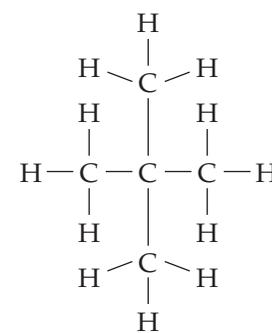
When larger numbers of carbons combine with hydrogen, however, more than one structure can result. There are two four-carbon alkanes with the formula  $\text{C}_4\text{H}_{10}$ , for instance. In one compound, the four carbons are in a row, while in the other they have a branched arrangement. Similarly, there are three alkanes with the formula  $\text{C}_5\text{H}_{12}$  and even more possibilities for larger alkanes. Compounds with all their carbons connected in a row are called **straight-chain alkanes**, and those with a branching connection of carbons are called **branched-chain alkanes**.



Butane (straight chain)



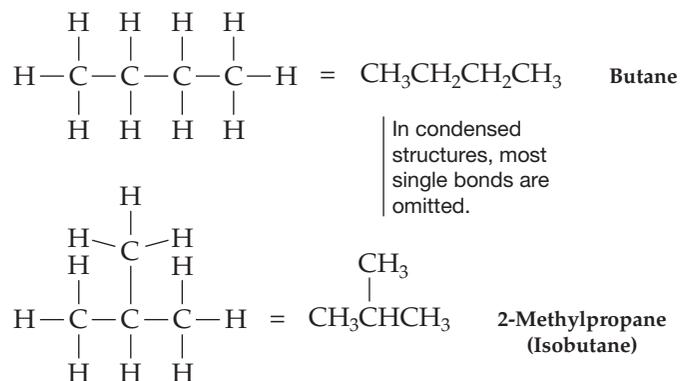
2-Methylpropane (branched chain)

Pentane  
(straight chain)2-Methylbutane  
(branched chain)2,2-Dimethylpropane  
(branched chain)**REMEMBER...**

**Isomers** are compounds that have the same formula but differ in the way their atoms are arranged. (Section 20.8)

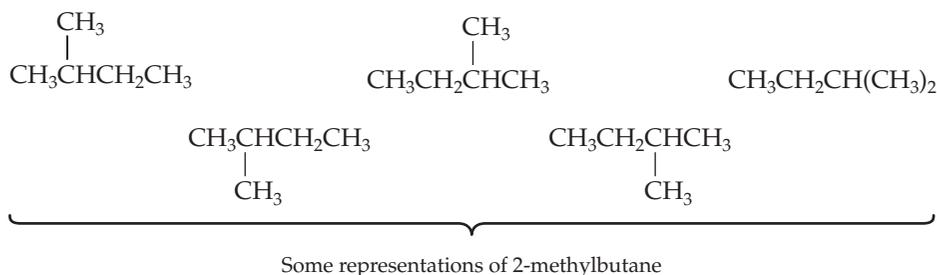
Compounds like the two different  $C_4H_{10}$  molecules and the three different  $C_5H_{12}$  molecules, which have the same molecular formula but different chemical structures, are called **isomers**. The number of possible alkane isomers grows rapidly as the number of carbon atoms increases, from five isomers for  $C_6H_{14}$  to more than 60 *trillion* possible isomers for  $C_{40}H_{82}$ ! As noted in Section 20.8, different isomers are different chemical compounds. They have different structures, different chemical properties, and different physical properties, such as melting point and boiling point.

Because it's both awkward and time-consuming to draw all the bonds and all the atoms in organic molecules, a shorthand way of drawing **condensed structures** is often used. In condensed structures, carbon-hydrogen and most carbon-carbon single bonds aren't shown; rather, they're "understood." If a carbon atom has three hydrogens bonded to it, we write  $CH_3$ ; if the carbon has two hydrogens bonded to it, we write  $CH_2$ ; and so on. For example, the four-carbon, straight-chain alkane (called butane) and its branched-chain isomer (called 2-methylpropane, or isobutane) can be written in the following way:

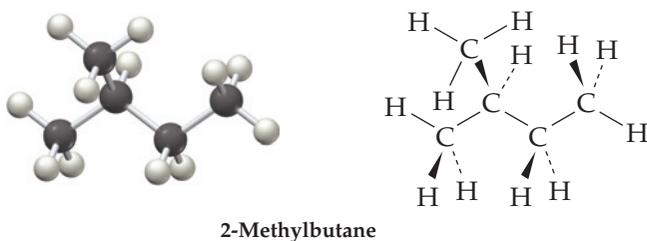


Note that the horizontal bonds between carbons aren't shown—the  $\text{CH}_3$  and  $\text{CH}_2$  units are simply placed next to each other—but the vertical bond in 2-methylpropane is shown for clarity.

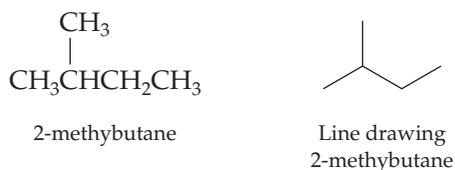
The condensed structure of an organic molecule indicates the connections among its atoms but implies nothing about its three-dimensional shape, which can be predicted by the **VSEPR model**. Thus, a molecule can be arbitrarily drawn in many different ways. The branched-chain alkane called 2-methylbutane, for instance, might be represented by any of the following structures. All have four carbons connected in a row, with a  $-\text{CH}_3$  branch on the second carbon from the end.



In fact, 2-methylbutane has no one single shape because rotation occurs around carbon-carbon single bonds. The two parts of a molecule joined by a  $\text{C}-\text{C}$  single bond are free to spin around the bond, giving rise to an infinite number of possible three-dimensional structures, or *conformations*. Thus, a large sample of 2-methylbutane contains a great many molecules that are constantly changing their shape. At any given instant, though, most of the molecules have an extended, zigzag shape, which is slightly more stable than other possibilities. The same is true for other alkanes. Remember when drawing three-dimensional structures that normal lines represent bonds in the plane of the page, wedges represent bonds coming out of the page toward the viewer, and dashed lines represent bonds receding into the page away from the viewer (Section 8.1).



**Line drawings** show only bonds in the carbon backbone and are another convenient shorthand representation of structure. These structures are also referred to as skeletal structures because they show only the carbon skeleton. A line drawing shows the carbon backbone as a zigzag shape because a chain of carbon atoms assumes this shape as shown in the structure of 2-methylbutane above. Each vertex or endpoint represents a carbon atom. Bonds to hydrogen atoms are not shown, but the number of hydrogen atoms can be determined because *carbon atoms form four bonds*. Therefore, a carbon atom with one bond to another carbon will also have three bonds to hydrogen. A carbon atom with two bonds to other carbon atoms will have two bonds to hydrogen. The line drawing for 2-methylbutane is:



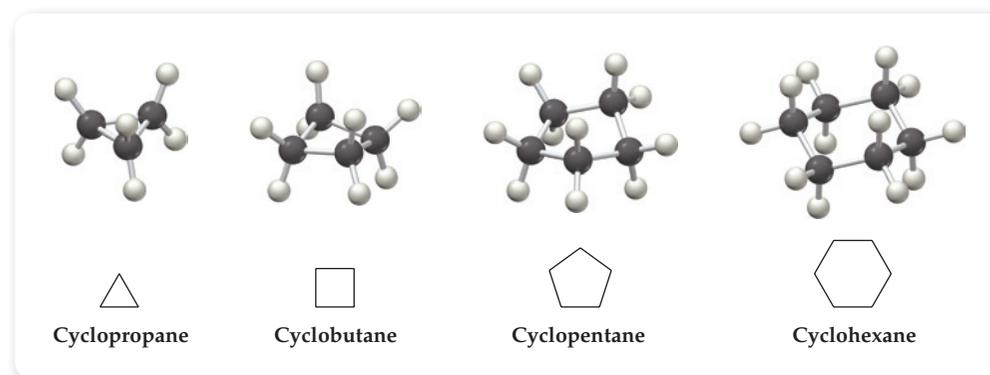
The alkanes we've seen thus far have been open-chain, or *acyclic*, compounds. *Cyclic* compounds, which contain *rings* of carbon atoms, are well known and widespread throughout nature. Compounds of all ring sizes from 3 through 30 carbons and beyond have been prepared.

### REMEMBER...

The **VSEPR model** predicts geometry by counting the number of charge clouds around an atom and assuming that those clouds orient in space as far away from one another as possible. When carbon has four single bonds, it has tetrahedral geometry with bond angles near  $109.5^\circ$ . When carbon has two single and one double bond, it has trigonal planar geometry with bond angles near  $120^\circ$ . When carbon has one single and one triple bond, it has linear geometry. (Section 8.1)

The simplest cyclic compounds are the **cycloalkanes** which, like their open-chain counterparts, contain only C—C and C—H single bonds. The compounds having three carbons (cyclopropane), four carbons (cyclobutane), five carbons (cyclopentane), and six carbons (cyclohexane) are shown in **FIGURE 23.1**. Condensed structures are awkward for cyclic molecules, so line drawings are typically used to represent the cycloalkanes. A carbon atom is at the junction of each line, and the number of hydrogen atoms can be determined because carbon forms *four* bonds. In a cyclic structure, each carbon atom has two bonds to other carbon atoms and therefore has two bonds to hydrogen.

► **FIGURE 23.1**  
Structures and line drawings of some simple cycloalkanes. The rings are shown as polygons.



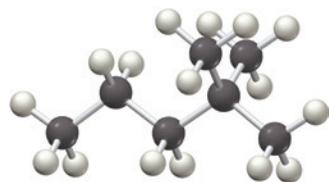
As you might imagine, the C—C—C bond angles in cyclopropane and cyclobutane are considerably distorted from the ideal  $109.5^\circ$  tetrahedral value. Cyclopropane, for example, has the shape of an equilateral triangle, with C—C—C angles of  $60^\circ$ . As a result, the bonds in three- and four-membered rings are weaker than normal, and the molecules are more reactive than other alkanes. Cyclopentane, cyclohexane, and larger cycloalkanes, however, pucker into shapes that allow bond angles to be near their normal tetrahedral value, as shown by the models in Figure 23.1.

### Conceptual WORKED EXAMPLE 23.1

#### Converting Molecular Models to Line Drawings

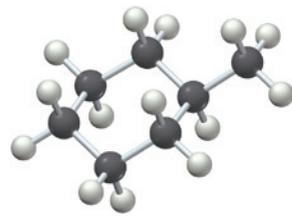
Convert the molecular models of the following alkanes into line drawings.

(a)



2,2-Dimethylpentane

(b)



Methylcyclohexane

#### STRATEGY

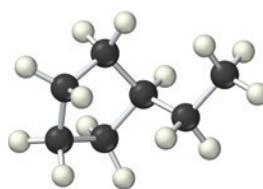
The first step is to draw the carbon backbone structure using each vertex or endpoint to represent a carbon atom. Connect the carbon atoms with single bonds.

#### SOLUTION

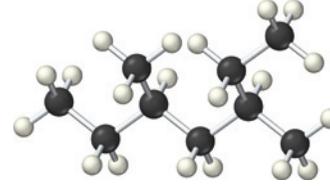


► **Conceptual PRACTICE 23.1** Convert the molecular models of the following alkanes into line drawings.

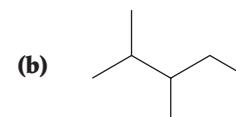
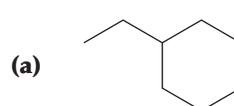
(a) Ethylcyclopentane



(b) 3,5-dimethylheptane



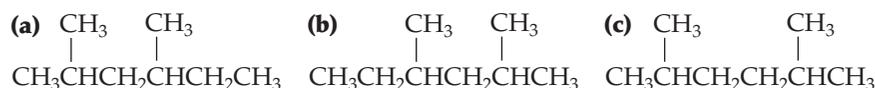
► **APPLY 23.2** Determine the molecular formula of the following alkanes from the line drawings.



### WORKED EXAMPLE 23.2

#### Identifying Isomeric Compounds

The following condensed structures have the same formula,  $C_8H_{18}$ . Which of them represent the same molecule and which are isomers?



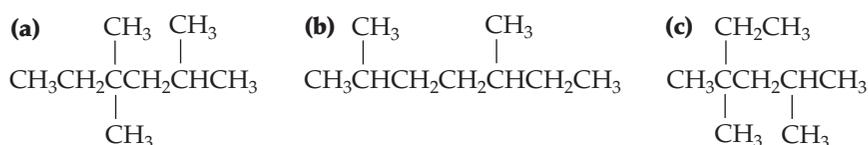
#### STRATEGY

Pay attention to the connections between atoms. Don't get confused by the apparent differences caused by writing a structure right-to-left versus left-to-right.

#### SOLUTION

Structure (a) has a straight chain of six carbons with  $-\text{CH}_3$  branches on the second and fourth carbons from the end. Structure (b) also has a straight chain of six carbons with  $-\text{CH}_3$  branches on the second and fourth carbons from the end and is therefore identical to (a). The only difference between (a) and (b) is that one is written "forward" and one is written "backward." Structure (c) has a straight chain of six carbons with  $-\text{CH}_3$  branches on the second and fifth carbons from the end, so it is an isomer of (a) and (b).

► **PRACTICE 23.3** Which of the following structures are identical?



► **APPLY 23.4** Draw the five isomers of the alkane with the formula  $C_6H_{14}$  as condensed structures and as line drawings.

## 23.2 ► FAMILIES OF ORGANIC COMPOUNDS: FUNCTIONAL GROUPS

Chemists have learned through experience that organic compounds can be classified into families according to their structural features and that the members of a given family often have similar chemical reactivity. Instead of 45 million compounds with random chemical behavior, there are a small number of families of compounds whose behavior is reasonably predictable.

The structural features that make it possible to classify compounds into families are called *functional groups*. A **functional group** is an atom or group of atoms within a molecule that has a characteristic chemical behavior and that undergoes the same kinds of reactions in every molecule where it occurs. Look at the carbon-carbon **double-bond** functional group, for instance. Ethylene ( $\text{H}_2\text{C}=\text{CH}_2$ ), the simplest compound with a double bond, undergoes reactions that are remarkably similar to those of menthene ( $\text{C}_{10}\text{H}_{18}$ ), a much larger and more complex molecule derived from peppermint oil. Both, for example, react with  $\text{Br}_2$  to give products in which a Br atom has added to each of the double-bond carbons (**FIGURE 23.2**).

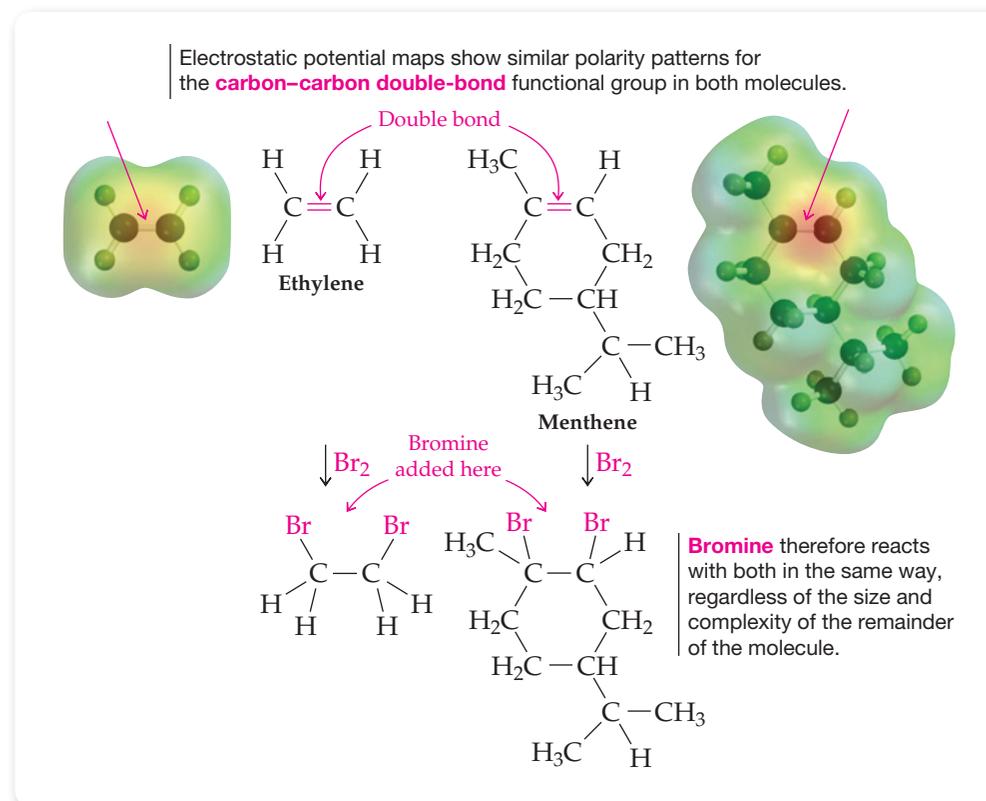
The example shown in Figure 23.2 is typical: the chemistry of an organic molecule, regardless of its size and complexity, is largely determined by the functional groups it contains.

#### REMEMBER...

A **double bond** is formed by sharing two pairs, or four electrons, between atoms. (Section 7.5)

▶ FIGURE 23.2

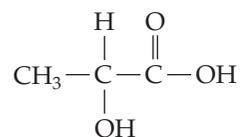
Reactions of the carbon–carbon double bond in ethylene and menthene with bromine.



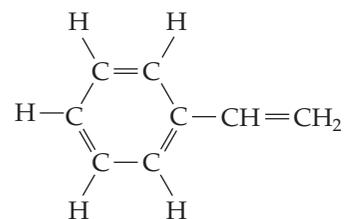
**TABLE 23.1** lists some of the most common functional groups and gives examples of their occurrence. Some functional groups such as alkenes, alkynes, and aromatic rings, have only carbon–carbon double or triple bonds; others contain single bonds to halogen, oxygen, or nitrogen atoms; and still others have carbon–oxygen double bonds. Most biological molecules, in particular, contain a  $\text{C}=\text{O}$ , called a **carbonyl**, which is present in several different functional groups.

**PROBLEM 23.5** Locate and identify the functional groups in the following molecules:

(a) Lactic acid, from sour milk



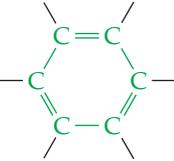
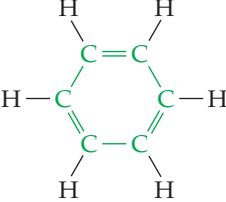
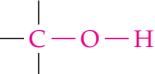
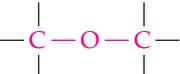
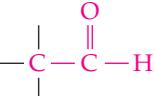
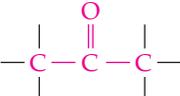
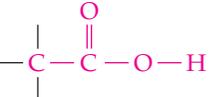
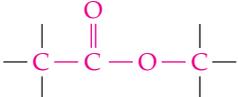
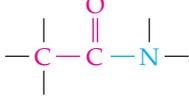
(b) Styrene, used to make polystyrene



**PROBLEM 23.6** Propose structures and represent structures with line drawings for molecules that fit the following descriptions:

- $\text{C}_3\text{H}_6\text{O}$ ; contains an aldehyde functional group
- $\text{C}_3\text{H}_6\text{O}_2$ ; contains a carboxylic acid functional group
- $\text{C}_4\text{H}_8\text{O}_2$ ; two isomers that contain ester groups
- $\text{C}_6\text{H}_{13}\text{N}$ , a cyclic structure with an amine group

TABLE 23.1 Some Families of Organic Compounds

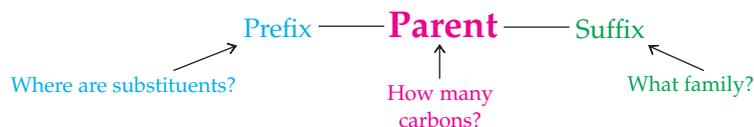
Family Name	Functional Group Structure	Simple Example	Name	Name Ending
Alkane	(contains only C—H and C—C single bonds)	CH <sub>3</sub> CH <sub>3</sub>	Ethane	-ane
Alkene		H <sub>2</sub> C=CH <sub>2</sub>	Ethene (Ethylene)	-ene
Alkyne		H—C≡C—H	Ethyne (Acetylene)	-yne
Arene (aromatic)			Benzene	None
Alcohol		CH <sub>3</sub> OH	Methanol	-ol
Ether		CH <sub>3</sub> OCH <sub>3</sub>	Dimethyl ether	ether
Amine		CH <sub>3</sub> NH <sub>2</sub>	Methylamine	-amine
Aldehyde		CH <sub>3</sub> CHO	Ethanal (Acetaldehyde)	-al
Ketone		CH <sub>3</sub> COCH <sub>3</sub>	Propanone (Acetone)	-one
Carboxylic acid		CH <sub>3</sub> COOH	Ethanoic acid (Acetic acid)	-oic acid
Ester		CH <sub>3</sub> COCH <sub>3</sub>	Methyl ethanoate (Methyl acetate)	-oate
Amide		CH <sub>3</sub> CONH <sub>2</sub>	Ethanamide (Acetamide)	-amide

The bonds whose connections aren't specified are assumed to be attached to carbon or hydrogen atoms in the rest of the molecule.

## 23.3 ► NAMING ORGANIC COMPOUNDS

Because there are so many organic compounds, it's particularly important to have a systematic way of assigning a unique and informative name to each. The system generally used for naming organic compounds is that devised by the International Union of Pure and Applied Chemistry, abbreviated IUPAC. In the IUPAC system, a chemical name has three parts: prefix, parent, and suffix. The parent name tells how many carbon atoms are present in the

longest continuous chain, the suffix identifies the family the molecule belongs to, and the prefix (if needed) specifies the various substituent groups attached to the parent chain:



## Naming Alkanes

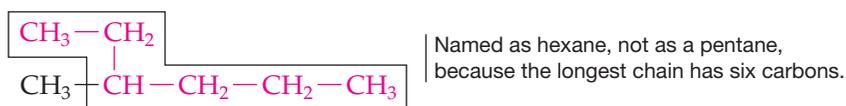
Let's use alkanes to illustrate the naming procedure. Straight-chain alkanes are named by counting the number of carbon atoms in the longest continuous chain and adding the family suffix *-ane*. With the exception of the first four compounds—methane, ethane, propane, and butane—whose names have historical origins, the alkanes are named from Greek numbers according to how many carbons they contain. Thus, *pentane* is the five-carbon alkane, *hexane* is the six-carbon alkane, *heptane* is the seven-carbon alkane, and so on, as shown in **TABLE 23.2**.

**TABLE 23.2** Names of Straight-Chain Alkanes

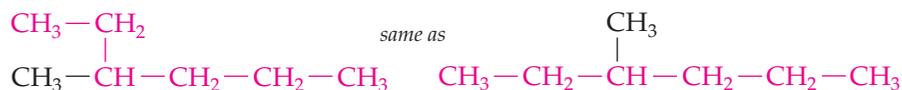
Number of Carbons	Structure	Name	Number of Carbons	Structure	Name
1	CH <sub>4</sub>	<i>Methane</i>	6	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	<i>Hexane</i>
2	CH <sub>3</sub> CH <sub>3</sub>	<i>Ethane</i>	7	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	<i>Heptane</i>
3	CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub>	<i>Propane</i>	8	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	<i>Octane</i>
4	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	<i>Butane</i>	9	CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub>	<i>Nonane</i>
5	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	<i>Pentane</i>	10	CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub>	<i>Decane</i>

Branched-chain alkanes are named by following four steps:

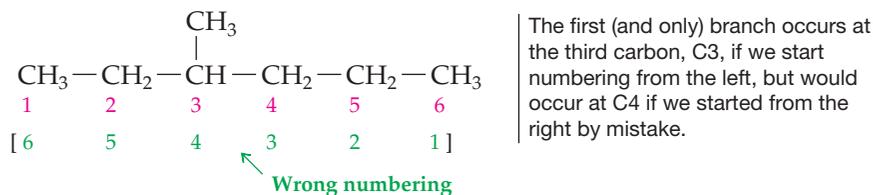
**Step 1. Name the parent chain.** Find the longest continuous chain of carbons in the molecule, and use the name of that chain as the parent. The longest chain may not always be obvious from the manner of writing; you may have to “turn corners” to find it.



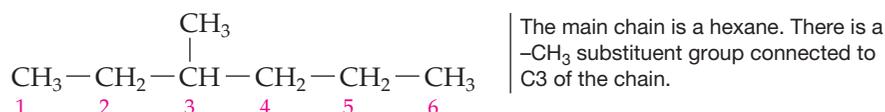
If you prefer, you can redraw the structure so that the longest chain is on one line.



**Step 2. Number the carbon atoms in the main chain.** Beginning at the end nearer the first branch point, number the carbon atoms in the parent chain.

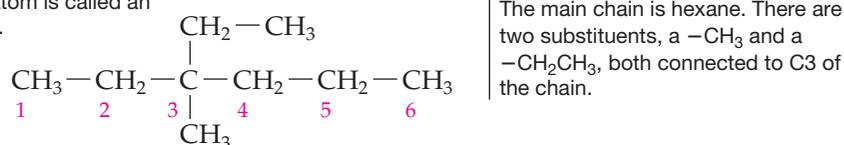


**Step 3. Identify and number the branching substituent.** Assign a number to each branching substituent on the parent chain according to its point of attachment.

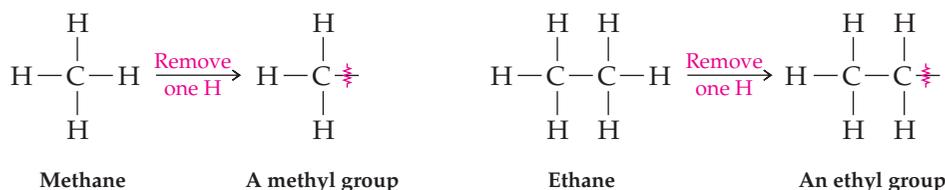


If there are two substituent groups on the same carbon, assign the same number to both. There must always be as many numbers in the name as there are substituents.

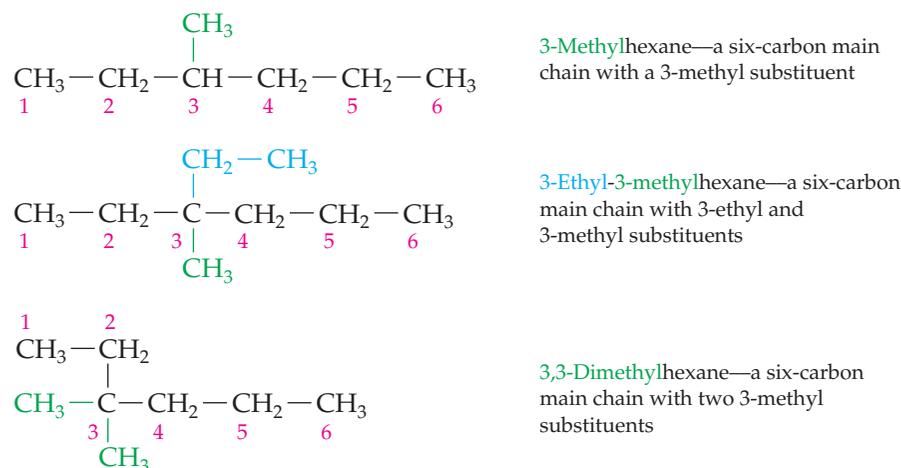
A substituent derived from an alkane by the removal of a hydrogen atom is called an alkyl group.



The  $-\text{CH}_3$  and  $-\text{CH}_2\text{CH}_3$  substituents that branch off the main chain are called **alkyl groups**. You can think of an alkyl group as the part of an alkane that remains when a hydrogen is removed. For example, removal of a hydrogen from methane,  $\text{CH}_4$ , gives the *methyl group*,  $-\text{CH}_3$ , and removal of a hydrogen from ethane,  $\text{CH}_3\text{CH}_3$ , gives the *ethyl group*,  $-\text{CH}_2\text{CH}_3$ . Alkyl groups are named by replacing the *-ane* ending of the parent alkane with a *-yl* ending.



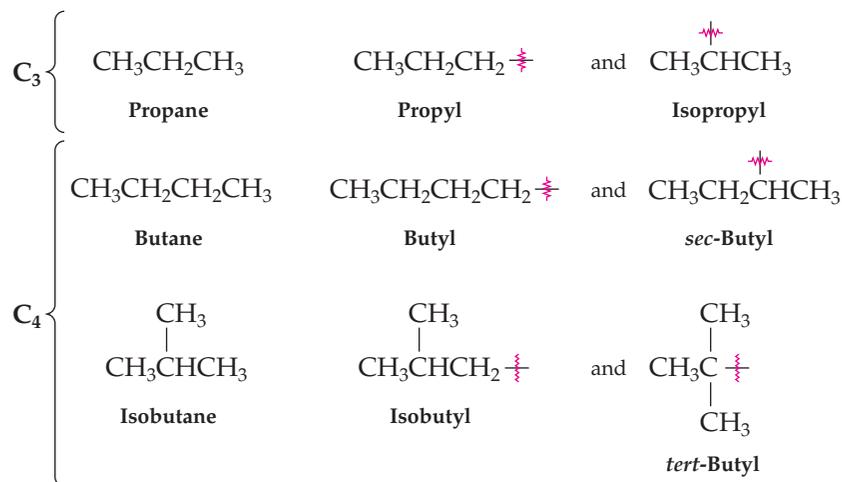
**Step 4. Write the name as a single word.** Use hyphens to separate the different prefixes, and use commas to separate numbers if there is more than one. If two or more different substituent groups are present, list them in alphabetical order. If two or more identical substituents are present, use a numerical prefix *di-*, *tri-*, *tetra-*, and so forth, but don't use these numerical prefixes for alphabetizing. That is, a prefix like "dimethyl" is listed alphabetically under "m" rather than under "d." Look at the following examples to see how names are written:



### More About Alkyl Groups

It doesn't matter which hydrogen is removed from  $\text{CH}_4$  to form a methyl group or which hydrogen is removed from  $\text{CH}_3\text{CH}_3$  to form an ethyl group because all the hydrogen atoms in both molecules are equivalent. The eight hydrogens in propane,  $\text{CH}_3\text{CH}_2\text{CH}_3$ , however, are not all equivalent. Propane has two sorts of hydrogens—six on the end carbons and two on the middle carbon. Depending on which hydrogen is removed, two different alkyl groups result. Removing one of the six hydrogens from an end carbon yields a straight-chain alkyl group called simply *propyl*, and removing one of the two hydrogens from the middle carbon yields a branched-chain alkyl group called *isopropyl*.

Similarly, there are four different butyl groups. Two (butyl and *sec*-butyl) are derived from straight-chain butane, and two (isobutyl and *tert*-butyl) are derived from branched-chain isobutane. The prefixes *sec*- (for *secondary*) and *tert*- (for *tertiary*) refer to the number of other carbon atoms attached to the branching carbon. The branch point in a *sec*-butyl group has two carbons attached to it, and the branch point in a *tert*-butyl group has three carbons attached.



Keep in mind that alkyl groups themselves are not stable compounds and that the “removal” of a hydrogen from an alkane is just a useful way of looking at things, not a chemical reaction. Alkyl groups are simply parts of molecules that help us to name compounds.

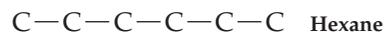
### WORKED EXAMPLE 23.3

#### Converting a Name into a Chemical Structure and Line Drawing

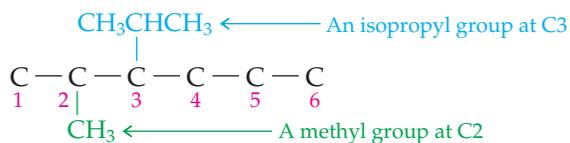
Draw the condensed structure and line drawing of 3-isopropyl-2-methylhexane.

##### STRATEGY AND SOLUTION

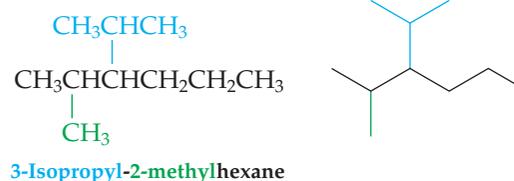
First, look at the parent name (hexane) and draw its carbon structure:



Next, find the substituents (3-isopropyl and 2-methyl) and place them on the proper carbons:



Finally, add hydrogens to complete the structure:



► **PRACTICE 23.7** Draw condensed structures and line drawings corresponding to the following IUPAC names:

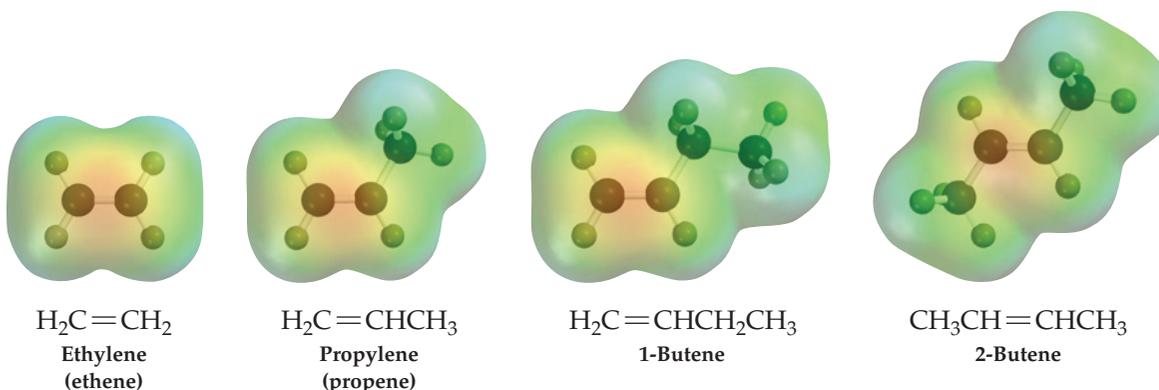
- (a) 3,4-Dimethylnonane      (b) 3-Ethyl-4,4-dimethylheptane  
(c) 2,2-Dimethyl-4-propyloctane      (d) 2,2,4-Trimethylpentane

► **APPLY 23.8** Draw three isomers of  $\text{C}_5\text{H}_{12}$  using the line drawing representation and give their IUPAC names.

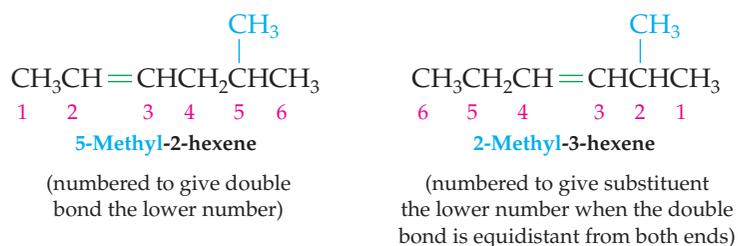
## Unsaturated Organic Compounds: Alkenes and Alkynes

In contrast to alkanes, which have only single bonds, alkenes and alkynes have multiple bonds. **Alkenes** are hydrocarbons that contain a carbon–carbon double bond, and **alkynes** are hydrocarbons that contain a carbon–carbon triple bond. Both groups of compounds are said to be **unsaturated**, meaning that they have fewer hydrogens per carbon than the related alkanes, which have the maximum possible number of hydrogens and are thus **saturated**. Ethylene ( $\text{H}_2\text{C}=\text{CH}_2$ ), for example, is unsaturated and has the formula  $\text{C}_2\text{H}_4$ , whereas ethane ( $\text{CH}_3\text{CH}_3$ ) is saturated and has the formula  $\text{C}_2\text{H}_6$ .

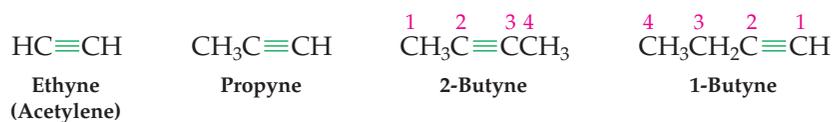
Alkenes are named by counting the longest chain of carbons that contains the double bond and adding the suffix *-ene*. Thus, ethylene, the simplest alkene, is followed by propene, butene, pentene, hexene, and so on. Note that ethylene should properly be called *ethene*, but the name ethylene has been used for so long that it is universally accepted. Similarly, the name *propylene* is often used for propene.



Isomers are possible for butene and higher alkenes depending on the position of the double bond in the chain, which must be specified by a numerical prefix. Numbering starts from the chain end nearer the double bond, and only the number of the first of the double-bond carbons is cited. If a substituent is present on the chain, its identity is noted and the position of its attachment is given. If the double bond is equidistant from both ends of the chain, numbering starts from the end nearer the substituent.



Isomers, called *cis-trans* isomers, that occur due to the geometry of the double bond in alkenes will be discussed in Section 23.5. Alkynes are similar in many respects to alkenes and are named using the suffix *-yne*. The simplest alkyne,  $\text{HC}\equiv\text{CH}$ , is often called by its alternative name *acetylene* rather than by its systematic name *ethyne*.

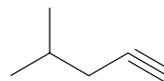


As with alkenes, isomers are also possible for butyne and higher alkynes, depending on the position of the triple bond in the chain.

### WORKED EXAMPLE 23.4

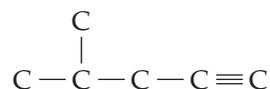
#### Naming and Drawing Unsaturated Compounds

Determine the condensed formula, molecular formula, and name for the following unsaturated organic compound.

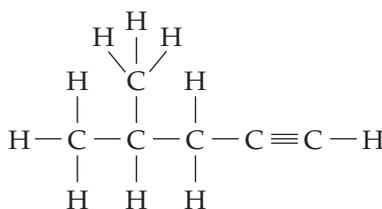


#### STRATEGY AND SOLUTION

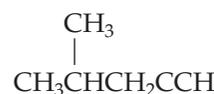
**Step 1. Determine the carbon backbone.** Find the number of carbon atoms by counting the number of vertices or endpoints and draw the backbone of carbon atoms. Add multiple bonds in the correct location.



**Step 2. Satisfy the octet rule by adding bonds to hydrogen.** Fulfill the octet for carbon by adding single bonds to hydrogen so that each carbon has a total of four bonds. To determine the molecular formula simply count up the atoms in the complete electron-dot structure.



Electron-dot structure  
4-Methyl-1-pentyne

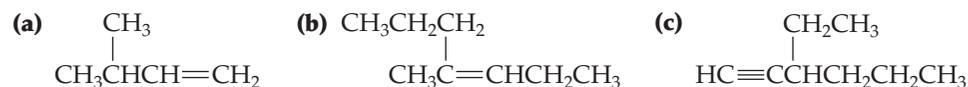


Condensed formula



Molecular formula

► **PRACTICE 23.9** What is the IUPAC name and line drawing for the following unsaturated organic compounds?



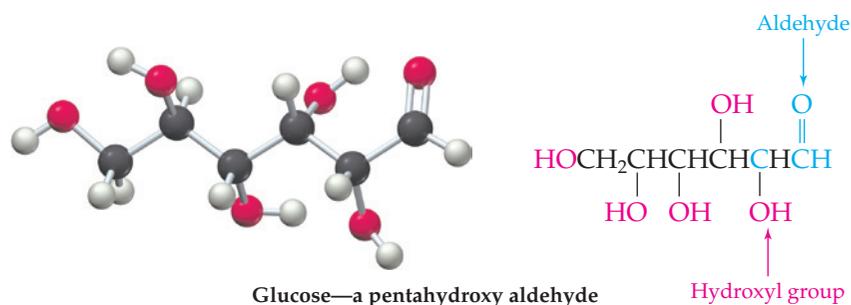
► **APPLY 23.10** What is the line drawing corresponding to the following IUPAC names?



## 23.4 ► CARBOHYDRATES: A BIOLOGICAL EXAMPLE OF ISOMERS

We have seen how isomers (Sections 21.1 and 21.3) result when the atoms of a molecule can be connected in different ways, as in variations in the branching of alkanes and in the positions of functional groups, such as the double bond in alkenes. *Carbohydrates*, which are molecules found in every living organism, exhibit several different types of isomerism. Familiar carbohydrates are starch in food and cellulose in grass. Modified carbohydrates form part of the coating around all living cells, and other carbohydrates are found in the DNA that carries genetic information from one generation to the next.

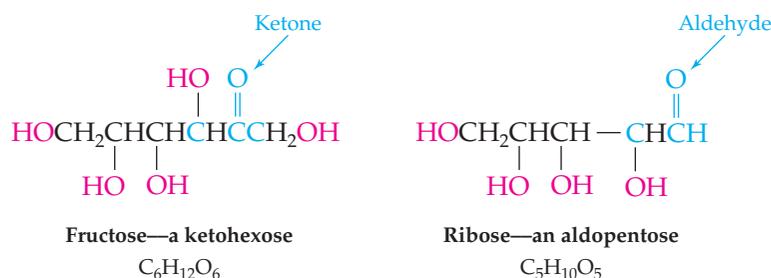
The word carbohydrate was used originally to describe glucose, which has the formula  $\text{C}_6\text{H}_{12}\text{O}_6$  and was once thought to be a “hydrate of carbon,” with a general formula of  $(\text{C}\cdot\text{H}_2\text{O})_n$  (where  $n \geq 3$ ) such as  $\text{C}_6(\text{H}_2\text{O})_6$  for glucose. This view was soon abandoned, but the word persisted; the term **carbohydrate** is now used to refer to the large class of polyhydroxylated aldehydes and ketones that we commonly call *sugars*. Glucose, for example, is a six-carbon aldehyde with five hydroxyl (OH) groups.



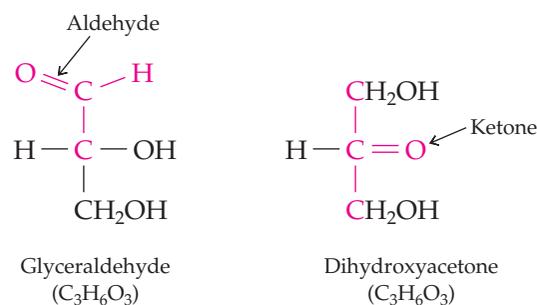
Carbohydrates are classified as either *simple* or *complex*. Simple sugars, or **monosaccharides**, are carbohydrates such as glucose and fructose that can't be broken down into smaller molecules by hydrolysis with aqueous acid. Complex carbohydrates, or **polysaccharides**, are compounds such as cellulose and starch that are made of many simple sugars linked together and *can* be broken down by hydrolysis.

### Monosaccharides

Monosaccharides are classified according to three different characteristics: the placement of its carbonyl group, the number of carbon atoms it contains, and its three-dimensional arrangement of atoms. An *aldose* contains a carbonyl group (C=O) in an aldehyde functional group; a *ketose* contains carbonyl group in a ketone functional group. The *-ose* suffix indicates a sugar, and the number of carbon atoms in the sugar is specified by using the appropriate numerical prefix *tri-*, *tetr-*, *pent-*, or *hex-*. Glucose, for example, is an aldohexose (a six-carbon aldehyde sugar), fructose is a ketohexose (a six-carbon ketone sugar), and ribose is an aldopentose (a five-carbon aldehyde sugar). Most commonly occurring sugars are either aldopentoses or aldohexoses.



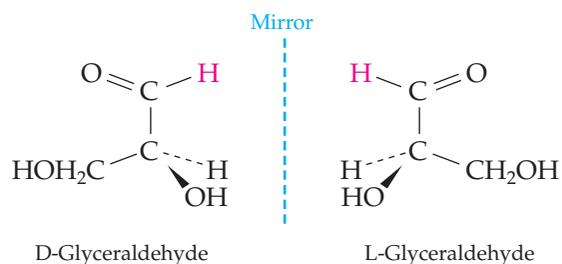
Carbohydrates can exist in a variety of isomeric forms, but we'll just consider three types—*constitutional isomers*, *enantiomers*, and *anomers*. Two compounds are **constitutional isomers** when they have the same chemical formula but different connections between atoms. Isomers of linear and branched alkanes are a good example of constitutional isomers (Section 23.1). The smallest monosaccharides consist of three carbon atoms. Two of these, glyceraldehyde and dihydroxyacetone, are examples of constitutional isomers because the atoms are connected in different ways.



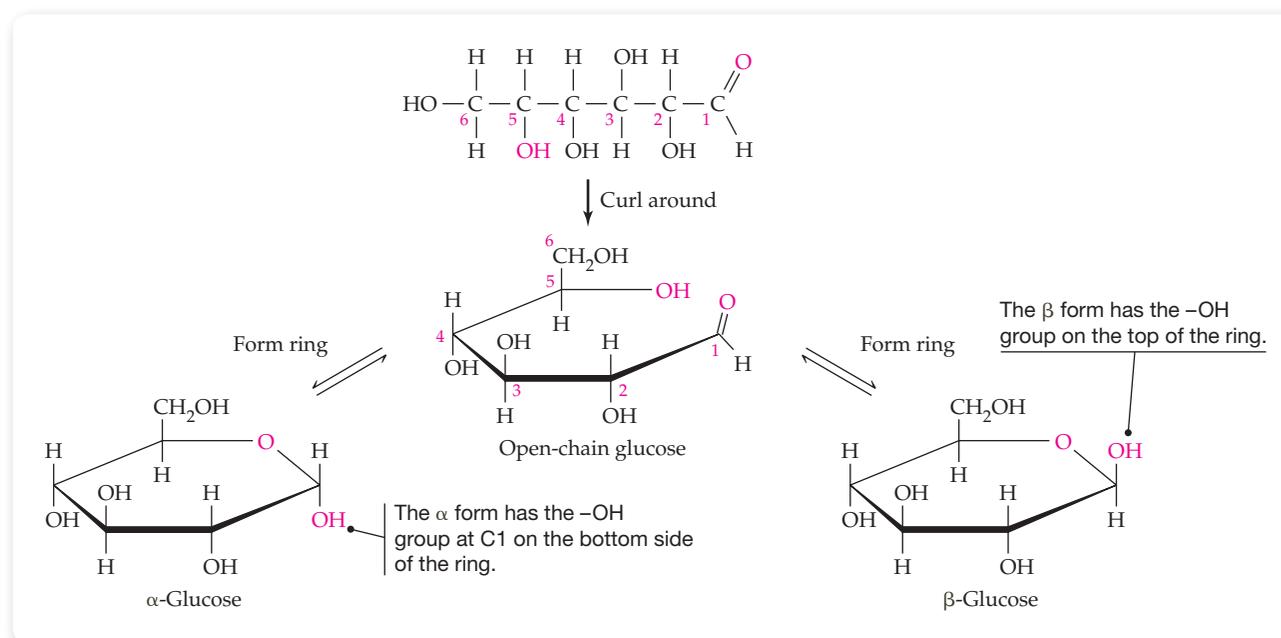
**REMEMBER...**

**Chiral** molecules are nonsuperimposable mirror images that occur when a central atom with tetrahedral geometry has four different groups attached (*Inquiry* Chapter 8).

Carbohydrates can also exist as **enantiomers**, nonidentical mirror images. **Chiral** molecules have enantiomers and are said to exhibit a “handedness” because just like your hands they are nonsuperimposable mirror images. The Latin prefixes *dextro* (D) and *levo* (L) mean “right” and “left,” respectively. Glyceraldehyde is a chiral molecule, and its enantiomers are:



Glucose and other monosaccharides are often shown for convenience as having open-chain structures. They actually exist, however, primarily as cyclic molecules in which an —OH group near one end of the chain adds to the carbonyl group at or near the other end of the chain to form a ring. In glucose, ring formation occurs between the —OH group on C5 and the C=O group at C1 (**FIGURE 23.3**).

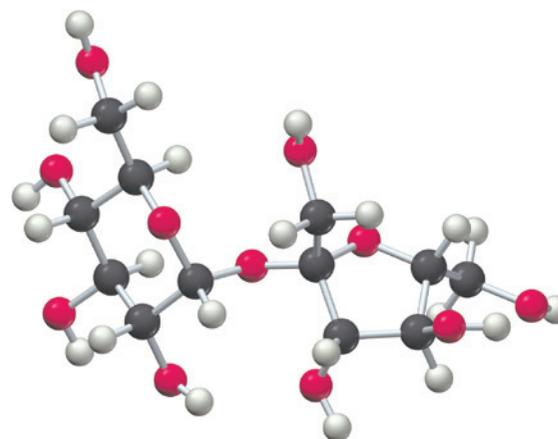
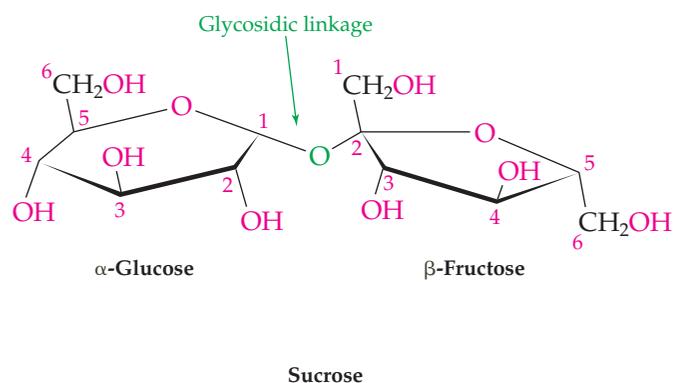


**▲ FIGURE 23.3**  
The cyclic  $\alpha$  and  $\beta$  forms of glucose.

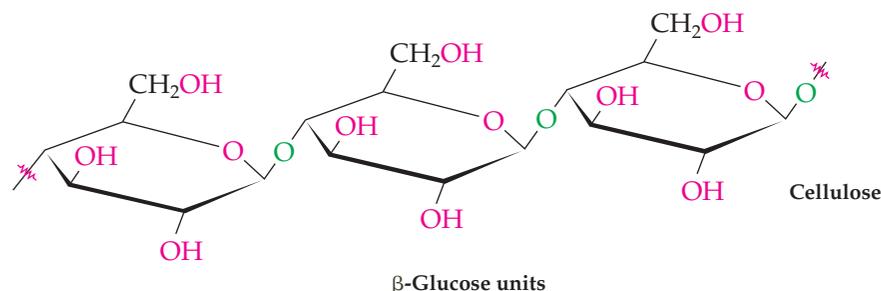
Two cyclic forms of glucose, called **anomers**, can result from ring formation, depending on whether the newly formed —OH group at C1 is on the bottom or top side of the ring. The ordinary crystalline glucose you might take from a bottle is entirely the cyclic  $\alpha$  form, in which the C1 —OH group is on the bottom side of the ring. At equilibrium in water solution, however, all three forms are present in the proportion 0.02% open-chain form, 36%  $\alpha$  form, and 64%  $\beta$  form.

### Polysaccharides

Sucrose, or plain table sugar, is probably the most common pure organic chemical in the world. Sucrose is found in many plants; sugar beets (20% by mass) and sugar cane (15% by mass) are the most common sources. Chemically, sucrose is a *disaccharide*, meaning a sugar composed of two monosaccharides—in this case, one molecule of glucose and one molecule of fructose join together with a glycosidic linkage. The 1:1 mixture of glucose and fructose that results from hydrolysis of sucrose, often called *invert sugar*, is commonly used as a food additive.

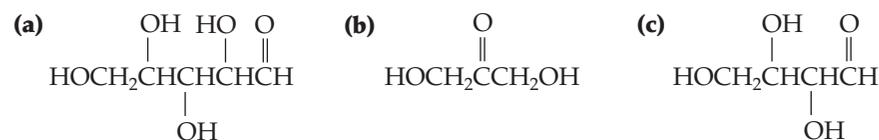


Cellulose, the fibrous substance that forms the structural material in grasses, leaves, and stems, is a polysaccharide composed of several thousand  $\beta$ -glucose molecules joined together to form an immense chain.



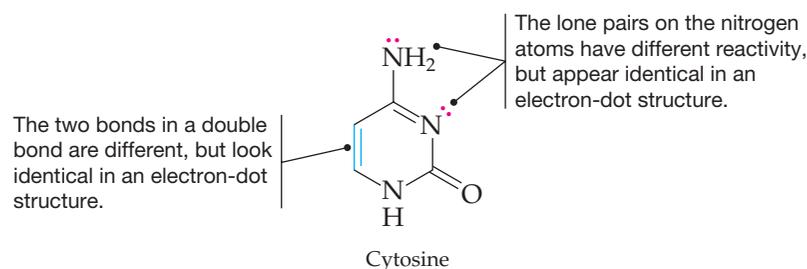
Starch is also made of several thousand glucose units but, unlike cellulose, is edible for humans. Indeed, the starch in such vegetables as beans, rice, and potatoes is an essential part of the human diet. The difference between the two polysaccharides is that cellulose contains  $\beta$ -glucose units, while starch contains  $\alpha$ -glucose units. Our stomach contains enzymes that are so specific in their action they are able to digest starch molecules while leaving cellulose untouched.

**PROBLEM 23.11** Classify each of the following monosaccharides as an aldose or a ketose:



## 23.5 ▶ VALENCE BOND THEORY AND ORBITAL OVERLAP PICTURES

Electron-dot structures and line drawings are relatively simple models that indicate the connectivity of atoms and locations of multiple bonds and lone pairs of electrons in a molecule. However, these simplistic models have limitations. Consider cytosine, a component in deoxyribonucleic acid (DNA):



In an electron-dot structure, the two bonds of the double bond (highlighted in blue) look identical. In reality, however, they are two kinds of bonds with different strengths and

reactivity. In a similar argument, we would have no reason to expect the lone pairs on the two nitrogen atoms (in pink) to have differences in structure or reactivity, but they are very different. If we want to understand these differences, we need a more complete picture of bonding and electron distribution in molecules.

Valence bond theory (Section 8.2) uses an orbital overlap picture to show how electron pairs are shared in a chemical bond. A covalent bond results when singly filled valence orbitals overlap spatially and electrons are attracted to both nuclei. Applying valence bond theory to organic molecules is not fundamentally different than what you have learned previously and visualizing orbital overlap is important in interpreting structure and reactivity. At this point, you should review valence bond theory and hybridization in Sections 8.2–8.4. You should be able to:

1. Determine the hybridization of a central atom in an electron-dot structure.
2. Describe the difference between a sigma ( $\sigma$ ) and a pi ( $\pi$ ) bond.
3. Sketch orbitals that overlap to form sigma ( $\sigma$ ) and pi ( $\pi$ ) bonds.

Worked Example 23.5 describes orbital overlap in an organic molecule with single bonds and Worked Example 23.6 describes orbital overlap in an organic molecule with double bonds.

### WORKED EXAMPLE 23.5

#### Visualizing Orbital Overlap in Organic Molecules with Single Bonds

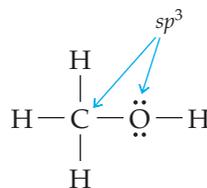
Draw an orbital overlap picture for methanol (commonly known as wood alcohol),  $\text{CH}_3\text{OH}$ .

#### STRATEGY

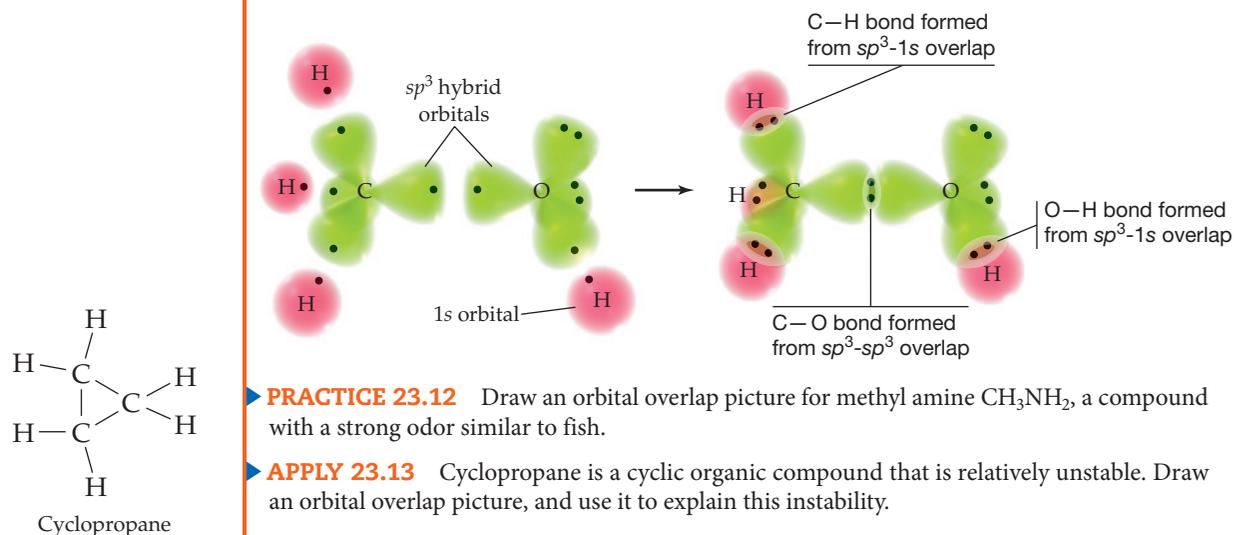
Draw the electron-dot structure for  $\text{CH}_3\text{OH}$  and determine the hybridization on each central atom. Overlap atomic or hybrid orbitals to make single bonds and fill in nonbonding orbitals with lone pairs as indicated by the electron-dot structure.

#### SOLUTION

The electron-dot structure for methanol is:



The carbon atom forms four bonds; three with hydrogen and one with oxygen and is therefore  $sp^3$  hybridized. Oxygen has two bonds and two lone pairs and is also  $sp^3$  hybridized. Overlap three carbon  $sp^3$  orbitals with  $1s$  orbitals of hydrogen to form  $\text{C}-\text{H}$  bonds. Overlap the remaining carbon  $sp^3$  orbital with an oxygen  $sp^3$  orbital to form the  $\text{C}-\text{O}$  bond. Account for the  $\text{O}-\text{H}$  bond by overlapping another oxygen  $sp^3$  orbital with the  $1s$  orbital of hydrogen. The two lone pairs on oxygen are placed in the two nonbonding  $sp^3$  orbitals of oxygen.



### WORKED EXAMPLE 23.6

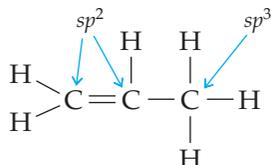
#### Visualizing Orbital Overlap in Unsaturated Organic Molecules

Draw an orbital overlap picture for propene, the monomer used to make plastics for garbage bags. The structure of propene is  $\text{CH}_2=\text{CHCH}_3$ .

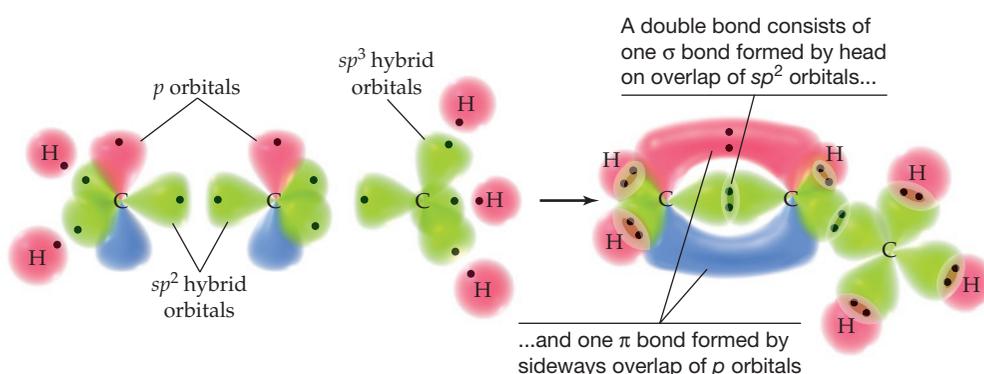
#### STRATEGY

Draw an electron-dot structure for propene and identify the hybridization of the central atoms. Overlap atomic or hybridized orbitals to make sigma ( $\sigma$ ) bonds and overlap unhybridized  $p$  orbitals to make pi ( $\pi$ ) bonds.

#### SOLUTION



To make the  $\text{C}=\text{C}$  double bond, overlap one  $sp^2$  hybrid orbital from each of the  $sp^2$  hybridized carbon atoms to make a  $\sigma$  bond, and then line up the  $p$  orbitals for sideways overlap to make a  $\pi$  bond. The remaining  $sp^2$  orbitals should all be in the same plane. Overlap three of them with the  $1s$  orbitals of three hydrogen atoms to make  $\text{C}-\text{H}$  bonds. Overlap the third  $sp^2$  orbital of the central carbon atom with an  $sp^3$  orbital from the carbon on the right to make a  $\text{C}-\text{C}$  single bond. Make the remaining  $\text{C}-\text{H}$  bonds by overlapping the carbon  $sp^3$  orbitals with the  $1s$  orbitals of three hydrogen atoms.



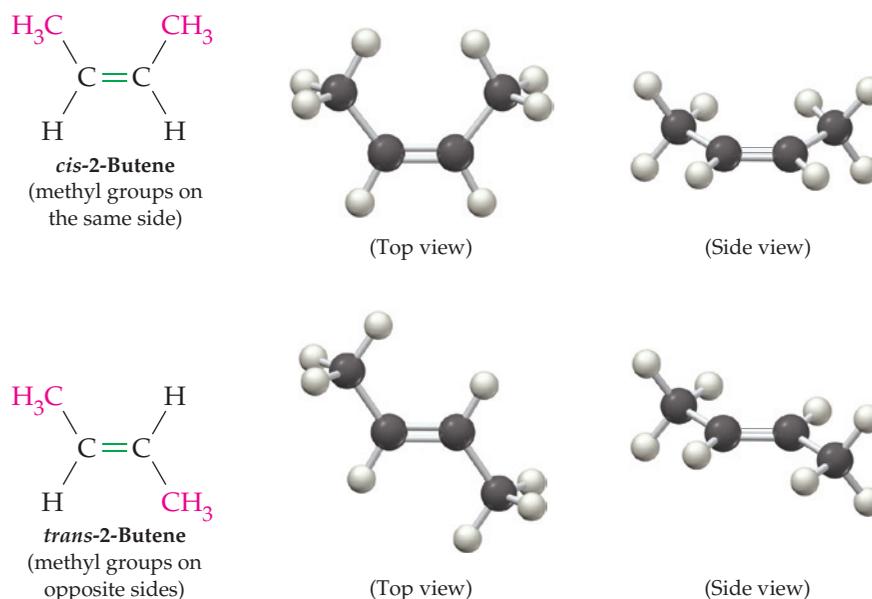
#### PRACTICE 23.14

- Draw an orbital overlap picture for formaldehyde,  $\text{O}=\text{CH}_2$ .
- Are the lone pair electrons in the same plane as the  $\pi$  bond?
- Are the lone pairs in the same plane as the hydrogen atoms?

#### APPLY 23.15

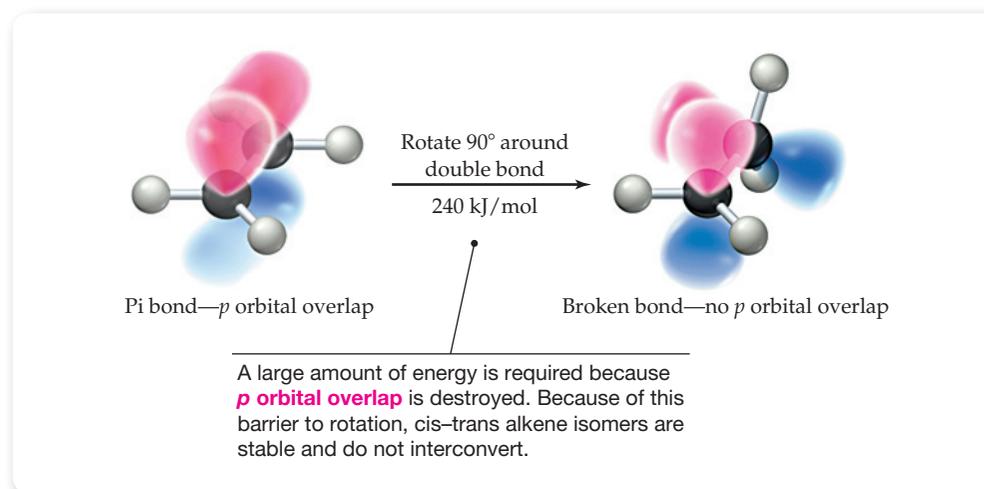
- Draw an electron-dot structure for the compound  $\text{C}_2\text{H}_2\text{O}$ . (The carbon atoms are connected.)
- Draw an orbital overlap picture.

Although  $sp$ -hybridized atoms do occur in organic molecules, they are relatively rare. However,  $sp^2$ -hybridized atoms are common and very important. The orbital overlap creating a  $\pi$  bond restricts rotation around the bond and has important implications in the structure of organic molecules. For instance, there are two geometrical isomers, or **cis-trans isomers**, of 2-butene, which differ in their geometry about the double bond. The cis isomer has its two  $-\text{CH}_3$  groups on the same side of the double bond, and the trans isomer has its two  $-\text{CH}_3$  groups on opposite sides.



Cis-trans isomerism in alkenes arises because of the electronic structure of the double bond, which makes bond rotation energetically unfavorable. Were rotation to occur, it would break the  $\pi$  part of the double bond by disrupting the sideways overlap of two parallel  $p$  orbitals (FIGURE 23.4). An energy input of 240 kJ/mol is needed to cause bond rotation in 2-butene.

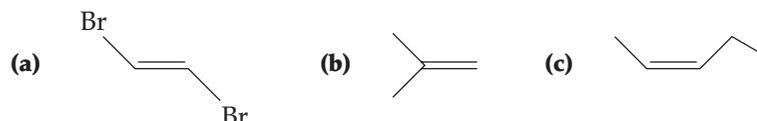
► **FIGURE 23.4**  
Rotation around a carbon-carbon double bond.



### WORKED EXAMPLE 23.7

#### Identifying and Drawing Cis-Trans Isomers

Which of the molecules (a-c) can exhibit cis-trans isomerism? For those that have this type of isomer, show the line drawing of the corresponding cis or trans isomer.

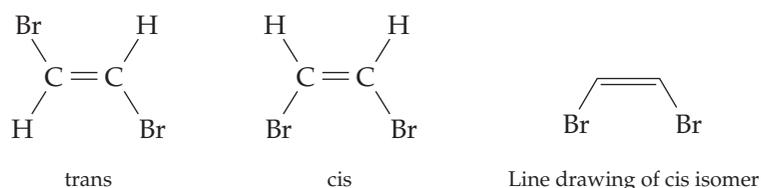


#### STRATEGY

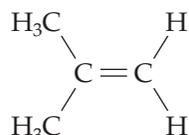
It is often easier to visualize organic line drawings by converting them back into structural formulas. The presence of cis-trans isomerism exists when each carbon atom in a double bond has two *different* substituents attached.

#### SOLUTION

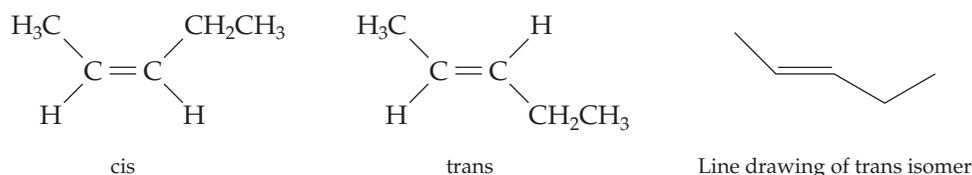
(a) Cis-trans isomers exist because the Br atoms can be placed on the same side or on opposite sides of the double bond.



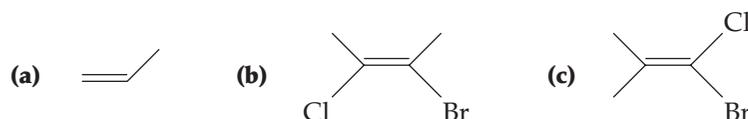
(b) This structure has two  $\text{—CH}_3$  (methyl) groups bonded to the same C atom, therefore cis-trans isomers do not exist.



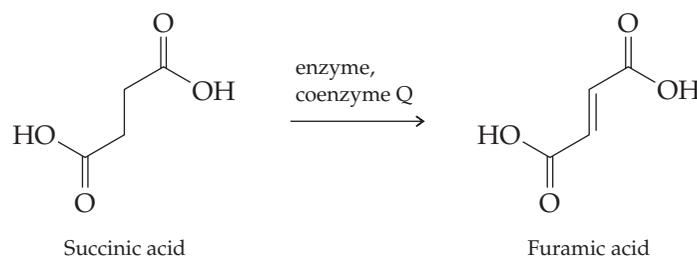
(c) Cis-trans isomers exist because each carbon has two different substituents attached.



► **PRACTICE 23.16** Which of the following molecules can exhibit cis-trans isomerism? If these isomers exist, show the line drawing of the corresponding cis or trans isomer.



► **APPLY 23.17** The Krebs cycle (citric acid cycle) is a metabolic pathway in which energy is harvested from carbohydrates. In the process, succinic acid is converted to fumaric acid.



- (a) Is fumaric acid cis or trans?  
 (b) Draw the structure of maleic acid, the geometric isomer of fumaric acid.  
 (c) Does succinic acid have cis and trans isomers? Explain.

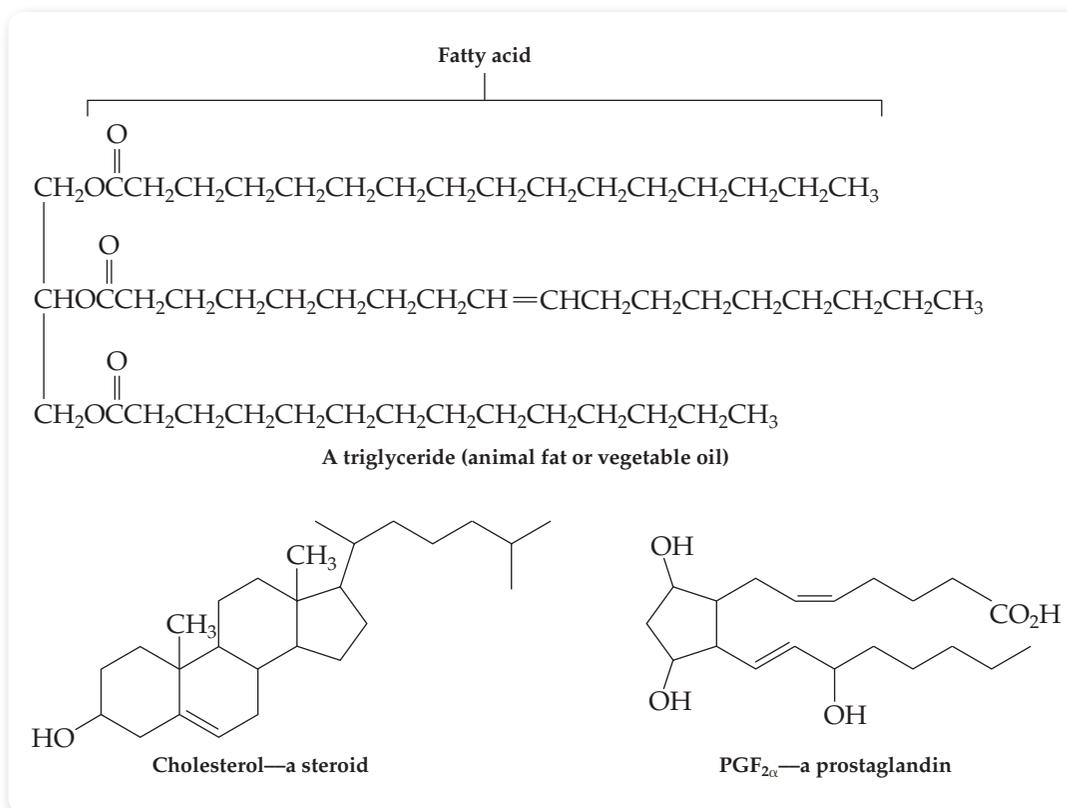
## 23.6 ► LIPIDS: A BIOLOGICAL EXAMPLE OF CIS-TRANS ISOMERISM

Lipids have many important biological functions, serving as sources of fuel, as protective coatings around many plants and insects, and as components of the membranes that enclose every living cell. Chemically, a **lipid** is a naturally occurring organic molecule that dissolves in a nonpolar organic solvent when a sample of plant or animal tissue is crushed or ground. Because they're defined by solubility, a physical property, rather than by chemical structure, it's not surprising that there are a great many different kinds of lipids (**FIGURE 23.5**). Note that all the lipids in Figure 23.5 contain large hydrocarbon portions, which accounts for their solubility behavior.

Animal fats and vegetable oils are the most abundant lipids in nature. Although they appear physically different—animal fats like butter and lard are usually solid while vegetable oils like corn and peanut oil are liquid—their structures are similar. All fats and oils are

▶ FIGURE 23.5

**Structures of some representative lipids.** All are isolated from plant and animal tissue by extraction with nonpolar organic solvents, and all have large hydrocarbon portions.



**triacylglycerols**, or *triglycerides*, esters of glycerol (1,2,3-propanetriol) with three long-chain carboxylic acids called **fatty acids**. The fatty acids are usually unbranched and have an even number of carbon atoms in the range 12–22.

As shown by the triacylglycerol structure in Figure 23.5, the three fatty acids of a given molecule need not be the same. Furthermore, the fat or oil from a given source is a complex mixture of many different triacylglycerols. TABLE 23.3 shows the structures of some commonly occurring fatty acids.

TABLE 23.3 Structures of Some Common Fatty Acids

Name	No. of Carbons	No. of Double Bonds	Structure
<b>Saturated</b>			
Myristic	14	0	$\text{CH}_3(\text{CH}_2)_{12}\text{CO}_2\text{H}$
Palmitic	16	0	$\text{CH}_3(\text{CH}_2)_{14}\text{CO}_2\text{H}$
Stearic	18	0	$\text{CH}_3(\text{CH}_2)_{16}\text{CO}_2\text{H}$
<b>Unsaturated</b>			
Oleic	18	1	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{CO}_2\text{H}$ (cis)
Linoleic	18	2	$\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{CO}_2\text{H}$ (all cis)
Linolenic	18	3	$\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{CO}_2\text{H}$ (all cis)

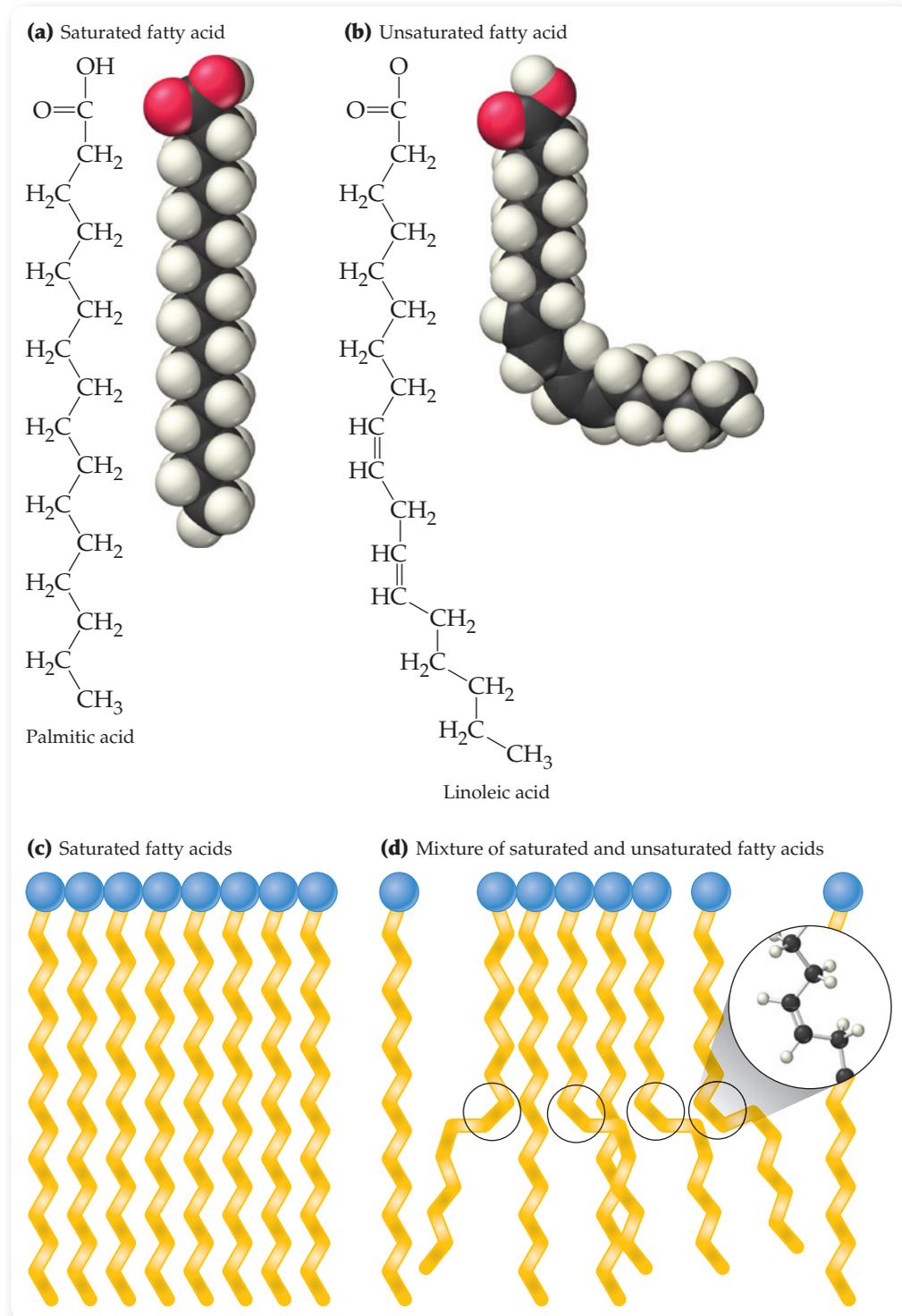
About 40 different fatty acids occur naturally. Palmitic acid ( $\text{C}_{16}$ ) and stearic acid ( $\text{C}_{18}$ ) are the most abundant saturated acids; oleic and linoleic acids (both  $\text{C}_{18}$ ) are the most abundant unsaturated ones. Oleic acid is monounsaturated because it has only one double bond, but linoleic and linolenic acids are *polyunsaturated fatty acids* because they have more than one carbon–carbon double bond. For reasons that are not yet clear, a diet rich in saturated fats leads to a higher level of blood cholesterol and consequent higher risk of heart attack than a diet rich in unsaturated fats.

The main difference between animal fats and vegetable oils is that vegetable oils generally have a higher proportion of unsaturated fatty acids than do animal fats. This is useful in explaining their macroscopic properties. Why is animal lard a solid at room temperature

while vegetable oil is a liquid? This can be explained by considering the number and geometry of the unsaturated fatty acids present in a fat. **FIGURE 23.6** shows that in a fat composed of mainly saturated fatty acids, the hydrocarbon tails are able to line up with one another to maximize **London dispersion forces**. Even though each individual London dispersion interaction is relatively weak, many interactions add up to strongly hold these fatty acid molecules together, making them solids. On the other hand, vegetable oils have a significant number of unsaturated fatty acids in the cis configuration. This geometry disrupts intermolecular forces substantially, making these oils liquid at room temperature.

**REMEMBER...**

**London dispersion forces** are intermolecular forces that occur when the distribution of electrons in a molecule temporarily shifts causing a temporary dipole. (Section 8.6)

**FIGURE 23.6**

(a) A saturated fatty acid, palmitic acid, showing a straight-chain hydrocarbon tail. (b) An unsaturated fatty acid, linoleic acid, showing bends at the double bonds in the hydrocarbon tails. (c) Saturated fatty acids pack tightly together leading to strong London dispersion forces. (d) The geometry of unsaturated fatty acids in the cis configuration disrupts packing.



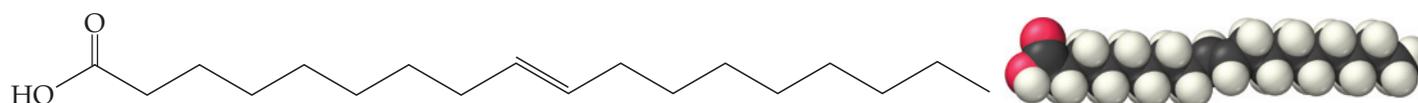
that they must be taken in through our diet because humans cannot biosynthesize them from other dietary building blocks.

One numbering system for lipids starts with the number “1” on the carboxylic acid functional group, and numbers until it reaches the last carbon in the chain. Another common numbering system uses Greek letters. Since the last letter in Greek is omega, this system numbers from the last carbon toward the carboxylic acid. Thus an “omega-3” fatty acid has a double bond starting on the third carbon from the end of the chain. Arachidonic acid can be called an omega-6 fatty acid. Both omega-3 and omega-6 fatty acids are essential fatty acids for humans.

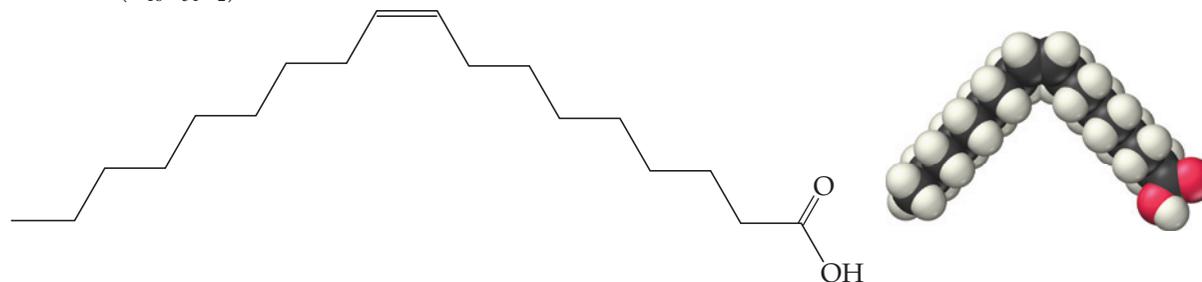
Arachidonic acid can be classified by **lipid number** as a 20:4( $\omega - 6$ ) fatty acid. The number 20 indicates the number of carbons, the number 4 indicates the number of unsaturations, and omega-6 indicates where the last double bond in the chain is located.

**PROBLEM 23.18** Label the configuration around the double bond in the fatty acids as cis or trans.

(a) Elaidic acid ( $C_{18}H_{34}O_2$ )



(b) Oleic acid ( $C_{18}H_{34}O_2$ )



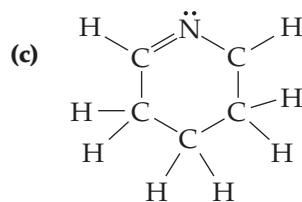
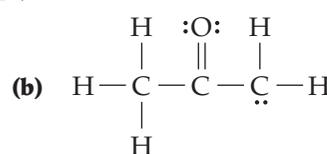
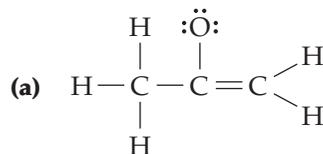
## 23.7 ► FORMAL CHARGE AND RESONANCE IN ORGANIC COMPOUNDS

**Formal charge** and **resonance** in organic compounds play an important role in understanding both structure and reactivity. In organic line drawings, formal charges must be indicated for correct interpretation. If formal charge is not indicated, the drawing is incorrect! Most organic reactions occur between regions of high and low electron density which is often shown by formal charge. Worked Example 23.8 shows how to calculate and represent formal charges in line drawings of organic molecules.

### WORKED EXAMPLE 23.8

#### Calculating Formal Charges in Organic Molecules

For the following electron-dot structures, give the line drawing and indicate any nonzero formal charges on atoms. (Note: It is possible to have resonance structures with electron-deficient carbon atoms because orbitals can be empty. However, carbon can never expand its octet.)



#### REMEMBER...

**Formal charge** is the number of valence electrons in an isolated atom minus the number of valence electrons assigned to an atom in an electron-dot structure. (Section 7.10)

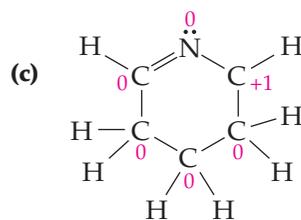
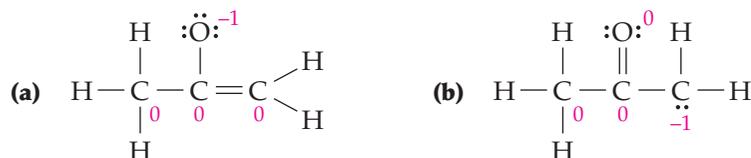
#### REMEMBER...

Different **resonance** forms of a substance differ only in the placement of bonding and nonbonding electrons. The connections between atoms and the relative positions of the atoms remain the same. (Section 7.9)

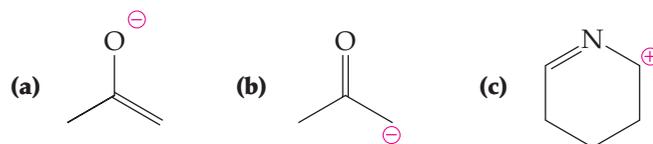
**STRATEGY**

**Step 1.** Apply the formula for calculating formal charge given in Section 7.10 to each carbon and oxygen atom in each structure as shown.

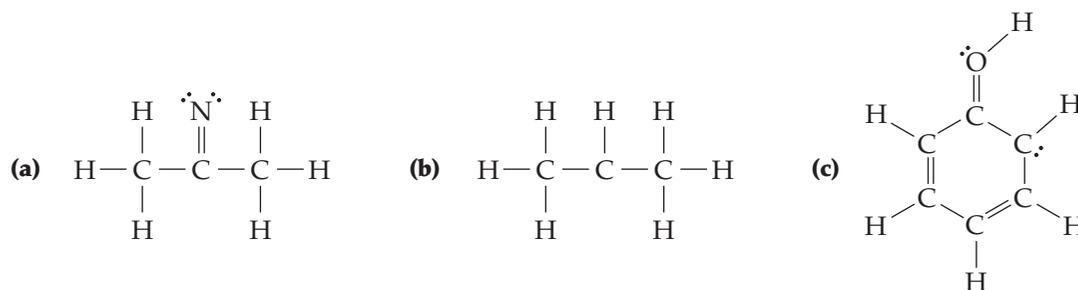
$$\text{Formal charge} = \left( \begin{array}{c} \text{Number of} \\ \text{valence electrons} \\ \text{in free atom} \end{array} \right) - \frac{1}{2} \left( \begin{array}{c} \text{Number of} \\ \text{bonding} \\ \text{electrons} \end{array} \right) - \left( \begin{array}{c} \text{Number of} \\ \text{nonbonding} \\ \text{electrons} \end{array} \right)$$



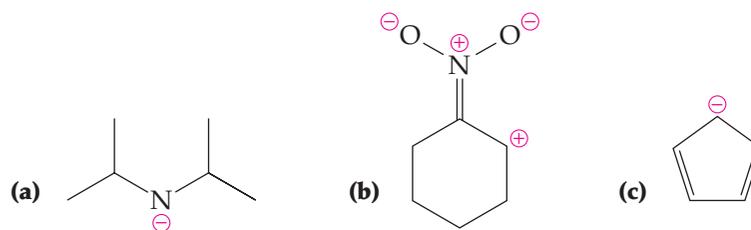
**Step 2.** Convert the electron-dot structure into a line drawing by indicating carbon-carbon bonds with a line. Do not show hydrogen atoms or lone pairs of electrons. Be sure to indicate all nonzero formal charges on atoms in the line drawing.

**SOLUTION**

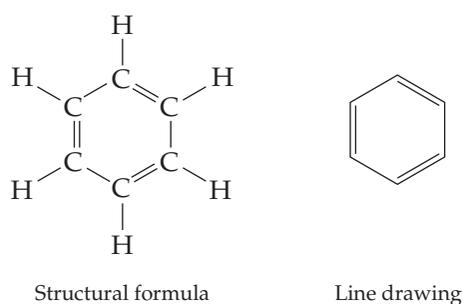
► **PRACTICE 23.19** For the following electron-dot structures, give the line drawing and indicate any nonzero formal charges on atoms.



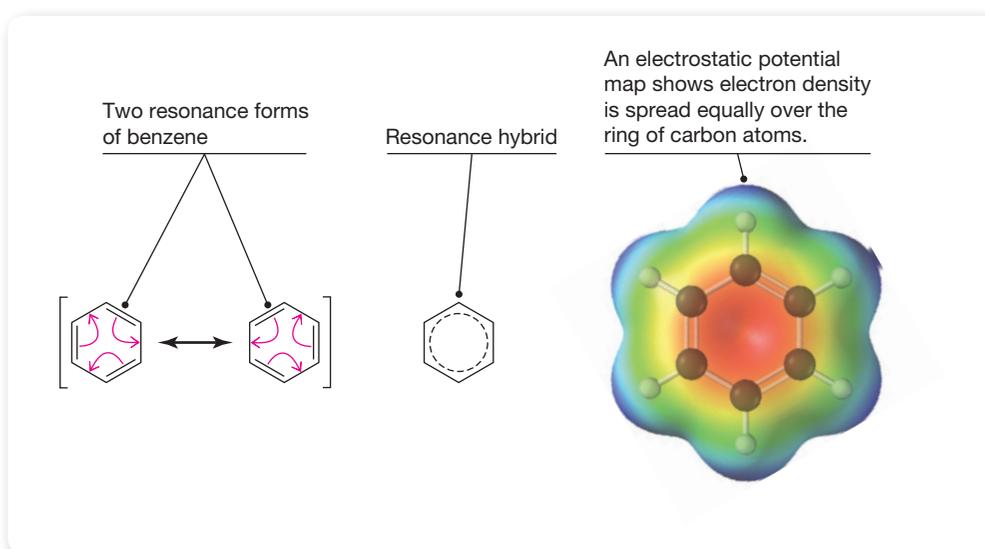
► **APPLY 23.20** Draw complete electron-dot structures from the line drawing by adding lone pairs of electrons and hydrogen atoms.



Resonance theory describes experimental observations about bond lengths and strengths in large organic molecules just as it does with small inorganic molecules like ozone (Section 7.9). It also helps explain how compounds react by predicting stability and sites of high and low electron density. The molecule benzene,  $C_6H_6$ , is a classic example of resonance in organic compounds. Benzene was first isolated from the oily residue in London street lamps in 1825 but is now an important industrial chemical used to manufacture pharmaceuticals, plastics, detergents, and pesticides. Benzene,  $C_6H_6$ , is a ring of six carbon atoms consisting of alternating single and double bonds:



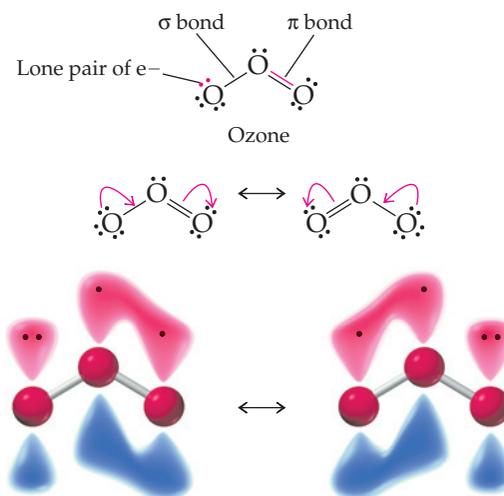
**FIGURE 23.8** shows that two resonance structures can be drawn for benzene and curved arrows show the interconversion of one form into another. The resonance hybrid for benzene is typically represented as a hexagon with a circle in the center, to convey it is a blend of the two contributing resonance structures. The circle represents the spreading or delocalization of electrons in the double bonds over all six carbon atoms in the ring. Electron delocalization diffuses electron density over a greater volume, which reduces electron–electron repulsions, stabilizing the molecule. The resonance hybrid can be thought of as an *average* of the two resonance structures, thus resulting in carbon–carbon bonds that are between a single and a double bond. Experimental determination of the structure of benzene verifies that there are six equivalent carbon–carbon bonds with a bond length of 139 pm, which is between a C—C single bond (154 pm) and a C=C double bond (134 pm). The electrostatic potential map shows the electron density is spread equally over the ring of carbon atoms.



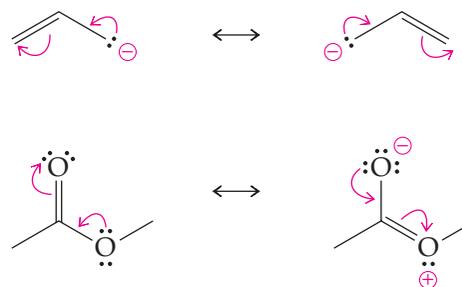
◀ **FIGURE 23.8**  
Resonance forms of benzene.

It is very helpful to recognize common patterns that indicate a resonance structure can be drawn for an organic molecule. Three important patterns are summarized below.

1. The first pattern occurs when there is a lone pair of electrons on an atom one  $\sigma$  bond away from a  $\pi$  bond. The ozone molecule (Section 7.9) is an example of this pattern and the resonance structures are:



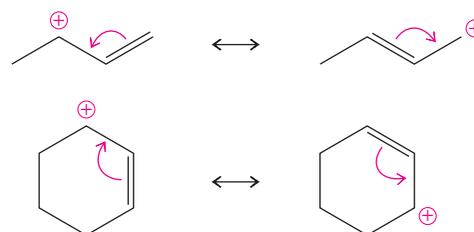
Examples of organic molecules that fit the same resonance pattern as ozone are shown:



2. A second resonance pattern occurs with a polar  $\pi$  bond, such as  $C=O$ . In this pattern, the  $\pi$  bond can be rewritten as a lone pair on the electronegative oxygen atom.



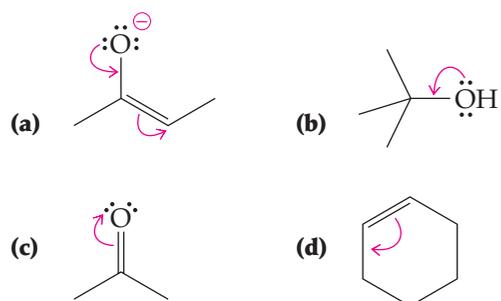
3. A third resonance pattern occurs when a positive formal charge resides on a carbon atom one  $\sigma$  bond away from a  $\pi$  bond as shown:



### WORKED EXAMPLE 23.6

#### Drawing Resonance Structures for Organic Molecules

Draw the electron-dot structure that results from the curved arrows shown below. If an incorrect structure results, explain why. For valid structures give the line drawing and indicate which resonance structure is preferred based on formal charge.



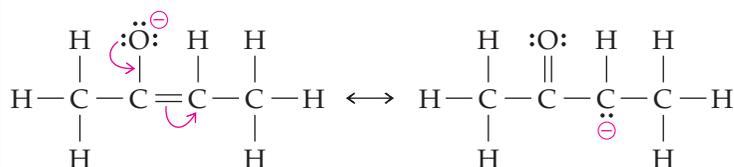
#### STRATEGY

Draw the complete electron-dot structure by adding hydrogen atoms and lone pairs. Then rearrange electrons as indicated by the curved arrows and check to make sure that the octet rule is not exceeded. Assign formal charges and evaluate the best structure based upon criteria given in Section 7.10 and summarized below.

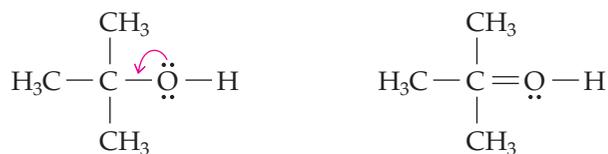
- Smaller formal charges (either positive or negative) are preferable to larger ones. Zero is preferred over  $-1$ , but  $-1$  is preferred over  $-2$ .
- Negative formal charges should reside on more electronegative atoms.
- Like charges should not be on adjacent atoms.

#### SOLUTION

- (a) The resonance structure on the left is preferred because the negative formal charge is on the more electronegative oxygen atom.

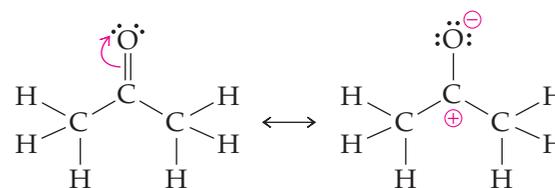


- (b) Arrow results in an incorrect electron-dot structure because carbon cannot have five bonds.

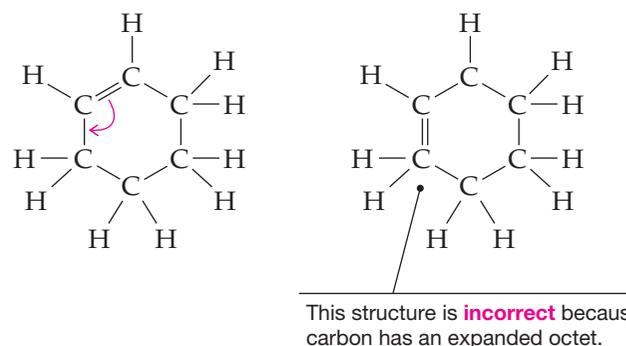


**Incorrect** electron-dot structure because carbon has five bonds (expanded octet)

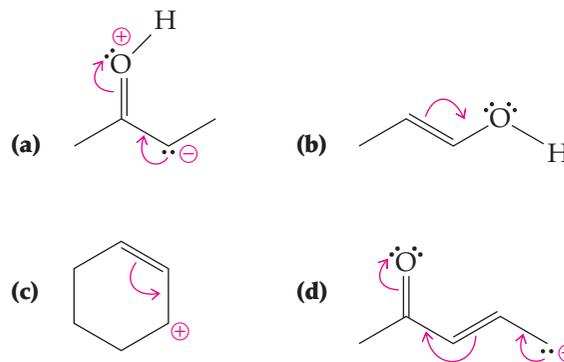
- (c) The resonance structure on the left is preferred since formal charge on all atoms is zero. Energy is required to separate  $+$  and  $-$  charges, so the structure without formal charges is probably lower in energy than the structure with formal charges.



- (d) Arrow results in an incorrect electron-dot structure because carbon cannot have five bonds.



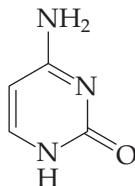
- **PRACTICE 23.21** Determine if the arrow depicting electron rearrangement to form a new electron-dot structure is valid. If an incorrect structure results, explain why. If it is valid, show the line drawing of the resonance structure. Indicate which resonance structure is preferred based on formal charge.



continued on next page

## ▶ APPLY 23.22

- (a) Draw a complete electron-dot structure for cytosine, a constituent of DNA, by adding lone pairs and hydrogen atoms to the line drawing.



- (b) Draw curved arrows in the electron-dot structure you drew in part (a) to generate the resonance structure shown.

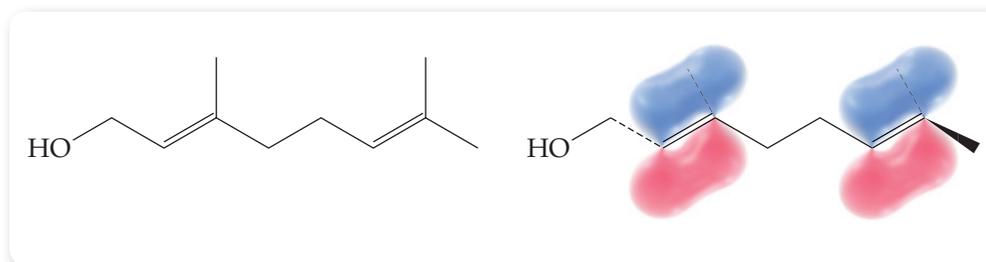


## 23.8 ▶ CONJUGATED SYSTEMS

Using both line drawings and orbital overlap pictures, we can get a pretty good picture of the bonding of organic molecules. The line drawing has the advantage of being simple while orbital overlap pictures help us to see the locations of electrons within molecules. When considering molecules with  $\pi$  bonds, it is sometimes beneficial to blend both approaches together. Because the electrons in  $\pi$  bonds are not directly between two nuclei, these electrons tend to be more reactive than the electrons in  $\sigma$  bonds. To make a picture that is both useful and as simple as possible, structures are sometimes drawn with  $\sigma$  bonds in a line drawing with the  $p$  orbitals superimposed on  $sp^2$  hybridized atoms. For instance, geraniol is a major component of rose and citronella oil. It would be difficult to draw a full orbital overlap picture for this molecule, but we can draw a picture that emphasizes the  $p$ -orbital overlap as shown in **FIGURE 23.9**.

## ▶ FIGURE 23.9

A simplified orbital overlap picture of the  $\pi$  bonds in geraniol.

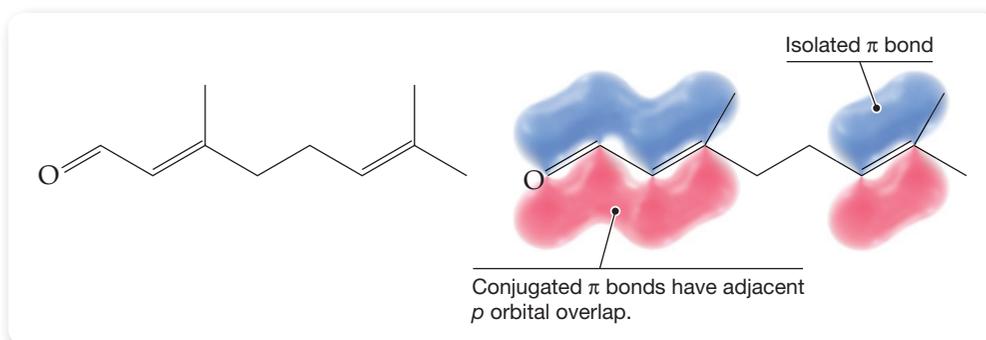


Pictures like this are even more useful in understanding a molecule like geranial, a molecule closely related to geraniol with a strong lemon smell (**FIGURE 23.10**). Geranial contains a **pi ( $\pi$ ) system**, in which there are more than two  $p$  orbitals adjacent to each other. In geranial, there are four  $sp^2$  hybridized atoms in a row. The two  $\pi$  bonds of this  $\pi$  system are not independent; they strongly affect one another.

The  $\pi$  system can be explained by examining the following picture of the  $p$  orbitals. Although the line drawing shows two distinct  $\pi$  bonds, one a  $C=O$   $\pi$  bond, and one a  $C=C$   $\pi$  bond, the orbital picture makes it clear that there is some overlap between the four  $p$  orbitals. All four of the atoms have been “joined together” in terms of their orbitals. **Conjugated systems** occur when  $p$  orbitals are connected in compounds with alternating single and multiple bonds. We therefore say that the two  $\pi$  bonds separated by a  $\sigma$  bond are **conjugated**.

## ▶ FIGURE 23.10

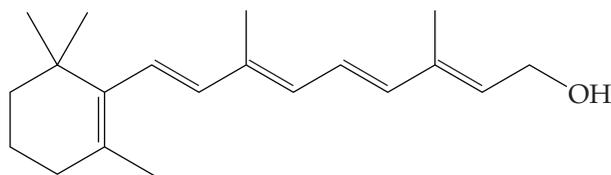
Conjugated  $\pi$  bonds and isolated  $\pi$  bonds in the molecule geranial.



### WORKED EXAMPLE 23.10

#### Drawing Simplified Orbital Overlap Pictures for $\pi$ Systems

Draw a simplified orbital overlap picture of vitamin A and identify any conjugated bonds.

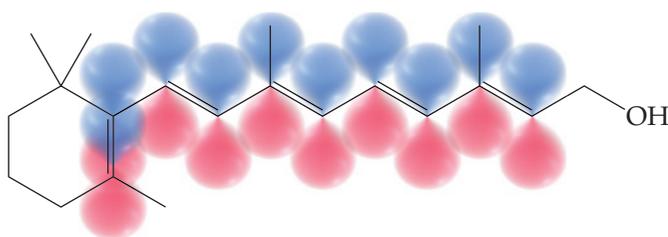


#### STRATEGY

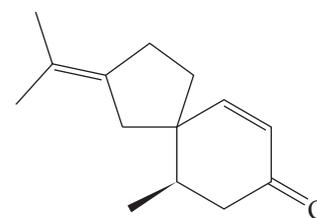
Superimpose  $p$  orbitals for the  $\pi$  bonds on the line drawing for vitamin A. Identify conjugation by finding all atoms with  $p$  orbitals that overlap each other.

#### SOLUTION

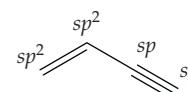
Vitamin A has 10 carbon atoms in one  $\pi$  system. We can also say that all 10 carbon atoms are conjugated.



► **PRACTICE 23.23** Draw a simplified orbital overlap picture of beta-vetivone, an ingredient in perfumes. Label the  $\pi$  bonds as conjugated or nonconjugated.



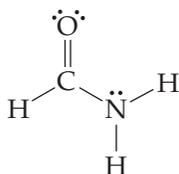
► **APPLY 23.24** In the molecule below, the triple bond has one  $\pi$  bond that is in conjugation with the neighboring double bond, and it has one  $\pi$  bond that is not conjugated. Visualize a simplified orbital overlap picture and explain why one  $\pi$  bond of the triple bond has delocalized electrons, but the other does not. (The hybridization of each atom is indicated.)



### Conjugation and Resonance

In line drawings, electrons appear to be localized in bonds between two atoms. However, in a conjugated system, the electrons are better described as **delocalized**, or associated with more than one or two atoms in a molecule. You have already been introduced to **molecular orbitals (MOs)** in Sections 8.7 and 8.8, which provide a good picture of delocalization and we'll explore this concept further in Section 23.10. For now, we can expand the concept of valence bond theory to explain delocalization.

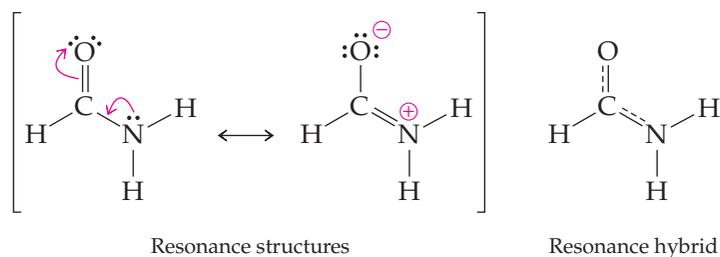
One of the most useful aspects of conjugation is its ability to give a structural basis to the concept of resonance. Consider the molecule formamide:



You learned to recognize the pattern of a lone pair of electrons on an atom one  $\sigma$  bond away from a  $\pi$  bond and to draw resonance structures in Section 23.7. Both structures are blended in a resonance hybrid, which is a better picture of electron distribution than either resonance structure by itself.

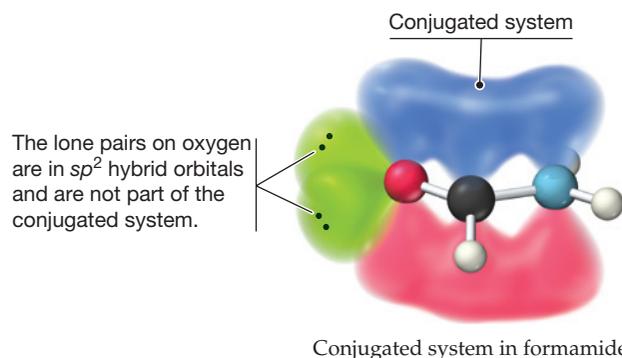
#### REMEMBER...

**Molecular orbitals (MOs)** are wave functions whose square gives the probability of finding an electron in a region of space spread over the entire molecule.

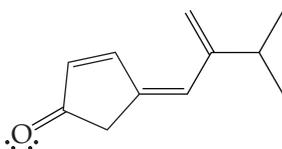


But what is the actual structure of the molecule? According to resonance theory, the double bond is not fluctuating between the  $C=O$  and  $C=N$ , but is in both places all the time. How is this possible? It is possible because the carbon, nitrogen, and oxygen atoms are all  $sp^2$  hybridized, and the  $p$  orbitals are conjugated. A simplified orbital picture of formamide shows localized electrons in the  $\sigma$  bonds and delocalized electrons in the  $\pi$  bonds.

We see that bonding is possible across all three  $p$  orbitals, since all three overlap. A simple electron-dot structure implies that the electrons exist as a discrete  $\pi$  bond and a discrete lone pair, but a conjugated picture shows all four of these electrons as spread out over all three atoms, supporting the resonance concept. According to resonance theory, there is not a lone pair on nitrogen. Rather, this lone pair is *resonance stabilized* by being delocalized over three atoms.



The simplified orbital overlap picture also provides a structural explanation of the double bond in the resonance hybrid. The hybrid model suggests double bond character between the carbon and nitrogen atoms as well as between the carbon and oxygen atoms. The lone pairs on oxygen, in contrast, are localized on one atom because they are in  $sp^2$  hybrid orbitals.



Molecule for problem 23.25

#### PROBLEM 23.25

- (a) Draw a resonance structure for the molecule shown.
- (b) How many electrons are delocalized?

### Conjugation and Hybridization

The major principle of valence bond theory is that *atoms will adopt the hybridization that makes the molecule most stable by lowering the overall energy*. To make the most stable structural picture of a molecule, keep in mind the following two principles:

1. *Conjugation is immensely stabilizing; therefore, always look for conjugated systems within a molecule first.* You can recognize conjugated systems by the same traits that characterize resonance structures: a lone pair of electrons on an atom one  $\sigma$  bond away from a  $\pi$  bond, two  $\pi$  bonds separated by a  $\sigma$  bond, or a positive formal charge on an atom one  $\sigma$  bond away from a  $\pi$  bond. Once you have identified the atoms in a conjugated system, remember that they must be  $sp$  or  $sp^2$  hybridized to have a  $p$  orbital for conjugation.
2. *If an atom is not conjugated, it will adopt a stable hybridization according to the VSEPR model.* Electrons that don't overlap in conjugated systems tend to repel each other as far as possible.

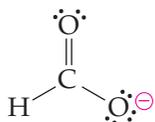
#### REMEMBER...

The **VSEPR (valence shell electron pair repulsion) model** considers electrons in bonds and lone pairs as charge clouds that repel one another causing molecules to assume specific shapes.

### WORKED EXAMPLE 23.11

#### Determining Hybridization of Atoms in Organic Molecules with $\pi$ Bonds

Formate is the compound that causes the sting of ant bites. Determine the hybridization of each atom in formate, then draw a simplified orbital overlap picture of formate, including lone pairs in appropriate orbitals.



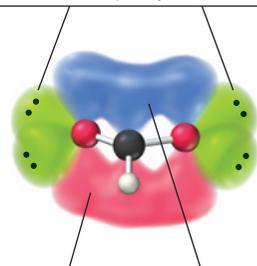
#### STRATEGY

First, determine the hybridization of each atom by looking for conjugation, then moving to VSEPR if necessary. Next, draw an orbital overlap picture.

#### SOLUTION

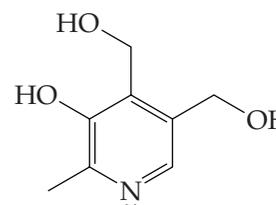
The electron-dot structure shows a  $\pi$  bond between the carbon atom and one of the oxygen atoms. The other oxygen atom has a lone pair of electrons one  $\sigma$  bond away from a  $\pi$  bond and is therefore in the conjugated system. Thus, the carbon atom and both oxygen atoms are  $sp^2$  hybridized. One lone pair on the oxygen atom is delocalized in the  $\pi$  system. All other lone pairs on oxygen are in  $sp^2$  hybridized orbitals.

These four lone pairs are localized in  $sp^2$  hybrid orbitals

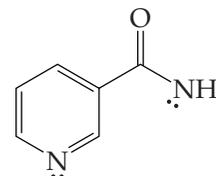


The  $\pi$  system is a series of three overlapped  $p$  orbitals with four delocalized electrons

► **PRACTICE 23.26** Pyridoxine, the precursor to vitamin B<sub>6</sub> is shown below. What is the hybridization of each oxygen atom?



► **APPLY 23.27** Niacinamide, the precursor for coenzyme NADH, is shown below. One of the nitrogen lone pairs is localized, and the other is delocalized. Label each lone pair on nitrogen and localized or delocalized.



## 23.9 ► PROTEINS: A BIOLOGICAL EXAMPLE OF CONJUGATION

A concept like “delocalized electrons” might seem a bit abstract. How could this apply to life? It turns out that conjugation and delocalization of electrons play a key role in the structure and function of an important class of biological molecules, proteins.

Taken from the Greek *proteios*, meaning “primary,” the name *protein* aptly describes a group of biological molecules that are of primary importance to all living organisms. Approximately 50% of the human body’s dry weight is protein, and almost all the reactions that occur in the body are catalyzed by proteins. In fact, a human body is thought to contain more than 150,000 different kinds of proteins.

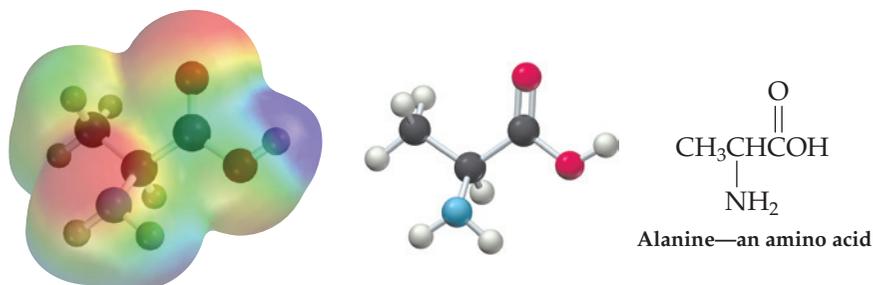
Proteins have many different biological functions. Some, such as the keratin in skin, hair, and fingernails, serve a structural purpose. Others, such as the insulin that controls carbohydrate metabolism, act as hormones—chemical messengers that coordinate the activities



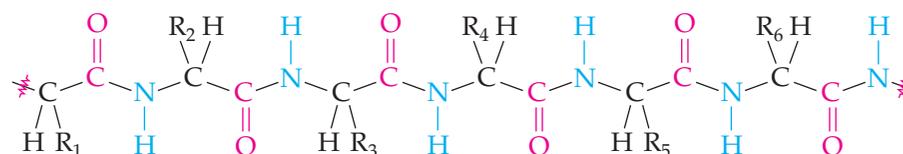
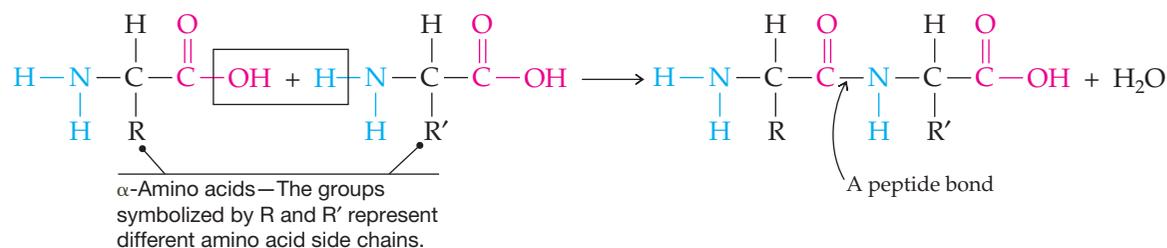
▲ Bird feathers are made largely of the protein keratin.

of different cells in an organism. And still other proteins, such as DNA polymerase, are **enzymes**, the biological catalysts that carry out body chemistry, as discussed in Section 13.14.

Chemically, **proteins** are made up of many *amino acid* molecules linked together to form a long chain. As their name implies, amino acids contain two functional groups, a basic amino group ( $-\text{NH}_2$ ) and an acidic  $-\text{CO}_2\text{H}$  group. Alanine is one of the simplest examples.



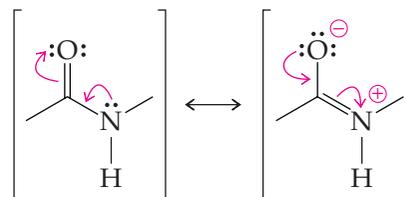
Two or more amino acids can link together by forming amide bonds, usually called **peptide bonds**, between the  $-\text{NH}_2$  group of one and the  $-\text{CO}_2\text{H}$  group of the other. A *dipeptide* results when two amino acids link together by one amide bond, a *tripeptide* results when three amino acids link together with two peptide bonds, and so on. Short chains of up to 50 amino acids are usually called **peptides**, while the terms *polypeptide* and *protein* are generally used for longer chains.



A segment of a protein backbone. The side-chain R groups of the individual amino acids are substituents on the backbone.

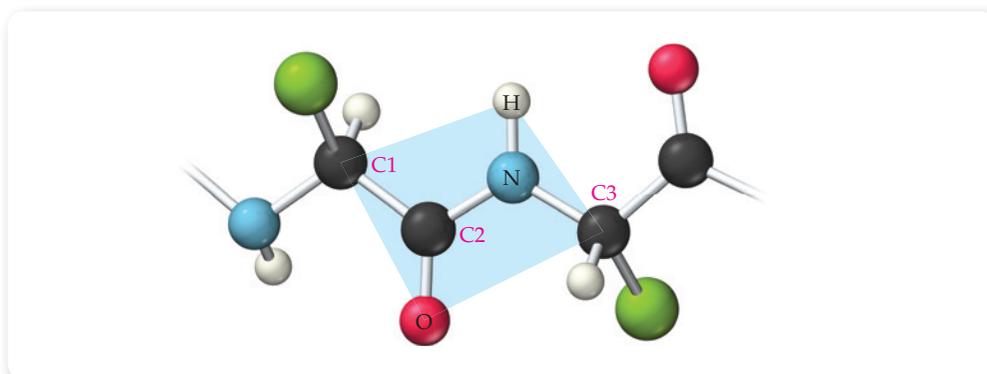
### A polypeptide

The concepts of conjugation and hybridization discussed in the previous section are essential to understanding the structure of the peptide bond. The nitrogen atom has a lone pair of electrons that is one  $\sigma$  bond away from a  $\pi$  bond and two resonance structures are shown:



Resonance shows us that the nitrogen atom in the peptide bond is  $sp^2$  hybridized, and its lone pair is in a conjugated system. Therefore, the carbon–nitrogen bond has significant  $p$  orbital overlap, giving the peptide bond significant double-bond character.

Several features of experimentally determined structure show that the (C—N) bond in a peptide has a significant degree of double-bond character. The (C—N) bond length is 132 pm, which is in between an average single (C—N) bond length of 147 pm and double (C=N) bond length of 127 pm. In addition, the atoms in the peptide bond all lie in one plane, as seen in the **FIGURE 23.11**.

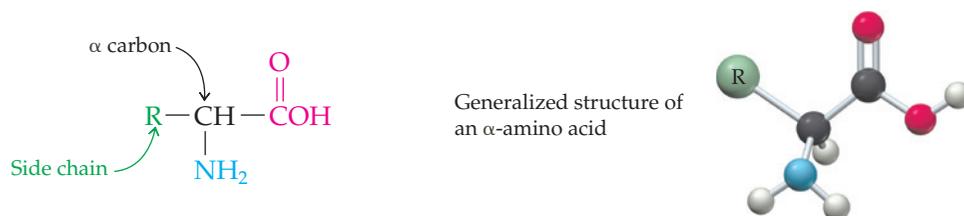


◀ **FIGURE 23.11**

**Structural representation of a peptide bond.** The peptide bond is planar because C2 and N are  $sp^2$  hybridized. In a pair of linked amino acids, C1, C2, O, N, H, and C3 lie in a plane. Green balls represent amino acid side chains.

Twenty different amino acids are commonly found in proteins, as shown in **FIGURE 23.12**. Our bodies can synthesize only 11 of the 20 amino acids. The remaining 9, highlighted in Figure 23.12, are called *essential amino acids* because they must be obtained from the diet. For convenience, there is a three-letter shorthand code for each amino acid, such as Ala (alanine), Gly (glycine), Pro (proline), and so on. All 20 are called **alpha-** ( $\alpha$ -) **amino acids** because the amine nitrogen atom in each is connected to the carbon atom *alpha to* (next to) the carboxylic acid group. Nineteen of the 20 have an  $\text{—NH}_2$  amino group, and one (proline) has an  $\text{—NH—}$  amino group as part of a ring.

The 20 amino acids differ in the nature of the group attached to the  $\alpha$  carbon. Called the *side chain*, this group can be symbolized in a general way by the letter **R**.



The 20 common amino acids are classified as *neutral*, *basic*, or *acidic*, depending on the structure of their side chains. Fifteen of the 20 have neutral side chains. Two (aspartic acid and glutamic acid) have an additional carboxylic acid group in their side chains and are classified as acidic amino acids. Three (lysine, arginine, and histidine) have an additional amine function in their side chains and are classified as basic amino acids. The 15 neutral amino acids can be further divided into those with nonpolar side chains and those with polar functional groups such as amide or hydroxyl groups. Nonpolar side chains are often described as *hydrophobic* (water fearing) because they are not attracted to water, while polar side chains are described as *hydrophilic* (water loving) because they are attracted to water. When a protein folds into a complex structure amino acids with hydrophobic side chains are often in the nonpolar interior of the protein, while amino acids with hydrophilic side chains are exposed to polar water molecules on the exterior.

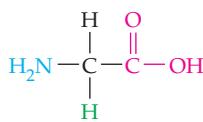
Because amino acids can be assembled in any order, depending on which  $\text{—CO}_2\text{H}$  group forms an amide bond with which  $\text{—NH}_2$  group, the number of possible isomeric peptides increases rapidly as the number of amino acids increases. There are six ways in which three different amino acids can be joined, more than 40,000 ways in which the eight amino acids present in the blood pressure-regulating hormone angiotensin II can be joined (**FIGURE 23.13**), and a staggering number of ways in which the 1800 amino acids in myosin, the major component of muscle filaments, can be arranged.

No matter how long the chain, all noncyclic proteins have an *N-terminal amino acid* with a free  $\text{—NH}_2$  on one end and a *C-terminal amino acid* with a free  $\text{—CO}_2\text{H}$  on the

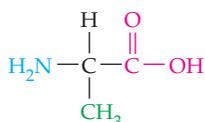


▲ Corn is particularly low in lysine, one of the essential amino acids.

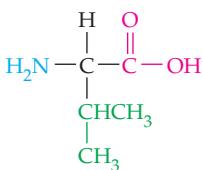
## Nonpolar side chains



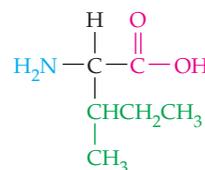
Glycine (Gly)



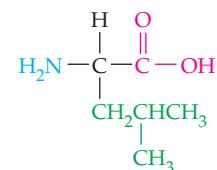
Alanine (Ala)



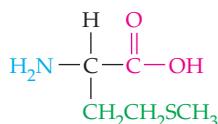
Valine (Val)



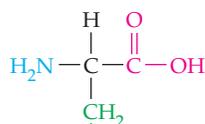
Isoleucine (Ile)



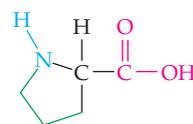
Leucine (Leu)



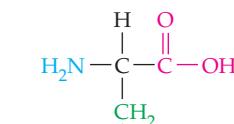
Methionine (Met)



Phenylalanine (Phe)

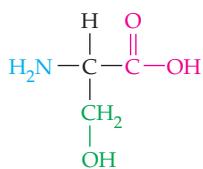


Proline (Pro)

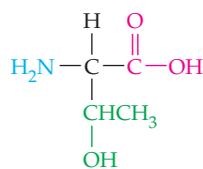


Tryptophan (Trp)

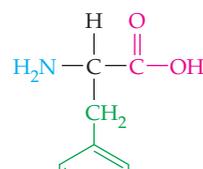
## Polar, neutral side chains



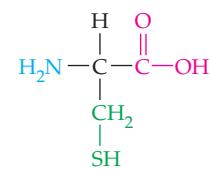
Serine (Ser)



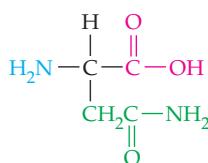
Threonine (Thr)



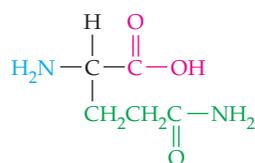
Tyrosine (Tyr)



Cysteine (Cys)

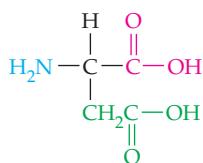


Asparagine (Asn)

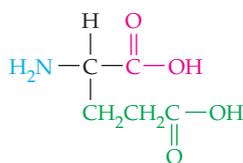


Glutamine (Gln)

## Acidic side chains

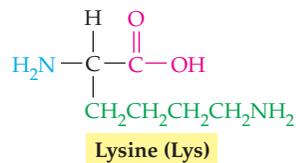


Aspartic acid (Asp)

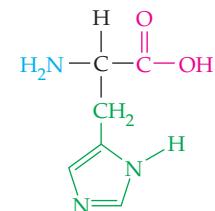


Glutamic acid (Glu)

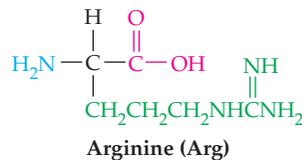
## Basic side chains



Lysine (Lys)



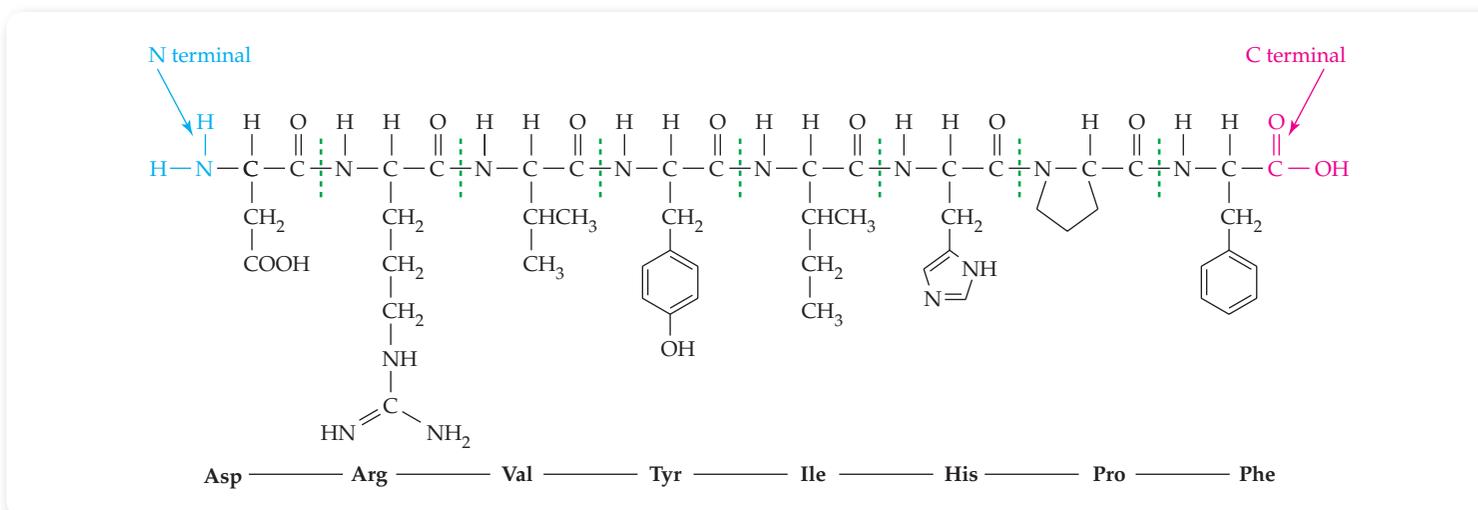
Histidine (His)



Arginine (Arg)

▲ FIGURE 23.12

Structures of the 20  $\alpha$ -amino acids found in proteins. Fifteen of the 20 have neutral side chains, 2 have acidic side chains, and 3 have basic side chains. The names of the 9 essential amino acids are highlighted.

▲ **FIGURE 23.13**

The structure of angiotensin II, an octapeptide present in blood plasma.

other end. By convention, a protein is written with the free  $\text{—NH}_2$  on the left and the free  $\text{—CO}_2\text{H}$  on the right, and its name is indicated using the three-letter abbreviations listed in Figure 23.12.

### WORKED EXAMPLE 23.12

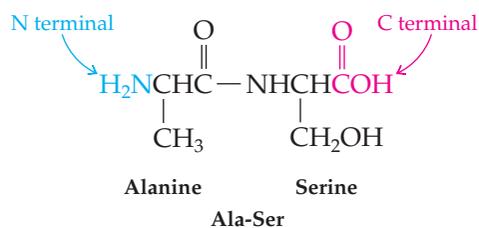
#### Drawing a Dipeptide Structure

Draw the structure of the dipeptide Ala-Ser.

#### STRATEGY

First, look up the names and structures of the two amino acids, Ala (alanine) and Ser (serine). Since alanine is N-terminal and serine is C-terminal, Ala-Ser must have an amide bond between the alanine  $\text{—CO}_2\text{H}$  and the serine  $\text{—NH}_2$ .

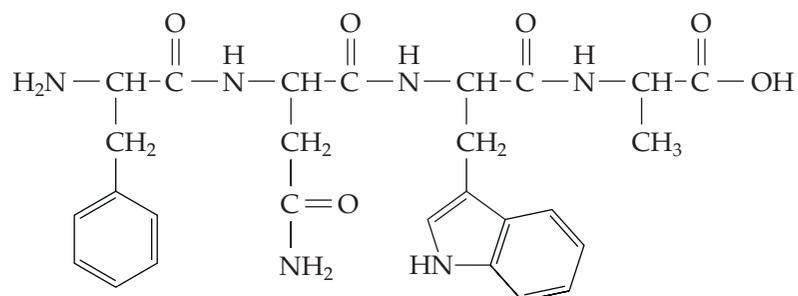
#### SOLUTION

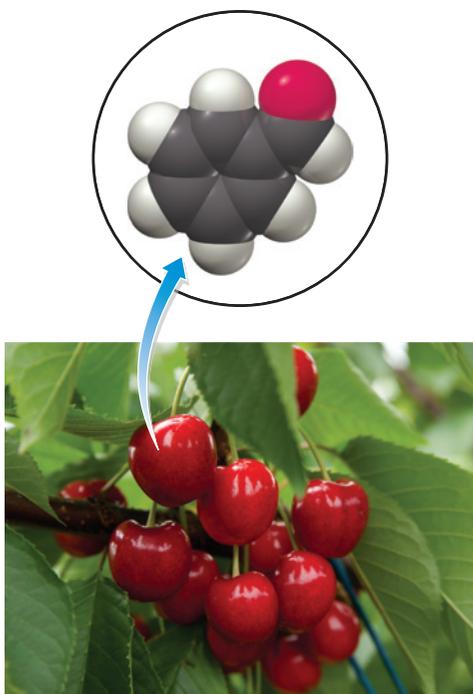


▶ **PRACTICE 23.28** Use the three-letter shorthand notations to name the two isomeric dipeptides that can be made from valine and cysteine. Draw both structures.

#### ▶ APPLY 23.29

- (a) How many amino acids are in the following peptide?  
 (b) Identify the amino acids and classify their side chains and polar or nonpolar.

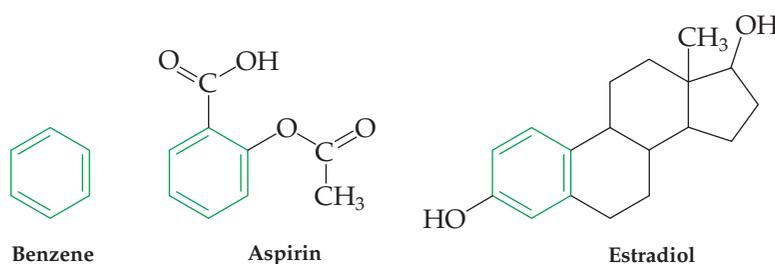




▲ Benzaldehyde, a close structural relative of benzene, is an aromatic compound responsible for the odor of cherries.

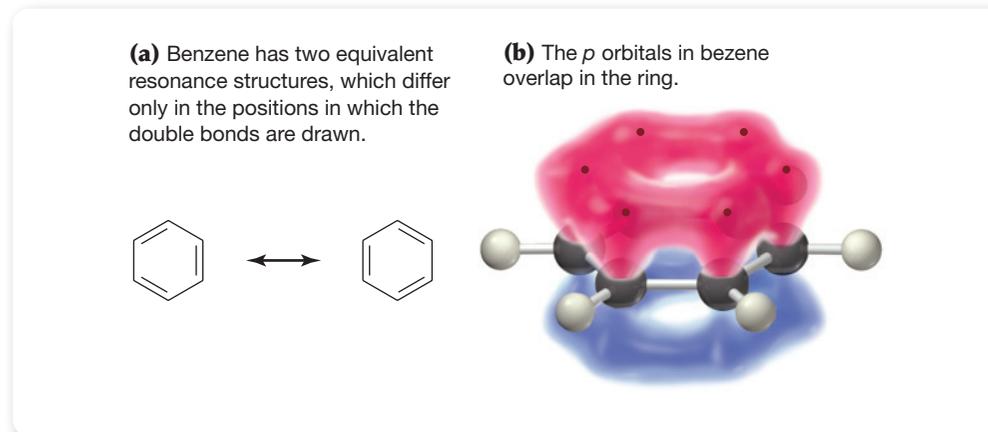
## 23.10 ► AROMATIC COMPOUNDS AND MOLECULAR ORBITAL THEORY

Although we have developed a fairly sophisticated view of molecular structure and bonding using electron-dot structures, hybridization, and valence bond theory, there are observations of molecular reactivity that cannot be explained with these models. Consider a group of highly unsaturated compounds, referred to as *aromatic compounds* in the early days of organic chemistry because they exist in fragrant substances found in fruits and other natural sources. Chemists soon realized, however, that substances grouped as aromatic behaved in a chemically different manner from most other organic compounds. Today, the term **aromatic** refers to a class of compounds that are cyclic, planar, and have adjacent  $p$  orbitals around a ring. Benzene, which has a six-membered ring with alternating single and double bonds, is the most common example of an aromatic compound. Aspirin, the steroid sex hormone estradiol, and many important biological molecules and pharmaceutical agents also contain aromatic rings.



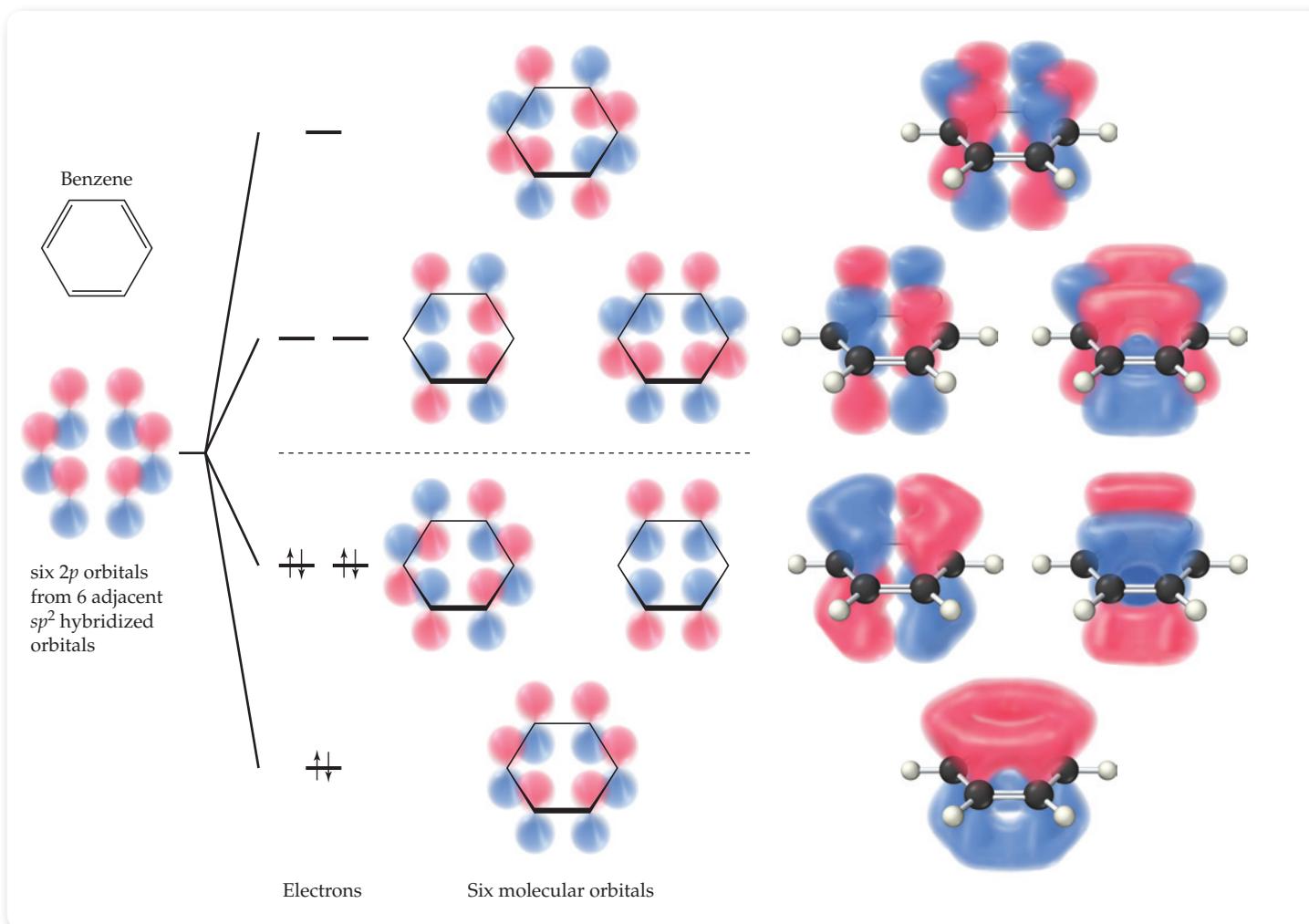
Benzene has two equivalent resonance structures; each of the six carbons in benzene is  $sp^2$ -hybridized and has a  $p$  orbital perpendicular to the ring (FIGURE 23.14). The sideways overlap of the  $p$  orbitals results in six electrons in a conjugated  $\pi$  system.

► FIGURE 23.14  
Some representations of benzene.



Although conjugation and resonance help us to understand the structure of benzene, valence bond theory does not explain its unusually high stability. If a molecule is more stable, it is less reactive. Molecular orbital (MO) theory is a more useful model in explaining electronic structure and reactivity of benzene. According to MO theory, electrons exist in molecular orbitals that cover the entire molecule. FIGURE 23.15 shows six new MOs formed from the mathematical combination of six atomic  $p$  orbitals in benzene. Three of the molecular orbitals are bonding orbitals and are lower in energy than the atomic  $p$  orbitals from which they were formed. Bonding MOs result from the interaction of lobes with the same phase and concentrate electron density between the nuclei. The other three molecular orbitals are antibonding orbitals and are higher in energy than the  $p$  orbitals from which they were formed. Antibonding MOs result from interaction of lobes with opposite phases and create nodes (or regions of zero electron probability) between the nuclei.

MO theory is mathematically complicated, but we can understand its implications qualitatively by focusing on the energy levels of the MOs. In benzene, there are six  $p$  orbitals with



▲ **FIGURE 23.15**  
Molecular orbitals of benzene.

one electron in each orbital, giving a total of six electrons. When the  $p$  orbitals combine to form molecular orbitals, the six electrons fill the MOs starting with the lowest energy. Therefore, the six electrons are paired in bonding MOs with lower energy than the atomic  $p$  orbitals, thus stabilizing the molecule.

The number of electrons in the  $\pi$  system is another very important characteristic of aromatic compounds. If there were only four electrons in the  $\pi$  system of benzene, two of the electrons would be unpaired in the MO diagram—a destabilizing configuration. If there were eight electrons in the  $\pi$  system, the last two electrons would be unpaired in antibonding MOs, which has a destabilizing effect as well. German physicist Erich Hückel articulated a requirement for the number of electron pairs in aromatic compounds. **Hückel's rule** states that a compound can only be aromatic if the number of  $\pi$  electrons in the ring is equal to  $4n + 2$ , where  $n$  equals zero or any positive integer. Therefore, the number of  $\pi$  electrons could be 2, 6, 10, 14, 18, and so on. Biological molecules that are aromatic most commonly have 6 or 10 electrons.

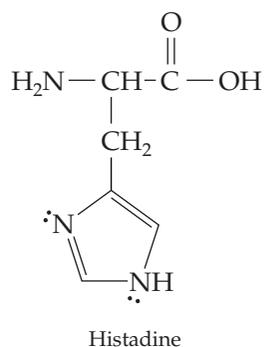
To summarize, aromatic compounds must have the following characteristics:

1. They must be cyclic.
2. They must be planar so  $p$  orbitals overlap and mathematically mix to form MOs.
3. They must have  $p$  orbitals on adjacent atoms around their ring.
4. They must have  $(4n + 2)\pi$  electrons in the ring.

## WORKED EXAMPLE 23.13

### Predicting if an Organic Compound Is Aromatic

A number of amino acids can be categorized as aromatic amino acids because they have aromatic groups in their side chains. Can the amino acid histidine be categorized as an aromatic amino acid?



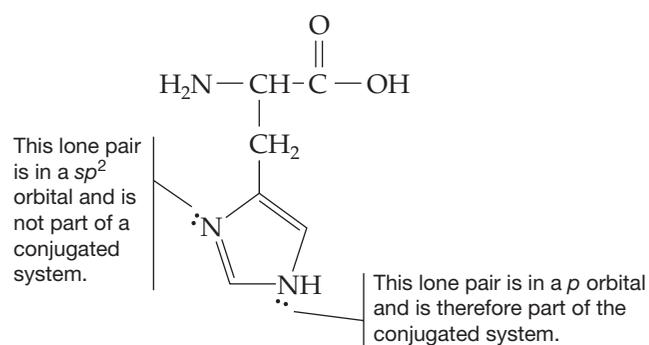
#### STRATEGY

Determine if there is a ring system in which all the atoms are  $sp^2$  hybridized and the  $\pi$  electrons part of a conjugated system. Next count the number of  $\pi$  electrons in the ring to evaluate if the  $4n + 2$  rule is satisfied.

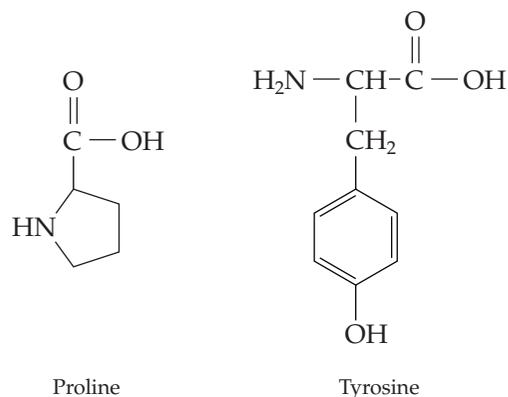
#### SOLUTION

The side chain in histidine has a five-membered ring with three carbon and two nitrogen atoms, all of which are  $sp^2$  hybridized. Two double bonds contribute four  $\pi$  electrons to the  $\pi$  system. Now evaluate lone pairs of electrons. Include lone pairs that are in  $p$  orbitals (these are the ones that are conjugated); *don't* include lone pairs in  $sp^2$  hybrid orbitals because they are not in the  $\pi$  system!

The electrons on the NH group are adjacent to a double bond and conjugated. Therefore, they are in a  $p$  orbital and part of the  $\pi$  system. The other lone pair on the N atom in the ring is in a  $sp^2$  hybrid orbital, and not part of the  $\pi$  system. Counting the four electrons in the  $\pi$  bonds and the two electrons in the lone pair of the NH group, there are a total of six electrons, making this amino acid aromatic.

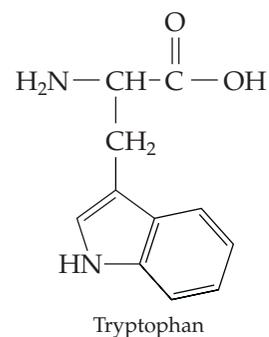


► **PRACTICE 23.30** Can either proline or tyrosine be considered aromatic amino acids? Explain.



► **APPLY 23.31** The structure of tryptophan is drawn below.

- Draw a simplified orbital overlap picture of the  $\pi$  system of tryptophan.
- Use this picture and the concepts from this section to explain why tryptophan is an aromatic amino acid.

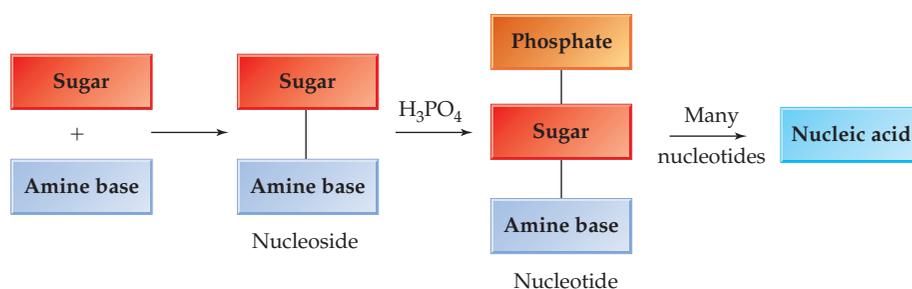


## 23.11 ► NUCLEIC ACIDS: A BIOLOGICAL EXAMPLE OF AROMATICITY

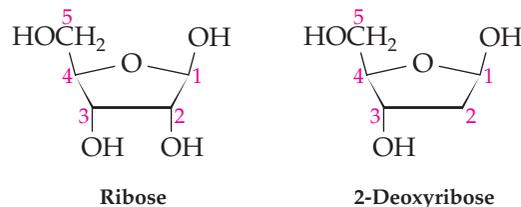
How does a seed “know” what kind of plant to become? How does a fertilized ovum know how to grow into a human being? How does a cell know what part of the body it’s in? The answers to such questions involve the biological molecules called **nucleic acids**, the information carrying molecules of the cell. We cannot understand the way nucleic acids function until we understand more about their structure and the key role of aromaticity.

**Deoxyribonucleic acid (DNA)** and **ribonucleic acid (RNA)** are the chemical carriers of an organism’s genetic information. Coded in an organism’s DNA is all the information that determines the nature of the organism and all the directions that are needed for producing the many thousands of different proteins required by the organism.

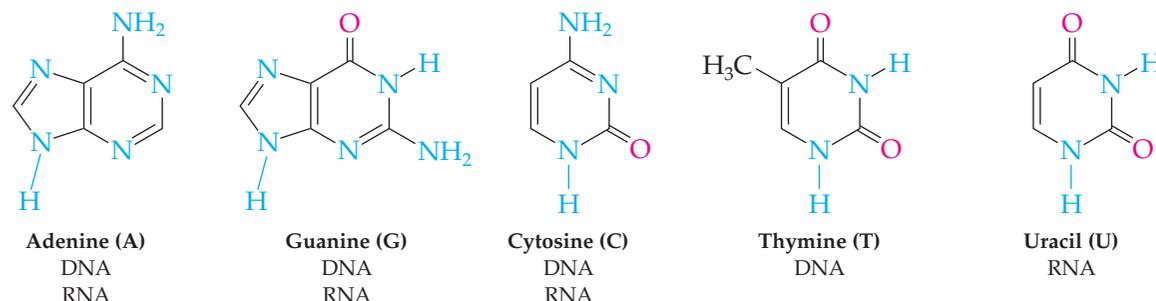
Just as proteins are made of amino acid units linked together, nucleic acids are made of **nucleotide** units linked together in a long chain. Each nucleotide is composed of a **nucleoside** plus phosphoric acid,  $\text{H}_3\text{PO}_4$ , and each nucleoside is composed of an aldopentose sugar plus an amine base.



The sugar component in RNA is ribose, and the sugar in DNA is 2-deoxyribose, where “2-deoxy” means that oxygen is missing from C2 of ribose.



Four different cyclic amine bases occur in DNA: adenine, guanine, cytosine, and thymine. Adenine, guanine, and cytosine also occur in RNA, but thymine is replaced in RNA by a related base called uracil.

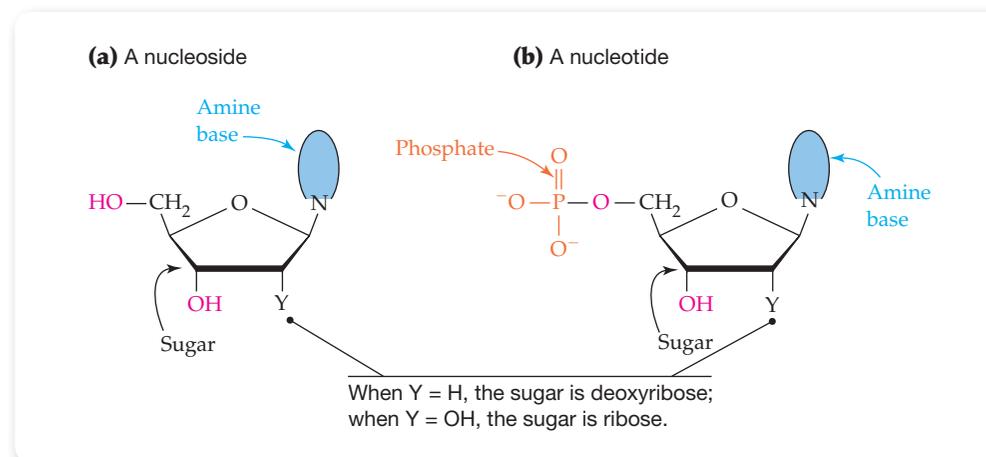


In both DNA and RNA, the cyclic amine base is bonded to C1' of the sugar, and the phosphoric acid is bonded to the C5' sugar position. Thus, nucleosides and nucleotides have the general structures shown in **FIGURE 23.16**. (Numbers with a prime superscript refer to positions on the sugar component of a nucleotide, and numbers without a prime refer to positions on the cyclic amine base.)

Nucleotides join together in nucleic acids by forming a bond between the phosphate group at the 5' position of one nucleotide and the hydroxyl group on the sugar component at the 3' position of another nucleotide (**FIGURE 23.17**).

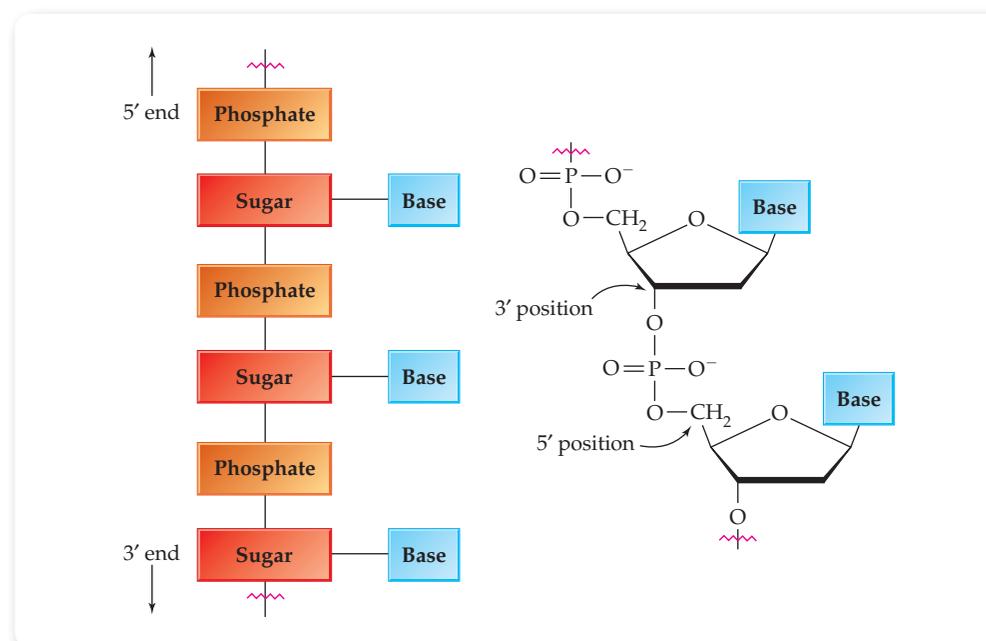
► FIGURE 23.16

General structures of (a) a nucleoside and (b) a nucleotide.



► FIGURE 23.17

Generalized structure of a nucleic acid.

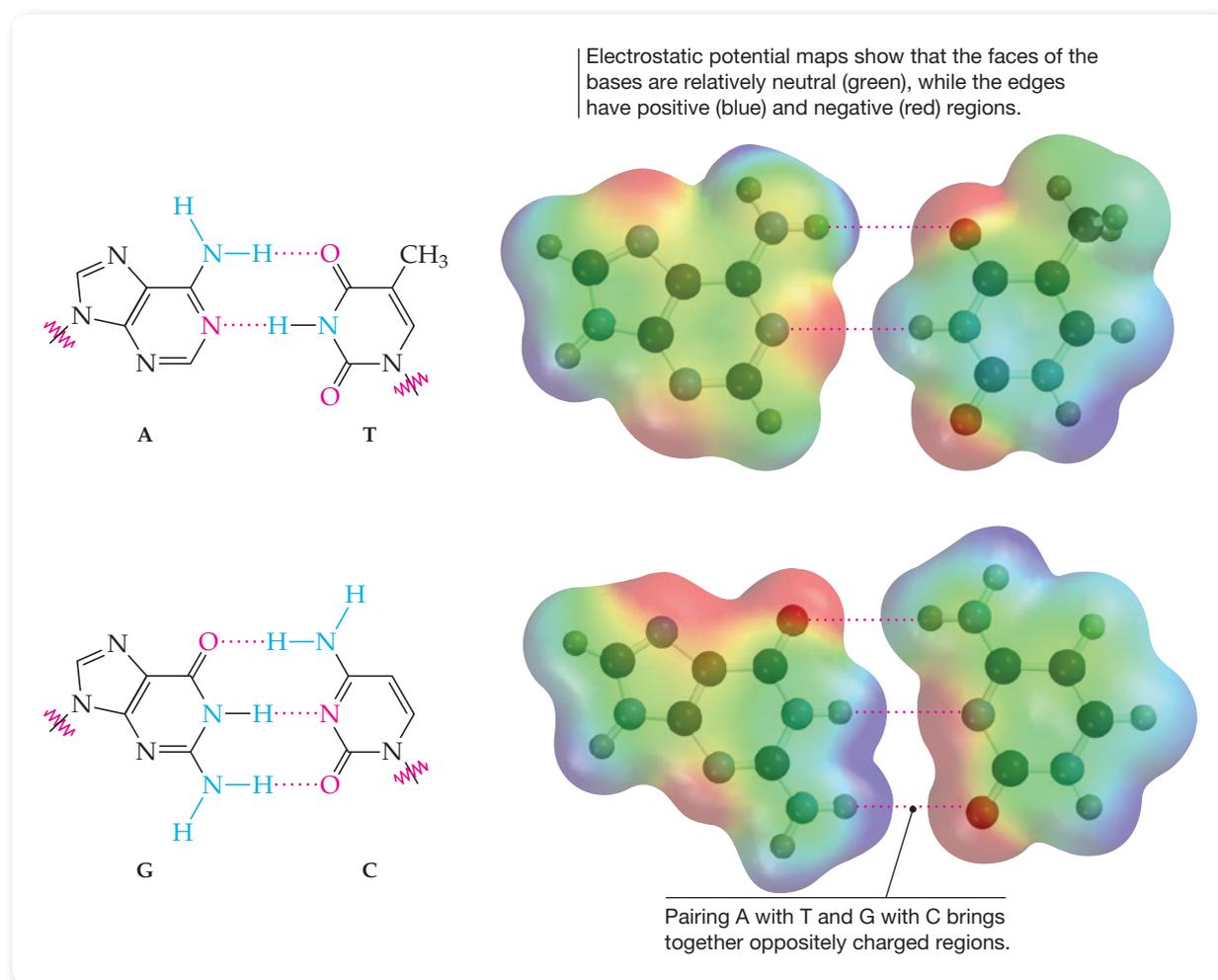


Just as the structure of a protein depends on the sequence of its individual amino acids, the structure of a nucleic acid depends on the sequence of its individual nucleotides. That sequence is described by starting at the 5' phosphate end of the chain and identifying the bases in order. Abbreviations are used for each nucleotide: A for adenosine, G for guanosine, C for cytosine, T for thymidine, and U for uracil. Thus, a typical DNA sequence might be written as -T-A-G-G-C-T-.

Interestingly, molecules of DNA isolated from different tissues of the same species have the same proportions of nucleotides, but molecules from different species can have quite different proportions. For example, human DNA contains about 30% each of A and T and about 20% each of G and C, but the bacterium *Clostridium perfringens* contains about 37% each of A and T and only 13% each of G and C. Note that in both cases, the bases occur in pairs. Adenine and thymine are usually present in equal amounts, as are guanine and cytosine. Why should this be?

According to the **Watson-Crick model**, DNA consists of two polynucleotide strands coiled around each other in a *double helix* like the handrails on a spiral staircase. The sugar-phosphate backbone is on the outside of the helix, and the amine bases are on the inside, so that a base on one strand points directly in toward a base on the second strand. The two strands run in opposite directions and are held together by hydrogen bonds between pairs of

bases. Adenine and thymine form two strong hydrogen bonds to each other, but not to G or C; G and C form three strong hydrogen bonds to each other, but not to A or T (FIGURE 23.18).



▲ FIGURE 23.18

Hydrogen bonding between base pairs in the DNA double helix.

The two strands of the DNA double helix aren't identical; rather, they're complementary. Whenever a G base occurs in one strand, a C base occurs opposite it in the other strand because of hydrogen bonding. When an A base occurs in one strand, a T base occurs in the other strand. This complementary pairing of bases explains why A and T are always found in equal amounts, as are G and C. FIGURE 23.19 shows how the two complementary strands coil into the double helix.

In order to fit into this complex structure, however, the bases must be planar so that they can stack on one another. This **base stacking** is the key to the stability of the DNA double helix, and the stacking interactions arise from the fact that all the bases are aromatic. These planar, aromatic bases stack exceptionally tightly for increased intermolecular interactions between bases.

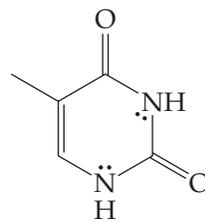
Thymine is incorporated into nucleosides to make thymidine, a building block of DNA. At first glance, this base might not appear to be aromatic due to the limitations of electron-dot structures. The nitrogen atoms appear to be  $sp^3$  hybridized if we do not consider resonance



▲ FIGURE 23.19

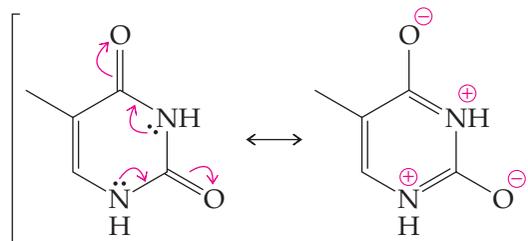
**The DNA double helix.** The coil of the sugar–phosphate backbone is visible on the outside of the DNA double helix, while the hydrogen-bonded pairs of amine bases lie flat on the inside.

structures. Remember the requirement of aromaticity is a planar, cyclic compound with  $sp^2$  hybridized atoms.



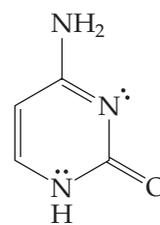
Thymine

Each nitrogen atom that is adjacent to a double bond has a lone pair and therefore a resonance structure for thymine can be drawn as shown:



The resonance structure on the right has a six-membered ring in which each atom is  $sp^2$  hybridized. Therefore, each atom has an atomic  $p$  orbital that will overlap with  $p$  orbitals on adjacent atoms, enabling the delocalization of electrons in the  $\pi$  system. The three  $\pi$  bonds drawn contribute a total of six  $\pi$  electrons and therefore thymine is aromatic and planar. The other amine bases in DNA can also be shown to be aromatic by drawing resonance structures.

**PROBLEM 23.32** Draw a resonance structure that shows cytosine is aromatic.



Cytosine

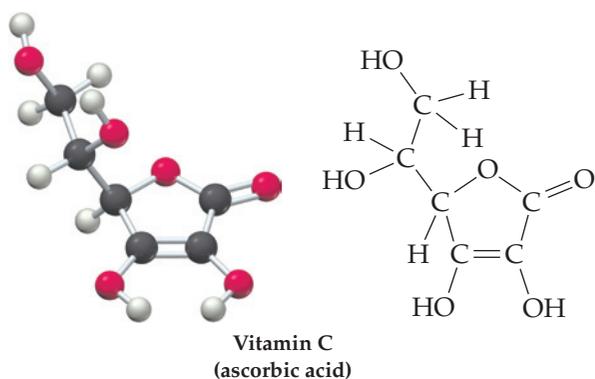
## INQUIRY ►►► WHICH IS BETTER, NATURAL OR SYNTHETIC?

Prior to the development of the chemical industry in the late nineteenth and early twentieth centuries, only substances from natural sources were available for treating our diseases, dying our clothes, cleansing and perfuming our bodies, and so forth. Extracts of the opium poppy, for instance, have been used since the seventeenth century for the relief of pain. The prized purple dye called *Tyrian purple*, obtained from a Middle Eastern mollusk, has been known since antiquity. Oils distilled from bergamot, sweet bay, rose, and lavender have been employed for centuries in making perfume.



▲ Whether from the laboratory or from food, the vitamin C is the same.

Many of these so-called *natural products* were first used without any knowledge of their chemical composition. As organic chemistry developed, though, chemists learned how to work out the structures of the compounds in natural products. The disease-curing properties of limes and other citrus fruits, for example, were known for centuries, but the chemical structure of vitamin C, the active ingredient, was not determined until 1933. Today there is a revival of interest in folk remedies, and a large effort is being made to identify medically important chemical compounds found in plants.

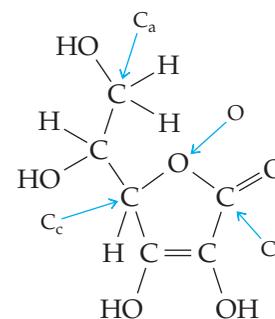


Once a structure is known, organic chemists try to synthesize the compound in the laboratory. If the starting materials are inexpensive and the synthesis process is simple enough, it may become more economical to manufacture a compound than to isolate it from a plant or bacterium. In the case of vitamin C, a

complete synthesis was achieved in 1933, and it is now much cheaper to synthesize it starting from glucose than to extract it from citrus or other natural sources. Worldwide, more than 110,000 metric tons of vitamin C are synthesized each year.

But is the “synthetic” vitamin C as good as the “natural” one? Some people still demand vitamins only from natural sources, assuming that natural is somehow better. Although eating an orange is probably better than taking a tablet, the difference lies in the many other substances present in the orange. The vitamin C itself is exactly the same, just as the NaCl produced by reacting sodium and chlorine in the laboratory is exactly the same as the NaCl found in the ocean. Natural and synthetic compounds are identical in all ways; neither is better than the other.

**PROBLEM 23.33** Refer to the structure of vitamin C to answer the following questions.

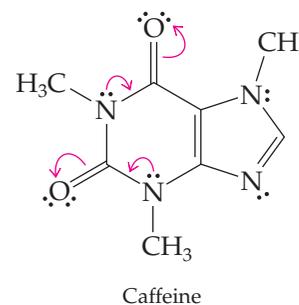


Ascorbic acid (Vitamin C)

- What functional groups are present in vitamin C?
- What is the hybridization of the atoms indicated in the structure as O, C<sub>a</sub>, C<sub>b</sub>, C<sub>c</sub>?
- Can resonance structures be drawn for vitamin C? If so, draw one.

**PROBLEM 23.34** Caffeine is the most widely used stimulant psychoactive drug in the United States. It is found naturally in the seeds and leaves of some plants such as tea and coffee and can be synthesized in the laboratory.

- What functional groups are present in caffeine?
- Draw the resonance structure that results from the following arrows. Include any relevant formal charges.
- What is the hybridization of each C and N atom in the two rings in the resonance structure?
- Is caffeine an aromatic compound?



## STUDY GUIDE

Section	Concept Summary	Learning Objectives	Test Your Understanding
<b>23.1</b> ▶ Organic Molecules and Their Structures: Alkanes	<b>Organic chemistry</b> is the study of carbon compounds. The simplest compounds are the <b>alkanes</b> , which contain only carbon and hydrogen ( <b>hydrocarbons</b> ) and have only single bonds. <b>Straight-chain alkanes</b> have all their carbons connected in a row, <b>branched-chain alkanes</b> have a branched connection of atoms in their chain, and <b>cycloalkanes</b> have a ring of carbon atoms.	<b>23.1</b> Represent the chemical structure of alkanes as condensed structures or line drawings. <b>23.2</b> Identify and draw isomers of alkanes.	Worked Example 23.1; Problems 23.35, 23.44, 23.45 Worked Example 23.2; Problems 23.46, 23.47, 23.52
<b>23.2</b> ▶ Families of Organic Compounds: Functional Groups	The more than 45 million known organic compounds can be organized into families according to the functional groups they contain. A <b>functional group</b> is an atom or group of atoms that has characteristic chemical behavior.	<b>23.3</b> Identify and name functional groups in organic molecules. <b>23.4</b> Represent molecules with functional groups using line drawings.	Problems 23.36, 23.49, 23.50, 23.54 Problems 23.51, 23.52, 23.64–23.69
<b>23.3</b> ▶ Naming Organic Compounds	Straight-chain alkanes are named in the IUPAC system by adding the family ending <i>-ane</i> to the Greek number that tells how many carbon atoms are present. Branched-chain alkanes are named by identifying the longest continuous chain of carbon atoms and then identifying what <b>alkyl groups</b> are present as branches. <b>Alkenes</b> are hydrocarbons that contain a carbon–carbon double bond, and <b>alkynes</b> are hydrocarbons that contain a carbon–carbon triple bond. Alkenes and alkynes are named by using the family ending <i>-ene</i> and <i>-yne</i> , respectively.	<b>23.5</b> Convert between the IUPAC name and condensed formula or line drawing of alkanes and unsaturated compounds.	Worked Example 23.3; Problems 23.37, 23.56, 23.58, 23.62, 23.64
<b>23.4</b> ▶ Carbohydrates: A Biological Example of Isomers	<b>Carbohydrates</b> are polyhydroxy aldehydes and ketones. Simple carbohydrates, or <b>monosaccharides</b> , can't be hydrolyzed to smaller molecules; complex carbohydrates such as starch and cellulose contain many simple sugars linked together. Monosaccharides exist in different isomeric forms including <b>constitutional isomers</b> , <b>enantiomers</b> , and <b>anomers</b> .	<b>23.6</b> Classify a monosaccharide as an aldose or ketose and draw a typical open chain structure. <b>23.7</b> Classify the type of isomerism in monosaccharides.	Problems 23.70–23.73 Problems 23.74 and 23.75
<b>23.5</b> ▶ Valence Bond Theory and Cis–Trans Isomerism of Alkenes	<b>Cis–trans isomers</b> are possible for substituted alkenes because of the lack of rotation about the carbon–carbon double bond. The cis isomer has two substituents on the same side of the double bond, and the trans isomer has two substituents on opposite sides.	<b>23.8</b> Draw orbital overlap pictures to describe bonding in organic compounds. <b>23.9</b> Identify and draw cis–trans isomers.	Worked Example 23.6; Problems 23.76–23.79 Worked Example 23.7; Problems 23.80–23.85
<b>23.6</b> ▶ Lipids: A Biological Example of Cis–Trans Isomerism	<b>Lipids</b> are the naturally occurring organic molecules that dissolve in a nonpolar solvent. Animal fats and vegetable oils are <b>triacylglycerols</b> —esters of glycerol with three long-chain <b>fatty acids</b> . The fatty acids are unbranched, have an even number of carbon atoms, and may be either saturated or unsaturated.	<b>23.10</b> Recognize and draw the structure of triacylglycerols. <b>23.11</b> Convert between chemical structure and name of lipids. <b>23.12</b> Relate lipid structure to physical properties.	Problems 23.88, 23.90, 23.98 Problems 23.92, 23.93, 23.96 Problems 23.94 and 23.95
<b>23.7</b> ▶ Formal Charge and Resonance in Organic Compounds	Resonance structures and formal charge are important concepts in understanding structure and reactivity of organic and biological compounds. Formal charge must be indicated in an organic line drawing for the structure to be correct. Formal charges are used to evaluate relative contributions of different resonance structures to the resonance hybrid.	<b>23.13</b> Used curved arrows to draw resonance structures and specify formal charges.	Worked Example 23.8, 23.9; Problems 23.100 and 23.111

Section	Concept Summary	Learning Objectives	Test Your Understanding
<b>23.8</b> ▶ Conjugated Systems	<b>Conjugated systems</b> consist of more than two <i>p</i> orbitals on adjacent atoms. The <i>p</i> orbitals overlap and delocalize electrons over all the atoms in the $\pi$ system. Resonance structures can be drawn for conjugated systems and atoms adopt the hybridization that lowers the overall energy. Electrons in <i>p</i> orbitals that are part of conjugated systems are delocalized and electrons that are in hybrid orbitals are localized.	<b>23.14</b> Draw orbital overlap pictures for conjugated systems and identify localized and delocalized electrons.	Worked Example 23.10; Problems 23.23, 23.24, 23.116, 23.117
<b>23.9</b> ▶Proteins: A Biological Example of Isomers	Proteins are large biomolecules consisting of $\alpha$ -amino acids linked together by amide, or peptide bonds. Twenty amino acids are commonly found in proteins.	<b>23.15</b> Identify conjugated systems and the hybridization of atoms included in the system.	Worked Example 23.11; Problems 23.25, 23.26, 23.112–23.115
<b>23.10</b> ▶Aromatic Compounds and Molecular Orbital Theory	<b>Aromatic</b> compounds are a class of compounds that are cyclic, planar, have adjacent <i>p</i> orbitals around a ring, and have $(4n + 2)$ $\pi$ electrons. Aromatic compounds have extra stability due to paired electrons in bonding molecular orbitals.	<b>23.16</b> Identify amino acids, show how they join together to form peptides, and name small peptides.	Worked Example 23.12; Problems 23.118–23.123
<b>23.11</b> ▶Nucleic Acids: A Biological Example of Aromaticity	<b>Deoxyribonucleic acid (DNA)</b> and <b>ribonucleic acid (RNA)</b> are the chemical carriers of an organism's genetic information. They are made up of <b>nucleotides</b> , linked together to form a long chain. Each nucleotide consists of a cyclic amine base linked to C1 of a sugar, with the sugar in turn linked to phosphoric acid. The sugar component in RNA is ribose; the sugar in DNA is 2-deoxyribose. The bases in DNA are adenine (A), guanine (G), cytosine (C), and thymine (T); the bases in RNA are adenine, guanine, cytosine, and uracil (U). Molecules of DNA consist of two complementary nucleotide strands held together by hydrogen bonds and coiled into a double helix.	<b>23.17</b> Predict if an organic compound is aromatic.	Worked Example 23.13; Problems 23.30, 23.31, 23.124–23.127
		<b>23.18</b> Identify the bases found in the nucleic acids, draw structures showing how different components of the nucleic acid are joined, and write the DNA sequence that is complementary to a specified strand.	Problems 23.128–23.134
		<b>23.19</b> Draw resonance structures to show that DNA bases are aromatic.	Problems 23.134 and 23.135

## KEY TERMS

alcohol 985  
aldehyde 985  
alkane 979  
alkene 979  
alkyl group 987  
alkyne 989  
alpha-( $\alpha$ -) amino acid 1011  
amide 985  
amine 985  
anomer 992  
aromatic 000  
base stacking 000  
biochemistry 000  
branched-chain alkane 979

carbohydrate 990  
carbonyl group 000  
carboxylic acid 985  
cis-trans isomers 995  
condensed structure 980  
conjugated systems 1006  
constitutional isomer 991  
cycloalkane 982  
delocalized 1007  
deoxyribonucleic acid (DNA) 000  
enantiomer 992  
enzyme 1010  
essential lipid 1000  
ester 985

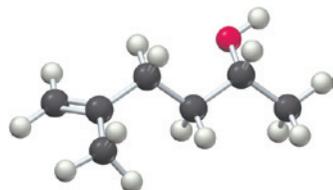
ether 985  
fatty acid 998  
functional group 983  
Hückel's rule 1015  
hydrocarbon 979  
hydrogenation 1000  
ketone 985  
line drawing 981  
lipid 997  
lipid number 1001  
monosaccharide 991  
nucleic acid 1017  
nucleoside 1017  
nucleotide 1017

organic chemistry 979  
peptide 1010  
peptide bond 1010  
pi system 000  
polysaccharide 991  
polyunsaturated fats 1000  
protein 1010  
ribonucleic acid (RNA) 1017  
saturated 989  
straight-chain alkane 979  
triacylglycerol 998  
unsaturated 989  
Watson-Crick model 1018

## CONCEPTUAL PROBLEMS

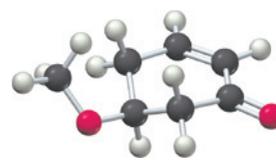
Problems 23.1–23.34 appear within the chapter.

**23.35** Convert the following model into a condensed structure and drawing. Draw the structures of two isomeric compounds.

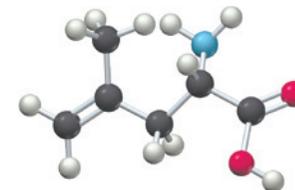


**23.36** Identify the functional groups in each of the following compounds:

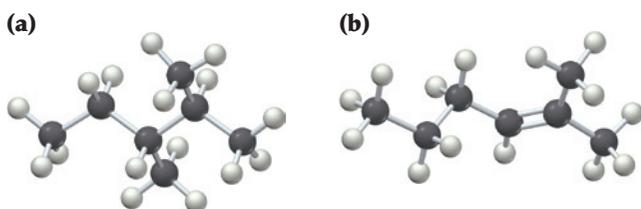
(a)



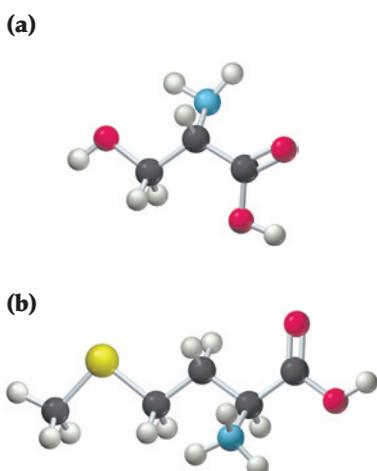
(b)



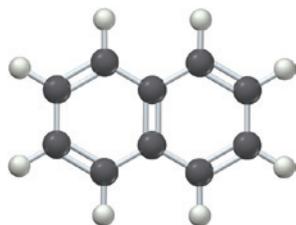
23.37 Give systematic names for the following compounds:



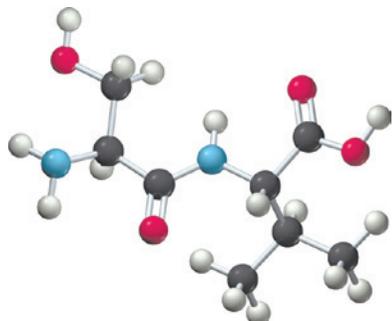
23.38 Identify the following amino acids (yellow = S):



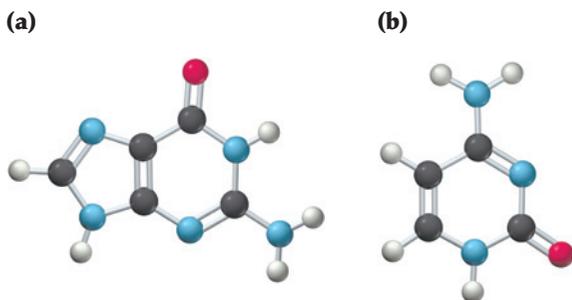
23.39 Draw three resonance forms for naphthalene, showing the positions of the double bonds.



23.40 Identify the following dipeptide:



23.41 Identify the following amine bases found in nucleic acids:



## SECTION PROBLEMS

### Isomers, Functional Groups, and Naming (Sections 23.1–23.3)

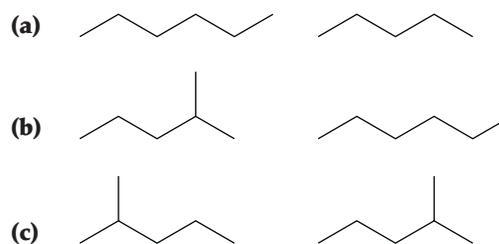
23.42 What is the difference between a straight-chain alkane and a branched-chain alkane?

23.43 What is the difference between an alkane and an alkyl group?

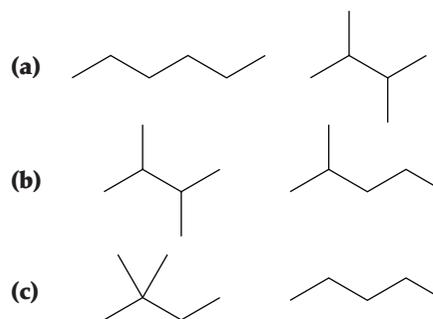
23.44 Draw the straight-chain alkane with the formula  $C_7H_{16}$  as a condensed structure and as a line drawing.

23.45 Draw the straight-chain alkane with the formula  $C_5H_{12}$  as a condensed structure and as a line drawing.

23.46 Decide whether the following pairs of alkanes are isomers. If not, explain why.



23.47 Decide whether the following pairs of alkanes are isomers. If not, explain why.



23.48 What are functional groups, and why are they important?

23.49 Describe the structure of the functional group in each of the following families:

- (a) Alkene (b) Alcohol  
(c) Ester (d) Amine

23.50 Propose structures and draw condensed formulas for molecules that meet the following descriptions:

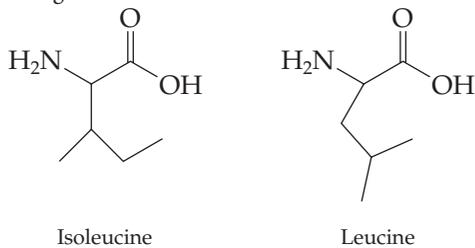
- (a) A ketone with the formula  $C_5H_{10}O$   
(b) An ester with the formula  $C_6H_{12}O_2$   
(c) A compound with formula  $C_2H_5NO_2$  that is both an amine and a carboxylic acid

23.51 Give line drawings for each of the following molecular formulas. You may have to use rings and/or multiple bonds in some instances.

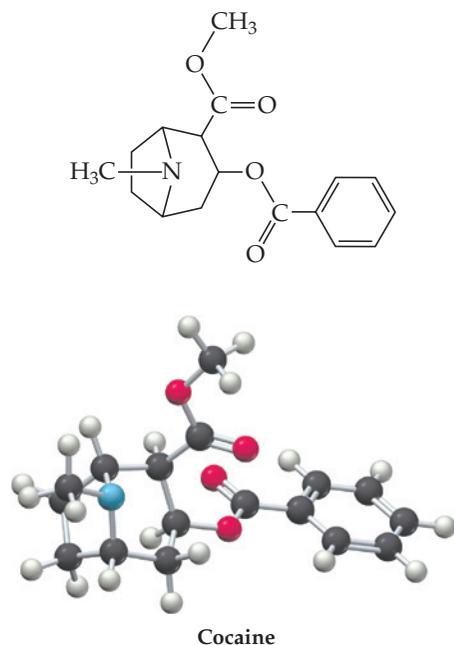
- (a)  $C_2H_7N$  (b)  $C_4H_8$   
(c)  $C_2H_4O$  (d)  $CH_2O_2$

23.52 Propose structures and draw condensed formulas of the three isomers with the formula  $C_3H_8O$ .

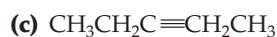
- 23.53 The following line drawings represent two amino acids, leucine and isoleucine. Are these two compounds isomers? Explain your reasoning.



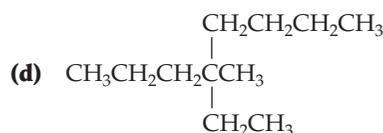
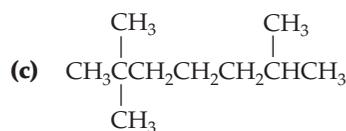
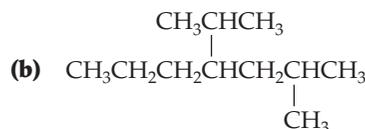
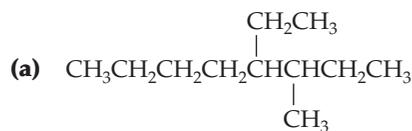
- 23.54 Identify the functional groups in cocaine.



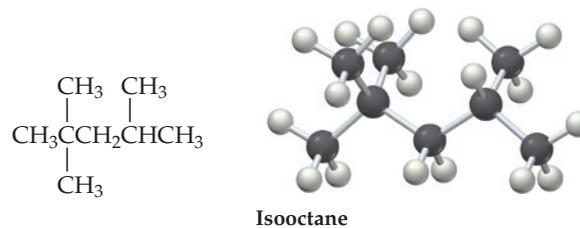
- 23.55 What is wrong with each of the following structures?



- 23.56 What are the IUPAC names of the following alkanes?



- 23.57 The following compound, known commonly as isooctane, is used as a reference substance for determining the octane rating of gasoline. What is the IUPAC name of isooctane?



- 23.58 Give line drawings for each of the following compounds:

(a) 3-Ethylhexane

(b) 2,2,3-Trimethylpentane

(c) 3-Ethyl-3,4-dimethylheptane

(d) 5-Isopropyl-2-methyloctane

- 23.59 Give line drawings for structures corresponding to the following IUPAC names:

(a) Cyclooctane

(b) 1,1-Dimethylcyclopentane

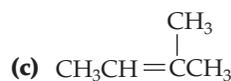
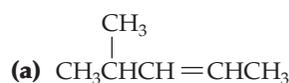
(c) 1,2,3,4-Tetramethylcyclobutane

(d) 4-Ethyl-1,1-dimethylcyclohexane

- 23.60 How many dienes (compounds with two double bonds) are there with the formula  $\text{C}_5\text{H}_8$ ? Draw structures of as many as you can.

- 23.61 If someone reported the preparation of a compound with the formula  $\text{C}_3\text{H}_9$ , most chemists would be skeptical. Why?

- 23.62 Give IUPAC names for the following compounds:



- 23.63 Give condensed structures corresponding to the following IUPAC names:

(a) *cis*-2-Hexene

(b) 2-Methyl-3-hexene

(c) 2-Methyl-1,3-butadiene

- 23.64 Give a line drawing and molecular formula for:

(a) A linear alkyne with three carbon atoms and one triple bond

(b) A linear alkene with four carbon atoms and one double bond

(c) An alkene with five carbons in a ring and two double bonds

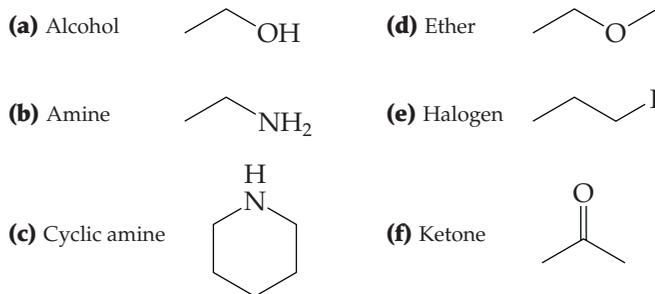
- 23.65 Give a line drawing and molecular formula for:

(a) A linear alkane with four carbon atoms

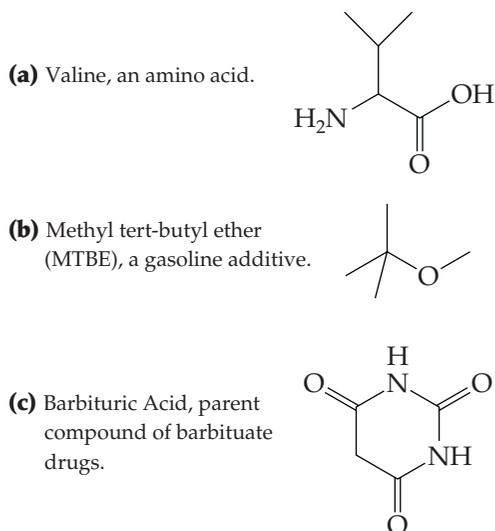
(b) An alkene with six carbon atoms in a ring and one double bond

(c) A linear alkyne with six carbon atoms and two triple bonds

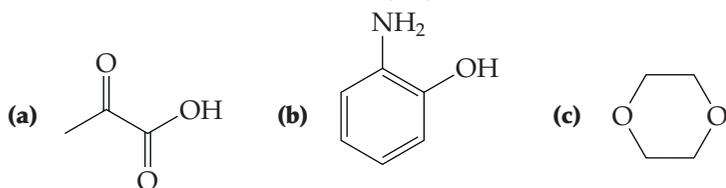
23.66 Draw the complete electron-dot structure and determine the molecular formulas for the following alkanes with functional groups.



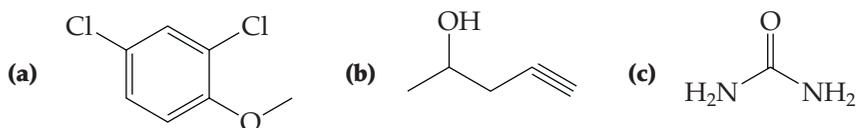
23.67 Draw the complete electron-dot structure and determine the molecular formulas for the following alkanes with functional groups.



23.68 Draw the complete electron-dot structure and determine the molecular formula for the following organic molecules.



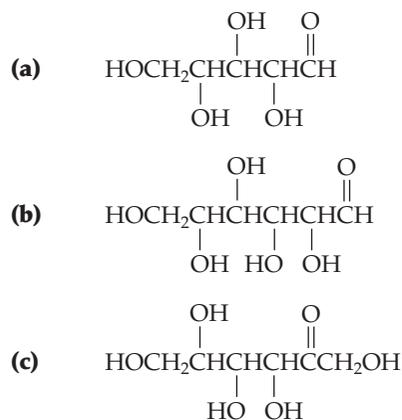
23.69 Draw the complete electron-dot structure and determine the molecular formula for the following organic molecules.



### Carbohydrates (Section 23.4)

23.70 What is the structural difference between an aldose and a ketose?

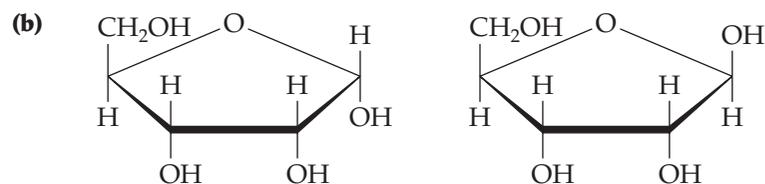
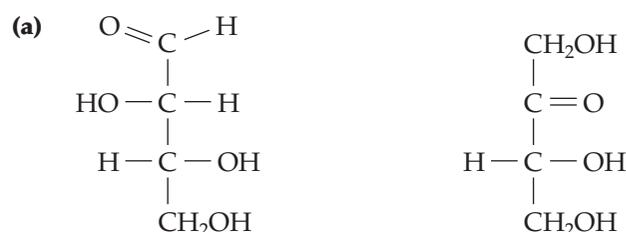
23.71 Classify each of the following carbohydrates by indicating the nature of its carbonyl group and the number of carbon atoms present. For example, glucose is an aldohexose.



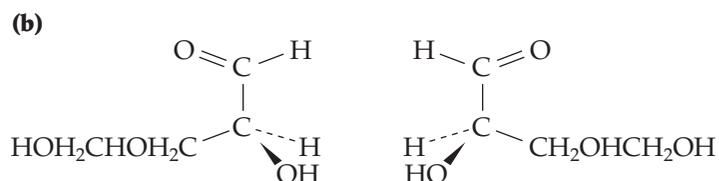
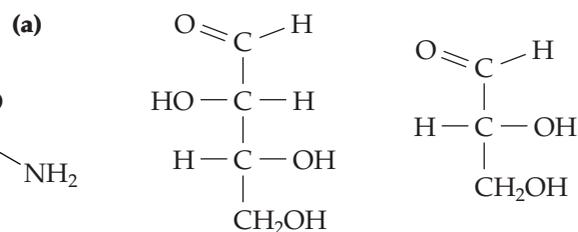
23.72 Write the open-chain structure of a ketotetrose.

23.73 Write the open-chain structure of a four-carbon deoxy sugar.

23.74 Are the following carbohydrates isomers? If so, classify the type of isomer.

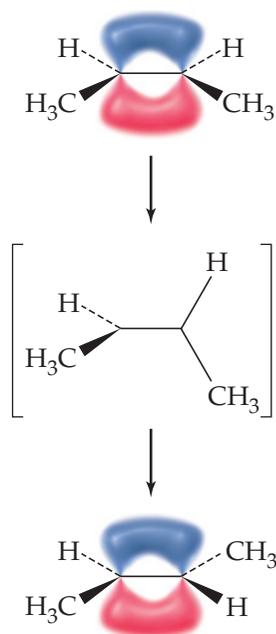


23.75 Are the following carbohydrates isomers? If so, classify the type of isomer.

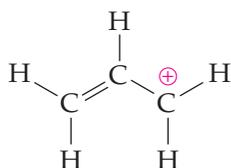


### Valence Bond Theory, Cis-Trans Isomers (Section 23.5)

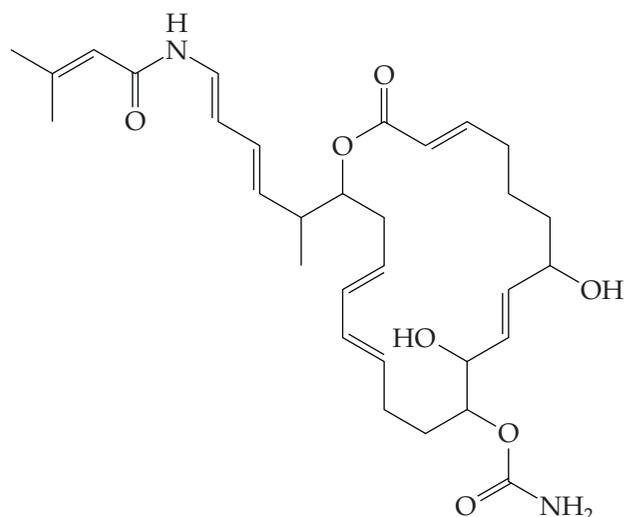
- 23.76 (a) Draw an orbital overlap picture of ethane ( $\text{CH}_3\text{CH}_3$ ) assuming both carbon atoms are  $sp^3$  hybridized. What are the C—H bond angles in this drawing?
- (b) Draw an orbital overlap picture of ethane assuming both carbon atoms are  $sp^2$  hybridized. What are the C—H bond angles in this drawing?
- (c) The real structure of ethane is like the picture you drew in part (a). Use VSEPR theory to explain why your picture from part (a) makes a more stable molecule than your picture in part (b).
- 23.77 Draw an orbital overlap picture of methane ( $\text{CH}_4$ ) with the carbon in  $sp^3$  hybridization and an orbital overlap picture of methane with carbon in  $sp^2$  hybridization. Explain why the carbon atom of methane is more stable in  $sp^3$  hybridization than in  $sp^2$  hybridization.
- 23.78 In order to convert a double bond in the cis configuration into a double bond in the trans configuration, the  $\pi$  bond must be broken. This would involve a transition state in which the two  $p$  orbitals do not overlap at all. Draw a simplified orbital overlap picture of the  $\pi$  bond broken by filling in the  $p$  orbitals in the transition state:



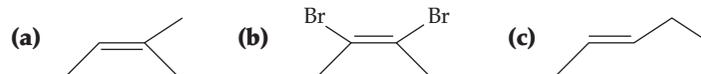
- 23.79 Draw a simplified orbital overlap picture of this molecule, and use it to explain why all the carbon and hydrogen atoms are in the same plane.



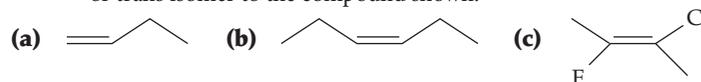
- 23.80 Palmerolide A is a chemical which has been isolated from marine organisms and shown to be able to kill melanoma cancer cells. A structure closely related to palmerolide A is shown. For each of its carbon-carbon double bonds, indicate whether they are cis, trans, or neither.



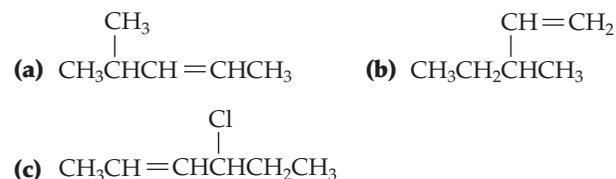
- 23.81 Unlike palmerolide A (Problem 23.80), which has a large ring, a cyclic molecule with only six atoms can only have a cis double bond, but not a trans double bond. Give a line drawing of a cyclic molecule with six carbon atoms and a cis double bond. Explain why it cannot have a trans double bond.
- 23.82 Which of the following compounds exhibit cis-trans isomerism? If isomers exist, show the line drawing for the corresponding cis or trans isomer to the compound shown.



- 23.83 Which of the following compounds exhibit cis-trans isomerism? If isomers exist, show the line drawing for the corresponding cis or trans isomer to the compound shown.



- 23.84 Which of the following compounds are capable of cis-trans isomerism?
- (a) 1-Hexene (b) 2-Hexene (c) 3-Hexene
- 23.85 Which of the following compounds are capable of cis-trans isomerism?



### Lipids (Section 23.6)

- 23.86 What is a fatty acid?
- 23.87 What does it mean to say that fats and oils are triacylglycerols?
- 23.88 Draw the structure of glycerol myristate, a fat made from glycerol and three myristic acid molecules (see Table 23.3).
- 23.89 Show the structure of glyceryl trioleate, a fat molecule whose components are glycerol and three oleic acid units.
- 23.90 Spermaceti, a fragrant substance isolated from sperm whales, was a common ingredient in cosmetics until its use was banned in 1976 to protect the whales from extinction. Chemically, spermaceti is cetyl palmitate, the ester of palmitic acid (see Table 23.3)

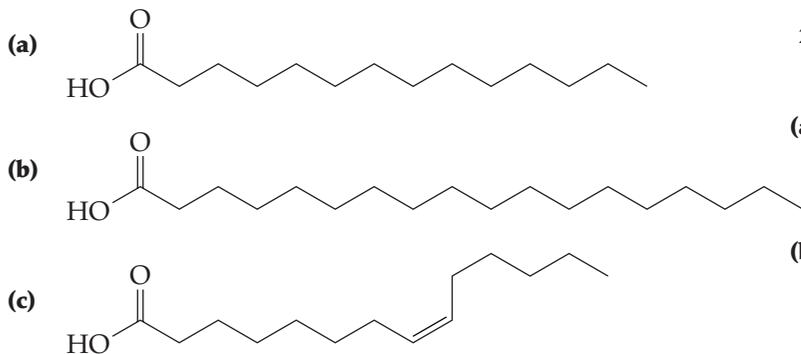
with cetyl alcohol (the straight-chain  $C_{16}$  alcohol). Show the structure of spermaceti.

**23.91** There are two isomeric fat molecules whose components are glycerol, one palmitic acid, and two stearic acids (see Table 23.3). Draw the structures of both, and explain how they differ.

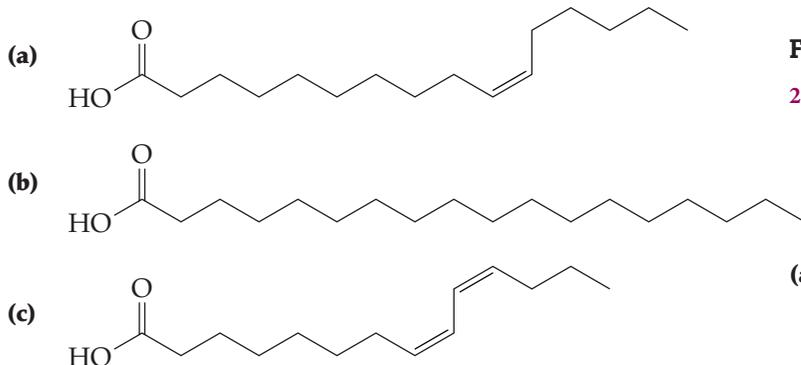
**23.92** Refer to Table 23.3 to determine the lipid number of  
(a) Linoleic acid (b) Palmitic acid

**23.93** Draw the structure of a fatty acid with a lipid number: 16:1( $\omega - 9$ ). Is it essential or nonessential?

**23.94** Which of the fatty acids below would most contribute to a triacylglyceride being an oil, rather than a fat, at room temperature?



**23.95** Which of the fatty acids below would most contribute to a triacylglyceride being a fat, rather than an oil, at room temperature?



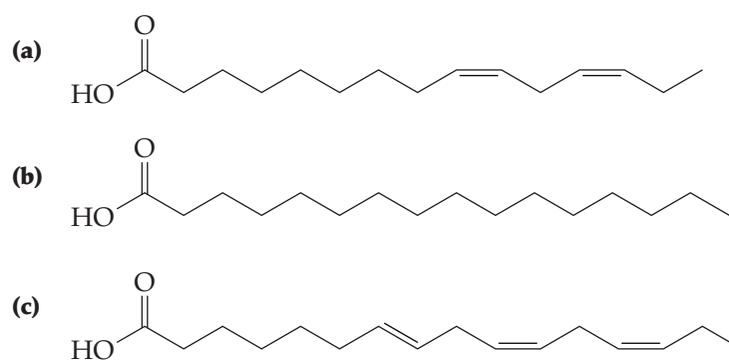
**23.96** Label each of the following statements about a fatty acid with lipid number 18:2( $\omega - 6$ ) as true, false, or cannot be determined.

- (a) This fatty acid is polyunsaturated.  
(b) This is an essential fatty acid.  
(c) This is a trans fatty acid.  
(d) This fat has an even number of carbon atoms.

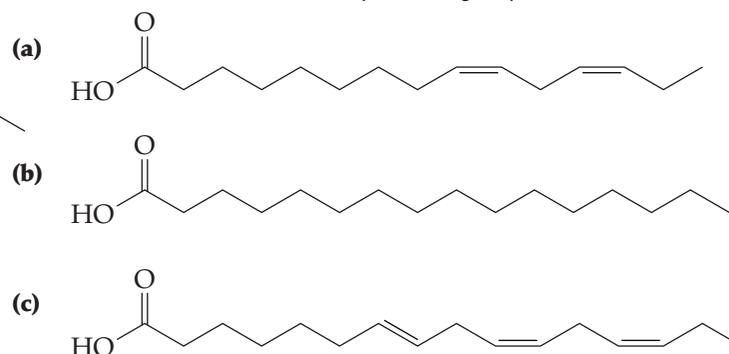
**23.97** Label each of the following statements about a fatty acid with lipid number 16:1( $\omega - 9$ ) as true, false, or cannot be determined.

- (a) This fatty acid is polyunsaturated.  
(b) This is an essential fatty acid.  
(c) This is a trans fatty acid.  
(d) This fat has an even number of carbon atoms.

**23.98** Partial hydrogenation of a cis fatty acid with lipid number 16:3( $\omega - 3$ ) could lead to all of the following except

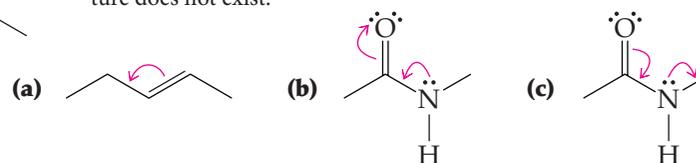


**23.99** Which of the following must be the product of a partial hydrogenation rather than a naturally occurring fatty acid?

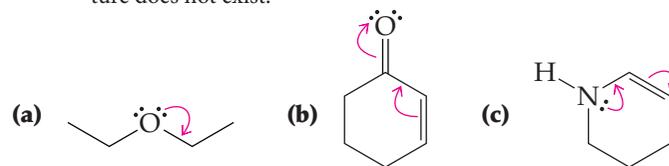


### Formal Charge and Resonance (Section 23.7)

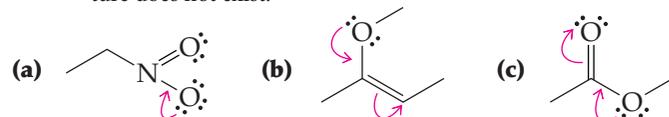
**23.100** Draw the electron-dot structure resulting from the curved arrows shown. If the arrow is valid, give the line drawing of the resonance structure. For incorrect structures, explain why the structure does not exist.



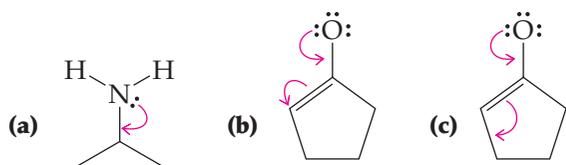
**23.101** Draw the electron-dot structure resulting from the curved arrows shown. If the arrow is valid, give the line drawing of the resonance structure. For incorrect structures, explain why the structure does not exist.



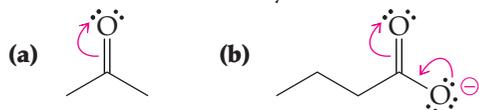
**23.102** Draw the electron-dot structure resulting from the curved arrows shown. If the arrow is valid, give the line drawing of the resonance structure. For incorrect structures, explain why the structure does not exist.



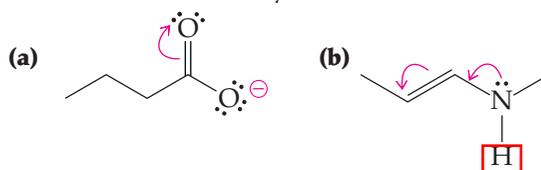
**23.103** Draw the electron-dot structure resulting from the curved arrows shown. If the arrow is valid, give the line drawing of the resonance structure. For incorrect structures, explain why the structure does not exist.



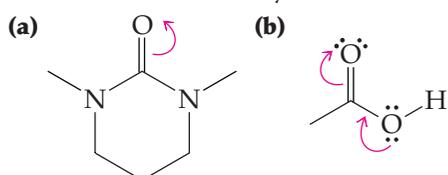
**23.104** Draw the resonance structure that results from indicated arrows. Show formal charge and evaluate the relative contribution of each structure to the resonance hybrid.



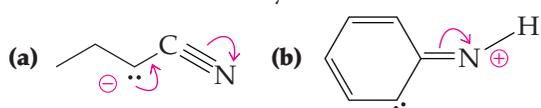
**23.105** Draw the resonance structure that results from indicated arrows. Show formal charge and evaluate the relative contribution of each structure to the resonance hybrid.



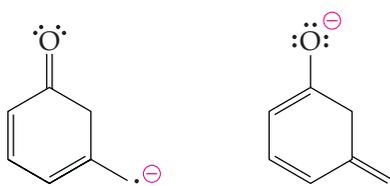
**23.106** Draw the resonance structure that results from indicated arrows. Show formal charge and evaluate the relative contribution of each structure to the resonance hybrid.



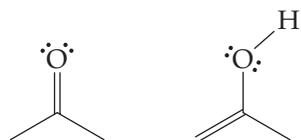
**23.107** Draw the resonance structure that results from indicated arrows. Show formal charge and evaluate the relative contribution of each structure to the resonance hybrid.



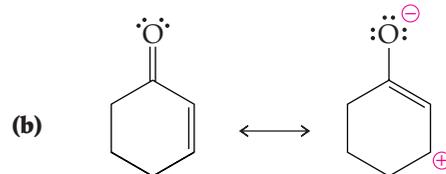
**23.108** Are the following two structures constitutional isomers or resonance structures?



**23.109** Are the following two structures constitutional isomers or resonance structures?

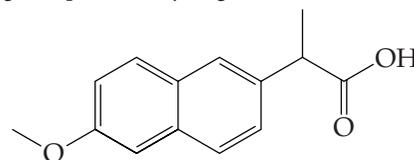


**23.110** Draw curved arrows showing how to convert the first structure into the resonance structure shown.

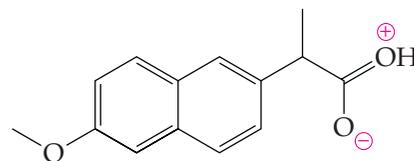
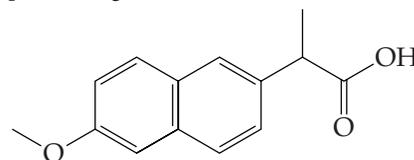


**23.111** Naproxen is a nonsteroidal anti-inflammatory drug (NSAID) commonly used to relieve pain and fever.

(a) Draw a complete electron-dot structure for naproxen by adding lone pairs and hydrogen atoms to the line drawing.

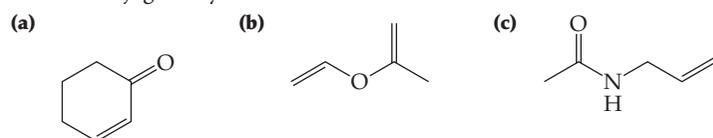


(b) Draw curved arrows in the electron-dot structure you drew in part (a) to generate the resonance structures shown.

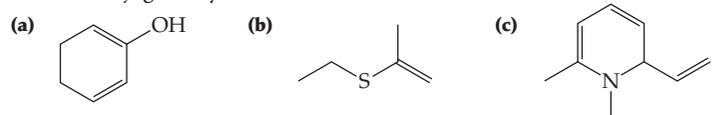


### Conjugation Systems (Section 23.8)

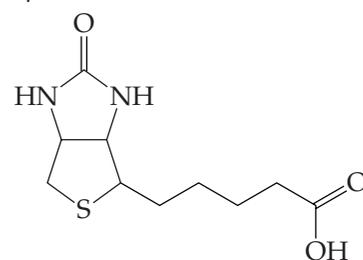
**23.112** In the following molecules, indicate which atoms are part of a conjugated system.



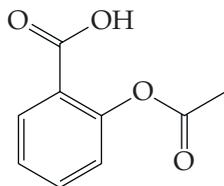
**23.113** In the following molecules, indicate which atoms are part of a conjugated system.



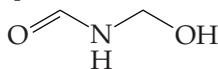
**23.114** Label the hybridization of each N, O, and S atom in vitamin B<sub>7</sub>:



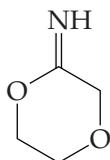
23.115 Label the hybridization of each O atom in aspirin:



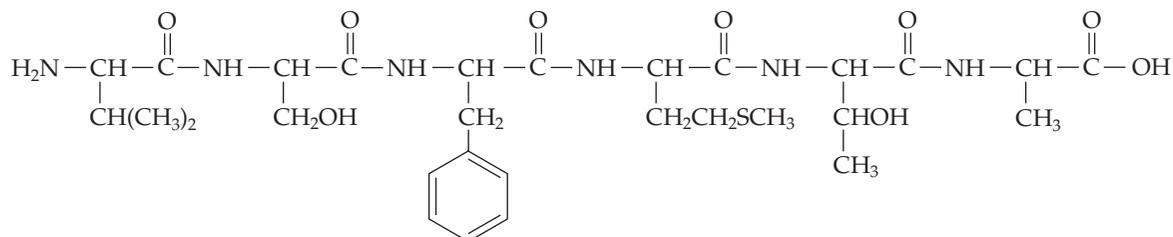
23.116 Draw simplified orbital overlap picture for this molecule, and indicate which lone pairs are localized and which are delocalized.



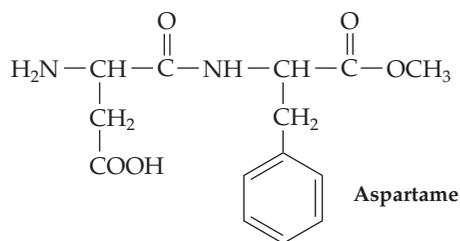
23.117 Draw simplified orbital overlap picture for this molecule, and indicate which lone pairs are localized and which are delocalized.



23.120 Identify the amino acids present in the following hexapeptide:



23.121 *Aspartame*, marketed for use as a nonnutritive sweetener under such trade names as Equal, NutraSweet, and Canderel, is the methyl ester of a simple dipeptide. Identify the two amino acids present in aspartame, and show all the products of digestion, assuming that both amide and ester bonds are hydrolyzed in the stomach.

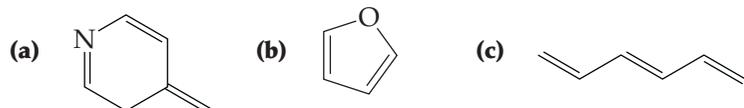


23.122 Use the three-letter abbreviations to name all tripeptides containing methionine, isoleucine, and lysine.

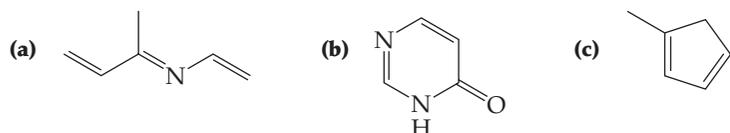
23.123 How many tetrapeptides containing alanine, serine, leucine, and glutamic acid do you think there are? Use the three-letter abbreviations to name three.

### Aromaticity and Molecular Orbital Theory (Section 23.10)

23.124 Which of the molecules below are aromatic?



23.125 Which of the molecules below are aromatic?



### Proteins (Section 23.9)

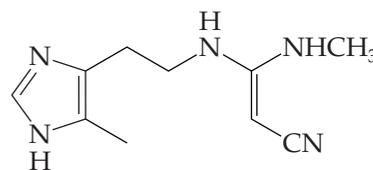
23.118 What amino acids do the following abbreviations stand for?

- (a) Ser (b) Thr (c) Pro  
(d) Phe (e) Cys

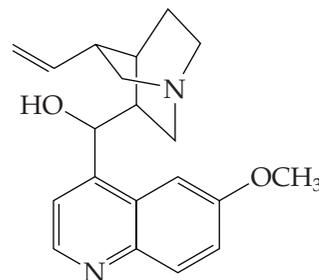
23.119 Name and draw the structures of amino acids that fit the following descriptions:

- (a) Contains an isopropyl group  
(b) Contains an alcohol group  
(c) Contains a thiol (—SH) group  
(d) Contains an aromatic ring

23.126 How many electrons are in the aromatic system of Tagamet®, a drug used to treat peptic ulcers and heartburn?



23.127 How many electrons are in the aromatic system of quinine, a drug used against malaria?



### Nucleic Acids (Section 23.11)

23.128 What is a nucleotide, and what three kinds of components does it contain?

23.129 What are the names of the sugars in DNA and RNA, and how do they differ?

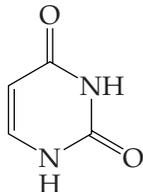
23.130 Show by drawing structures how the phosphate and sugar components of a nucleic acid are joined.

23.131 Show by drawing structures how the sugar and amine base components of a nucleic acid are joined.

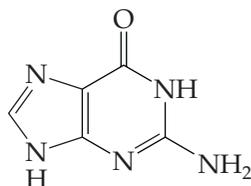
23.132 If the sequence T-A-C-C-G-A appeared on one strand of DNA, what sequence would appear opposite it on the other strand?

23.133 The DNA from sea urchins contains about 32% A and about 18% G. What percentages of T and C would you expect in sea urchin DNA? Explain.

23.134 Draw a resonance structure for the RNA base uracil showing its aromatic conjugated double bonds. Give the hybridization for each atom in the ring in the resonance structure.



23.135 Draw a resonance structure for the DNA base guanine that shows its aromatic conjugated double bonds. Give the hybridization for each atom in the rings in the resonance structure.

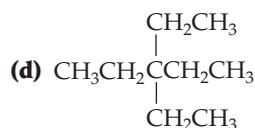
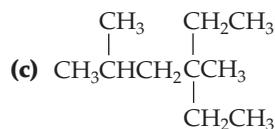
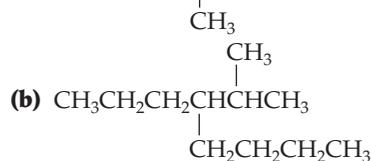


## CHAPTER PROBLEMS

23.136 Draw structural formulas for the following compounds:

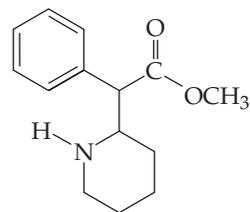
- 2-Methylheptane
- 4-Ethyl-2-methylhexane
- 4-Ethyl-3,4-dimethyloctane
- 2,4,4-Trimethylheptane
- 1,1-Dimethylcyclopentane
- 4-Isopropyl-3-methylheptane

23.137 Give IUPAC names for the following alkanes:



23.138 One of the constituents of the carnauba wax used in floor and furniture polish is an ester of a  $\text{C}_{32}$  straight-chain alcohol with a  $\text{C}_{20}$  straight-chain carboxylic acid. Draw the structure of this ester.

23.139 Methylphenidate is the active ingredient in Ritalin, a medication prescribed for attention deficit disorder.

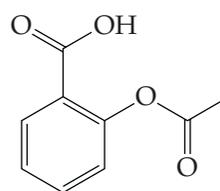


Methylphenidate

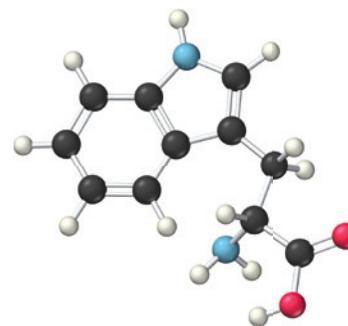
What functional groups are present in methylphenidate?

23.140 Benzynes,  $\text{C}_6\text{H}_4$ , is a highly energetic and reactive molecule. The carbon atoms are connected in six-membered ring. Give a line drawing for benzyne. What functional group is present?

23.141 Draw the complete electron-dot structure and determine the molecular formula for aspirin.

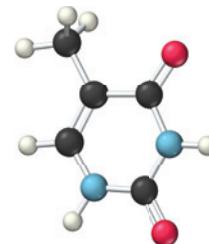


23.142 The following structure is a representation of tryptophan, an amino acid constituent of proteins. Complete the structure by showing where lone pairs are located (red = O, gray = C, blue = N, ivory = H). Give the line drawing and molecular formula.



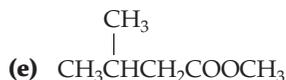
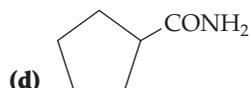
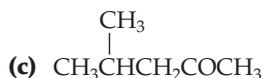
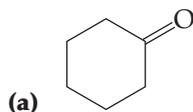
Tryptophan

23.143 The following structure is a representation of thymine, a constituent of DNA. Complete the structure by showing where lone pairs are located (red = O, gray = C, blue = N, ivory = H). Give the line drawing and molecular formula.

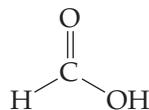


Thymine

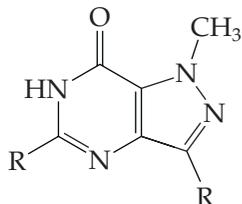
- 23.144 Identify the kinds of carbonyl groups in the following molecules (aldehyde, amide, ester, or ketone):



- 23.145 For the following molecule:



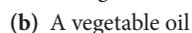
- (a) Draw simplified orbital overlap pictures to indicate the  $\pi$  system and localized lone pairs.  
 (b) Indicate which lone pairs are localized and which are delocalized.  
 (c) Draw a resonance structure for this compound.
- 23.146 An abbreviated chemical structure of Viagra® is shown below. Is the portion shown aromatic or not? Explain, using Hückel's rule. (Hint: Remember to consider conjugation and resonance!)



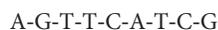
- 23.147 Write full structures for the following peptides, and indicate the positions of the amide bonds:



- 23.148 Write representative structures for the following:



- 23.149 What DNA sequence is complementary to the following sequence?



- 23.150 Jojoba wax, used in candles and cosmetics, is partially composed of the ester of stearic acid and a straight-chain  $\text{C}_{22}$  alcohol. Draw the structure of this ester.

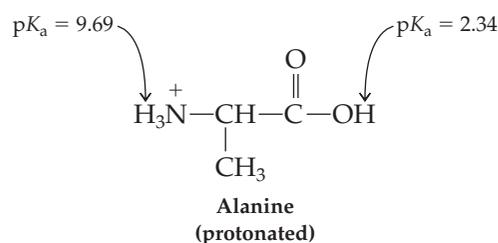
- 23.151 Elaidic acid, a component of so-called trans fats, is the trans isomer of oleic acid (Table 23.3). Draw both isomers using condensed structures.

### MULTICONCEPT PROBLEMS

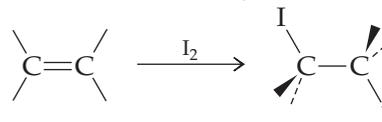
- 23.152 Fumaric acid is an organic substance widely used as a food additive. Its elemental composition is 41.4% C, 3.5% H, and 55.1% O. A solution made by dissolving 0.1500 g of fumaric acid in water and diluting to a volume of 100.0 mL gave rise to an osmotic pressure of 240.3 mm Hg at 298 K. On titration of a sample weighing

0.573 g, 94.1 mL of 0.105 M NaOH was required to reach an equivalence point. Fumaric acid reacts with 1 mol of  $\text{H}_2$  to give a hydrogenation product.

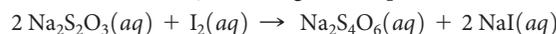
- (a) What is the empirical formula of fumaric acid?  
 (b) What is the molecular weight of fumaric acid?  
 (c) Draw three possible structures for fumaric acid.  
 (d) If fumaric acid contains a trans double bond, which of your structures is correct?
- 23.153 Cytochrome *c* is an important enzyme found in the cells of all aerobic organisms. Elemental analysis of cytochrome *c* shows that it contains 0.43% iron. What is the minimum molecular weight of this enzyme?
- 23.154 The protonated form of a neutral amino acid such as alanine is a diprotic acid,  $\text{H}_2\text{A}^+$ , with two acid dissociation constants, one for the  $-\text{NH}_3^+$  group and one for the  $-\text{CO}_2\text{H}$  group.



- (a) Which group is more acidic, the  $-\text{NH}_3^+$  or the  $-\text{CO}_2\text{H}$ ?  
 (b) What percentage of each form—protonated ( $\text{H}_2\text{A}^+$ ), neutral (HA), and deprotonated ( $\text{A}^-$ )—is present in aqueous solution at pH = 4.00?  
 (c) What percentage of each form—protonated ( $\text{H}_2\text{A}^+$ ), neutral (HA), and deprotonated ( $\text{A}^-$ )—is present in aqueous solution at pH = 8.50?  
 (d) At what pH is the neutral form present in maximum amount?
- 23.155 The relative amount of unsaturation in a fat or oil is expressed as an *iodine number*. Olive oil, for instance, is highly unsaturated and has an iodine number of 172, while butter is much less unsaturated and has an iodine number of 37. Defined as the number of grams of  $\text{I}_2$  absorbed per 100 grams of fat, the iodine number is based on the fact that the carbon-carbon double bonds in fats and oils undergo an addition reaction with  $\text{I}_2$ . The larger the number of double bonds, the larger the amount of  $\text{I}_2$  that reacts.



To determine an iodine number, a known amount of fat is treated with a known amount of  $\text{I}_2$ . When the addition reaction is complete, the amount of excess  $\text{I}_2$  remaining is determined by titration with  $\text{Na}_2\text{S}_2\text{O}_3$  according to the equation



Knowing both the amount of  $\text{I}_2$  originally added and the amount remaining after reaction, the iodine number can be calculated.

Assume that 0.500 g of human milk fat is allowed to react with 25.0 mL of 0.200 M  $\text{I}_2$  solution and that 81.99 mL of 0.100 M  $\text{Na}_2\text{S}_2\text{O}_3$  is required for complete reaction with the excess  $\text{I}_2$ .

- (a) What amount (in grams) of  $\text{I}_2$  was added initially?  
 (b) How many grams of  $\text{I}_2$  reacted with the milk fat, and how many grams were in excess?  
 (c) What is the iodine number of human milk fat?  
 (d) Assuming a molecular weight of 800, how many double bonds does an average molecule of milk fat contain?