

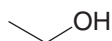


Families of Carbon Compounds

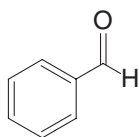
FUNCTIONAL GROUPS, INTERMOLECULAR FORCES, AND INFRARED (IR) SPECTROSCOPY

In this chapter we introduce one of the great simplifying concepts of organic chemistry—the functional group. Functional groups are common and specific arrangements of atoms that impart predictable reactivity and properties to a molecule. Even though there are millions of organic compounds, you may be relieved to know that we can readily understand much about whole families of compounds simply by learning about the properties of the common functional groups.

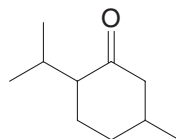
For example, all alcohols contain an —OH (hydroxyl) functional group attached to a saturated carbon bearing nothing else but carbon or hydrogen. Alcohols as simple as ethanol in alcoholic beverages and as complex as ethinyl estradiol (Section 2.1C) in birth control pills have this structural unit in common. All aldehydes have a —C(=O)— (carbonyl) group with one bond to a hydrogen and the other to one or more carbons, such as in benzaldehyde (which comes from almonds). All ketones include a carbonyl group bonded by its carbon to one or more other carbons on each side, as in the natural oil menthone, found in geraniums and spearmint.



Ethanol



Benzaldehyde



Menthone

Members of each functional group family share common chemical properties and reactivity, and this fact helps greatly in organizing our knowledge of organic chemistry. As you progress in this chapter it will serve you well to learn the arrangements of atoms that define the common functional groups. This knowledge will be invaluable to your study of organic chemistry.

IN THIS CHAPTER WE WILL CONSIDER:

- the major functional groups
- the correlation between properties of functional groups and molecules and intermolecular forces
- infrared (IR) spectroscopy, which can be used to determine what functional groups are present in a molecule

[**WHY DO THESE TOPICS MATTER?**] At the end of the chapter, we will see how these important concepts merge together to explain how the world's most powerful antibiotic behaves and how bacteria have evolved to escape its effects.

2.1 HYDROCARBONS: REPRESENTATIVE ALKANES, ALKENES, ALKYNES, AND AROMATIC COMPOUNDS

We begin this chapter by introducing the class of compounds that contains only carbon and hydrogen, and we shall see how the -ane, -ene, or -yne ending in a name tells us what kinds of carbon-carbon bonds are present.

- **Hydrocarbons** are compounds that contain only carbon and hydrogen atoms.

Methane (CH_4) and ethane (C_2H_6) are hydrocarbons, for example. They also belong to a subgroup of compounds called alkanes.

- **Alkanes** are hydrocarbons that do not have multiple bonds between carbon atoms, and we can indicate this in the family name and in names for specific compounds by the **-ane** ending.

Other hydrocarbons may contain double or triple bonds between their carbon atoms.

- **Alkenes** contain at least one carbon-carbon double bond, and this is indicated in the family name and in names for specific compounds by an **-ene** ending.
- **Alkynes** contain at least one carbon-carbon triple bond, and this is indicated in the family name and in names for specific compounds by an **-yne** ending.
- **Aromatic compounds** contain a special type of ring, the most common example of which is a benzene ring. There is no special ending for the general family of aromatic compounds.

We shall introduce representative examples of each of these classes of hydrocarbons in the following sections.

Generally speaking, compounds such as alkanes, whose molecules contain only single bonds, are referred to as **saturated compounds** because these compounds contain the maximum number of hydrogen atoms that the carbon compound can possess. Compounds with multiple bonds, such as alkenes, alkynes, and aromatic hydrocarbons, are called **unsaturated compounds** because they possess fewer than the maximum number of hydrogen atoms, and they are capable of reacting with hydrogen under the proper conditions. We shall have more to say about this in Chapter 7.



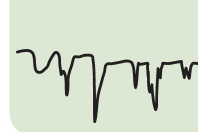
Methane



2.1A Alkanes

The primary sources of alkanes are natural gas and petroleum. The smaller alkanes (methane through butane) are gases under ambient conditions. Methane is the principal component of natural gas. Higher molecular weight alkanes are obtained largely by refining petroleum. Methane, the simplest alkane, was one major component of the early atmosphere of this planet. Methane is still found in Earth's atmosphere, but no longer in appreciable amounts. It is, however, a major component of the atmospheres of Jupiter, Saturn, Uranus, and Neptune.

Some living organisms produce methane from carbon dioxide and hydrogen. These very primitive creatures, called *methanogens*, may be Earth's oldest organisms, and they



may represent a separate form of evolutionary development. Methanogens can survive only in an anaerobic (i.e., oxygen-free) environment. They have been found in ocean trenches, in mud, in sewage, and in cows' stomachs.

2.1B Alkenes

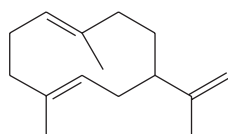
Ethene and propene, the two simplest alkenes, are among the most important industrial chemicals produced in the United States. Each year, the chemical industry produces more than 30 billion pounds of ethene and about 15 billion pounds of propene. Ethene is used as a starting material for the synthesis of many industrial compounds, including ethanol, ethylene oxide, ethanal, and the polymer polyethylene (Section 10.10). Propene is used in making the polymer polypropylene (Section 10.10 and Special Topic B*), and, in addition to other uses, propene is the starting material for a synthesis of acetone and cumene (Section 21.4B).

Ethene also occurs in nature as a plant hormone. It is produced naturally by fruits such as tomatoes and bananas and is involved in the ripening process of these fruits. Much use is now made of ethene in the commercial fruit industry to bring about the ripening of tomatoes and bananas picked green because the green fruits are less susceptible to damage during shipping.

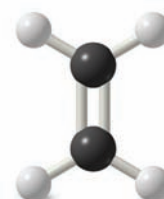
There are many naturally occurring alkenes. Two examples are the following:



β -Pinene
(a component of turpentine)



An aphid alarm pheromone



Ethene

SOLVED PROBLEM 2.1

Propene, $\text{CH}_3\text{CH}=\text{CH}_2$, is an alkene. Write the structure of a constitutional isomer of propene that is not an alkene. (*Hint*: It does not have a double bond.)

STRATEGY AND ANSWER: A compound with a ring of n carbon atoms will have the same molecular formula as an alkene with the same number of carbons.



Cyclopropane
 C_3H_6

is a constitutional isomer of



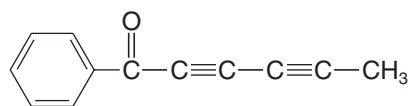
Propene
 C_3H_6

Cyclopropane has anesthetic properties.

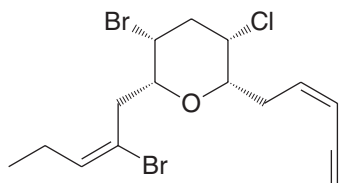
2.1C Alkynes

The simplest alkyne is ethyne (also called acetylene). Alkynes occur in nature and can be synthesized in the laboratory.

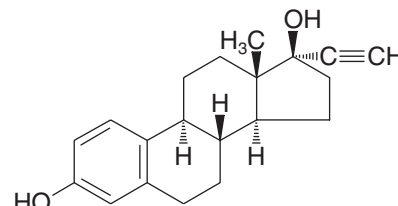
Two examples of alkynes among thousands that have a biosynthetic origin are capillin, an antifungal agent, and dactylyne, a marine natural product that is an inhibitor of pentobarbital metabolism. Ethinyl estradiol is a synthetic alkyne whose estrogen-like properties have found use in oral contraceptives.



Capillin



Dactylyne



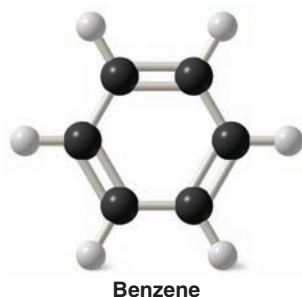
Ethinyl estradiol
[17 α -ethynyl-1,3,5(10)-estratriene-3,17 β -diol]



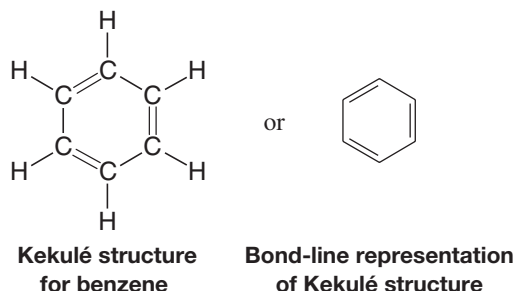
Ethyne

*Special Topics A–F and H are in *WileyPLUS*; Special Topic G can be found later in this volume.

2.1D Benzene: A Representative Aromatic Hydrocarbon

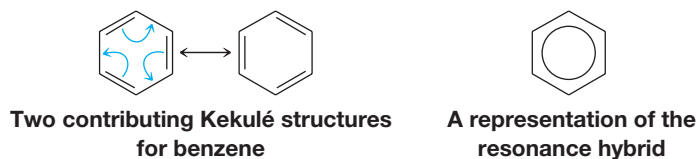


In Chapter 14 we shall study in detail a group of unsaturated cyclic hydrocarbons known as **aromatic compounds**. The compound known as **benzene** is the prototypical aromatic compound. Benzene can be written as a six-membered ring with alternating single and double bonds, called a **Kekulé structure** after August Kekulé, who first conceived of this representation:



Even though the Kekulé structure is frequently used for benzene compounds, there is much evidence that this representation is inadequate and incorrect. For example, if benzene had alternating single and double bonds as the Kekulé structure indicates, we would expect the lengths of the carbon–carbon bonds around the ring to be alternately longer and shorter, as we typically find with carbon–carbon single and double bonds (Fig. 1.31). In fact, the carbon–carbon bonds of benzene are all the same length (1.39 Å), a value in between that of a carbon–carbon single bond and a carbon–carbon double bond. There are two ways of dealing with this problem: with resonance theory or with molecular orbital theory.

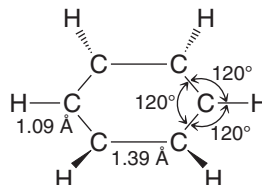
If we use resonance theory, we visualize benzene as being represented by either of two equivalent Kekulé structures:

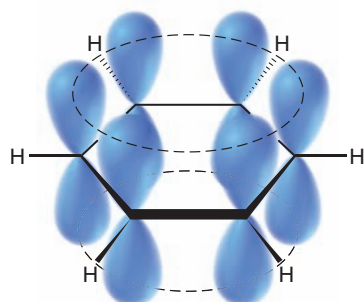
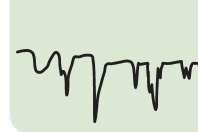
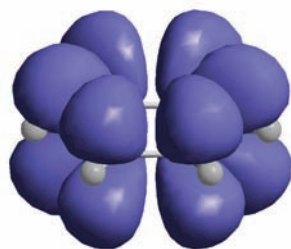


Based on the principles of resonance theory (Section 1.8) we recognize that benzene cannot be represented adequately by either structure, but that, instead, *it should be visualized as a hybrid of the two structures*. We represent this hybrid by a hexagon with a circle in the middle. Resonance theory, therefore, solves the problem we encountered in understanding how all of the carbon–carbon bonds are the same length. According to resonance theory, the bonds are not alternating single and double bonds, they are a resonance hybrid of the two. Any bond that is a single bond in the first contributor is a double bond in the second, and vice versa.

- All of the carbon–carbon bonds in benzene are one and one-half bonds, have a bond length in between that of a single bond and a double bond, and have bond angles of 120° .

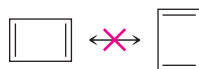
In the molecular orbital explanation, which we shall describe in much more depth in Chapter 14, we begin by recognizing that the carbon atoms of the benzene ring are sp^2 hybridized. Therefore, each carbon has a p orbital that has one lobe above the plane of the ring and one lobe below, as shown on the next page in the schematic and calculated p orbital representations.



Schematic representation of benzene p orbitalsCalculated p orbital shapes in benzeneCalculated benzene molecular orbital resulting from favorable overlap of p orbitals above and below plane of benzene ring

The lobes of each p orbital above and below the ring overlap with the lobes of p orbitals on the atoms to either side of it. This kind of overlap of p orbitals leads to a set of bonding molecular orbitals that encompass all of the carbon atoms of the ring, as shown in the calculated molecular orbital. Therefore, the six electrons associated with these p orbitals (one electron from each orbital) are **delocalized** about all six carbon atoms of the ring. This delocalization of electrons explains how all the carbon–carbon bonds are equivalent and have the same length. In Section 14.7B, when we study nuclear magnetic resonance spectroscopy, we shall present convincing physical evidence for this delocalization of the electrons.

Cyclobutadiene (below) is like benzene in that it has alternating single and double bonds in a ring. However, its bonds are not the same length, the double bonds being shorter than the single bonds; the molecule is rectangular, not square. Explain why it would be incorrect to write resonance structures as shown.



PRACTICE PROBLEM 2.1

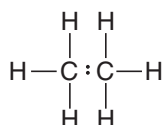
2.2 POLAR COVALENT BONDS

In our discussion of chemical bonds in Section 1.3, we examined compounds such as LiF in which the bond is between two atoms with very large electronegativity differences. In instances like these, a complete transfer of electrons occurs, giving the compound an **ionic bond**:



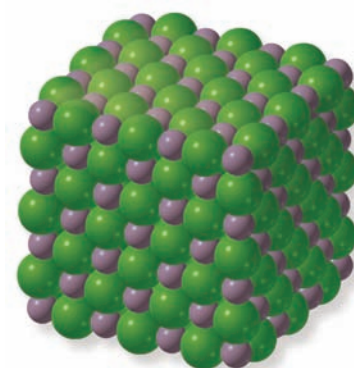
Lithium fluoride has an ionic bond.

We also described molecules in which electronegativity differences are not large, or in which they are the same, such as the carbon–carbon bond of ethane. Here the electrons are shared equally between the atoms.



Ethane has a covalent bond.
The electrons are shared equally
between the carbon atoms.

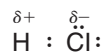
Until now, we have not considered the possibility that the electrons of a covalent bond might be shared unequally.



Lithium fluoride crystal model

- If electronegativity differences exist between two bonded atoms, and they are not large, the electrons are not shared equally and a **polar covalent bond** is the result.
- Remember: one definition of **electronegativity** is *the ability of an atom to attract electrons that it is sharing in a covalent bond.*

An example of such a polar covalent bond is the one in hydrogen chloride. The chlorine atom, with its greater electronegativity, pulls the bonding electrons closer to it. This makes the hydrogen atom somewhat electron deficient and gives it a *partial* positive charge (δ^+). The chlorine atom becomes somewhat electron rich and bears a *partial* negative charge (δ^-):



Because the hydrogen chloride molecule has a partially positive end and a partially negative end, it is a **dipole**, and it has a **dipole moment**.

The direction of polarity of a polar bond can be symbolized by a vector quantity \longleftrightarrow . The crossed end of the arrow is the positive end and the arrowhead is the negative end:

(positive end) \longleftrightarrow (negative end)

In HCl, for example, we would indicate the direction of the dipole moment in the following way:



The dipole moment is a physical property that can be measured experimentally. It is defined as the product of the magnitude of the charge in electrostatic units (esu) and the distance that separates them in centimeters (cm):

$$\text{Dipole moment} = \text{charge (in esu)} \times \text{distance (in cm)}$$

$$\mu = e \times d$$

The charges are typically on the order of 10^{-10} esu and the distances are on the order of 10^{-8} cm. Dipole moments, therefore, are typically on the order of 10^{-18} esu cm. For convenience, this unit, 1×10^{-18} esu cm, is defined as one **debye** and is abbreviated D. (The unit is named after Peter J. W. Debye, a chemist born in the Netherlands and who taught at Cornell University from 1936 to 1966. Debye won the Nobel Prize in Chemistry in 1936.) In SI units $1 \text{ D} = 3.336 \times 10^{-30}$ coulomb meter (C · m).

If necessary, the length of the arrow can be used to indicate the magnitude of the dipole moment. Dipole moments, as we shall see in Section 2.3, are very useful quantities in accounting for physical properties of compounds.

PRACTICE PROBLEM 2.2

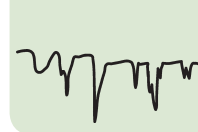
Write δ^+ and δ^- by the appropriate atoms and draw a dipole moment vector for any of the following molecules that are polar:

- (a) HF (b) IBr (c) Br₂ (d) F₂

Polar covalent bonds strongly influence the physical properties and reactivity of molecules. In many cases, these polar covalent bonds are part of **functional groups**, which we shall study shortly (Sections 2.5–2.13). Functional groups are defined groups of atoms in a molecule that give rise to the function (reactivity or physical properties) of the molecule. Functional groups often contain atoms having different electronegativity values and unshared electron pairs. (Atoms such as oxygen, nitrogen, and sulfur that form covalent bonds and have unshared electron pairs are called **heteroatoms**.)

2.2A Maps of Electrostatic Potential

One way to visualize the distribution of charge in a molecule is with a **map of electrostatic potential (MEP)**. Regions of an electron density surface that are more negative than others in an MEP are colored red. These regions would attract a positively charged species (or repel a negative charge). Regions in the MEP that are less negative (or are



positive) are blue. Blue regions are likely to attract electrons from another molecule. The spectrum of colors from red to blue indicates the trend in charge from most negative to least negative (or most positive).

Figure 2.1 shows a map of electrostatic potential for the low-electron-density surface of hydrogen chloride. We can see clearly that negative charge is concentrated near the chlorine atom and that positive charge is localized near the hydrogen atom, as we predict based on the difference in their electronegativity values. Furthermore, because this MEP is plotted at the low-electron-density surface of the molecule (the van der Waals surface, Section 2.13B), it also gives an indication of the molecule's overall shape.

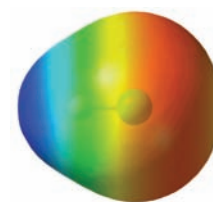


FIGURE 2.1 A calculated map of electrostatic potential for hydrogen chloride showing regions of relatively more negative charge in red and more positive charge in blue. Negative charge is clearly localized near the chlorine, resulting in a strong dipole moment for the molecule.

2.3 POLAR AND NONPOLAR MOLECULES

In the discussion of dipole moments in the previous section, our attention was restricted to simple diatomic molecules. Any *diatomic* molecule in which the two atoms are *different* (and thus have different electronegativities) will, of necessity, have a dipole moment. In general, a molecule with a dipole moment is a **polar molecule**. If we examine Table 2.1, however, we find that a number of molecules (e.g., CCl_4 , CO_2) consist of more than two atoms, have *polar* bonds, *but have no dipole moment*. With our knowledge of the shapes of molecules (Sections 1.12–1.16) we can understand how this can occur.

TABLE 2.1 DIPOLE MOMENTS OF SOME SIMPLE MOLECULES

Formula	μ (D)	Formula	μ (D)
H_2	0	CH_4	0
Cl_2	0	CH_3Cl	1.87
HF	1.83	CH_2Cl_2	1.55
HCl	1.08	CHCl_3	1.02
HBr	0.80	CCl_4	0
HI	0.42	NH_3	1.47
BF_3	0	NF_3	0.24
CO_2	0	H_2O	1.85

Consider a molecule of carbon tetrachloride (CCl_4). Because the electronegativity of chlorine is greater than that of carbon, each of the carbon–chlorine bonds in CCl_4 is polar. Each chlorine atom has a partial negative charge, and the carbon atom is considerably positive. Because a molecule of carbon tetrachloride is tetrahedral (Fig. 2.2), however, *the center of positive charge and the center of negative charge coincide, and the molecule has no net dipole moment*.

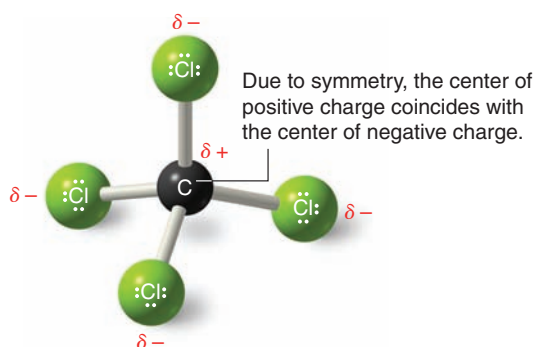


FIGURE 2.2 Charge distribution in carbon tetrachloride. The molecule has no net dipole moment.

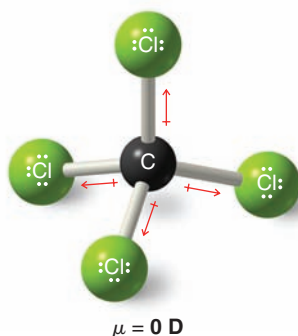


FIGURE 2.3 A tetrahedral orientation of equal bond moments causes their effects to cancel.

This result can be illustrated in a slightly different way: if we use arrows (\rightarrow) to represent the direction of polarity of each bond, we get the arrangement of bond moments shown in Fig. 2.3. Since the bond moments are vectors of equal magnitude arranged tetrahedrally, their effects cancel. Their vector sum is zero. The molecule has *no net dipole moment*.

The chloromethane molecule (CH_3Cl) has a net dipole moment of 1.87 D. Since carbon and hydrogen have electronegativities (Table 1.1) that are nearly the same, the contribution of three C—H bonds to the net dipole is negligible. The electronegativity difference between carbon and chlorine is large, however, and the highly polar C—Cl bond accounts for most of the dipole moment of CH_3Cl (Fig. 2.4).

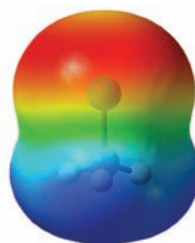
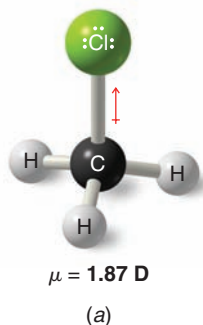
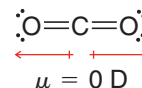


FIGURE 2.4 (a) The dipole moment of chloromethane arises mainly from the highly polar carbon–chlorine bond. (b) A map of electrostatic potential illustrates the polarity of chloromethane.

SOLVED PROBLEM 2.2

Although molecules of CO_2 have polar bonds (oxygen is more electronegative than carbon), carbon dioxide (Table 2.1) has no dipole moment. What can you conclude about the geometry of a carbon dioxide molecule?

STRATEGY AND ANSWER: For a CO_2 molecule to have a zero dipole moment, the bond moments of the two carbon–oxygen bonds must cancel each other. This can happen only if molecules of carbon dioxide are linear.



PRACTICE PROBLEM 2.3 Boron trifluoride (BF_3) has no dipole moment ($\mu = 0 \text{ D}$). Explain how this observation confirms the geometry of BF_3 predicted by VSEPR theory.

PRACTICE PROBLEM 2.4 Tetrachloroethene ($\text{CCl}_2=\text{CCl}_2$) does not have a dipole moment. Explain this fact on the basis of the shape of $\text{CCl}_2=\text{CCl}_2$.

PRACTICE PROBLEM 2.5 Sulfur dioxide (SO_2) has a dipole moment ($\mu = 1.63 \text{ D}$); on the other hand, carbon dioxide (see Solved Problem 2.2) has no dipole moment ($\mu = 0 \text{ D}$). What do these facts indicate about the geometry of sulfur dioxide?

Unshared pairs of electrons make large contributions to the dipole moments of water and ammonia. Because an unshared pair has no other atom attached to it to partially neutralize its negative charge, an unshared electron pair contributes a large moment directed away from the central atom (Fig. 2.5). (The O—H and N—H moments are also appreciable.)

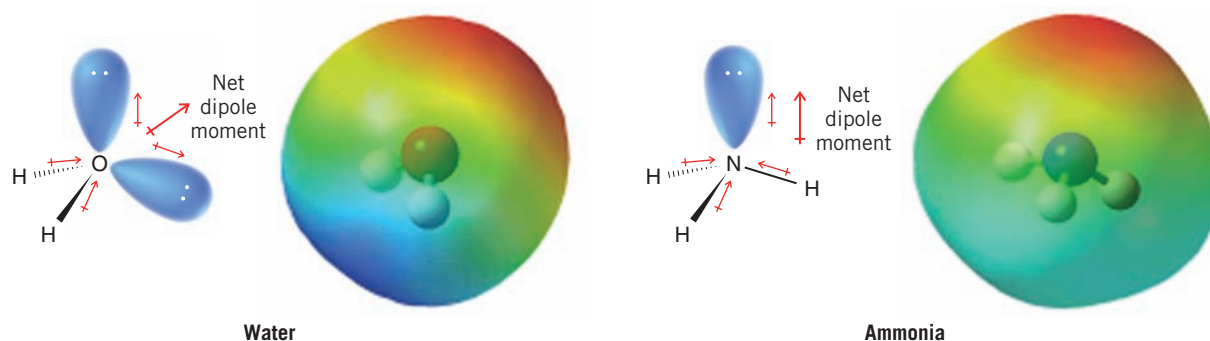


FIGURE 2.5 Bond moments and the resulting dipole moments of water and ammonia.

Using a three-dimensional formula, show the direction of the dipole moment of CH_3OH . Write δ^+ and δ^- signs next to the appropriate atoms.

PRACTICE PROBLEM 2.6

Trichloromethane (CHCl_3 , also called *chloroform*) has a larger dipole moment than CFCl_3 . Use three-dimensional structures and bond moments to explain this fact.

PRACTICE PROBLEM 2.7

2.3A Dipole Moments in Alkenes

Cis–trans isomers of alkenes (Section 1.13B) have different physical properties. They have different melting points and boiling points, and often cis–trans isomers differ markedly in the magnitude of their dipole moments. Table 2.2 summarizes some of the physical properties of two pairs of cis–trans isomers.

TABLE 2.2 PHYSICAL PROPERTIES OF SOME CIS–TRANS ISOMERS

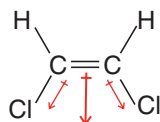
Compound	Melting Point ($^{\circ}\text{C}$)	Boiling Point ($^{\circ}\text{C}$)	Dipole Moment (D)
<i>cis</i> -1,2-Dichloroethene	−80	60	1.90
<i>trans</i> -1,2-Dichloroethene	−50	48	0
<i>cis</i> -1,2-Dibromoethene	−53	112	1.35
<i>trans</i> -1,2-Dibromoethene	−6	108	0

SOLVED PROBLEM 2.3

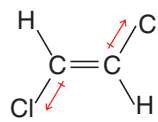
Explain why *cis*-1,2-dichloroethene (Table 2.2) has a large dipole moment whereas *trans*-1,2-dichloroethene has a dipole moment equal to zero.

STRATEGY AND ANSWER: If we examine the net dipole moments (shown in red) for the bond moments (black), we see that in *trans*-1,2-dichloroethene the bond moments cancel each other, whereas in *cis*-1,2-dichloroethene they augment each other.

Bond moments (black) are in same general direction. Resultant dipole moment (red) is large.



cis-1,2-Dichloroethene
 $\mu = 1.9 \text{ D}$



Bond moments cancel each other. Net dipole is zero.

trans-1,2-Dichloroethene
 $\mu = 0 \text{ D}$

PRACTICE PROBLEM 2.8 Indicate the direction of the important bond moments in each of the following compounds (neglect C—H bonds). You should also give the direction of the net dipole moment for the molecule. If there is no net dipole moment, state that $\mu = 0$ D.

- (a) *cis*-CHF=CHF (b) *trans*-CHF=CHF (c) CH₂=CF₂ (d) CF₂=CF₂

PRACTICE PROBLEM 2.9 Write structural formulas for all of the alkenes with (a) the formula C₂H₂Br₂ and (b) the formula C₂Br₂Cl₂. In each instance designate compounds that are *cis*–*trans* isomers of each other. Predict the dipole moment of each one.

2.4 FUNCTIONAL GROUPS

- **Functional groups** are common and specific arrangements of atoms that impart predictable reactivity and properties to a molecule.

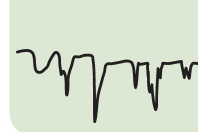
The functional group of an alkene, for example, is its carbon–carbon double bond. When we study the reactions of alkenes in greater detail in Chapter 8, we shall find that most of the chemical reactions of alkenes are the chemical reactions of the carbon–carbon double bond.

The functional group of an alkyne is its carbon–carbon triple bond. Alkanes do not have a functional group. Their molecules have carbon–carbon single bonds and carbon–hydrogen bonds, but these bonds are present in molecules of almost all organic compounds, and C—C and C—H bonds are, in general, much less reactive than common functional groups. We shall introduce other common functional groups and their properties in Sections 2.5–2.11. Table 2.3 (Section 2.12) summarizes the most important functional groups. First, however, let us introduce some common alkyl groups, which are specific groups of carbon and hydrogen atoms that are not part of functional groups.

2.4A Alkyl Groups and the Symbol R

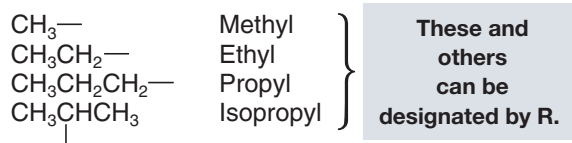
Alkyl groups are the groups that we identify for purposes of naming compounds. They are groups that would be obtained by removing a hydrogen atom from an alkane:

Alkane	Alkyl Group	Abbreviation	Bond-line	Model
CH ₃ —H Methane	H ₃ C— Methyl	Me-		
CH ₃ CH ₂ —H Ethane	CH ₃ CH ₂ — Ethyl	Et-		
CH ₃ CH ₂ CH ₂ —H Propane	CH ₃ CH ₂ CH ₂ — Propyl	Pr-		
CH ₃ CH ₂ CH ₂ CH ₂ —H Butane	CH ₃ CH ₂ CH ₂ CH ₂ — Butyl	Bu-		



While only one alkyl group can be derived from methane or ethane (the **methyl** and **ethyl** groups, respectively), two groups can be derived from propane. Removal of a hydrogen from one of the end carbon atoms gives a group that is called the **propyl** group; removal of a hydrogen from the middle carbon atom gives a group that is called the **isopropyl** group. The names and structures of these groups are used so frequently in organic chemistry that you should learn them now. See Section 4.3C for names and structures of branched alkyl groups derived from butane and other hydrocarbons.

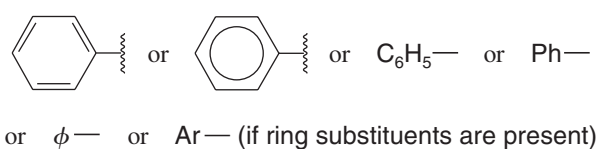
We can simplify much of our future discussion if, at this point, we introduce a symbol that is widely used in designating general structures of organic molecules: the symbol **R**. **R is used as a general symbol to represent any alkyl group.** For example, R might be a methyl group, an ethyl group, a propyl group, or an isopropyl group:



Thus, the general formula for an alkane is R—H.

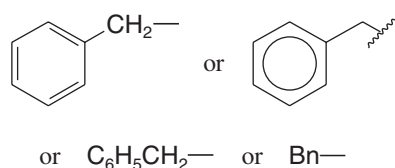
2.4B Phenyl and Benzyl Groups

When a benzene ring is attached to some other group of atoms in a molecule, it is called a **phenyl group**, and it is represented in several ways:

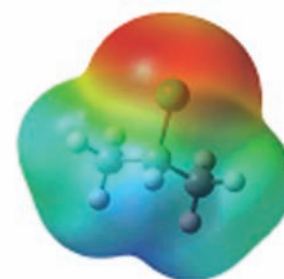
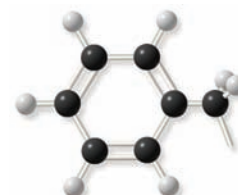
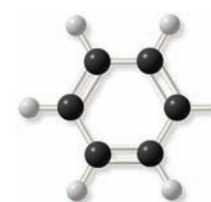


Ways of representing a phenyl group

The combination of a phenyl group and a **methylene group** (—CH₂—) is called a **benzyl group**:



Ways of representing a benzyl group



2-Chloropropane

2.5 ALKYL HALIDES OR HALOALKANES

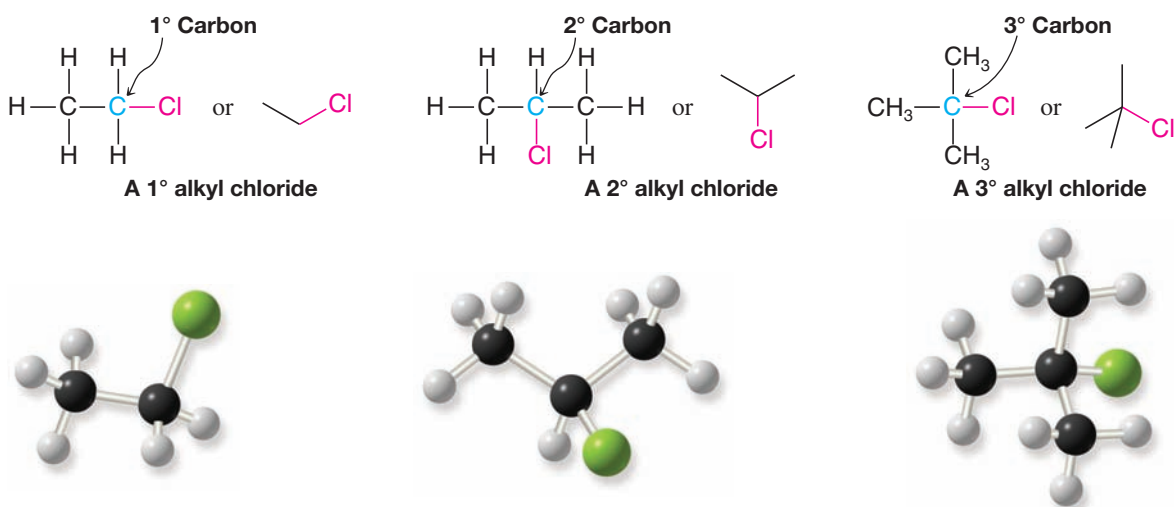
Alkyl halides are compounds in which a halogen atom (fluorine, chlorine, bromine, or iodine) replaces a hydrogen atom of an alkane. For example, CH₃Cl and CH₃CH₂Br are alkyl halides. Alkyl halides are also called **haloalkanes**. The generic formula for an alkyl halide is R—Ẍ: where X = fluorine, chlorine, bromine, or iodine.

Alkyl halides are classified as being primary (1°), secondary (2°), or tertiary (3°). **This classification is based on the carbon atom to which the halogen is directly attached.** If the carbon atom that bears the halogen is directly attached to only one other carbon, the carbon atom is said to be a **primary carbon atom** and the alkyl halide is classified as a **primary alkyl halide**. If the carbon that bears the halogen is itself directly attached to two other carbon atoms, then the carbon is a **secondary carbon** and the alkyl halide is a **secondary alkyl halide**. If the carbon that bears the halogen is directly attached to three other carbon atoms, then the carbon is a **tertiary**

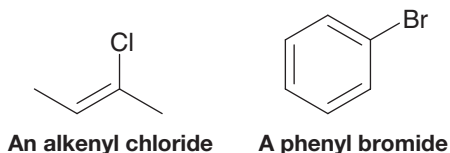
Helpful Hint

Although we use the symbols 1°, 2°, 3°, we do not say first degree, second degree, and third degree; we say *primary*, *secondary*, and *tertiary*.

carbon and the alkyl halide is a **tertiary alkyl halide**. Examples of primary, secondary, and tertiary alkyl halides are the following:



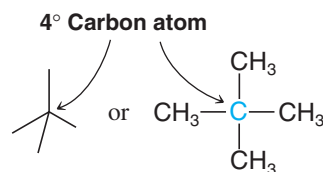
An **alkenyl halide** is a compound with a halogen atom bonded to an alkene carbon. In older nomenclature such compounds were sometimes referred to as vinyl halides. An **aryl halide** is a compound with a halogen atom bonded to an aromatic ring such as a benzene ring.



SOLVED PROBLEM 2.4

Write the structure of an alkane with the formula C_5H_{12} that has no secondary or tertiary carbon atoms. *Hint:* The compound has a quaternary (4°) carbon.

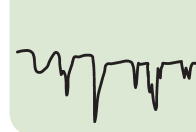
STRATEGY AND ANSWER: Following the pattern of designations for carbon atoms given above, a 4° carbon atom must be one that is directly attached to four other carbon atoms. If we start with this carbon atom, and then add four carbon atoms with their attached hydrogens, there is only one possible alkane. The other four carbons are all primary carbons; none is secondary or tertiary.



PRACTICE PROBLEM 2.10 Write bond-line structural formulas for (a) two constitutionally isomeric primary alkyl bromides with the formula C_4H_9Br , (b) a secondary alkyl bromide, and (c) a tertiary alkyl bromide with the same formula. Build handheld molecular models for each structure and examine the differences in their connectivity.

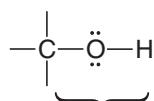
PRACTICE PROBLEM 2.11 Although we shall discuss the naming of organic compounds later when we discuss the individual families in detail, one method of naming alkyl halides is so straightforward that it is worth describing here. We simply name the alkyl group attached to the halogen and add the word *fluoride*, *chloride*, *bromide*, or *iodide*. Write formulas for (a) ethyl fluoride and (b) isopropyl chloride.

What are the names for (c) Br, (d) F, and (e) C_6H_5I ?

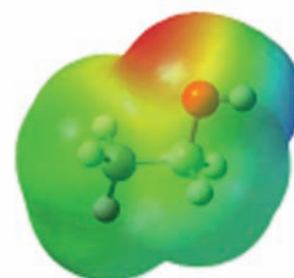


2.6 ALCOHOLS AND PHENOLS

Methyl alcohol (also called methanol) has the structural formula CH_3OH and is the simplest member of a family of organic compounds known as **alcohols**. The characteristic functional group of this family is the hydroxyl ($-\text{OH}$) group attached to an sp^3 -hybridized carbon atom. Another example of an alcohol is ethyl alcohol, $\text{CH}_3\text{CH}_2\text{OH}$ (also called ethanol).

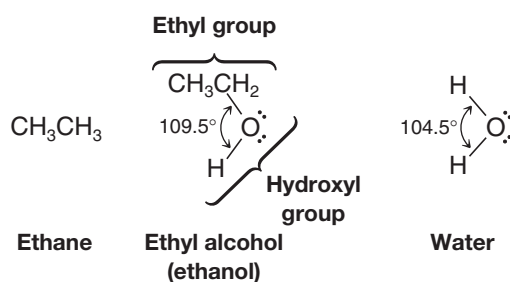


This is the functional group of an alcohol.

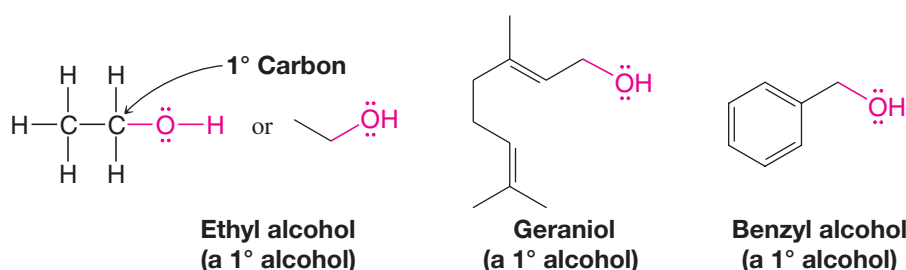


Ethanol

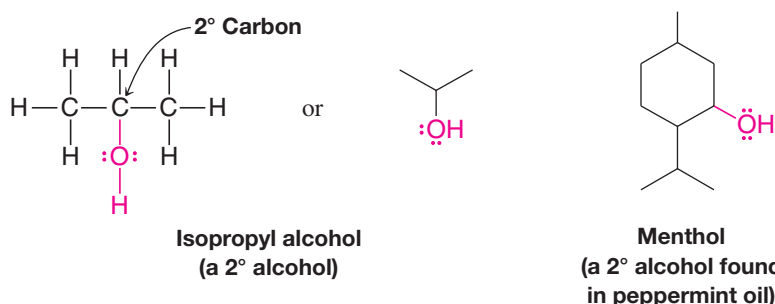
Alcohols may be viewed structurally in two ways: (1) as hydroxyl derivatives of alkanes and (2) as alkyl derivatives of water. Ethyl alcohol, for example, can be seen as an ethane molecule in which one hydrogen has been replaced by a hydroxyl group or as a water molecule in which one hydrogen has been replaced by an ethyl group:



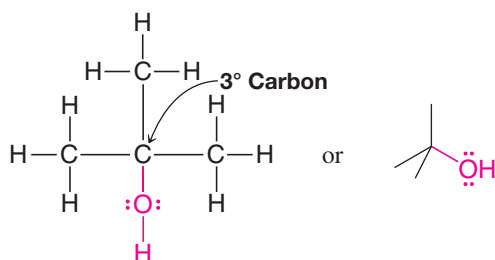
As with alkyl halides, alcohols are classified into three groups: primary (1°), secondary (2°), and tertiary (3°) alcohols. *This classification is based on the degree of substitution of the carbon to which the hydroxyl group is directly attached.* If the carbon has only one other carbon attached to it, the carbon is said to be a **primary carbon** and the alcohol is a **primary alcohol**:



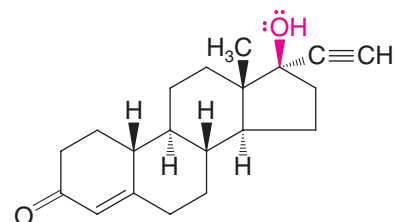
If the carbon atom that bears the hydroxyl group also has two other carbon atoms attached to it, this carbon is called a secondary carbon, and the alcohol is a secondary alcohol:



If the carbon atom that bears the hydroxyl group has three other carbons attached to it, this carbon is called a tertiary carbon, and the alcohol is a tertiary alcohol:



tert-Butyl alcohol
(a 3° alcohol)



Norethindrone
(an oral contraceptive that contains a 3° alcohol group as well as a ketone group and carbon-carbon double and triple bonds)

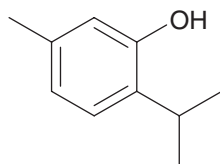
Helpful Hint

Practice with handheld molecular models by building models of as many of the compounds on this page as you can.

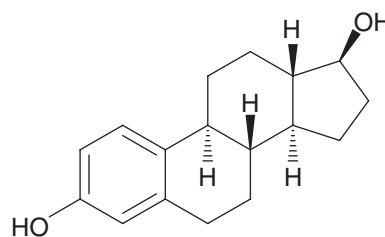
PRACTICE PROBLEM 2.12 Write bond-line structural formulas for (a) two primary alcohols, (b) a secondary alcohol, and (c) a tertiary alcohol—all having the molecular formula $C_4H_{10}O$.

PRACTICE PROBLEM 2.13 One way of naming alcohols is to name the alkyl group that is attached to the $-OH$ and add the word *alcohol*. Write bond-line formulas for (a) propyl alcohol and (b) isopropyl alcohol.

When a hydroxyl group is bonded to a benzene ring the combination of the ring and the hydroxyl is called a phenol. Phenols differ significantly from alcohols in terms of their relative acidity, as we shall see in Chapter 3, and thus they are considered a distinct functional group.



Thymol
(a phenol found in thyme)

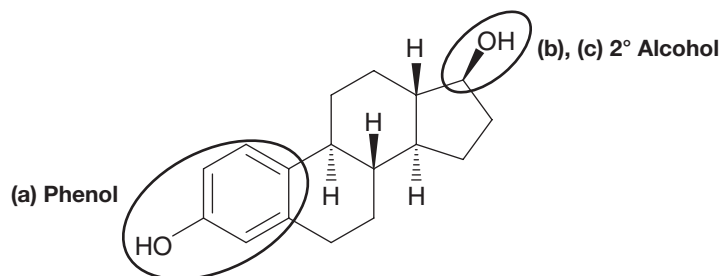


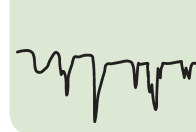
Estradiol
(a sex hormone that contains both alcohol and phenol groups)

SOLVED PROBLEM 2.5

Circle the atoms that comprise (a) the phenol and (b) the alcohol functional groups in estradiol. (c) What is the class of the alcohol?

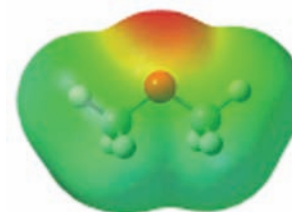
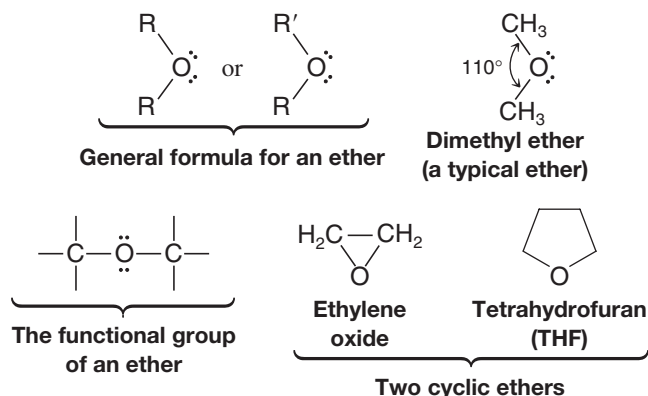
STRATEGY AND ANSWER: (a) A phenol group consists of a benzene ring and a hydroxyl group, hence we circle these parts of the molecule together. (b) The alcohol group is found in the five-membered ring of estradiol. (c) The carbon bearing the alcohol hydroxyl group has two carbons directly bonded to it, thus it is a secondary alcohol.





2.7 ETHERS

Ethers have the general formula $R-O-R$ or $R-O-R'$, where R' may be an alkyl (or phenyl) group different from R . Ethers can be thought of as derivatives of water in which both hydrogen atoms have been replaced by alkyl groups. The bond angle at the oxygen atom of an ether is only slightly larger than that of water:

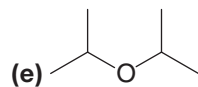


Dimethyl ether

One way of naming ethers is to name the two alkyl groups attached to the oxygen atom in alphabetical order and add the word *ether*. If the two alkyl groups are the same, we use the prefix *di-*, for example, as in *dimethyl ether*. Write bond-line structural formulas for (a) diethyl ether, (b) ethyl propyl ether, and (c) ethyl isopropyl ether. What name would

PRACTICE PROBLEM 2.14

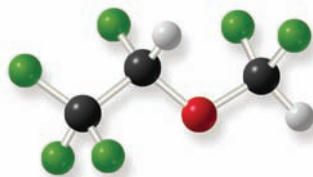
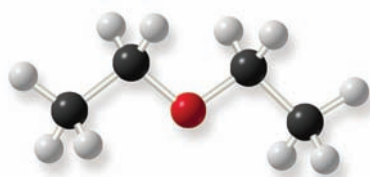
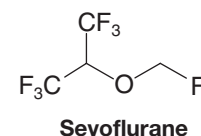
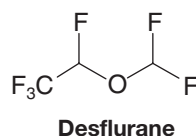
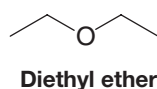
you give to (d)



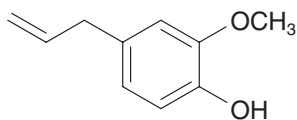
and (f) $\text{CH}_3\text{OC}_6\text{H}_5$?

THE CHEMISTRY OF... Ethers as General Anesthetics

Nitrous oxide (N_2O), also called laughing gas, was first used as an anesthetic in 1799, and it is still in use today, even though when used alone it does not produce deep anesthesia. The first use of an ether, diethyl ether, to produce deep anesthesia occurred in 1842. In the years that have passed since then, several different ethers, usually with halogen substituents, have replaced diethyl ether as anesthetics of choice. One reason: unlike diethyl ether, which is highly flammable, the halogenated ethers are not. Two halogenated ethers that are currently used for inhalation anesthesia are desflurane and sevoflurane.

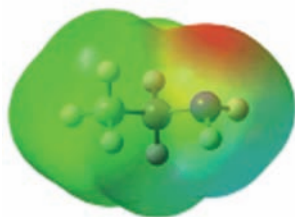


PRACTICE PROBLEM 2.15 Eugenol is the main constituent of the natural oil from cloves. Circle and label all of the functional groups in eugenol.



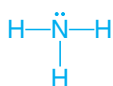
Eugenol (found in cloves)

2.8 AMINES

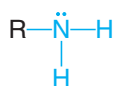


Ethylamine

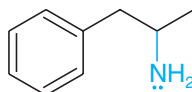
Just as alcohols and ethers may be considered as organic derivatives of water, amines may be considered as organic derivatives of ammonia:



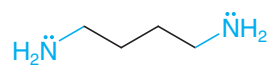
Ammonia



An amine

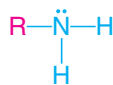


Amphetamine
(a dangerous stimulant)

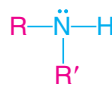


Putrescine
(found in decaying meat)

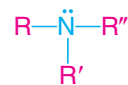
Amines are classified as primary, secondary, or tertiary amines. **This classification is based on the number of organic groups that are attached to the nitrogen atom:**



A primary (1°)
amine

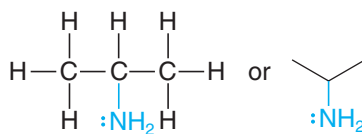


A secondary (2°)
amine

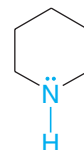


A tertiary (3°)
amine

Notice that this is quite different from the way alcohols and alkyl halides are classified. Isopropylamine, for example, is a primary amine even though its $-\text{NH}_2$ group is attached to a secondary carbon atom. It is a primary amine because only one organic group is attached to the nitrogen atom:

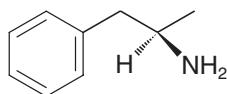


Isopropylamine
(a 1° amine)

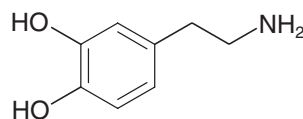


Piperidine
(a cyclic 2° amine)

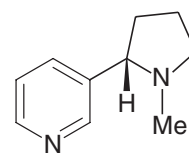
Amphetamine (below), a powerful and dangerous stimulant, is a primary amine. Dopamine, an important neurotransmitter whose depletion is associated with Parkinson's disease, is also a primary amine. Nicotine, a toxic compound found in tobacco that makes smoking addictive, has a secondary amine group and a tertiary one.



Amphetamine

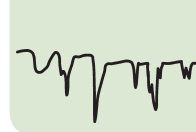


Dopamine

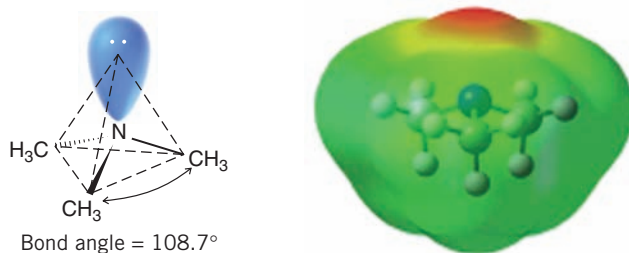


Nicotine

Amines are like ammonia (Section 1.16B) in having a trigonal pyramidal shape. The $\text{C}-\text{N}-\text{C}$ bond angles of trimethylamine are 108.7° , a value very close to the



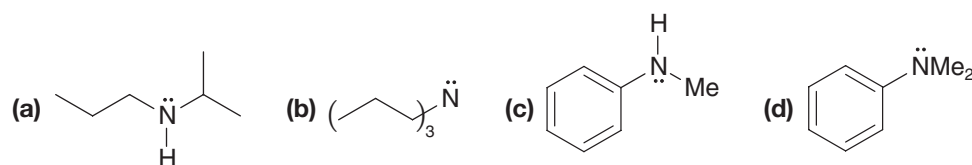
H—C—H bond angles of methane. Thus, for all practical purposes, the nitrogen atom of an amine can be considered to be sp^3 hybridized with the unshared electron pair occupying one orbital (see below). This means that the unshared pair is relatively exposed, and as we shall see this is important because it is involved in almost all of the reactions of amines.



Trimethylamine

One way of naming amines is to name in alphabetical order the alkyl groups attached to the nitrogen atom, using the prefixes *di-* and *tri-* if the groups are the same. An example is *isopropylamine*, whose formula is shown above. What are names for **(a)**, **(b)**, **(c)**, and **(d)**? Build hand-held molecular models for the compounds in parts **(a)**–**(d)**.

PRACTICE PROBLEM 2.16



Write bond-line formulas for **(e)** propylamine, **(f)** trimethylamine, and **(g)** ethylisopropylmethylamine.

Which amines in Practice Problem 2.16 are **(a)** primary amines, **(b)** secondary amines, and **(c)** tertiary amines?

PRACTICE PROBLEM 2.17

Amines are like ammonia in being weak bases. They do this by using their unshared electron pair to accept a proton. **(a)** Show the reaction that would take place between trimethylamine and HCl. **(b)** What hybridization state would you expect for the nitrogen atom in the product of this reaction?

PRACTICE PROBLEM 2.18

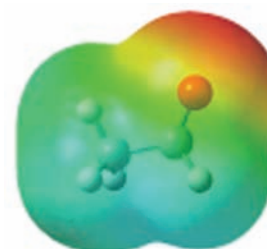
2.9 ALDEHYDES AND KETONES

Aldehydes and ketones both contain the **carbonyl group**—a group in which a carbon atom has a double bond to oxygen:



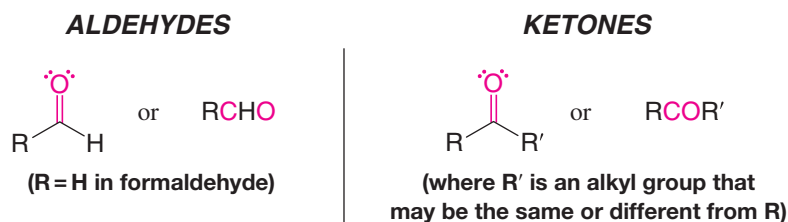
The carbonyl group

The carbonyl group of an aldehyde is bonded to one hydrogen atom and one carbon atom (except for formaldehyde, which is the only aldehyde bearing two hydrogen atoms).

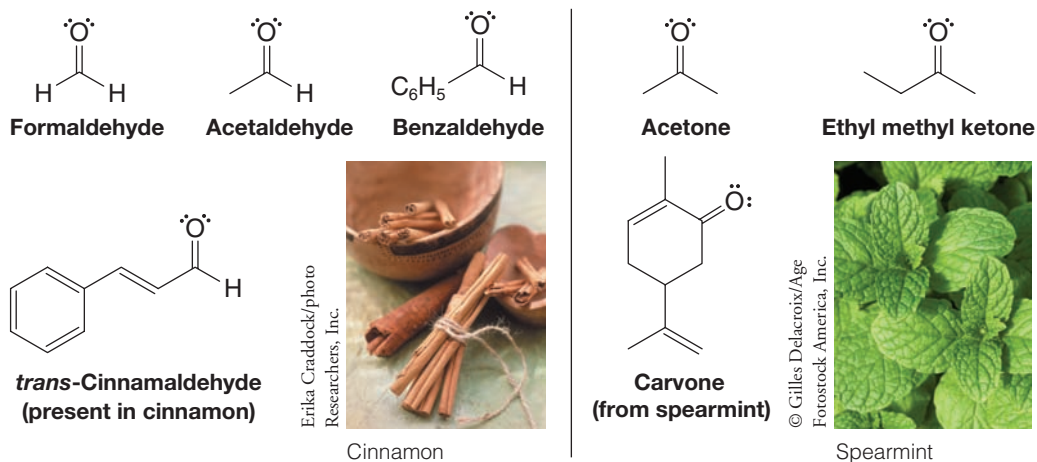


Acetaldehyde

The carbonyl group of a ketone is bonded to two carbon atoms. Using R, we can designate the general formulas for aldehydes and ketones as follows:



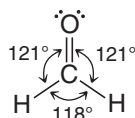
Some specific examples of aldehydes and ketones are the following:



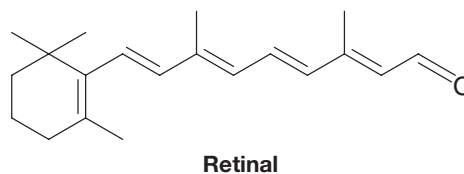
Helpful Hint

Computer molecular models can be found in the 3D Models section of the book's website for these and many other compounds we discuss in this book.

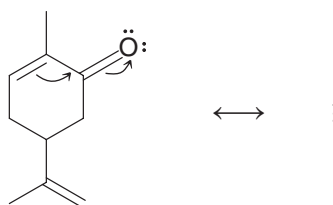
Aldehydes and ketones have a trigonal planar arrangement of groups around the carbonyl carbon atom. The carbon atom is sp^2 hybridized. In formaldehyde, for example, the bond angles are as follows:



Retinal (below) is an aldehyde made from vitamin A that plays a vital role in vision. We discuss this further in Chapter 13.



PRACTICE PROBLEM 2.19 Write the resonance structure for carvone that results from moving the electrons as indicated. Include all formal charges.



SOLVED PROBLEM 2.6

When formic acid (see above) donates a proton to a base, the result is the formation of a formate ion (HCO_2^-). **(a)** Write two resonance structures for the formate ion, and two resonance structures for formic acid. **(b)** Review the Rules for Resonance in Chapter 1, and identify which species, formate ion or formic acid, is most stabilized by resonance.

STRATEGY AND ANSWER: **(a)** We move the electron pairs as indicated below.

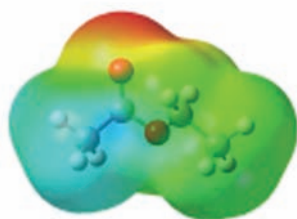
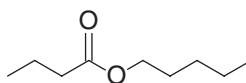
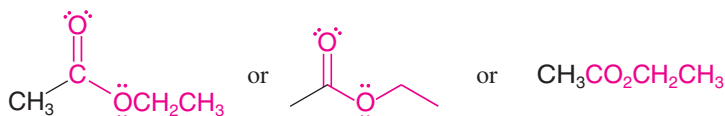
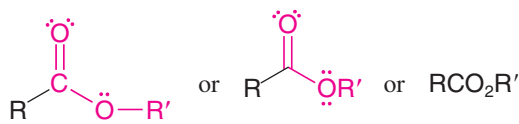


(b) The formate ion would be most stabilized because it does not have separated charges.

PRACTICE PROBLEM 2.21 Write bond-line formulas for four carboxylic acids with the formula $\text{C}_5\text{H}_{10}\text{O}_2$.

2.10B Esters

Esters have the general formula $\text{RCO}_2\text{R}'$ (or RCOOR'), where a carbonyl group is bonded to an alkoxy ($-\text{OR}$) group:



Ethyl acetate



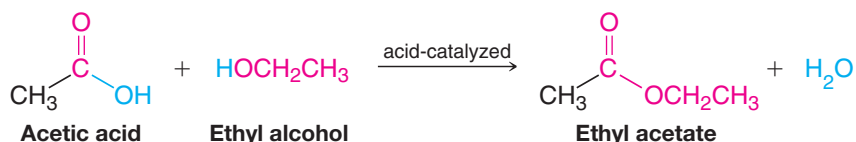
Media Bakery

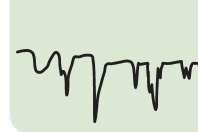
The ester pentyl butanoate has the odor of apricots and pears.

PRACTICE PROBLEM 2.22 Write bond-line formulas for three esters with the formula $\text{C}_5\text{H}_{10}\text{O}_2$.

PRACTICE PROBLEM 2.23 Write another resonance structure for ethyl acetate. Include formal charges.

Esters can be made from a carboxylic acid and an alcohol through the acid-catalyzed loss of a molecule of water. For example:

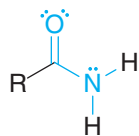




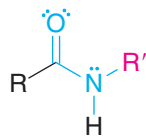
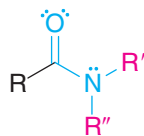
Your body makes esters from long-chain carboxylic acids called “fatty acids” by combining them with glycerol. We discuss their chemistry in detail in Chapter 23.

2.10C Amides

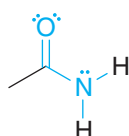
Amides have the formulas RCONH_2 , RCONHR' , or $\text{RCONR}'\text{R}''$ where a carbonyl group is bonded to a nitrogen atom bearing hydrogen and/or alkyl groups. General formulas and some specific examples are shown below.



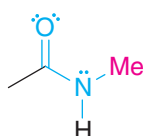
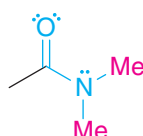
An unsubstituted amide

An *N*-substituted amideAn *N,N*-disubstituted amide

General formulas for amides



Acetamide

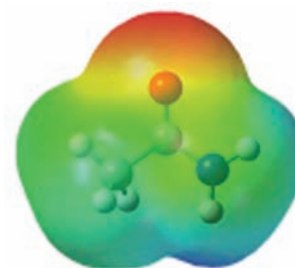
*N*-Methylacetamide*N,N*-Dimethylacetamide

Specific examples of amides

Media Bakery



Nylon is a polymer comprised of regularly repeating amide groups.



Acetamide

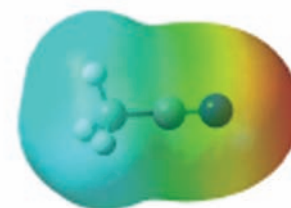
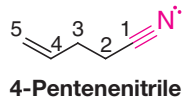
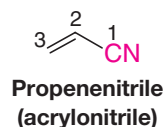
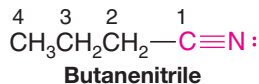
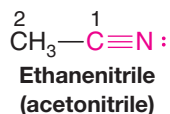
N- and *N,N*- indicate that the substituents are attached to the nitrogen atom.

Write another resonance structure for acetamide.

PRACTICE PROBLEM 2.24

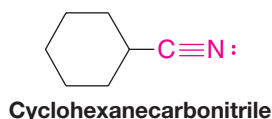
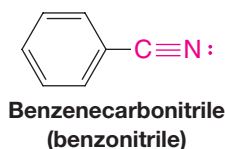
2.11 NITRILES

A nitrile has the formula $\text{R}-\text{C}\equiv\text{N}$: (or $\text{R}-\text{CN}$). The carbon and the nitrogen of a nitrile are *sp* hybridized. In IUPAC systematic nomenclature, acyclic nitriles are named by adding the suffix *-nitrile* to the name of the corresponding hydrocarbon. The carbon atom of the $-\text{C}\equiv\text{N}$ group is assigned number 1. The name acetonitrile is an acceptable common name for CH_3CN , and acrylonitrile is an acceptable common name for $\text{CH}_2=\text{CHCN}$:



Acetonitrile

Cyclic nitriles are named by adding the suffix *-carbonitrile* to the name of the ring system to which the $-\text{CN}$ group is attached. Benzonitrile is an acceptable common name for $\text{C}_6\text{H}_5\text{CN}$:



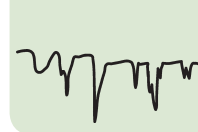
2.12 SUMMARY OF IMPORTANT FAMILIES OF ORGANIC COMPOUNDS

A summary of the important families of organic compounds is given in Table 2.3. You should learn to identify these common functional groups as they appear in other, more complicated molecules.

TABLE 2.3 IMPORTANT FAMILIES OF ORGANIC COMPOUNDS

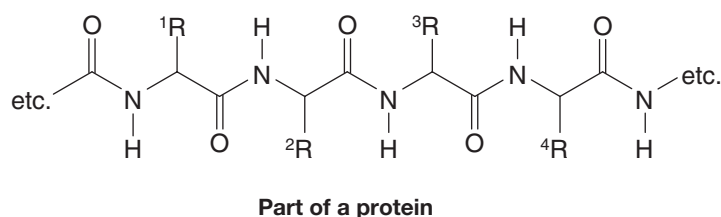
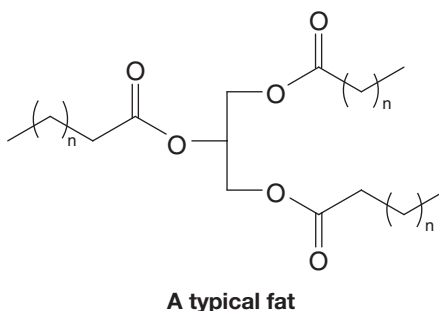
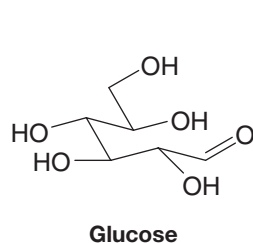
		Family							
		Alkane	Alkene	Alkyne	Aromatic	Haloalkane	Alcohol	Phenol	Ether
Functional group	$\begin{array}{c} \text{C}-\text{H} \\ \text{and} \\ \text{C}-\text{C} \\ \text{bonds} \end{array}$			$-\text{C}\equiv\text{C}-$	Aromatic ring				
General formula	RH	$\text{RCH}=\text{CH}_2$ $\text{RCH}=\text{CHR}$ $\text{R}_2\text{C}=\text{CHR}$ $\text{R}_2\text{C}=\text{CR}_2$	$\text{RC}\equiv\text{CH}$ $\text{RC}\equiv\text{CR}$	ArH	RX	ROH	ArOH	ROR	
Specific example	CH_3CH_3	$\text{CH}_2=\text{CH}_2$	$\text{HC}\equiv\text{CH}$		$\text{CH}_3\text{CH}_2\text{Cl}$	$\text{CH}_3\text{CH}_2\text{OH}$		CH_3OCH_3	
IUPAC name	Ethane	Ethene	Ethyne	Benzene	Chloroethane	Ethanol	Phenol	Methoxymethane	
Common name ^a	Ethane	Ethylene	Acetylene	Benzene	Ethyl chloride	Ethyl alcohol	Phenol	Dimethyl ether	
		Amine	Aldehyde	Ketone	Carboxylic Acid	Ester	Amide	Nitrile	
Functional group							$-\text{C}\equiv\text{N:}$		
General formula	RNH_2 R_2NH R_3N	$\text{RCH}=\text{O}$	$\text{RCH}'=\text{O}$	RCOH	RCOR'	RCNH_2 RCNHR' $\text{RCNR}'\text{R}''$	RCN		
Specific example	CH_3NH_2	CH_3CHO	CH_3COCH_3	CH_3COOH	CH_3COCH_3	CH_3CONH_2	$\text{CH}_3\text{C}\equiv\text{N}$		
IUPAC name	Methanamine	Ethanal	Propanone	Ethanoic acid	Methyl ethanoate	Ethanamide	Ethanenitrile		
Common name	Methylamine	Acetaldehyde	Acetone	Acetic acid	Methyl acetate	Acetamide	Acetonitrile		

^aThese names are also accepted by the IUPAC.



2.12A Functional Groups in Biologically Important Compounds

Many of the functional groups we have listed in Table 2.3 are central to the compounds of living organisms. A typical sugar, for example, is glucose. Glucose contains several alcohol hydroxyl groups (—OH) and in one of its forms contains an aldehyde group. Fats and oils contain ester groups, and proteins contain amide groups. See if you can identify alcohol, aldehyde, ester, and amide groups in the following examples.



2.13 PHYSICAL PROPERTIES AND MOLECULAR STRUCTURE

So far, we have said little about one of the most obvious characteristics of organic compounds—that is, *their physical state or phase*. Whether a particular substance is a solid, or a liquid, or a gas would certainly be one of the first observations that we would note in any experimental work. The temperatures at which transitions occur between phases—that is, melting points (mp) and boiling points (bp)—are also among the more easily measured **physical properties**. Melting points and boiling points are also useful in identifying and isolating organic compounds.

Suppose, for example, we have just carried out the synthesis of an organic compound that is known to be a liquid at room temperature and 1 atm pressure. If we know the boiling point of our desired product and the boiling points of by-products and solvents that may be present in the reaction mixture, we can decide whether or not simple distillation will be a feasible method for isolating our product.

In another instance our product might be a solid. In this case, in order to isolate the substance by crystallization, we need to know its melting point and its solubility in different solvents.

The physical constants of known organic substances are easily found in handbooks and other reference books.* Table 2.4 lists the melting and boiling points of some of the compounds that we have discussed in this chapter.

Often in the course of research, however, the product of a synthesis is a new compound—one that has never been described before. In these instances, success in isolating the new compound depends on making reasonably accurate estimates of its melting point, boiling point, and solubilities. Estimations of these macroscopic physical properties are based on the most likely structure of the substance and on the forces that act between molecules and ions. The temperatures at which phase changes occur are an indication of the strength of these intermolecular forces.

Helpful Hint

Understanding how molecular structure influences physical properties is very useful in practical organic chemistry.

*Two useful handbooks are *Handbook of Chemistry*, Lange, N. A., Ed., McGraw-Hill: New York; and *CRC Handbook of Chemistry and Physics*, CRC: Boca Raton, FL.

TABLE 2.4 PHYSICAL PROPERTIES OF REPRESENTATIVE COMPOUNDS

Compound	Structure	mp (°C)	bp (°C) (1 atm) ^a
Methane	CH ₄	-182.6	-162
Ethane	CH ₃ CH ₃	-172	-88.2
Ethene	CH ₂ =CH ₂	-169	-102
Ethyne	HC≡CH	-82	-84 subl
Chloromethane	CH ₃ Cl	-97	-23.7
Chloroethane	CH ₃ CH ₂ Cl	-138.7	13.1
Ethyl alcohol	CH ₃ CH ₂ OH	-114	78.5
Acetaldehyde	CH ₃ CHO	-121	20
Acetic acid	CH ₃ CO ₂ H	16.6	118
Sodium acetate	CH ₃ CO ₂ Na	324	dec
Ethylamine	CH ₃ CH ₂ NH ₂	-80	17
Diethyl ether	(CH ₃ CH ₂) ₂ O	-116	34.6
Ethyl acetate	CH ₃ CO ₂ CH ₂ CH ₃	-84	77

^aIn this table dec = decomposes and subl = sublimes.

2.13A Ionic Compounds: Ion–Ion Forces

- The **melting point** of a substance is the temperature at which an equilibrium exists between the well-ordered crystalline state and the more random liquid state.

If the substance is an ionic compound, such as sodium acetate (Table 2.4), the **ion–ion forces** that hold the ions together in the crystalline state are the strong electrostatic lattice forces that act between the positive and negative ions in the orderly crystalline structure. In Fig. 2.6 each sodium ion is surrounded by negatively charged acetate ions, and each acetate ion is surrounded by positive sodium ions. A large amount of thermal energy is required to break up the orderly structure of the crystal into the disorderly open structure of a liquid. As a result, the temperature at which sodium acetate melts is quite high, 324 °C. The **boiling points** of ionic compounds are higher still, so high that most ionic organic compounds decompose (are changed by undesirable chemical reactions) before they boil. Sodium acetate shows this behavior.

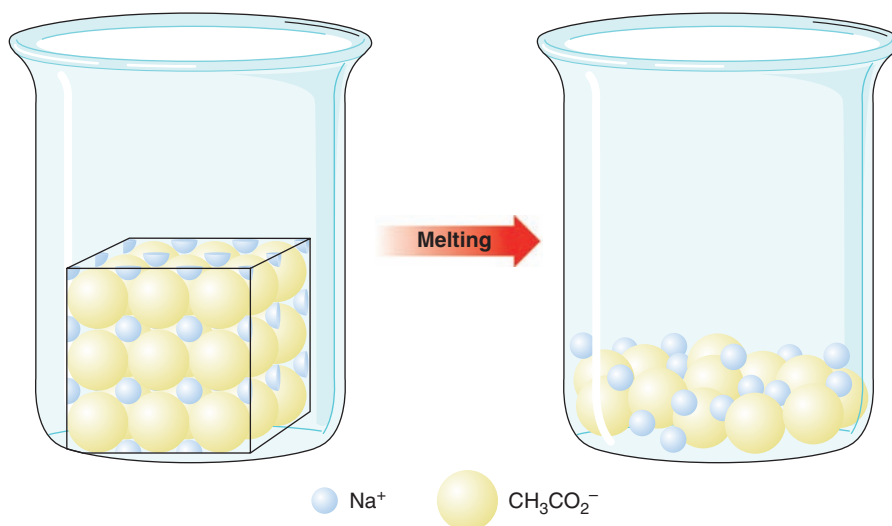


FIGURE 2.6 The melting of sodium acetate.

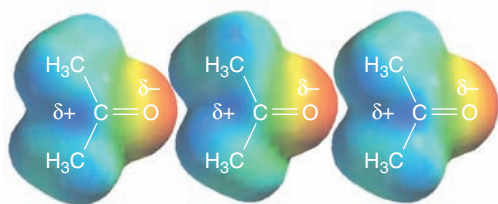


FIGURE 2.7 Electrostatic potential models for acetone molecules that show how acetone molecules might align according to attractions of their partially positive regions and partially negative regions (dipole–dipole interactions).

2.13B Intermolecular Forces (van der Waals Forces)

The forces that act between molecules are not as strong as those between ions, but they account for the fact that even completely nonpolar molecules can exist in liquid and solid states. These **intermolecular forces**, collectively called **van der Waals forces**, are all electrical in nature. We will focus our attention on three types:

1. Dipole–dipole forces
2. Hydrogen bonds
3. Dispersion forces

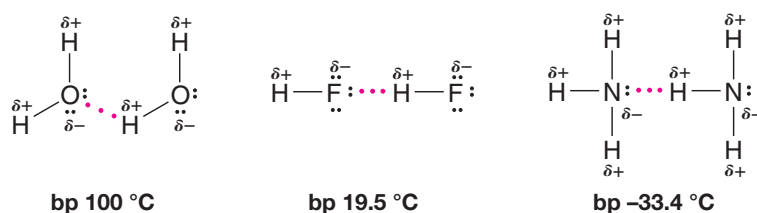
Dipole–Dipole Forces Most organic molecules are not fully ionic but have instead a *permanent dipole moment* resulting from a nonuniform distribution of the bonding electrons (Section 2.3). Acetone and acetaldehyde are examples of molecules with permanent dipoles because the carbonyl group that they contain is highly polarized. In these compounds, the attractive forces between molecules are much easier to visualize. In the liquid or solid state, **dipole–dipole** attractions cause the molecules to orient themselves so that the positive end of one molecule is directed toward the negative end of another (Fig. 2.7).

Hydrogen Bonds

- Very strong dipole–dipole attractions occur between hydrogen atoms bonded to small, strongly electronegative atoms (O, N, or F) and nonbonding electron pairs on other such electronegative atoms. This type of intermolecular force is called a **hydrogen bond**.

Hydrogen bonds (bond dissociation energies of about $4\text{--}38\text{ kJ mol}^{-1}$) are weaker than ordinary covalent bonds but much stronger than the dipole–dipole interactions that occur above, for example, in acetone.

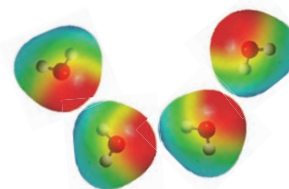
Hydrogen bonding explains why water, ammonia, and hydrogen fluoride all have far higher boiling points than methane (bp $-161.6\text{ }^{\circ}\text{C}$), even though all four compounds have similar molecular weights.



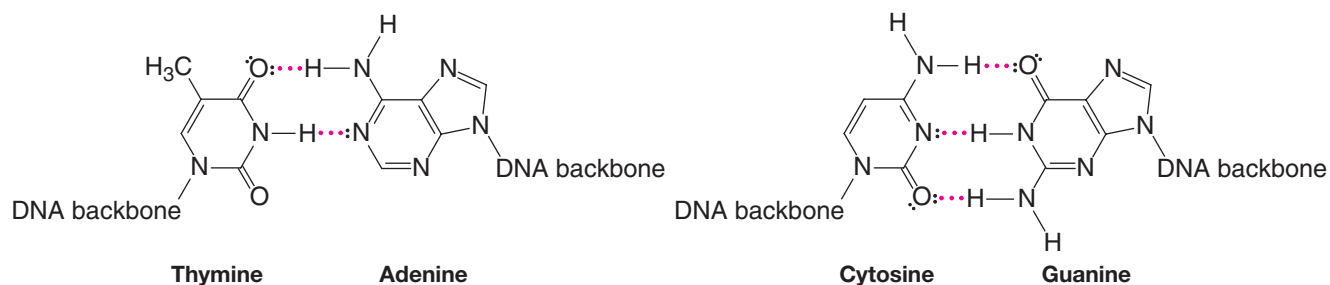
Hydrogen bonds are shown by the red dots.

One of the most important consequences of hydrogen bonding is that it causes water to be a liquid rather than a gas at $25\text{ }^{\circ}\text{C}$. Calculations indicate that in the absence of hydrogen bonding, water would have a boiling point near $-80\text{ }^{\circ}\text{C}$ and would not exist as a liquid unless the temperature were lower than that temperature. Had this been the case, it is highly unlikely that life, as we know it, could have developed on the planet Earth.

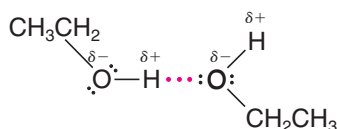
Hydrogen bonds hold the base pairs of double-stranded DNA together (see Section 25.4). Thymine hydrogen bonds with adenine. Cytosine hydrogen bonds with guanine.



Water molecules associated by attraction of opposite partial charges.



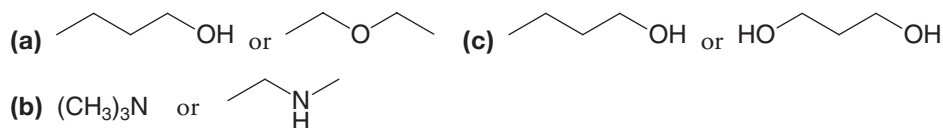
Hydrogen bonding accounts for the fact that ethyl alcohol has a much higher boiling point (78.5 °C) than dimethyl ether (24.9 °C) even though the two compounds have the same molecular weight. Molecules of ethyl alcohol, because they have a hydrogen atom covalently bonded to an oxygen atom, can form strong hydrogen bonds to each other.



The red dots represent a hydrogen bond. Strong hydrogen bonding is limited to molecules having a hydrogen atom attached to an O, N, or F atom.

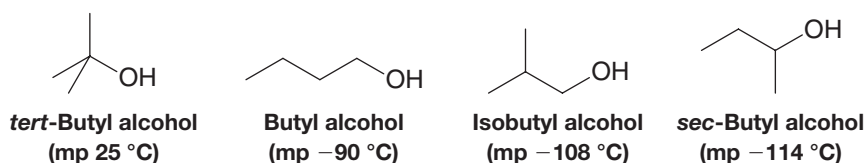
Molecules of dimethyl ether, because they lack a hydrogen atom attached to a strongly electronegative atom, cannot form strong hydrogen bonds to each other. In dimethyl ether the intermolecular forces are weaker dipole–dipole interactions.

PRACTICE PROBLEM 2.25 The compounds in each part below have the same (or similar) molecular weights. Which compound in each part would you expect to have the higher boiling point? Explain your answers.



A factor (in addition to polarity and hydrogen bonding) that affects the *melting point* of many organic compounds is the compactness and rigidity of their individual molecules.

- Molecules that are symmetrical generally have abnormally high melting points. *tert*-Butyl alcohol, for example, has a much higher melting point than the other isomeric alcohols shown here:



PRACTICE PROBLEM 2.26 Which compound would you expect to have the higher melting point, propane or cyclopropane? Explain your answer.

Dispersion Forces If we consider a substance like methane where the particles are non-polar molecules, we find that the melting point and boiling point are very low: –182.6 °C and –162 °C, respectively. Instead of asking, “Why does methane melt and boil at low

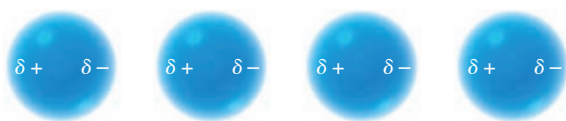
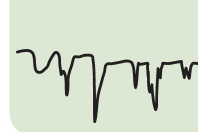


FIGURE 2.8 Temporary dipoles and induced dipoles in nonpolar molecules resulting from an uneven distribution of electrons at a given instant.

temperatures?” a more appropriate question might be “Why does methane, a nonionic, nonpolar substance, become a liquid or a solid at all?” The answer to this question can be given in terms of attractive intermolecular forces called **dispersion forces** or London forces.

An accurate account of the nature of dispersion forces requires the use of quantum mechanics. We can, however, visualize the origin of these forces in the following way. The average distribution of charge in a nonpolar molecule (such as methane) over a period of time is uniform. At any given instant, however, *because electrons move*, the electrons and therefore the charge may not be uniformly distributed. Electrons may, in one instant, be slightly accumulated on one part of the molecule, and, as a consequence, *a small temporary dipole will occur* (Fig. 2.8). This temporary dipole in one molecule can induce opposite (attractive) dipoles in surrounding molecules. It does this because the negative (or positive) charge in a portion of one molecule will distort the electron cloud of an adjacent portion of another molecule, causing an opposite charge to develop there. These temporary dipoles change constantly, but the net result of their existence is to produce attractive forces between nonpolar molecules and thus make possible the existence of their liquid and solid states.

Two important factors determine the magnitude of dispersion forces.

- 1. The relative polarizability of electrons of the atoms involved.** *By polarizability we mean how easily the electrons respond to a changing electric field.* The electrons of large atoms such as iodine are loosely held and are easily polarized, while the electrons of small atoms such as fluorine are more tightly held and are much less polarizable.

CF_4 and Cl_4 are both nonpolar molecules. But if we were to consider the intermolecular forces between two Cl_4 molecules, which contain polarizable iodine atoms, we would find that the dispersion forces are much larger than between two CF_4 molecules, which contains fluorine atoms that are not very polarizable.

- 2. The relative surface area of the molecules involved.** The larger the surface area, the larger is the overall attraction between molecules caused by dispersion forces. Molecules that are generally longer, flatter, or cylindrical have a greater surface area available for intermolecular interactions than more spherical molecules, and consequently have greater attractive forces between them than the tangential interactions between branched molecules. This is evident when comparing pentane, the unbranched C_5H_{12} hydrocarbon, with neopentane, the most highly branched C_5H_{12} isomer (in which one carbon bears four methyl groups). Pentane has a boiling point of 36.1°C . Neopentane has a boiling point of 9.5°C . The difference in their boiling points indicates that the attractive forces between pentane molecules are stronger than between neopentane molecules.

For large molecules, the cumulative effect of these small and rapidly changing dispersion forces can lead to a large net attraction.

2.13C Boiling Points

- The **boiling point** of a liquid is the temperature at which the vapor pressure of the liquid equals the pressure of the atmosphere above it.

The boiling points of liquids are *pressure dependent*, and boiling points are always reported as occurring at a particular pressure, at 1 atm (or at 760 torr), for example. A substance that boils at 150°C at 1 atm pressure will boil at a substantially lower temperature if the pressure is reduced to, for example, 0.01 torr (a pressure easily obtained with a vacuum pump). The normal boiling point given for a liquid is its boiling point at 1 atm.

In passing from a liquid to a gaseous state, the individual molecules (or ions) of the substance must separate. Because of this, we can understand why ionic organic compounds often decompose before they boil. The thermal energy required to completely separate (volatilize) the ions is so great that chemical reactions (decompositions) occur first.



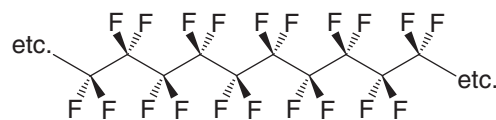
© Rfcompany/Age Fotostock America, Inc.

Dispersion forces are what provides a gecko's grip to smooth surfaces.

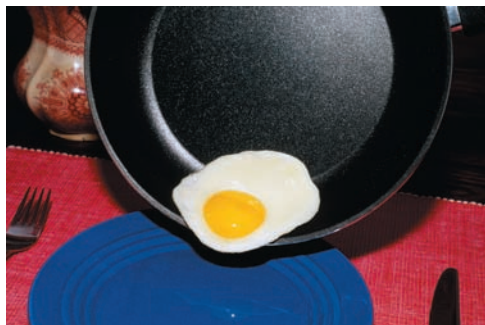
THE CHEMISTRY OF... Fluorocarbons and Teflon

Fluorocarbons (compounds containing only carbon and fluorine) have extraordinarily low boiling points when compared to hydrocarbons of the same molecular weight. The fluorocarbon C_5F_{12} has a slightly lower boiling point than pentane (C_5H_{12}) even though it has a far higher molecular weight. The important factor in explaining this behavior is the very low polarizability of fluorine atoms that we mentioned earlier, resulting in very small dispersion forces.

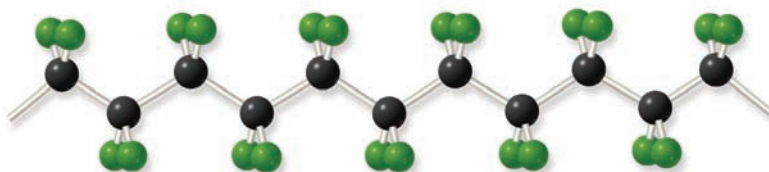
The fluorocarbon called *Teflon* [CF_2CF_2] $_n$ (see Section 10.10) has self-lubricating properties that are exploited in making “nonstick” frying pans and lightweight bearings.



Teflon



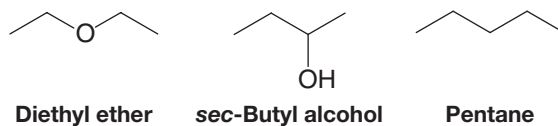
Leonard Lessin/Photo Researchers, Inc.



Nonpolar compounds, where the intermolecular forces are very weak, usually boil at low temperatures even at 1 atm pressure. This is not always true, however, because of other factors that we have not yet mentioned: the effects of molecular weight and molecular shape and surface area. Heavier molecules require greater thermal energy in order to acquire velocities sufficiently great to escape the liquid phase, and because the surface areas of larger molecules can be much greater, intermolecular dispersion attractions can also be much larger. These factors explain why nonpolar ethane (bp $-88.2\text{ }^\circ\text{C}$) boils higher than methane (bp $-162\text{ }^\circ\text{C}$) at a pressure of 1 atm. It also explains why, at 1 atm, the even heavier and larger nonpolar molecule decane ($C_{10}H_{22}$) boils at $174\text{ }^\circ\text{C}$. The relationship between dispersion forces and surface area helps us understand why neopentane (2,2-dimethylpropane) has a lower boiling point ($9.5\text{ }^\circ\text{C}$) than pentane ($36.1\text{ }^\circ\text{C}$), even though they have the same molecular weight. The branched structure of neopentane allows less surface interaction between neopentane molecules, hence lower dispersion forces, than does the linear structure of pentane.

SOLVED PROBLEM 2.7

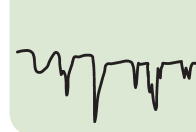
Arrange the following compounds according to their expected boiling points, with the lowest boiling point first, and explain your answer. Notice that the compounds have similar molecular weights.



STRATEGY AND ANSWER:

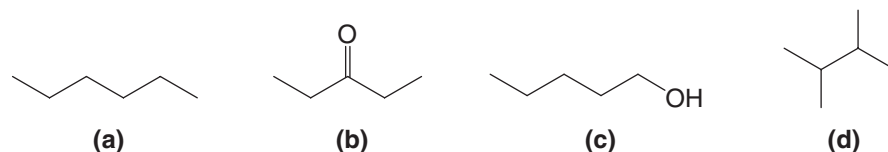


Pentane has no polar groups and has only dispersion forces holding its molecules together. It would have the lowest boiling point. Diethyl ether has the polar ether group that provides dipole–dipole forces which are greater than dispersion forces, meaning it would have a higher boiling point than pentane. *sec*-Butyl alcohol has an $-\text{OH}$ group that can form strong hydrogen bonds; therefore, it would have the highest boiling point.



Arrange the following compounds in order of increasing boiling point. Explain your answer in terms of the intermolecular forces in each compound.

PRACTICE PROBLEM 2.27



2.13D Solubilities

Intermolecular forces are of primary importance in explaining the **solubilities** of substances. Dissolution of a solid in a liquid is, in many respects, like the melting of a solid. The orderly crystal structure of the solid is destroyed, and the result is the formation of the more disorderly arrangement of the molecules (or ions) in solution. In the process of dissolving, too, the molecules or ions must be separated from each other, and energy must be supplied for both changes. The energy required to overcome lattice energies and intermolecular or interionic attractions comes from the formation of new attractive forces between solute and solvent.

Consider the dissolution of an ionic substance as an example. Here both the lattice energy and interionic attractions are large. We find that water and only a few other very polar solvents are capable of dissolving ionic compounds. These solvents dissolve ionic compounds by **hydrating** or **solvating** the ions (Fig. 2.9).

Water molecules, by virtue of their great polarity as well as their very small, compact shape, can very effectively surround the individual ions as they are freed from the crystal surface. Positive ions are surrounded by water molecules with the negative end of the water dipole pointed toward the positive ion; negative ions are solvated in exactly the opposite way. Because water is highly polar, and because water is capable of forming strong hydrogen bonds, the **ion-dipole forces** of attraction are also large. The energy supplied by the formation of these forces is great enough to overcome both the lattice energy and interionic attractions of the crystal.

A general rule for solubility is that “like dissolves like” in terms of comparable polarities.

- Polar and ionic solids are usually soluble in polar solvents.
- Polar liquids are usually miscible.
- Nonpolar solids are usually soluble in nonpolar solvents.
- Nonpolar liquids are usually miscible.
- Polar and nonpolar liquids, like oil and water, are usually not soluble to large extents.

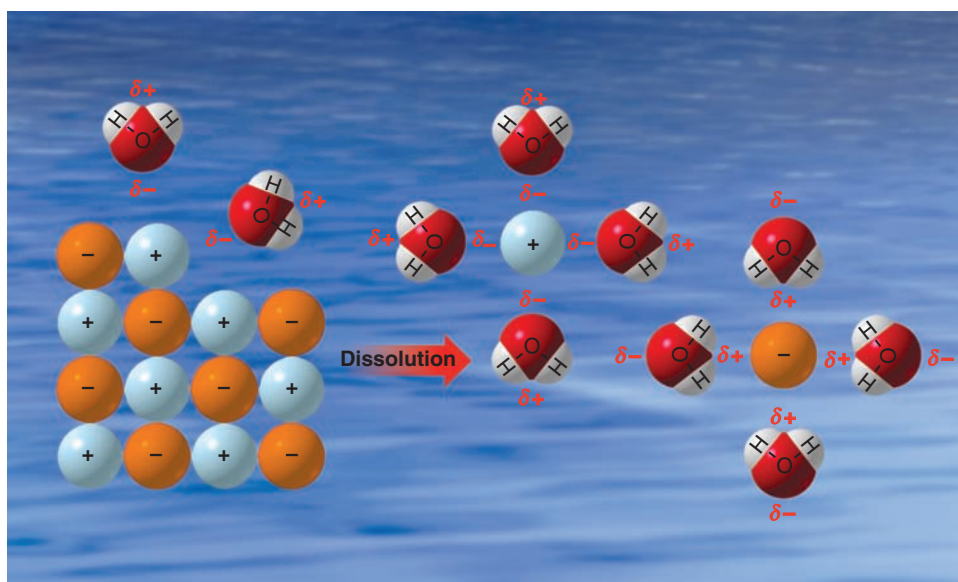
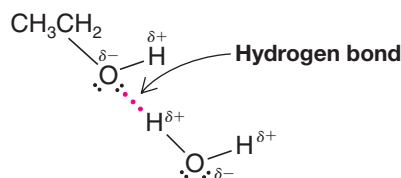


FIGURE 2.9 The dissolution of an ionic solid in water, showing the hydration of positive and negative ions by the very polar water molecules. The ions become surrounded by water molecules in all three dimensions, not just the two shown here.

Helpful Hint

Your ability to make qualitative predictions regarding solubility will prove very useful in the organic chemistry laboratory.

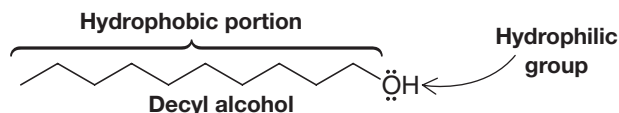
Methanol and water are miscible in all proportions; so too are mixtures of ethanol and water and mixtures of both propyl alcohols and water. In these cases the alkyl groups of the alcohols are relatively small, and the molecules therefore resemble water more than they do an alkane. Another factor in understanding their solubility is that the molecules are capable of forming strong hydrogen bonds to each other:



We often describe molecules or parts of molecules as being hydrophilic or hydrophobic. The alkyl groups of methanol, ethanol, and propanol are hydrophobic. Their hydroxyl groups are hydrophilic.

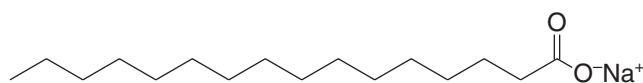
- **Hydrophobic** means incompatible with water (*hydro*, water; *phobic*, fearing or avoiding).
- **Hydrophilic** means compatible with water (*philic*, loving or seeking).

Decyl alcohol, with a chain of 10 carbon atoms, is a compound whose hydrophobic alkyl group overshadows its hydrophilic hydroxyl group in terms of water solubility.

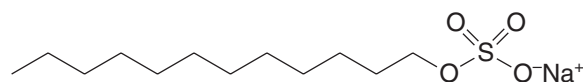


An explanation for why nonpolar groups such as long alkane chains avoid an aqueous environment—that is, for the so-called **hydrophobic effect**—is complex. The most important factor seems to involve an **unfavorable entropy change** in the water. Entropy changes (Section 3.10) have to do with changes from a relatively ordered state to a more disordered one or the reverse. Changes from order to disorder are favorable, whereas changes from disorder to order are unfavorable. For a nonpolar hydrocarbon chain to be accommodated by water, the water molecules have to form a more ordered structure around the chain, and for this, the entropy change is unfavorable.

We will see in Section 23.2C that the presence of a **hydrophobic group** and a hydrophilic group are essential components of soaps and detergents.



A typical soap molecule

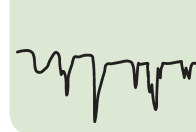


A typical detergent molecule

The hydrophobic long carbon chains of a soap or detergent embed themselves in the oily layer that typically surrounds the thing we want to wash away. The hydrophilic ionic groups at the ends of the chains are then left exposed on the surface and make the surface one that water molecules find attractive. Oil and water don't mix, but now the oily layer looks like something ionic and the water can take it "right down the drain."

2.13E Guidelines for Water Solubility

Organic chemists usually define a compound as water soluble if at least 3 g of the organic compound dissolves in 100 mL of water. We find that for compounds containing one hydrophilic group—and thus capable of forming strong **hydrogen bonds**—the following approximate guidelines hold: compounds with one to three carbon atoms are water

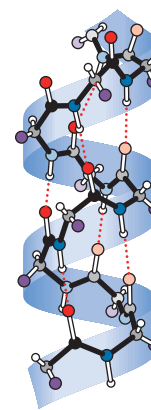


soluble, compounds with four or five carbon atoms are borderline, and compounds with six carbon atoms or more are insoluble.

When a compound contains more than one hydrophilic group, these guidelines do not apply. Polysaccharides (Chapter 22), proteins (Chapter 24), and nucleic acids (Chapter 25) all contain thousands of carbon atoms *and many are water soluble*. They dissolve in water because they also contain thousands of hydrophilic groups.

2.13F Intermolecular Forces in Biochemistry

Later, after we have had a chance to examine in detail the properties of the molecules that make up living organisms, we shall see how **intermolecular forces** are extremely important in the functioning of cells. **Hydrogen bond** formation, the hydration of polar groups, and the tendency of nonpolar groups to avoid a polar environment all cause complex protein molecules to fold in precise ways—ways that allow them to function as biological catalysts of incredible efficiency. The same factors allow molecules of hemoglobin to assume the shape needed to transport oxygen. They allow proteins and molecules called lipids to function as cell membranes. Hydrogen bonding gives certain carbohydrates a globular shape that makes them highly efficient food reserves in animals. It gives molecules of other carbohydrates a rigid linear shape that makes them perfectly suited to be structural components in plants.


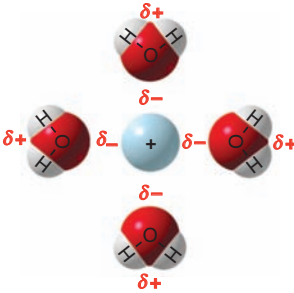

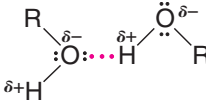

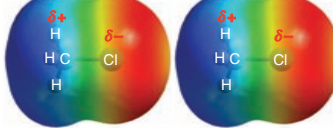


Hydrogen bonding (red dotted lines) in the α -helix structure of proteins

(Illustration, Irving Geis. Image from the Irving Geis Collection, HHMI. Rights owned by Howard Hughes Medical Institute. Not to be reproduced without permission.)

2.14 SUMMARY OF ATTRACTIVE ELECTRIC FORCES

The attractive forces occurring between molecules and ions that we have studied so far are summarized in Table 2.5.

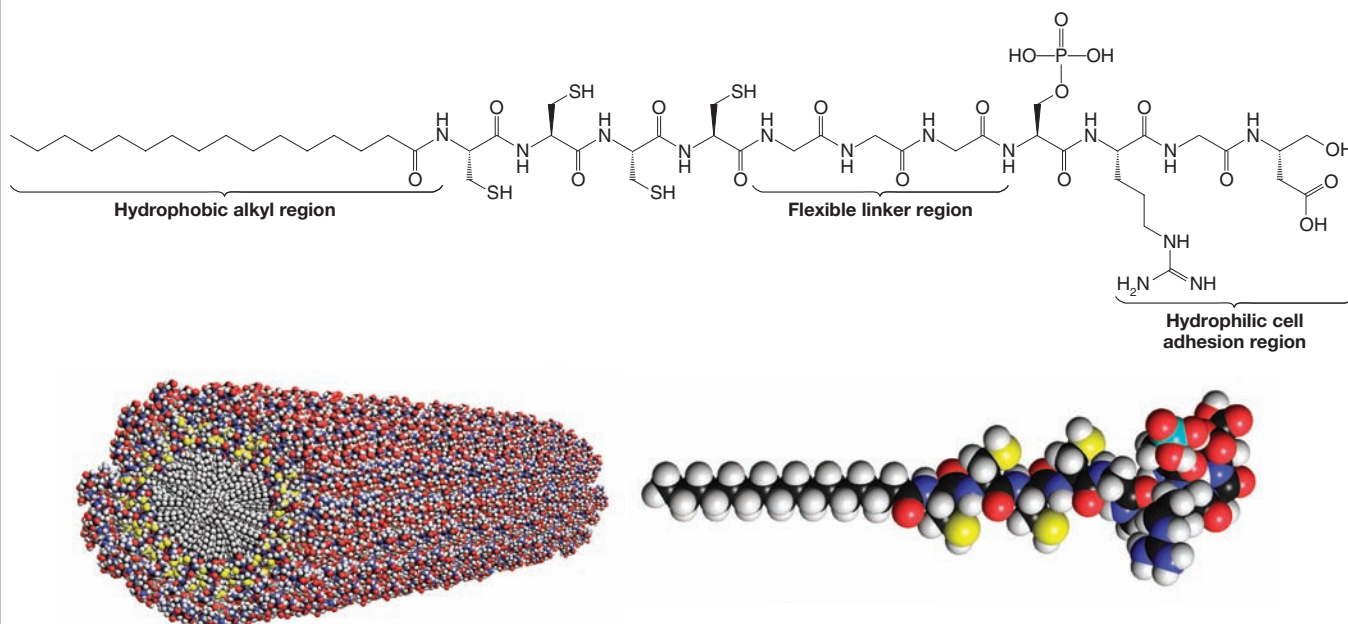
Electric Force	Relative Strength	Type	Example
Cation–anion (in a crystal)	Very strong		Sodium chloride crystal lattice
Covalent bonds	Strong (140–523 kJ mol ⁻¹)	Shared electron pairs	H—H (436 kJ mol ⁻¹) CH ₃ —CH ₃ (378 kJ mol ⁻¹) I—I (151 kJ mol ⁻¹)
Ion–dipole	Moderate		Na ⁺ in water (see Fig. 2.9)
Hydrogen bonds	Moderate to weak (4–38 kJ mol ⁻¹)		
Dipole–dipole	Weak		
Dispersion	Variable	Transient dipole	Interactions between methane molecules

THE CHEMISTRY OF... Organic Templates Engineered to Mimic Bone Growth

Intermolecular forces play a myriad of roles in life and in the world around us. Intermolecular forces hold together the strands of our DNA, provide structure to our cell membranes, cause the feet of gecko lizards to stick to walls and ceilings, keep water from boiling at room temperature and ordinary pressure, and literally provide the adhesive forces that hold our cells, bones, and tissues together. As these examples show, the world around us provides exquisite instruction in nanotechnology and bioengineering, and scientists throughout the ages have been inspired to create and innovate based on nature. One target of recent research in bioengineering is the development of synthetic materials that mimic nature's template for bone growth. A synthetic material with bone-promoting properties could be used to help repair broken bones, offset osteoporosis, and treat bone cancer.

Both natural bone growth and the synthetic system under development depend strongly on intermolecular forces. In living systems, bones grow by adhesion of specialized cells to a long fibrous natural template called collagen. Certain functional groups along the collagen promote the binding of

bone-growing cells, while other functional groups facilitate calcium crystallization. Chemists at Northwestern University (led by S. I. Stupp) have engineered a molecule that can be made in the laboratory and that mimics this process. The molecule shown below spontaneously self-assembles into a long tubular aggregate, imitating the fibers of collagen. Dispersion forces between hydrophobic alkyl tails on the molecule cause self-assembly of the molecules into tubules. At the other end of the molecule, the researchers included functional groups that promote cell binding and still other functional groups that encourage calcium crystallization. Lastly, they included functional groups that allow one molecule to be covalently linked to its neighbors after the self-assembly process has occurred, thus adding further stabilization to the initially noncovalent structure. Designing all of these features into the molecular structure has paid off, because the self-assembled fiber promotes calcium crystallization along its axis, much like nature's collagen template. This example of molecular design is just one exciting development at the intersection of nanotechnology and bioengineering.

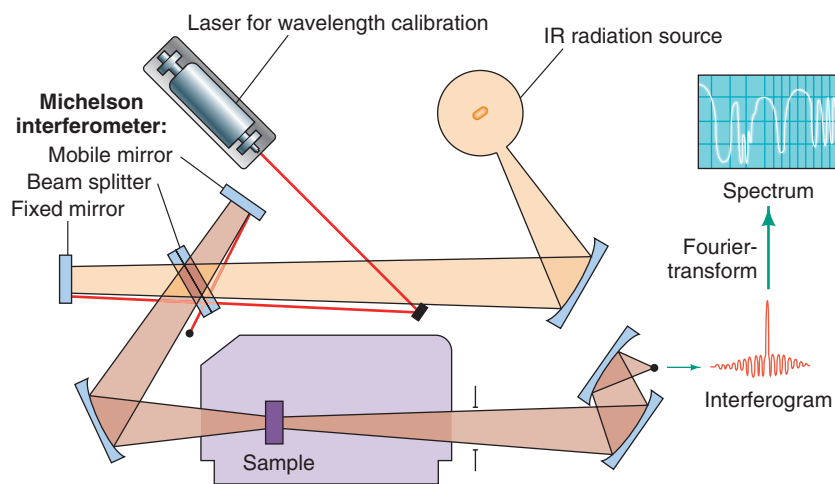


(From Hartgerink, J.D., Beniash, E. J., Stupp, S.I.: Self-assembly and Mineralization of Peptide-Amphiphile Nanofibers. *SCIENCE* 294:1684-1688, Figure 1 (2001). Reprinted with permission from AAAS.)

2.15 INFRARED SPECTROSCOPY: AN INSTRUMENTAL METHOD FOR DETECTING FUNCTIONAL GROUPS

Infrared (IR) spectroscopy is a simple, rapid, and nondestructive instrumental technique that can give evidence for the presence of various functional groups. If you had a sample of unknown identity, among the first things you would do is obtain an infrared spectrum, along with determining its solubility in common solvents and its melting and/or boiling point.

Infrared spectroscopy, as with all forms of spectroscopy, depends on the interaction of molecules or atoms with electromagnetic radiation. Infrared radiation causes atoms and groups of atoms of organic compounds to vibrate with increased amplitude about the



(Diagram adapted from the computer program IR Tutor, Columbia University.)

FIGURE 2.10 A diagram of a Fourier transform infrared (FTIR) spectrometer. FTIR spectrometers employ a Michelson interferometer, which splits the radiation beam from the IR source so that it reflects simultaneously from a moving mirror and a fixed mirror, leading to interference. After the beams recombine, they pass through the sample to the detector and are recorded as a plot of time versus signal intensity, called an interferogram. The overlapping wavelengths and the intensities of their respective absorptions are then converted to a spectrum by applying a mathematical operation called a Fourier transform.

The FTIR method eliminates the need to scan slowly over a range of wavelengths, as was the case with older types of instruments called dispersive IR spectrometers, and therefore FTIR spectra can be acquired very quickly. The FTIR method also allows greater throughput of IR energy. The combination of these factors gives FTIR spectra strong signals as compared to background noise (i.e., a high signal to noise ratio) because radiation throughput is high and rapid scanning allows multiple spectra to be averaged in a short period of time. The result is enhancement of real signals and cancellation of random noise.

covalent bonds that connect them. (Infrared radiation is not of sufficient energy to excite electrons, as is the case when some molecules interact with visible, ultraviolet, or higher energy forms of light.) Since the functional groups of organic molecules include specific arrangements of bonded atoms, absorption of IR radiation by an organic molecule will occur at specific frequencies characteristic of the types of bonds and atoms present in the specific functional groups of that molecule. These vibrations are *quantized*, and as they occur, the compounds absorb IR energy in particular regions of the IR portion of the spectrum.

An infrared spectrometer (Fig. 2.10) operates by passing a beam of IR radiation through a sample and comparing the radiation transmitted through the sample with that transmitted in the absence of the sample. Any frequencies absorbed by the sample will be apparent by the difference. The spectrometer plots the results as a graph showing absorbance versus frequency or wavelength.

- The position of an absorption band (peak) in an IR spectrum is specified in units of **wavenumbers** ($\bar{\nu}$).

Wavenumbers are the reciprocal of wavelength when wavelength is expressed in centimeters (the unit is cm^{-1}), and therefore give the number of wave cycles per centimeter. The larger the wavenumber, the higher is the frequency of the wave, and correspondingly the higher is the frequency of the bond absorption. IR absorptions are sometimes, though less commonly, reported in terms of **wavelength** (λ), in which case the units are micrometers (μm ; old name micron, μ). Wavelength is the distance from crest to crest of a wave.

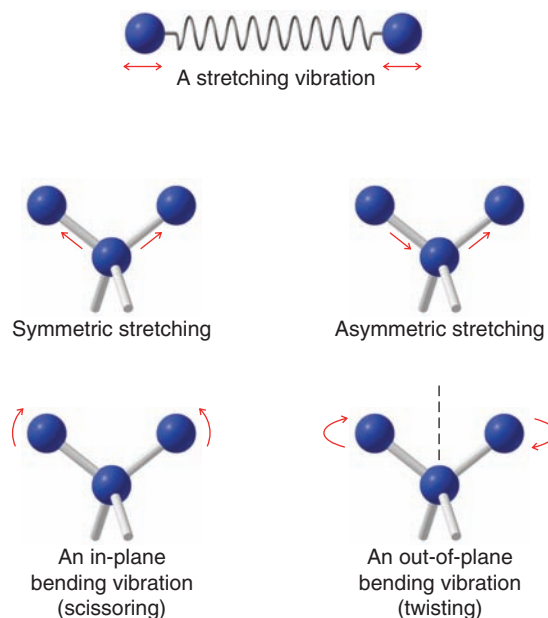
$$\bar{\nu} = \frac{1}{\lambda} \quad (\text{with } \lambda \text{ in cm}) \quad \text{or} \quad \bar{\nu} = \frac{10,000}{\lambda} \quad (\text{with } \lambda \text{ in } \mu\text{m})$$

In their vibrations covalent bonds behave as if they were tiny springs connecting the atoms. When the atoms vibrate, they can do so only at certain frequencies, as if the bonds

were “tuned.” Because of this, covalently bonded atoms have only particular vibrational energy levels; that is, the levels are quantized.

The excitation of a molecule from one vibrational energy level to another occurs only when the compound absorbs IR radiation of a particular energy, meaning a particular wavelength or frequency. Note that the energy (E) of absorption is directly proportional to the **frequency** of radiation (ν) because $\Delta E = h\nu$, and inversely proportional to the wavelength (λ) because $\frac{c}{\lambda}$, and therefore $\Delta E = \frac{hc}{\lambda}$.

Molecules can vibrate in a variety of ways. Two atoms joined by a covalent bond can undergo a stretching vibration where the atoms move back and forth as if joined by a spring. Three atoms can also undergo a variety of stretching and bending vibrations.



The *frequency* of a given stretching vibration *in an IR spectrum* can be related to two factors. These are *the masses of the bonded atoms*—light atoms vibrate at higher frequencies than heavier ones—and *the relative stiffness of the bond*. (These factors are accounted for in Hooke’s law, a relationship you may study in introductory physics.) Triple bonds are stiffer (and vibrate at higher frequencies) than double bonds, and double bonds are stiffer (and vibrate at higher frequencies) than single bonds. We can see some of these effects in Table 2.6. Notice that stretching frequencies of groups involving hydrogen (a light atom) such as C—H, N—H, and O—H all occur at relatively high frequencies:

GROUP	BOND	FREQUENCY RANGE (cm^{-1})
Alkyl	C—H	2853–2962
Alcohol	O—H	3590–3650
Amine	N—H	3300–3500

Notice, too, that triple bonds vibrate at higher frequencies than double bonds:

GROUP	BOND	FREQUENCY RANGE (cm^{-1})
Alkyne	C \equiv C	2100–2260
Nitrile	C \equiv N	2220–2260
Alkene	C=C	1620–1680
Carbonyl	C=O	1630–1780

- Not all molecular vibrations result in the absorption of IR energy. ***In order for a vibration to occur with the absorption of IR energy, the dipole moment of the molecule must change as the vibration occurs.***

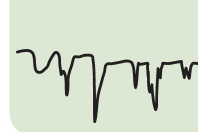


TABLE 2.6 CHARACTERISTIC INFRARED ABSORPTIONS OF GROUPS

Group	Frequency Range (cm ⁻¹)	Intensity ^a
A. Alkyl		
C—H (stretching)	2853–2962	(m–s)
Isopropyl, —CH(CH ₃) ₂	1380–1385	(s)
	and 1365–1370	(s)
<i>tert</i> -Butyl, —C(CH ₃) ₃	1385–1395	(m)
	and ~1365	(s)
B. Alkenyl		
C—H (stretching)	3010–3095	(m)
C=C (stretching)	1620–1680	(v)
R—CH=CH ₂	985–1000	(s)
R ₂ C=CH ₂	and 905–920	(s)
		880–900
<i>cis</i> -RCH=CHR	and 675–730	(s)
		960–975
<i>trans</i> -RCH=CHR		
C. Alkynyl		
≡C—H (stretching)	~3300	(s)
C≡C (stretching)	2100–2260	(v)
D. Aromatic		
Ar—H (stretching)	~3030	(v)
C=C (stretching)	1450–1600	(m)
Aromatic substitution type (C—H out-of-plane bendings)		
Monosubstituted	690–710	(very s)
	and 730–770	(very s)
<i>o</i> -Disubstituted	735–770	(s)
<i>m</i> -Disubstituted	680–725	(s)
	and 750–810	(very s)
<i>p</i> -Disubstituted	800–860	(very s)
E. Alcohols, Phenols, and Carboxylic Acids		
O—H (stretching)		
Alcohols, phenols (dilute solutions)	3590–3650	(sharp, v)
Alcohols, phenols (hydrogen bonded)	3200–3550	(broad, s)
Carboxylic acids (hydrogen bonded)	2500–3000	(broad, v)
F. Ethers, Alcohols, and Esters		
C—O (stretching)	1020–1275	(s)
G. Aldehydes, Ketones, Esters, Carboxylic Acids, and Amides		
C=O (stretching)	1630–1780	(s)
Aldehydes	1690–1740	(s)
Ketones	1680–1750	(s)
Esters	1735–1750	(s)
Carboxylic acids	1710–1780	(s)
Amides	1630–1690	(s)
H. Amines		
N—H	3300–3500	(m)
I. Nitriles		
C≡N	2220–2260	(m)

^aAbbreviations: s = strong, m = medium, w = weak, v = variable, ~ = approximately.

Thus, methane does not absorb IR energy for symmetric stretching of the four C—H bonds; asymmetric stretching, on the other hand, does lead to an IR absorption. Symmetrical vibrations of the carbon–carbon double and triple bonds of ethene and ethyne do not result in the absorption of IR radiation, either.

SOLVED PROBLEM 2.8

The infrared spectrum of 1-hexyne shows a sharp absorption peak near 2100 cm^{-1} due to stretching of its triple bond. However, 3-hexyne shows no absorption in that region. Explain.



STRATEGY AND ANSWER: For an infrared absorption to occur there must be a change in the dipole moment of the molecule during the stretching process. Since 3-hexyne is symmetrical about its triple bond, there is no change in its dipole moment as stretching takes place, hence there is no IR absorption from the triple bond.

Vibrational absorption may occur outside the region measured by a particular IR spectrometer, and vibrational absorptions may occur so closely together that peaks fall on top of peaks.

Other factors bring about even more absorption peaks. Overtones (harmonics) of fundamental absorption bands may be seen in IR spectra even though these overtones occur with greatly reduced intensity. Bands called combination bands and difference bands also appear in IR spectra.

Because IR spectra of even relatively simple compounds contain so many peaks, the possibility that two different compounds will have the same IR spectrum is exceedingly small. It is because of this that an IR spectrum has been called the “fingerprint” of a molecule. Thus, with organic compounds, if two pure samples give different IR spectra, one can be certain that they are different compounds. If they give the same IR spectrum, then they are very likely to be the same compound.

2.16 INTERPRETING IR SPECTRA

IR spectra contain a wealth of information about the structures of compounds. We show some of the information that can be gathered from the spectra of octane and methylbenzene (commonly called toluene) in Figs. 2.11 and 2.12. In this section we shall learn how

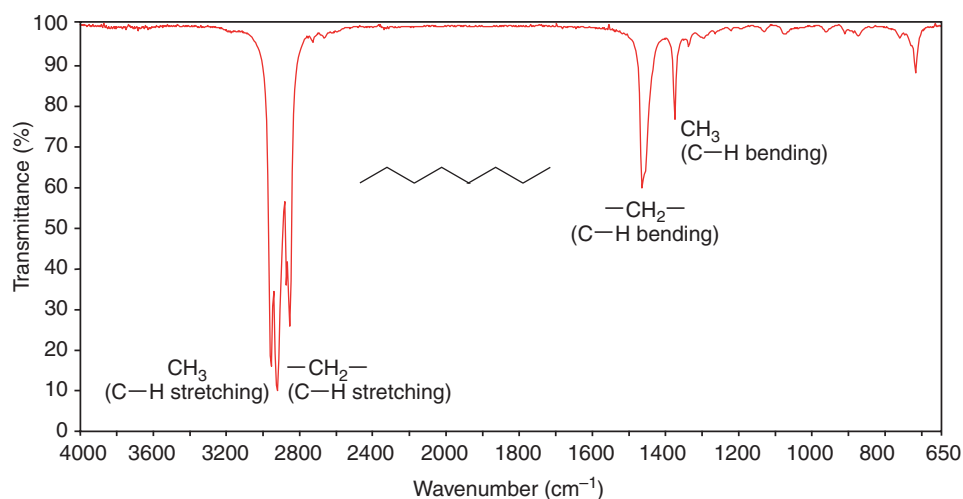


FIGURE 2.11 The IR spectrum of octane. (Notice that, in IR spectra, the peaks are usually measured in % transmittance. Thus, the peak at 2900 cm^{-1} has 10% transmittance—that is, an absorbance, A , of 0.90.)

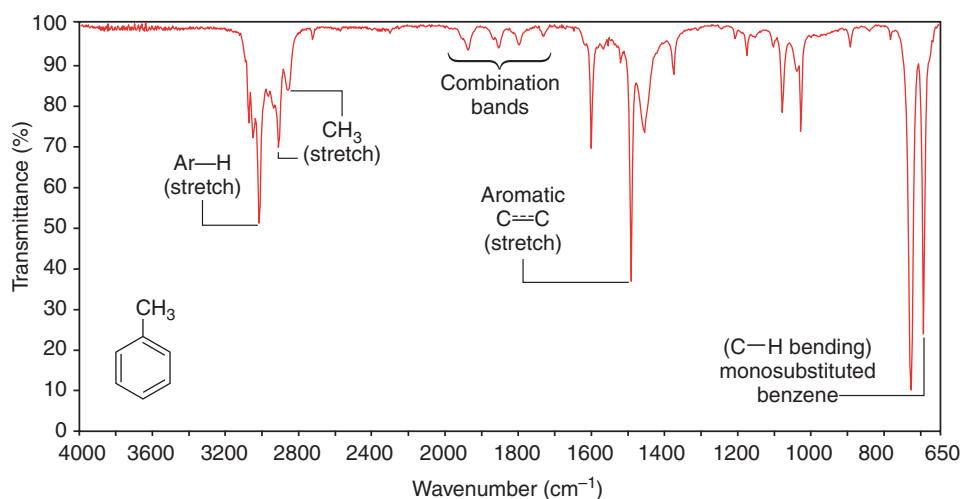
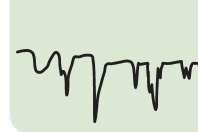


FIGURE 2.12 The IR spectrum of methylbenzene (toluene).

to recognize the presence of characteristic IR absorption peaks that result from vibrations of alkyl and functional groups. The data given in Table 2.6 will provide us with key information to use when correlating actual spectra with IR absorption frequencies that are typical for various groups.

2.16A Infrared Spectra of Hydrocarbons

- All hydrocarbons give absorption peaks in the $2800\text{--}3300\text{-cm}^{-1}$ region that are associated with carbon–hydrogen stretching vibrations.

We can use these peaks in interpreting IR spectra because the exact location of the peak depends on the strength (and stiffness) of the C—H bond, which in turn depends on the hybridization state of the carbon that bears the hydrogen. The C—H bonds involving sp -hybridized carbon are strongest and those involving sp^3 -hybridized carbon are weakest. The order of bond strength is

$$sp > sp^2 > sp^3$$

This, too, is the order of the bond stiffness.

- The carbon–hydrogen stretching peaks of hydrogen atoms attached to sp -hybridized carbon atoms occur at highest frequencies, about 3300 cm^{-1} .

The carbon–hydrogen bond of a terminal alkyne ($\equiv\text{C—H}$) gives an absorption in the 3300-cm^{-1} region. We can see the absorption of the acetylenic (alkynyl) C—H bond of 1-heptyne at 3320 cm^{-1} in Fig. 2.13.

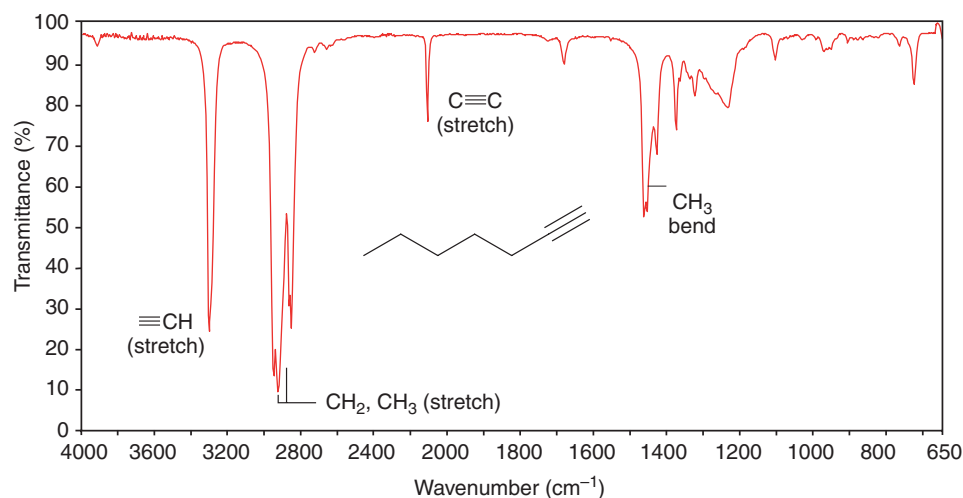
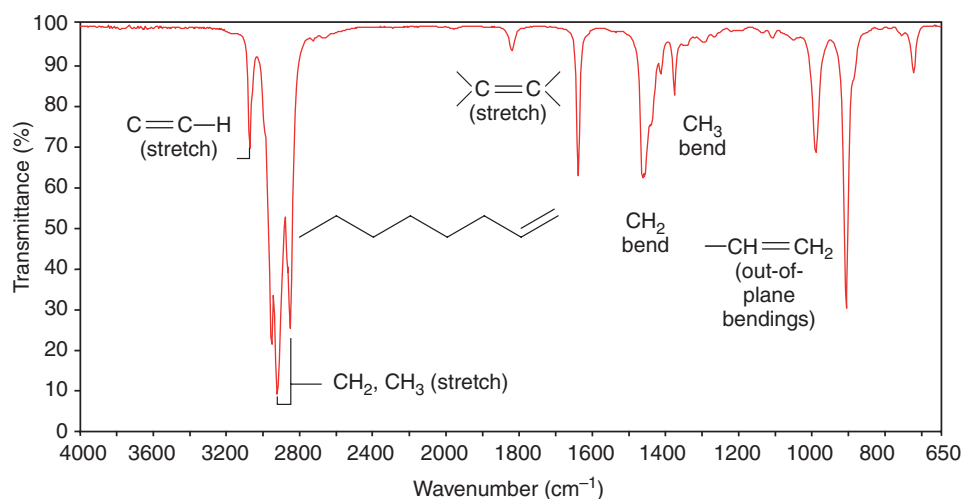


FIGURE 2.13 The IR spectrum of 1-heptyne.

FIGURE 2.14 The IR spectrum of 1-octene.



- The carbon–hydrogen stretching peaks of hydrogen atoms attached to sp^2 -hybridized carbon atoms occur in the $3000\text{--}3100\text{-cm}^{-1}$ region.

Thus, alkenyl C—H bonds and the C—H groups of aromatic rings give absorption peaks in this region. We can see the alkenyl C—H absorption peak at 3080 cm^{-1} in the spectrum of 1-octene (Fig. 2.14), and we can see the C—H absorption of the aromatic hydrogen atoms at 3090 cm^{-1} in the spectrum of methylbenzene (Fig. 2.12).

- The carbon–hydrogen stretching bands of hydrogen atoms attached to sp^3 -hybridized carbon atoms occur at lowest frequencies, in the $2800\text{--}3000\text{-cm}^{-1}$ region.

We can see methyl and methylene absorption peaks in the spectra of octane (Fig. 2.11), methylbenzene (Fig. 2.12), 1-heptyne (Fig. 2.13), and 1-octene (Fig. 2.14).

Hydrocarbons also give absorption peaks in their IR spectra that result from carbon–carbon bond stretchings. Carbon–carbon single bonds normally give rise to very weak peaks that are usually of little use in assigning structures. More useful peaks arise from carbon–carbon multiple bonds, however.

- Carbon–carbon double bonds give absorption peaks in the $1620\text{--}1680\text{-cm}^{-1}$ region, and carbon–carbon triple bonds give absorption peaks between 2100 and 2260 cm^{-1} .

These absorptions are not usually strong ones, and they are absent if the double or triple bond is symmetrically substituted. (No dipole moment change will be associated with the vibration.) The stretchings of the carbon–carbon bonds of benzene rings usually give a set of characteristic sharp peaks in the $1450\text{--}1600\text{-cm}^{-1}$ region.

- Absorptions arising from carbon–hydrogen bending vibrations of alkenes occur in the $600\text{--}1000\text{-cm}^{-1}$ region. With the aid of a spectroscopy handbook, the exact location of these peaks can often be used as evidence for the *substitution pattern of the double bond and its configuration*.

Helpful Hint

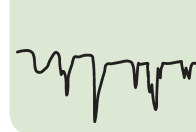
IR spectroscopy is an exceedingly useful tool for detecting functional groups.

2.16B IR Spectra of Some Functional Groups Containing Heteroatoms

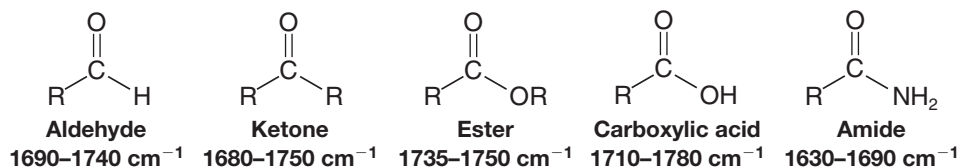
Infrared spectroscopy gives us an invaluable method for recognizing quickly and simply the presence of certain functional groups in a molecule.

Carbonyl Functional Groups One important functional group that gives a prominent absorption peak in IR spectra is the **carbonyl group**, $\text{C}=\text{O}$. This group is present in aldehydes, ketones, esters, carboxylic acids, amides, and others.

- The carbon–oxygen double-bond stretching frequency of carbonyl groups gives a strong peak between 1630 and 1780 cm^{-1} .



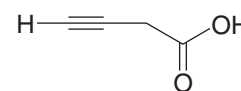
The exact location of the absorption depends on whether it arises from an aldehyde, ketone, ester, and so forth.



SOLVED PROBLEM 2.9

A compound with the molecular formula C₄H₄O₂ has a strong sharp absorbance near 3300 cm⁻¹, absorbances in the 2800–3000-cm⁻¹ region, and a sharp absorbance peak near 2200 cm⁻¹. It also has a strong broad absorbance in the 2500–3600-cm⁻¹ region and a strong peak in the 1710–1780-cm⁻¹ region. Propose a possible structure for the compound.

STRATEGY AND ANSWER: The sharp peak near 3300 cm⁻¹ is likely to arise from the stretching of a hydrogen attached to the *sp*-hybridized carbon of a triple bond. The sharp peak near 2200 cm⁻¹, where the triple bond of an alkyne stretches, is consistent with this. The peaks in the 2800–3000-cm⁻¹ region suggest stretchings of the C—H bonds of alkyl groups, either CH₂ or CH₃ groups. The strong, broad absorbance in the 2500–3600-cm⁻¹ region suggests a hydroxyl group arising from a carboxylic acid. The strong peak around 1710–1780 cm⁻¹ is consistent with this since it could arise from the carbonyl group of a carboxylic acid. Putting all this together with the molecular formula suggests the compound is as shown at the right.



Use arguments based on resonance and electronegativity effects to explain the trend in carbonyl IR stretching frequencies from higher frequency for esters and carboxylic acids to lower frequencies for amides. (*Hint:* Use the range of carbonyl stretching frequencies for aldehydes and ketones as the “base” frequency range of an unsubstituted carbonyl group and consider the influence of electronegative atoms on the carbonyl group and/or atoms that alter the resonance hybrid of the carbonyl.) What does this suggest about the way the nitrogen atom influences the distribution of electrons in an amide carbonyl group?

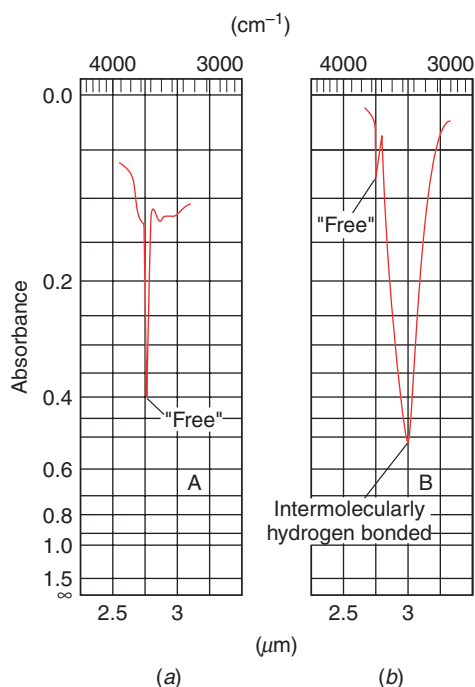
PRACTICE PROBLEM 2.28

Alcohols and Phenols The **hydroxyl groups** of alcohols and phenols are also easy to recognize in IR spectra by their O—H stretching absorptions. These bonds also give us direct evidence for hydrogen bonding (Section 2.13B).

- The IR absorption of an alcohol or phenol O—H group is in the 3200–3550-cm⁻¹ range, and most often it is broad.

The typical broadness of the peak is due to association of the molecules through hydrogen bonding (Section 2.13B), which causes a wider distribution of stretching frequencies for the O—H bond. If an alcohol or phenol is present as a very dilute solution in a solvent that cannot contribute to hydrogen bonding (e.g., CCl₄), O—H absorption occurs as a very sharp peak in the 3590–3650-cm⁻¹ region. In very dilute solution in such a solvent or in the gas phase, formation of intermolecular hydrogen bonds does not take place because molecules of the analyte are too widely separated. A sharp peak in the 3590–3650-cm⁻¹ region, therefore, is attributed to “free” (unassociated) hydroxyl groups. Increasing the concentration of the alcohol or phenol causes the sharp peak to be replaced by a broad band in the 3200–3550-cm⁻¹ region. Hydroxyl absorptions in IR spectra of cyclohexylcarbinol (cyclohexylmethanol) run in dilute and concentrated solutions (Fig. 2.15) exemplify these effects.

FIGURE 2.15 (a) The IR spectrum of an alcohol (cyclohexylcarbinol) in a dilute solution shows the sharp absorption of a "free" (non-hydrogen-bonded) hydroxyl group at 3600 cm^{-1} . (b) The IR spectrum of the same alcohol as a concentrated solution shows a broad hydroxyl group absorption at 3300 cm^{-1} due to hydrogen bonding. (Reprinted with permission of John Wiley & Sons, Inc. From Silverstein, R., and Webster, F. X., *Spectrometric Identification of Organic Compounds*, Sixth Edition, p. 89. Copyright 1998.)



Carboxylic Acids The **carboxylic acid group** can also be detected by IR spectroscopy. If both carbonyl and hydroxyl stretching absorptions are present in an IR spectrum, there is good evidence for a carboxylic acid functional group (although it is possible that isolated carbonyl and hydroxyl groups could be present in the molecule).

- The hydroxyl absorption of a carboxylic acid is often very broad, extending from 3600 cm^{-1} to 2500 cm^{-1} .

Figure 2.16 shows the IR spectrum of propanoic acid.

Amines IR spectroscopy also gives evidence for N—H bonds (see Figure 2.17).

- Primary (1°) and secondary (2°) amines give absorptions of moderate strength in the $3300\text{--}3500\text{-cm}^{-1}$ region.
- Primary amines exhibit two peaks in this region due to symmetric and asymmetric stretching of the two N—H bonds.
- Secondary amines exhibit a single peak.
- Tertiary amines show no N—H absorption because they have no such bond.
- A basic pH is evidence for any class of amine.

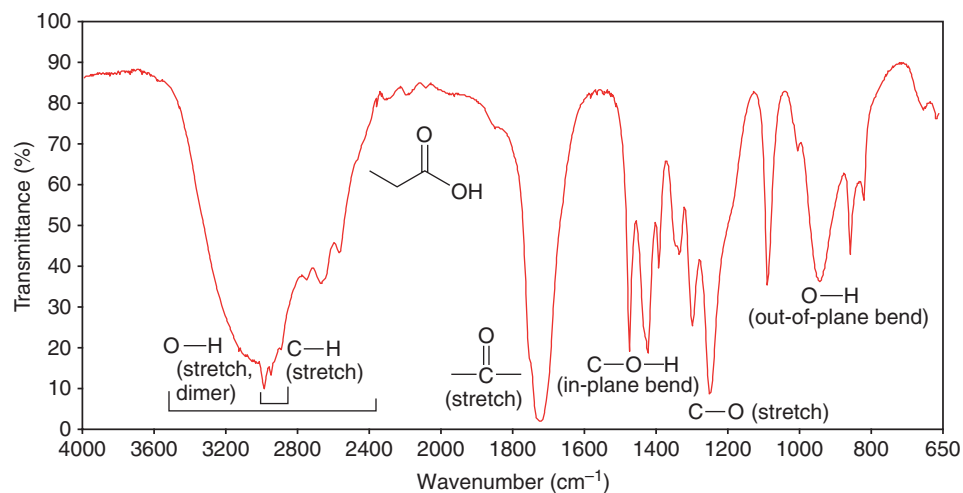


FIGURE 2.16 The IR spectrum of propanoic acid.

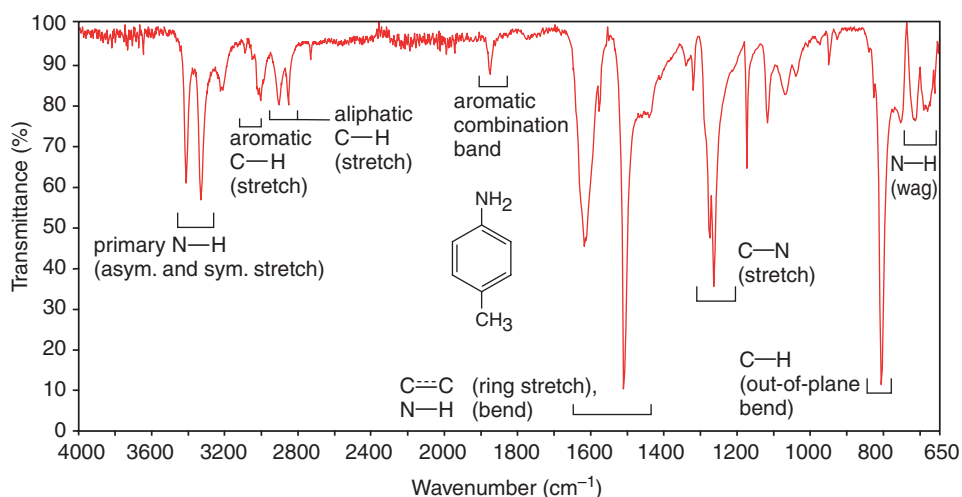
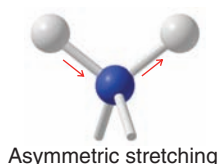
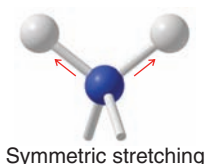


FIGURE 2.17 Annotated IR spectrum of 4-methylaniline.

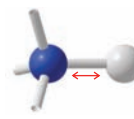
RNH_2 (1° Amine)

Two peaks in $3300\text{--}3500\text{-cm}^{-1}$ region



R_2NH (2° Amine)

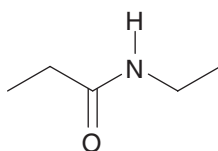
One peak in $3300\text{--}3500\text{-cm}^{-1}$ region



Hydrogen bonding causes N—H stretching peaks of 1° and 2° amines to broaden. The NH groups of **amides** give similar absorption peaks and include a carbonyl absorption as well.

SOLVED PROBLEM 2.10

What key peaks would you expect to find in the IR spectrum of the following compound?



STRATEGY AND ANSWER: The compound is an amide. We should expect a strong peak in the $1630\text{--}1690\text{ cm}^{-1}$ region arising from the carbonyl group and a single peak of moderate strength in the $3300\text{--}3500\text{ cm}^{-1}$ region for the N—H group.

HOW TO INTERPRET AN IR SPECTRUM WITHOUT ANY KNOWLEDGE OF THE STRUCTURE

IR spectroscopy is an incredibly powerful tool for functional group identification, as we have seen in the preceding sections. However, in introducing this technique, we have explored IR spectra from the perspective of compounds of known structure, explaining the peaks observed in reference to each critical grouping of atoms that we know to be present. In the real world, one often encounters brand new materials of unknown structure. How IR can help in this scenario is something that a forensics scientist or natural products isolation chemist might need to worry about on a daily basis.

We certainly cannot use IR spectroscopy by itself to determine complete structure (techniques in Chapter 9 will help with that problem), but an IR spectrum can often point toward the presence of certain functional groups if one pays particular attention to signals whose peak positions are distinct from other groups and is consistently strong enough to be observed. The latter is an important consideration as there can be variations in signal strength for certain groups dependent on what other groups are in the molecule, and some signals overlap with others, making a definitive assignment impossible. For example, most organic molecules contain C—H bonds in one form or another, so peaks below 1450 cm^{-1} and signals in the range $2800\text{--}3000\text{ cm}^{-1}$ are not particularly definitive other than to indicate that the molecule is organic and contains C—H bonds.

Here are some examples of what one might consider in a first-pass assessment of any IR spectrum to generate what are likely to be correct answers about some of the functional groups that are present:

- Only C=O stretches tend to have a tight, strong absorbance in the $1630\text{--}1780\text{ cm}^{-1}$ range. We may not be able to identify what kind of carbonyl group is present, but we can tell that there is at least one carbonyl group.
- Only the stretches of nitrile or alkyne bonds tend to appear between 2000 and 2300 cm^{-1} , so these can be fairly readily assigned.
- Only hydroxyl groups as in alcohols or carboxylic acids tend to create a large and broad signal at about 3300 cm^{-1} ; these groups are easy to identify assuming the sample is not contaminated with water.
- Only amines tend to produce broad but smaller peaks than hydroxyl peaks around 3300 cm^{-1} . The number of those peaks can sometimes tell if there is one or two hydrogens attached to that nitrogen atom.

The examples below allow us to put these general principles into practice.

The IR spectrum of Unknown 1 (Fig. 2.18) has broad signals centered around 3300 cm^{-1} and a medium absorption at 2250 cm^{-1} . Based on the information above, we can surmise that the molecule likely contains a hydroxyl group and a group with a triple bond. Most likely the triply-bonded group is a nitrile since nitriles tend to appear at about 2250 cm^{-1} , whereas alkynes appear slightly lower at around 2000 cm^{-1} . We cannot be strictly sure that it is a nitrile, but that would be a good hypothesis in the absence of any other chemical evidence. Indeed, this turns out to be correct, as the molecule is 3-hydroxypropionitrile in this case.

In the IR spectrum of Unknown 2 (Fig. 2.19) there is a hydroxyl absorption once again centered around 3300 cm^{-1} , as well as a carbonyl peak at 1705 cm^{-1} . And, although we cannot always tell what kind of carbonyl is present, when the hydroxyl peak is extremely broad and has a ragged appearance (due to overlap of the C—H absorptions that extend below it, in contrast to the first spectrum where the hydroxyl was smooth, it is usually safe to assume that this hydroxyl group is attached to the

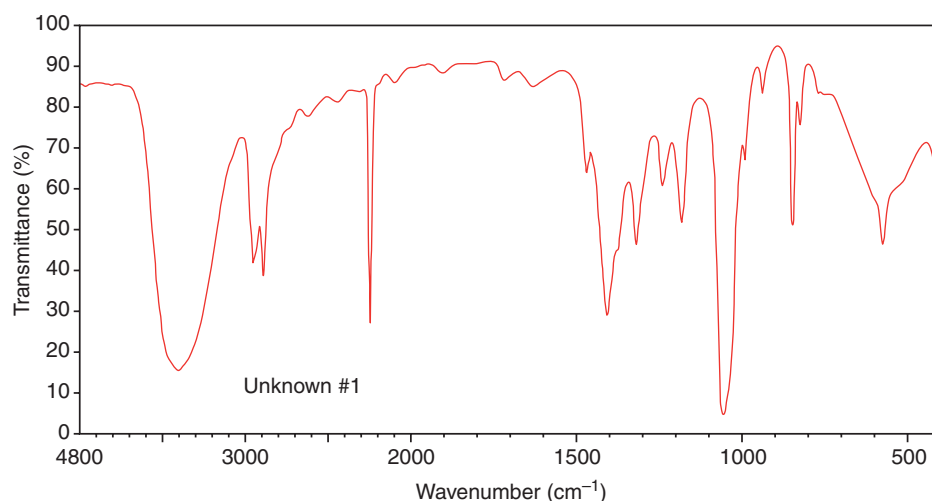


FIGURE 2.18 The IR Spectrum of Unknown 1. (SDBS, National Institute of Advanced Industrial Science and Technology)

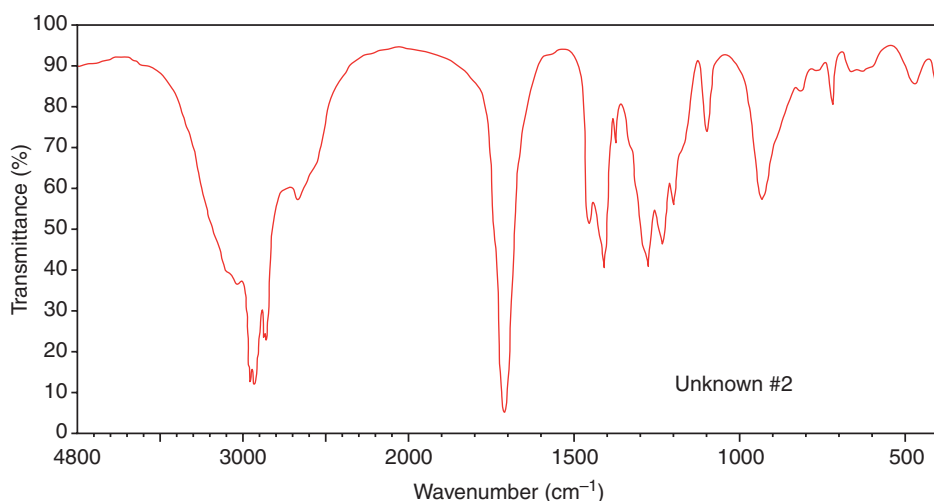
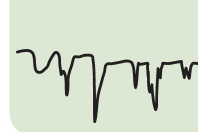


FIGURE 2.19 The IR Spectrum of Unknown 2. (SDBS, National Institute of Advanced Industrial Science and Technology)

carbonyl group; thus, these two groups are together part of a carboxylic acid functional group. Once again, we were able to identify the key functional group of the molecule since this is heptanoic acid.

2.17 APPLICATIONS OF BASIC PRINCIPLES

We now review how certain basic principles apply to phenomena that we have studied in this chapter.

Polar Bonds Are Caused by Electronegativity Differences We saw in Section 2.2 that when atoms with different electronegativities are covalently bonded, the more electronegative atom will be negatively charged and the less electronegative atom will be positively charged. The bond will be a *polar bond* and it will have a *dipole moment*.

Dipole moments are important in explaining physical properties of molecules (as we shall review below), and in explaining infrared spectra. For a vibration to occur with the absorption of IR energy, the dipole moment of the molecule must change during the course of the vibration.

Opposite Charges Attract This principle is central to understanding physical properties of organic compounds (Section 2.13). All of the forces that operate between individual molecules (and thereby affect boiling points, melting points, and solubilities) are between oppositely charged molecules (ions) or between oppositely charged portions of molecules. Examples are ion–ion forces (Section 2.13A) that exist between oppositely charged ions in crystals of ionic compounds, dipole–dipole forces (Section 2.13B) that exist between oppositely charged portions of polar molecules and that include the very strong dipole–dipole forces that we call *hydrogen bonds*, and the weak *dispersion* or *London forces* that exist between portions of molecules that bear small temporary opposite charges.

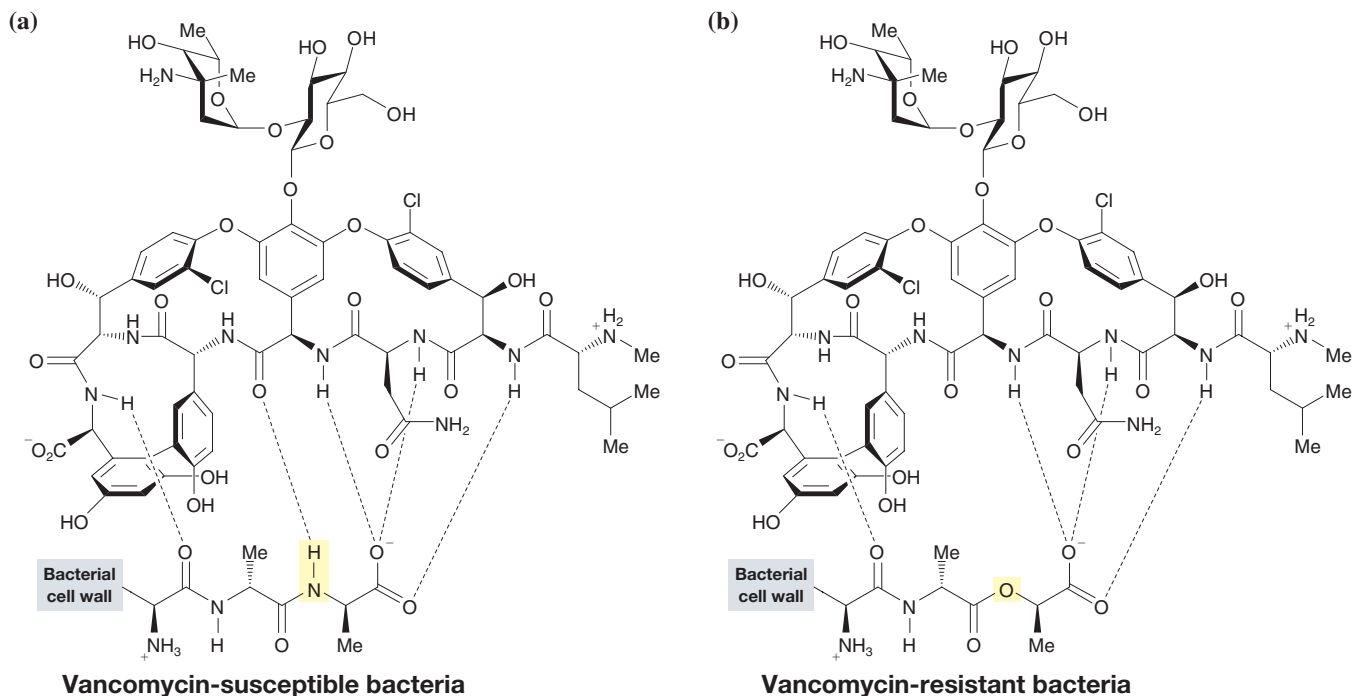
Molecular Structure Determines Properties We learned in Section 2.13 how physical properties are related to molecular structure.

[WHY Do These Topics Matter?

VANCOMYCIN AND ANTIBIOTIC RESISTANCE

Just as hydrogen bonds are critical in the pairing of nucleotides, they also play a major role in how one of the world's most powerful antibiotics kills bacteria. That antibiotic is vancomycin, a compound first isolated in 1956 by scientists at the Eli Lilly pharmaceutical company from the fermentation broth of a microbe found in the jungles of Borneo. Its name was derived from the verb “to vanquish,” because it could kill every strain of gram-positive bacteria thrown at it, including the deadly strain known as MRSA (for methicillin-resistant *Staphylococcus aureus*), one of the so-called flesh-eating bacteria.

Vancomycin's success is due to its structure, a carefully designed arrangement of atoms that allows it to attack diverse bacterial strains. As bacteria move about their hosts, their cell walls are constantly being assembled and disassembled. Vancomycin targets one particular peptide sequence found on the surface of the cell walls, forming a network of five specific hydrogen bonds that allows it to lock onto the bacterium. These bonds are shown as dashed lines in the structures below. Once attached to vancomycin, bacteria can no longer build and strengthen their cell walls, leading to eventual lysis of the cell membrane and their death.



Unfortunately, while vancomycin has proven effective for many decades in combating bacterial infections, in the past few years some bacteria have become resistant to it. These resistant bacteria have evolved a different set of peptides on their cell surface. The highlighted N—H group in (a) has been instead replaced with an O, as shown in (b). Although we will have much more to say about peptides and amino acids in Chapter 24, for now realize that this change has turned one hydrogen-bond donor (the N—H) into an atom that is a hydrogen-bond acceptor (O). As a result, vancomycin can form only four hydrogen bonds with the target. Although this constitutes a loss of just 20% of its hydrogen-bonding capacity, it turns out that its overall effectiveness in terms of its bacterial-killing ability is reduced by a factor of 1000. As a result, these bacteria are resistant to vancomycin, meaning that new chemical weapons are needed if patients infected with certain resistant gram-positive bacteria are to survive. Fortunately, there are several leads being explored in clinical trials, but given the ability of bacteria to constantly evolve and evade our therapies, we will need to keep developing new and better antibiotics.

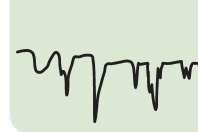


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Vancomycin was discovered in microbes from the jungles in Borneo.

To learn more about these topics, see:

1. Nicolaou, K. C.; Boddy, C. N. C., "Behind enemy lines" in *Scientific American*, May 2001, pp. 54–61.
2. Nicolaou, K. C.; Snyder, S. A. *Classics in Total Synthesis II*. Wiley-VCH: Weinheim, 2003, pp. 239–300.



SUMMARY AND REVIEW TOOLS

In Chapter 2 you learned about families of organic molecules, some of their physical properties, and how we can use an instrumental technique called infrared spectroscopy to study them.

You learned that functional groups define the families to which organic compounds belong. At this point you should be able to name functional groups when you see them in structural formulas, and, when given the name of a functional group, draw a general example of its structure.

You also built on your knowledge of how electronegativity influences charge distribution in a molecule and how, together with three-dimensional structure, charge distribution influences the overall polarity of a molecule. Based on polarity and three-dimensional structure, you should be able to predict the kind and relative strength of electrostatic forces between molecules. With this understanding you will be able to roughly estimate physical properties such as melting point, boiling point, and solubility.

Last, you learned to use IR spectroscopy as an indicator of the family to which an organic compound belongs. IR spectroscopy provides signatures (in the form of spectra) that suggest which functional groups are present in a molecule.

If you know the concepts in Chapters 1 and 2 well, you will be on your way to having the solid foundation you need for success in organic chemistry. Keep up the good work (including your diligent homework habits)!

The study aids for this chapter include key terms and concepts (which are hyperlinked to the glossary from the bold, blue terms in the *WileyPLUS* version of the book at wileyplus.com) and a Concept Map after the end-of-chapter problems.

KEY TERMS AND CONCEPTS

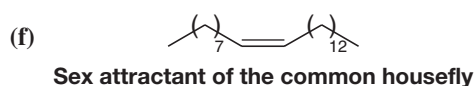
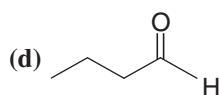
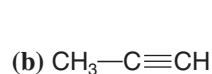
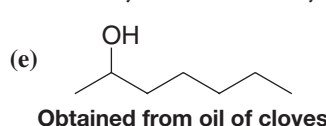
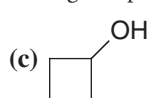
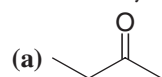
The key terms and concepts that are highlighted in bold, blue text within the chapter are defined in the glossary (at the back of the book) and have hyperlinked definitions in the accompanying *WileyPLUS* course (www.wileyplus.com).

PROBLEMS

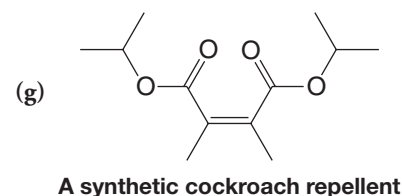
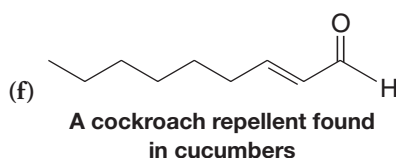
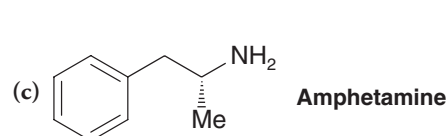
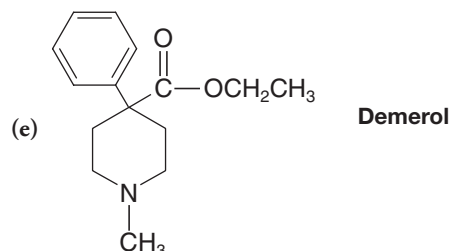
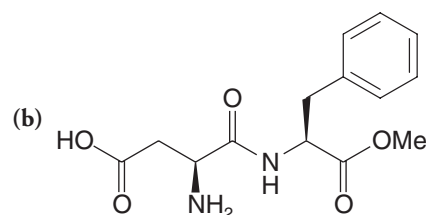
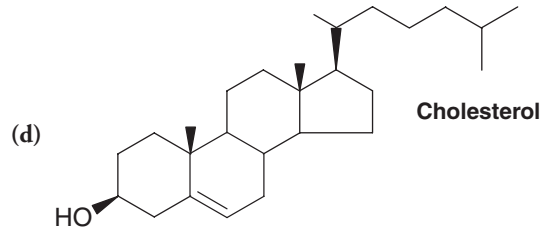
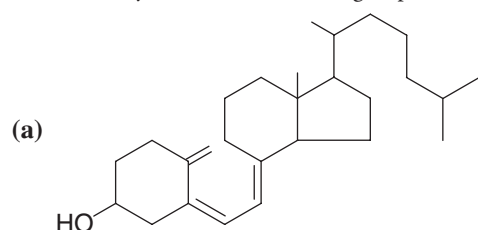
Note to Instructors: Many of the homework problems are available for assignment via *WileyPLUS*, an online teaching and learning solution.

FUNCTIONAL GROUPS AND STRUCTURAL FORMULAS

2.29 Classify each of the following compounds as an alkane, alkene, alkyne, alcohol, aldehyde, amine, and so forth.



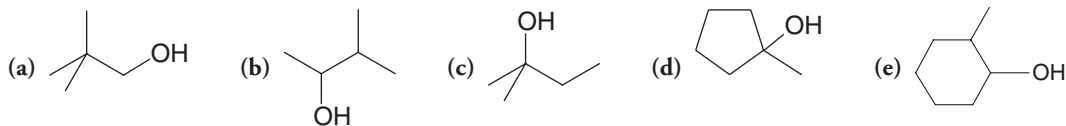
2.30 Identify all of the functional groups in each of the following compounds:



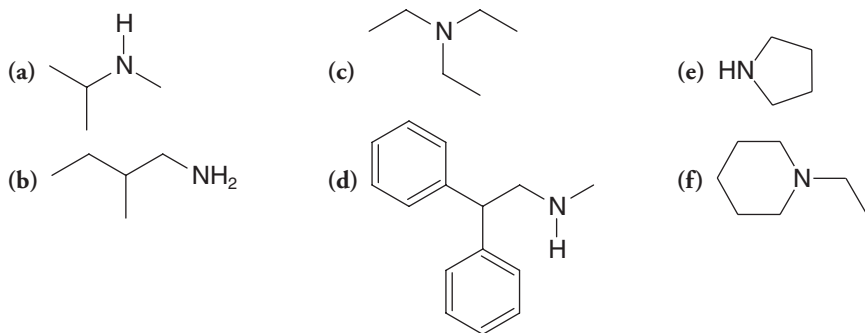
2.31 There are four alkyl bromides with the formula C_4H_9Br . Write their structural formulas and classify each as to whether it is a primary, secondary, or tertiary alkyl bromide.

2.32 There are seven isomeric compounds with the formula $C_4H_{10}O$. Write their structures and classify each compound according to its functional group.

2.33 Classify the following alcohols as primary, secondary, or tertiary:



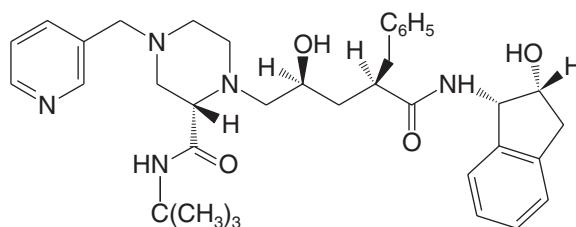
2.34 Classify the following amines as primary, secondary, or tertiary:



2.35 Write structural formulas for each of the following:

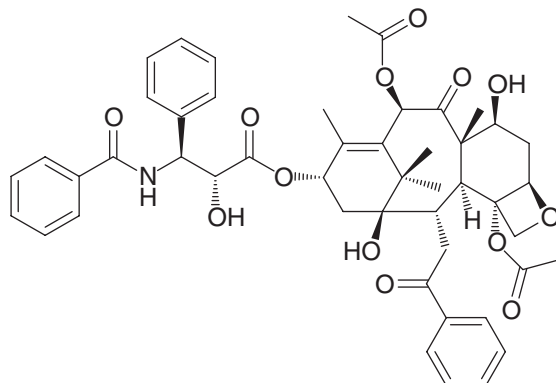
- (a) Three ethers with the formula $C_4H_{10}O$.
 (b) Three primary alcohols with the formula C_4H_8O .
 (c) A secondary alcohol with the formula C_3H_6O .
 (d) A tertiary alcohol with the formula C_4H_8O .
 (e) Two esters with the formula $C_3H_6O_2$.
 (f) Four primary alkyl halides with the formula $C_5H_{11}Br$.
 (g) Three secondary alkyl halides with the formula $C_5H_{11}Br$.
 (h) A tertiary alkyl halide with the formula $C_5H_{11}Br$.
 (i) Three aldehydes with the formula $C_5H_{10}O$.
 (j) Three ketones with the formula $C_5H_{10}O$.
 (k) Two primary amines with the formula C_3H_9N .
 (l) A secondary amine with the formula C_3H_9N .
 (m) A tertiary amine with the formula C_3H_9N .
 (n) Two amides with the formula C_2H_5NO .

2.36 Identify all of the functional groups in Crixivan, an important drug in the treatment of AIDS.



Crixivan (an HIV protease inhibitor)

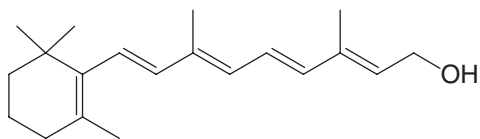
2.37 Identify all of the functional groups in the following molecule.



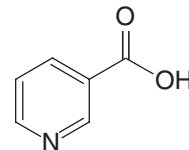


PHYSICAL PROPERTIES

2.38 (a) Indicate the hydrophobic and hydrophilic parts of vitamin A and comment on whether you would expect it to be soluble in water. (b) Do the same for vitamin B₃ (also called niacin).



Vitamin A

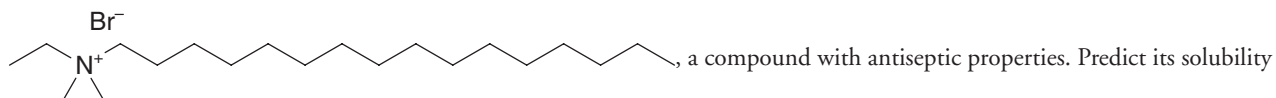


Vitamin B₃ or niacin

2.39 Hydrogen fluoride has a dipole moment of 1.83 D; its boiling point is 19.34 °C. Ethyl fluoride (CH₃CH₂F) has an almost identical dipole moment and has a larger molecular weight, yet its boiling point is -37.7 °C. Explain.

2.40 Why does one expect the cis isomer of an alkene to have a higher boiling point than the trans isomer?

2.41 Cetylalcohol is the common name for



behavior in water and in diethyl ether.

2.42 Which of the following solvents should be capable of dissolving ionic compounds?

- (a) Liquid SO₂ (b) Liquid NH₃ (c) Benzene (d) CCl₄

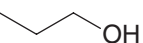
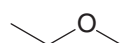
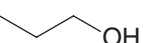
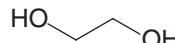
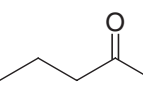
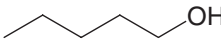



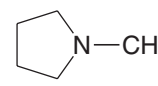
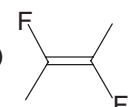
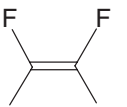
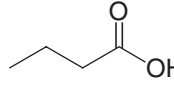
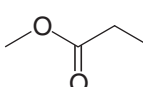


2.43 Write a three-dimensional formula for each of the following molecules using the wedge-dashed wedge-line formalism. If the molecule has a net dipole moment, indicate its direction with an arrow, \longleftrightarrow . If the molecule has no net dipole moment, you should so state. (You may ignore the small polarity of C—H bonds in working this and similar problems.)

- (a) CH₃F (c) CHF₃ (e) CH₂FCI (g) BeF₂ (i) CH₃OH
 (b) CH₂F₂ (d) CF₄ (f) BCl₃ (h) CH₃OCH₃ (j) CH₂O

2.44 Consider each of the following molecules in turn: (a) dimethyl ether, (CH₃)₂O; (b) trimethylamine, (CH₃)₃N; (c) trimethylboron, (CH₃)₃B; and (d) dimethylberyllium, (CH₃)₂Be. Describe the hybridization state of the central atom (i.e., O, N, B, or Be) of each molecule, tell what bond angles you would expect at the central atom, and state whether the molecule would have a dipole moment.

2.45 Analyze the statement: For a molecule to be polar, the presence of polar bonds is necessary, but it is not a sufficient requirement.

2.46 Which compound in each of the following pairs would have the higher boiling point? Explain your answers.

- (a)  or 
- (b)  or 
- (c)  or 
- (d)  or 
- (e)  or 
- (f)  or 
- (g)  or 
- (h) Hexane, CH₃(CH₂)₄CH₃, or nonane, CH₃(CH₂)₇CH₃
- (i)  or 

IR SPECTROSCOPY

2.47 Predict the key IR absorption bands whose presence would allow each compound in pairs (a), (c), (d), (e), (g), and (i) from Problem 2.46 to be distinguished from each other.

2.48 The IR spectrum of propanoic acid (Fig. 2.17) indicates that the absorption for the O—H stretch of the carboxylic acid functional group is due to a hydrogen-bonded form. Draw the structure of two propanoic acid molecules showing how they could dimerize via hydrogen bonding.

2.49 In infrared spectra, the carbonyl group is usually indicated by a single strong and sharp absorption. However, in the case of carboxylic acid anhydrides, $\text{R}-\text{C}(=\text{O})-\text{O}-\text{C}(=\text{O})-\text{R}$, two peaks are observed even though the two carbonyl groups are chemically equivalent.



Explain this fact, considering what you know about the IR absorption of primary amines.

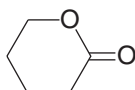
MULTICONCEPT PROBLEMS

2.50 Write structural formulas for four compounds with the formula $\text{C}_3\text{H}_6\text{O}$ and classify each according to its functional group. Predict IR absorption frequencies for the functional groups you have drawn.

2.51 There are four amides with the formula $\text{C}_3\text{H}_7\text{NO}$. (a) Write their structures. (b) One of these amides has a melting and a boiling point that are substantially lower than those of the other three. Which amide is this? Explain your answer. (c) Explain how these amides could be differentiated on the basis of their IR spectra.

2.52 Write structures for all compounds with molecular formula $\text{C}_4\text{H}_6\text{O}$ that would not be expected to exhibit infrared absorption in the $3200\text{--}3550\text{-cm}^{-1}$ and $1620\text{--}1780\text{-cm}^{-1}$ regions.

2.53 Cyclic compounds of the general type shown here are called lactones. What functional group does a lactone contain?



CHALLENGE PROBLEMS

2.54 Two constitutional isomers having molecular formula $\text{C}_4\text{H}_6\text{O}$ are both symmetrical in structure. In their infrared spectra, neither isomer when in dilute solution in CCl_4 (used because it is nonpolar) has absorption in the 3600-cm^{-1} region. Isomer A has absorption bands at approximately 3080 , 1620 , and 700 cm^{-1} . Isomer B has bands in the 2900-cm^{-1} region and at 1780 cm^{-1} . Propose a structure for A and two possible structures for B.

2.55 When two substituents are on the same side of a ring skeleton, they are said to be *cis*, and when on opposite sides, *trans* (analogous to use of those terms with 1,2-disubstituted alkene isomers). Consider stereoisomeric forms of 1,2-cyclopentanediol (compounds having a five-membered ring and hydroxyl groups on two adjacent carbons that are *cis* in one isomer and *trans* in the other). At high dilution, both isomers have an infrared absorption band at approximately 3626 cm^{-1} but only one isomer has a band at 3572 cm^{-1} .

(a) Assume for now that the cyclopentane ring is coplanar (the interesting actuality will be studied later) and then draw and label the two isomers using the wedge-dashed wedge method of depicting the OH groups. (b) Designate which isomer will have the 3572-cm^{-1} band and explain its origin.

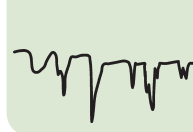
2.56 Compound C is asymmetric, has molecular formula $\text{C}_5\text{H}_{10}\text{O}$, and contains two methyl groups and a 3° functional group. It has a broad infrared absorption band in the $3200\text{--}3550\text{-cm}^{-1}$ region and no absorption in the $1620\text{--}1680\text{-cm}^{-1}$ region. Propose a structure for C.

2.57 Examine the diagram showing an α -helical protein structure in Section 2.13E. Between what specific atoms and of what functional groups are the hydrogen bonds formed that give the molecule its helical structure?

LEARNING GROUP PROBLEMS

Consider the molecular formula $\text{C}_4\text{H}_8\text{O}_2$.

- Write structures for at least 15 different compounds that all have the molecular formula $\text{C}_4\text{H}_8\text{O}_2$ and contain functional groups presented in this chapter.
- Provide at least one example each of a structure written using the dash format, the condensed format, the bond-line format, and the full three-dimensional format. Use your choice of format for the remaining structures.
- Identify four different functional groups from among your structures. Circle and name them on the representative structures.
- Predict approximate frequencies for IR absorptions that could be used to distinguish the four compounds representing these functional groups.
- If any of the 15 structures you drew have atoms where the formal charge is other than zero, indicate the formal charge on the appropriate atom(s) and the overall charge for the molecule.
- Identify which types of intermolecular forces would be possible in pure samples of all 15 compounds.
- Pick five formulas you have drawn that represent a diversity of structures, and predict their order with respect to trend in increasing boiling point.
- Explain your order of predicted boiling points on the basis of intermolecular forces and polarity.



[CONCEPT MAP]

