CHAPTER

1

The Basics

BONDING AND MOLECULAR STRUCTURE

Organic chemistry plays a role in all aspects of our lives, from the clothing we wear, to the pixels of our television and computer screens, to preservatives in food, to the inks that color the pages of this book. If you take the time to understand organic chemistry, to learn its overall logic, then you will truly have the power to change society. Indeed, organic chemistry provides the power to synthesize new drugs, to engineer molecules that can make computer processors run more quickly, to understand why grilled meat can cause cancer and how its effects can be combated, and to design ways to knock the calories out of sugar while still making food taste deliciously sweet. It can explain biochemical processes like aging, neural functioning, and cardiac arrest, and show how we can prolong and improve life. It can do almost anything.

IN THIS CHAPTER WE WILL CONSIDER:

- what kinds of atoms make up organic molecules
- the principles that determine how the atoms in organic molecules are bound together
- how best to depict organic molecules

[WHY DO THESE TOPICS MATTER?] At the end of the chapter, we will see how some of the unique organic structures that nature has woven together possess amazing properties that we can harness to aid human health.

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1.1 LIFE AND THE CHEMISTRY OF CARBON COMPOUNDS—WE ARE STARDUST


NASA/Photo Researchers, Inc.

Supernovae were the crucibles in which the heavy elements were formed.

Organic chemistry is the chemistry of compounds that contain the element carbon. If a compound does not contain the element carbon, it is said to be *inorganic.*

Look for a moment at the periodic table inside the front cover of this book. More than a hundred elements are listed there. The question that comes to mind is this: why should an entire field of chemistry be based on the chemistry of compounds that contain this one element, carbon? There are several reasons, the primary one being this: **carbon compounds are central to the structure of living organisms and therefore to the existence of life on Earth. We exist because of carbon compounds.**

What is it about carbon that makes it the element that nature has chosen for living organisms? There are two important reasons: carbon atoms can form strong bonds to other carbon atoms to form rings and chains of carbon atoms, and carbon atoms can also form strong bonds to elements such as hydrogen, nitrogen, oxygen, and sulfur. Because of these bond-forming properties, carbon can be the basis for the huge diversity of compounds necessary for the emergence of living organisms.

From time to time, writers of science fiction have speculated about the possibility of life on other planets being based on the compounds of another element—for example, silicon, the element most like carbon. However, the bonds that silicon atoms form to each other are not nearly as strong as those formed by carbon, and therefore it is very unlikely that silicon could be the basis for anything equivalent to life as we know it.

1.1A What Is the Origin of the Element Carbon?

Through the efforts of physicists and cosmologists, we now understand much of how the elements came into being. The light elements hydrogen and helium were formed at the beginning, in the Big Bang. Lithium, beryllium, and boron, the next three elements, were formed shortly thereafter when the universe had cooled somewhat. All of the heavier elements were formed millions of years later in the interiors of stars through reactions in which the nuclei of lighter elements fuse to form heavier elements.

The energy of stars comes primarily from the fusion of hydrogen nuclei to produce helium nuclei. This nuclear reaction explains why stars shine. Eventually some stars begin to run out of hydrogen, collapse, and explode—they become supernovae. Supernovae explosions scatter heavy elements throughout space. Eventually, some of these heavy elements drawn by the force of gravity became part of the mass of planets like the Earth.

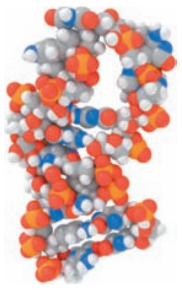
1.1B How Did Living Organisms Arise?

This question is one for which an adequate answer cannot be given now because there are many things about the emergence of life that we do not understand. However, we do know this. Organic compounds, some of considerable complexity, are detected in outer space, and meteorites containing organic compounds have rained down on Earth since it was formed. A meteorite that fell near Murchison, Victoria, Australia, in 1969 was found to contain over 90 different amino acids, 19 of which are found in living organisms on Earth. While this does not mean that life arose in outer space, it does suggest that events in outer space may have contributed to the emergence of life on Earth.

In 1924 Alexander Oparin, a biochemist at the Moscow State University, postulated that life on Earth may have developed through the gradual evolution of carbon-based molecules in a “primordial soup” of the compounds that were thought to exist on a prebiotic Earth: methane, hydrogen, water, and ammonia. This idea was tested by experiments carried out at the University of Chicago in 1952 by Stanley Miller and Harold Urey. They showed that amino acids and other complex organic compounds are synthesized when an electric spark (think of lightning) passes through a flask containing a mixture of these four compounds (think of the early atmosphere). Miller and Urey in their 1953 publication reported that five amino acids (essential constituents of proteins) were formed. In 2008, examination of archived solutions from Miller and Urey’s original experiments have shown that 22 amino acids, rather than the 5 amino acids originally reported, were actually formed.

Similar experiments have shown that other precursors of biomolecules can also arise in this way—compounds such as ribose and adenine, two components of RNA. Some RNA molecules can not only store genetic information as DNA does, they can also act as catalysts, as enzymes do.

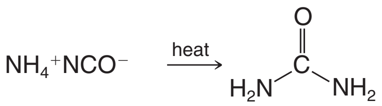
There is much to be discovered to explain exactly how the compounds in this soup became living organisms, but one thing seems certain. The carbon atoms that make up our bodies were formed in stars, so, in a sense, we are stardust.



An RNA molecule

1.1C Development of the Science of Organic Chemistry

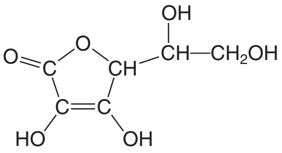
The science of organic chemistry began to flower with the demise of a nineteenth century theory called vitalism. According to vitalism, organic compounds were only those that came from living organisms, and only living things could synthesize organic compounds through intervention of a vital force. Inorganic compounds were considered those compounds that came from nonliving sources. Friedrich Wöhler, however, discovered in 1828 that an organic compound called urea (a constituent of urine) could be made by evaporating an aqueous solution of the inorganic compound ammonium cyanate. With this discovery, the synthesis of an organic compound, began the evolution of organic chemistry as a scientific discipline.



Ammonium cyanate **Urea**

THE CHEMISTRY OF... Natural Products

Despite the demise of vitalism in science, the word "organic" is still used today by some people to mean "coming from living organisms" as in the terms "organic vitamins" and "organic fertilizers." The commonly used term "organic food" means that the food was grown without the use of synthetic fertilizers and pesticides. An "organic vitamin" means to these people that the vitamin was isolated from a natural source and not synthesized by a chemist. While there are sound arguments to be made against using food contaminated with certain pesticides, while there may be environmental benefits to be obtained from organic farming, and while "natural" vitamins may contain beneficial substances not present in synthetic vitamins, it is impossible to argue that pure "natural" vitamin C, for example, is healthier than pure "synthetic" vitamin C, since the two substances are identical in all respects. In science today, the study of compounds from living organisms is called natural products chemistry. In the closer to this chapter we will consider more about why natural products chemistry is important.



Vitamin C

FOODCOLLECTION/Image Source

Vitamin C is found in various citrus fruits.

1.2 ATOMIC STRUCTURE

Before we begin our study of the compounds of carbon we need to review some basic but familiar ideas about the chemical elements and their structure.

- The **compounds** we encounter in chemistry are made up of **elements** combined in different proportions.
- **Elements** are made up of **atoms**. An atom (Fig. 1.1) consists of a dense, positively charged *nucleus* containing **protons** and **neutrons** and a surrounding cloud of **electrons**.

Each proton of the nucleus bears one positive charge; electrons bear one negative charge. Neutrons are electrically neutral; they bear no charge. Protons and neutrons have

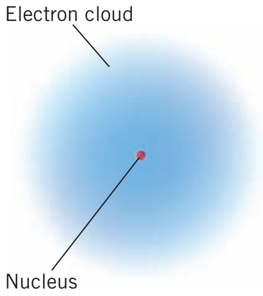


FIGURE 1.1 An atom is composed of a tiny nucleus containing protons and neutrons and a large surrounding volume containing electrons. The diameter of a typical atom is about 10,000 times the diameter of its nucleus.

nearly equal masses (approximately 1 atomic mass unit each) and are about 1800 times as heavy as electrons. Most of the **mass** of an atom, therefore, comes from the mass of the nucleus; the atomic mass contributed by the electrons is negligible. Most of the **volume** of an atom, however, comes from the electrons; the volume of an atom occupied by the electrons is about 10,000 times larger than that of the nucleus.

The elements commonly found in organic molecules are carbon, hydrogen, nitrogen, oxygen, phosphorus, and sulfur, as well as the halogens: fluorine, chlorine, bromine, and iodine.

Each **element** is distinguished by its **atomic number** (Z), a **number equal to the number of protons in its nucleus**. Because an atom is electrically neutral, **the atomic number also equals the number of electrons surrounding the nucleus**.

1.2A Isotopes

Before we leave the subject of atomic structure and the periodic table, we need to examine one other observation: **the existence of atoms of the same element that have different masses**.

For example, the element carbon has six protons in its nucleus giving it an atomic number of 6. Most carbon atoms also have six neutrons in their nuclei, and because each proton and each neutron contributes one atomic mass unit (1 amu) to the mass of the atom, carbon atoms of this kind have a mass number of 12 and are written as ^{12}C.

- **Although all the nuclei of all atoms of the same element will have the same number of protons**, some atoms of the same element **may have different masses** because they have **different numbers of neutrons**. Such atoms are called **isotopes**.

For example, about 1% of the atoms of elemental carbon have nuclei containing 7 neutrons, and thus have a mass number of 13. Such atoms are written ^{13}C. A tiny fraction of carbon atoms have 8 neutrons in their nucleus and a mass number of 14. Unlike atoms of carbon-12 and carbon-13, atoms of carbon-14 are radioactive. The ^{14}C isotope is used in *carbon dating*. The three forms of carbon, ^{12}C, ^{13}C, and ^{14}C, are isotopes of one another.

Most atoms of the element hydrogen have one proton in their nucleus and have no neutron. They have a mass number of 1 and are written ^{1}H. A very small percentage (0.015%) of the hydrogen atoms that occur naturally, however, have one neutron in their nucleus. These atoms, called *deuterium* atoms, have a mass number of 2 and are written ^{2}H. An unstable (and radioactive) isotope of hydrogen, called *tritium* (^{3}H), has two neutrons in its nucleus.

PRACTICE PROBLEM 1.1 There are two stable isotopes of nitrogen, ^{14}N and ^{15}N. How many protons and neutrons does each isotope have?

1.2B Valence Electrons

We discuss the electron configurations of atoms in more detail in Section 1.10. For the moment we need only to point out that the electrons that surround the nucleus exist in **shells** of increasing energy and at increasing distances from the nucleus. The most important shell, called the **valence shell**, is the outermost shell because the electrons of this shell are the ones that an atom uses in making chemical bonds with other atoms to form compounds.

- How do we know how many electrons an atom has in its valence shell? We look at the periodic table. The number of electrons in the valence shell (called **valence electrons**) is equal to the group number of the atom. For example, carbon is in group **IVA** and carbon has *four* valence electrons; oxygen is in group **VIA** and oxygen has *six* valence electrons. The halogens of group **VIIA** all have *seven* electrons.

PRACTICE PROBLEM 1.2 How many valence electrons does each of the following atoms have?

(a) Na **(b)** Cl **(c)** Si **(d)** B **(e)** Ne **(f)** N

1.3 CHEMICAL BONDS: THE OCTET RULE

The first explanations of the nature of chemical bonds were advanced by G. N. Lewis (of the University of California, Berkeley) and W. Kössel (of the University of Munich) in 1916. Two major types of chemical bonds were proposed:

1. **Ionic** (or electrovalent) bonds are formed by the transfer of one or more electrons from one atom to another to create ions.
2. **Covalent** bonds result when atoms share electrons.

The central idea in their work on bonding is that atoms without the electronic configuration of a noble gas generally react to produce such a configuration because these configurations are known to be highly stable. For all of the noble gases except helium, this means achieving an octet of electrons in the valence shell.

- The **valence shell** is the outermost shell of electrons in an atom.
- The tendency for an atom to achieve a configuration where its valence shell contains eight electrons is called the **octet rule**.

The concepts and explanations that arise from the original propositions of Lewis and Kössel are satisfactory for explanations of many of the problems we deal with in organic chemistry today. For this reason we shall review these two types of bonds in more modern terms.

1.3A Ionic Bonds

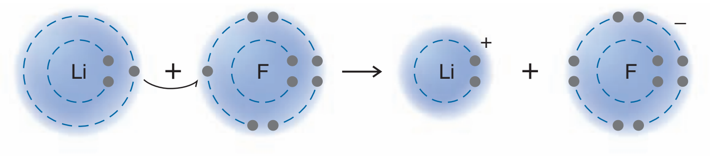
Atoms may gain or lose electrons and form charged particles called **ions**.

- An **ionic bond** is an attractive force between oppositely charged ions.

One source of such ions is a reaction between atoms of widely differing electronegativities (Table 1.1).

- **Electronegativity** ***is a measure of the ability of an atom to attract electrons.***
- Electronegativity increases as we go across a horizontal row of the periodic table from left to right and it increases as we go up a vertical column (Table 1.1).

An example of the formation of an ionic bond is the reaction of lithium and fluorine atoms:



Lithium, a typical metal, has a very low electronegativity; fluorine, a nonmetal, is the most electronegative element of all. The loss of an electron (a negatively charged species)

Helpful Hint

Terms and concepts that are fundamentally important to your learning organic chemistry are set in bold blue type. You should learn them as they are introduced. These terms are also defined in the glossary.

Helpful Hint

We will use electronegativity frequently as a tool for understanding the properties and reactivity of organic molecules.

TABLE 1.1 ELECTRONEGATIVITIES OF SOME OF THE ELEMENTS

Increasing electronegativity →

H
2.1

Li 1.0	Be 1.5	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	↑ Increasing electronegativity
Na 0.9	Mg 1.2	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	
K 0.8						Br 2.8	

by the lithium atom leaves a lithium cation (Li^+); the gain of an electron by the fluorine atom gives a fluoride anion (F^-).

- Ions form because atoms can achieve the electronic configuration of a noble gas by gaining or losing electrons.

The lithium cation with two electrons in its valence shell is like an atom of the noble gas helium, and the fluoride anion with eight electrons in its valence shell is like an atom of the noble gas neon. Moreover, crystalline lithium fluoride forms from the individual lithium and fluoride ions. In this process negative fluoride ions become surrounded by positive lithium ions, and positive lithium ions by negative fluoride ions. In this crystalline state, the ions have substantially lower energies than the atoms from which they have been formed. Lithium and fluorine are thus "stabilized" when they react to form crystalline lithium fluoride.

We represent the formula for lithium fluoride as LiF, because that is the simplest formula for this ionic compound.

Ionic substances, because of their strong internal electrostatic forces, are usually very high melting solids, often having melting points above 1000 °C. In polar solvents, such as water, the ions are solvated (see Section 2.13D), and such solutions usually conduct an electric current.

- Ionic compounds, often called **salts**, form only when atoms of very different electronegativities transfer electrons to become ions.

PRACTICE PROBLEM 1.3 Using the periodic table, which element in each pair is more electronegative?

(a) Si, O **(b)** N, C **(c)** Cl, Br **(d)** S, P

1.3B Covalent Bonds and Lewis Structures

When two or more atoms of the same or similar electronegativities react, a complete transfer of electrons does not occur. In these instances the atoms achieve noble gas configurations by *sharing electrons*.

- **Covalent bonds** form by sharing of electrons between atoms of similar electronegativities to achieve the configuration of a noble gas.
- **Molecules** are composed of atoms joined exclusively or predominantly by covalent bonds.

Molecules may be represented by electron-dot formulas or, more conveniently, by formulas where each pair of electrons shared by two atoms is represented by a line.

- A **dash structural formula** has lines that show bonding electron pairs and includes elemental symbols for the atoms in a molecule.

Some examples are shown here:

1. Hydrogen, being in group IA of the periodic table, has one valence electron. Two hydrogen atoms share electrons to form a hydrogen molecule, H_2.

H_2 $\quad H\cdot + \cdot H \longrightarrow H{:}H$ usually written $H{-}H$

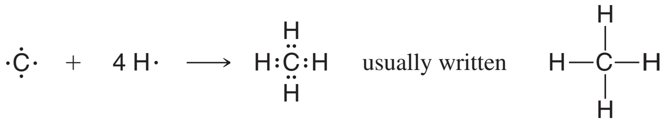
2. Because chlorine is in group VIIA, its atoms have seven valence electrons. Two chlorine atoms can share electrons (one electron from each) to form a molecule of Cl_2.

Cl_2

$:\ddot{\underset{..}{Cl}}\cdot + \cdot\ddot{\underset{..}{Cl}}: \longrightarrow :\ddot{\underset{..}{Cl}}:\ddot{\underset{..}{Cl}}:$ usually written $:\ddot{\underset{..}{Cl}}-\ddot{\underset{..}{Cl}}:$

3. And a carbon atom (group IVA) with four valence electrons can share each of these electrons with four hydrogen atoms to form a molecule of methane, CH_4.

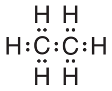
CH_4



$\cdot\dot{\underset{\cdot}{C}}\cdot + 4\,H\cdot \longrightarrow H{:}\overset{H}{\underset{H}{\ddot{\underset{..}{C}}}}{:}H$ usually written $H-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}-H$

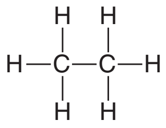
Two carbon atoms can use one electron pair between them to form a **carbon–carbon single bond** while also bonding hydrogen atoms or other groups to achieve an octet of valence electrons. Consider the example of ethane below.

C_2H_6



$\mathrm{H{:}\overset{H}{\underset{H}{C}}{:}\overset{H}{\underset{H}{C}}{:}H}$

and as a dash formula



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

Ethane

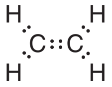
These formulas are often called **Lewis structures**; in writing them we show all of the valence electrons. Unshared electron pairs are shown as dots, and in dash structural formulas, bonding electron pairs are shown as lines.

4. Atoms can share *two or more pairs of electrons* to form **multiple covalent bonds**. For example, two nitrogen atoms possessing five valence electrons each (because nitrogen is in group VA) can share electrons to form a **triple bond** between them.

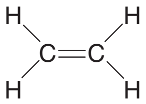
N_2 $\mathrm{{:}N{\vdots}{\vdots}N{:}}$ and as a dash formula $\mathrm{{:}N{\equiv}N{:}}$

Carbon atoms can also share more than one electron pair with another atom to form a multiple covalent bond. Consider the examples of a **carbon–carbon double bond** in ethene (ethylene) and a **carbon–carbon triple bond** in ethyne (acetylene).

C_2H_4



and as a dash formula



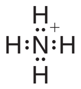
Ethene

C_2H_2 $\mathrm{H{:}C{::}{:}C{:}H}$ and as a dash formula $\mathrm{H{-}C{\equiv}C{-}H}$

Ethyne

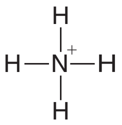
5. Ions, themselves, may contain covalent bonds. Consider, as an example, the ammonium ion.

$\overset{+}{NH_4}$



$\mathrm{H{:}\overset{H}{\underset{H}{N}}{}^{+}{:}H}$

and as a dash formula



$\mathrm{H{-}\overset{H}{\underset{H}{N}}{}^{+}{-}H}$

PRACTICE PROBLEM 1.4

Consider the following compounds and decide whether the bond in them would be ionic or covalent.

(a) KCl **(b)** F_2 **(c)** PH_3 **(d)** CBr_4

1.4 HOW TO WRITE LEWIS STRUCTURES

Several simple rules allow us to draw proper Lewis structures:

1. **Lewis structures show the connections between atoms in a molecule or ion using only the valence electrons of the atoms involved.** Valence electrons are those of an atom's outermost shell.
2. **For main group elements, the number of valence electrons a neutral atom brings to a Lewis structure is the same as its group number in the periodic table.**

Helpful Hint

The ability to write proper **Lewis structures** is one of the most important tools for learning organic chemistry.

Carbon, for example, is in group IVA and has four valence electrons; the halogens (e.g., fluorine) are in group VIIA and each has seven valence electrons; hydrogen is in group IA and has one valence electron.

3. **If the structure we are drawing is a negative ion (an anion), we add one electron for each negative charge to the original count of valence electrons. If the structure is a positive ion (a cation), we subtract one electron for each positive charge.**
4. **In drawing Lewis structures we try to give each atom the electron configuration of a noble gas**. To do so, we draw structures where atoms share electrons to form covalent bonds or transfer electrons to form ions.
   - **a.** Hydrogen forms one covalent bond by sharing its electron with an electron of another atom so that it can have two valence electrons, the same number as in the noble gas helium.
   - **b.** Carbon forms four covalent bonds by sharing its four valence electrons with four valence electrons from other atoms, so that it can have eight electrons (the same as the electron configuration of neon, satisfying the octet rule).
   - **c.** To achieve an octet of valence electrons, elements such as nitrogen, oxygen, and the halogens typically share only some of their valence electrons through covalent bonding, leaving others as unshared electron pairs.

The following problems illustrate the rules above.

SOLVED PROBLEM 1.1

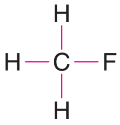
Write the Lewis structure of CH_3F.

STRATEGY AND ANSWER:

1. We find the total number of valence electrons of all the atoms:

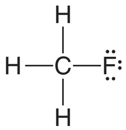
$$\underset{\substack{\uparrow \\ \text{C}}}{4} + \underset{\substack{\uparrow \\ 3\text{H}}}{3(1)} + \underset{\substack{\uparrow \\ \text{F}}}{7} = 14$$

2. We use pairs of electrons to form bonds between all atoms that are bonded to each other. We represent these bonding pairs with lines. In our example this requires four pairs of electrons (8 of the 14 valence electrons).



$$\begin{array}{c} \text{H} \\ | \\ \text{H}-\text{C}-\text{F} \\ | \\ \text{H} \end{array}$$

3. We then add the remaining electrons in pairs so as to give each hydrogen 2 electrons (a duet) and every other atom 8 electrons (an octet). In our example, we assign the remaining 6 valence electrons to the fluorine atom in three nonbonding pairs.



$$\begin{array}{c} \text{H} \\ | \\ \text{H}-\text{C}-\ddot{\underset{\cdot\cdot}{\text{F}}}\colon \\ | \\ \text{H} \end{array}$$

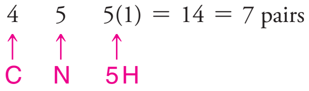
PRACTICE PROBLEM 1.5 Write the Lewis structure of (a) CH_2F_2 (difluoromethane) and (b) $CHCl_3$ (chloroform).

SOLVED PROBLEM 1.2

Write a Lewis structure for methylamine (CH_3NH_2).

STRATEGY AND ANSWER:

1. We find the total number of valence electrons for all the atoms.

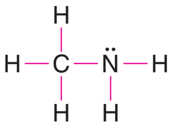


$$\underset{\underset{C}{\uparrow}}{4}\quad \underset{\underset{N}{\uparrow}}{5}\quad \underset{\underset{5H}{\uparrow}}{5(1)} = 14 = 7 \text{ pairs}$$

2. We use one electron pair to join the carbon and nitrogen.

$$C-N$$

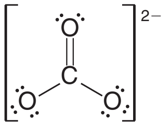
3. We use three pairs to form single bonds between the carbon and three hydrogen atoms.
4. We use two pairs to form single bonds between the nitrogen atom and two hydrogen atoms.
5. This leaves one electron pair, which we use as a lone pair on the nitrogen atom.



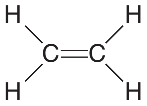
PRACTICE PROBLEM 1.6

Write the Lewis structure of CH_3OH.

5. **If necessary, we use multiple bonds to satisfy the octet rule (i.e., give atoms the noble gas configuration)**. The carbonate ion ($CO_3{}^{2-}$) illustrates this:



The organic molecules ethene (C_2H_4) and ethyne (C_2H_2), as mentioned earlier, have a double and triple bond, respectively:



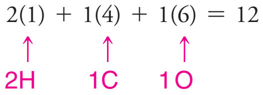
and $H-C\equiv C-H$

SOLVED PROBLEM 1.3

Write the Lewis structure of CH_2O (formaldehyde).

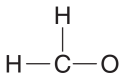
STRATEGY AND ANSWER:

1. Find the total number of valence electrons of all the atoms:



$$\underset{\underset{2H}{\uparrow}}{2(1)} + \underset{\underset{1C}{\uparrow}}{1(4)} + \underset{\underset{1O}{\uparrow}}{1(6)} = 12$$

2. **(a)** Use pairs of electrons to form single bonds.

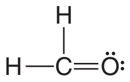


$$H-\overset{H}{\overset{|}{C}}-O$$

(continues on next page)

(b) Determine which atoms already have a full valence shell and which ones do not, and how many valence electrons we have used so far. In this case, we have used 6 valence electrons, and the valence shell is full for the hydrogen atoms but not for the carbon and oxygen.

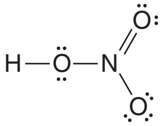
(c) We use the remaining electrons as bonds or unshared electron pairs, to fill the valence shell of any atoms whose valence shell is not yet full, taking care not to exceed the octet rule. In this case 6 of the initial 12 valence electrons are left to use. We use 2 electrons to fill the valence shell of the carbon by another bond to the oxygen, and the remaining 4 electrons as two unshared electron pairs with the oxygen, filling its valence shell.



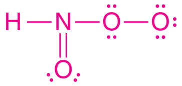
$$\mathrm{H}-\overset{\mathrm{H}}{\overset{|}{\mathrm{C}}}=\ddot{\mathrm{O}}:$$

PRACTICE PROBLEM 1.7 Write a dash structural formula showing all valence electrons for CH_3CHO (acetaldehyde).

6. **Before we can write some Lewis structures, *we must know how the atoms are connected to each other*.** Consider nitric acid, for example. Even though the formula for nitric acid is often written HNO_3, the hydrogen is actually connected to an oxygen, not to the nitrogen. The structure is $HONO_2$ and not HNO_3. Thus the correct Lewis structure is:



and not



This knowledge comes ultimately from experiments. If you have forgotten the structures of some of the common inorganic molecules and ions (such as those listed in Practice Problem 1.8), this may be a good time for a review of the relevant portions of your general chemistry text.

Helpful Hint

Check your progress by doing each Practice Problem as you come to it in the text.

SOLVED PROBLEM 1.4

Assume that the atoms are connected in the same way they are written in the formula, and write a Lewis structure for the toxic gas hydrogen cyanide (HCN).

STRATEGY AND ANSWER:

1. We find the total number of valence electrons on all of the atoms:

$$\underset{\mathrm{H}}{\underset{\uparrow}{1}} + \underset{\mathrm{C}}{\underset{\uparrow}{4}} + \underset{\mathrm{N}}{\underset{\uparrow}{5}} = 10$$

2. We use one pair of electrons to form a single bond between the hydrogen atom and the carbon atom (see below), and we use three pairs to form a triple bond between the carbon atom and the nitrogen atom. This leaves two electrons. We use these as an unshared pair on the nitrogen atom. Now each atom has the electronic structure of a noble gas. The hydrogen atom has two electrons (like helium) and the carbon and nitrogen atoms each have eight electrons (like neon).

$$\mathrm{H}-\mathrm{C}\equiv\mathrm{N}:$$

PRACTICE PROBLEM 1.8

Write a Lewis structure for each of the following:

(a) HF **(c)** CH_3F **(e)** H_2SO_3 **(g)** H_3PO_4
(b) F_2 **(d)** HNO_2 **(f)** BH_4^- **(h)** H_2CO_3

1.4A Exceptions to the Octet Rule

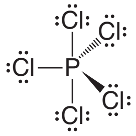
Atoms share electrons, not just to obtain the configuration of an inert gas, but because sharing electrons produces increased electron density between the positive nuclei. The resulting attractive forces of nuclei for electrons is the "glue" that holds the atoms together (cf. Section 1.11).

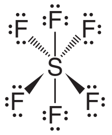
- Elements of the second period of the periodic table can have a maximum of four bonds (i.e., have eight electrons around them) because these elements have only one 2*s* and three 2*p* orbitals available for bonding.

Each orbital can contain two electrons, and a total of eight electrons fills these orbitals (Section 1.10A). The **octet rule**, therefore, only applies to these elements, and even here, as we shall see in compounds of beryllium and boron, fewer than eight electrons are possible.

- Elements of the third period and beyond have *d* orbitals that can be used for bonding.

These elements can accommodate more than eight electrons in their valence shells and therefore can form more than four covalent bonds. Examples are compounds such as PCl_5 and SF_6. Bonds written as ⋰ (dashed wedges) project behind the plane of the paper. Bonds written as ◢ (solid wedges) project in front of the paper.





SOLVED PROBLEM 1.5

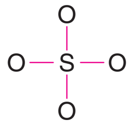
Write a Lewis structure for the sulfate ion (SO_4^{2-}). (*Note*: The sulfur atom is bonded to all four oxygen atoms.)

STRATEGY AND ANSWER:

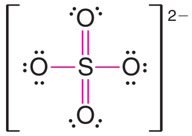
1. We find the total number of valence electrons including the extra 2 electrons needed to give the ion the double negative charge:

$$\underset{\underset{\text{S}}{\uparrow}}{6} + \underset{\underset{4\,\text{O}}{\uparrow}}{4(6)} + \underset{\underset{2e^-}{\uparrow}}{2} = 32$$

2. We use four pairs of electrons to form bonds between the sulfur atom and the four oxygen atoms:



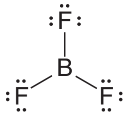
3. We add the remaining 24 electrons as unshared pairs on oxygen atoms and as **double bonds** between the sulfur atom and two oxygen atoms. This gives each oxygen 8 electrons and the sulfur atom 12:



PRACTICE PROBLEM 1.9

Write a Lewis structure for the phosphate ion (PO_4^{3-}).

Some highly reactive molecules or ions have atoms with fewer than eight electrons in their outer shell. An example is boron trifluoride (BF_3). In a BF_3 molecule the central boron atom has only six electrons around it:



1.5 FORMAL CHARGES AND HOW TO CALCULATE THEM

Helpful Hint

Proper assignment of **formal charges** is another essential tool for learning organic chemistry.

Many **Lewis structures** are incomplete until we decide whether any of their atoms have a **formal charge**. Calculating the formal charge on an atom in a Lewis structure is simply a bookkeeping method for its valence electrons.

- First, we examine each atom and, using the periodic table, we determine how many **valence electrons** it would have if it were an atom not bonded to any other atoms. **This is equal to the group number of the atom in the periodic table**. For hydrogen this number equals 1, for carbon it equals 4, for nitrogen it equals 5, and for oxygen it equals 6.

Next, we examine the atom in the Lewis structure and we assign the valence electrons in the following way:

- **We assign to each atom half of the electrons it is sharing with another atom and all of its unshared (lone) electron pairs.**

Then we do the following calculation for the atom:

Formal charge = number of valence electrons − 1/2 number of shared electrons − number of unshared electrons

or

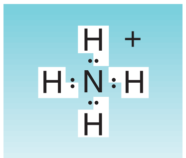
$$F = Z - (1/2)S - U$$

where F is the formal charge, Z is the group number of the element, S equals the number of shared electrons, and U is the number of unshared electrons.

- It is important to note, too, that **the arithmetic sum of all the formal charges in a molecule or ion will equal the overall charge on the molecule or ion**.

Let us consider several examples showing how this is done.

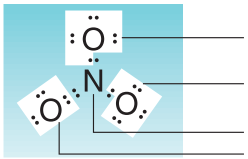
The Ammonium Ion (NH_4^+) As we see below, the ammonium ion has no unshared electron pairs. We divide all of the electrons in bonds equally between the atoms that share them. Thus, each hydrogen is assigned one electron. We subtract this from one (the number of valence electrons in a hydrogen atom) to give each hydrogen atom a formal charge of zero. The nitrogen atom is assigned four electrons (one from each bond). We subtract four from five (the number of valence electrons in a nitrogen atom) to give the nitrogen a formal charge of +1.



For hydrogen:	valence electrons of free atom	=	1
	subtract assigned electrons	=	-1
	Formal charge on each hydrogen	=	0
For nitrogen:	valence electrons of free atom	=	5
	subtract assigned electrons	=	$-(1/2)8$
	Formal charge on nitrogen	=	+1

Overall charge on ion = 4(0) + 1 = +1

The Nitrate Ion (NO_3^-) Let us next consider the nitrate ion (NO_3^-), an ion that has oxygen atoms with unshared electron pairs. Here we find that the nitrogen atom has a formal charge of +1, that two oxygen atoms have formal charges of −1, and that one oxygen has a formal charge equal to 0.



Formal charge = $6 - (\frac{1}{2})2 - 6 = -1$

Formal charge = $6 - (\frac{1}{2})2 - 6 = -1$

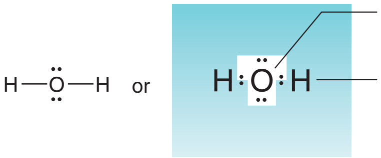
Formal charge = $5 - (\frac{1}{2})8 = +1$

Formal charge = $6 - (\frac{1}{2})4 - 4 = 0$

Charge on ion = $2(-1) + 1 + 0 = -1$

Water and Ammonia The sum of the formal charges on each atom making up a molecule must be zero. Consider the following examples:

Water

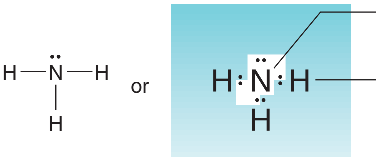


Formal charge = $6 - (\frac{1}{2})4 - 4 = 0$

Formal charge = $1 - (\frac{1}{2})2 = 0$

Charge on molecule = $0 + 2(0) = 0$

Ammonia



Formal charge = $5 - (\frac{1}{2})6 - 2 = 0$

Formal charge = $1 - (\frac{1}{2})2 = 0$

Charge on molecule = $0 + 3(0) = 0$

PRACTICE PROBLEM 1.10

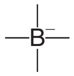
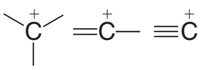
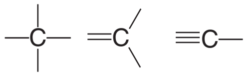
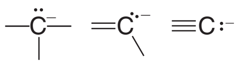
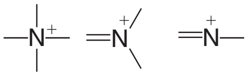
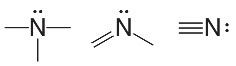
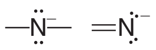
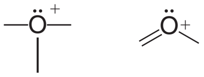
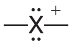
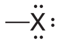
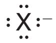
Write a Lewis structure for each of the following negative ions, and assign the formal negative charge to the correct atom:

(a) CH_3O^- **(b)** NH_2^- **(c)** CN^- **(d)** HCO_2^- **(e)** HCO_3^- **(f)** HC_2^-

1.5A A Summary of Formal Charges

With this background, it should now be clear that each time an oxygen atom of the type $-\ddot{\underset{\cdot\cdot}{\mathrm{O}}}\!:$ appears in a molecule or ion, it will have a formal charge of −1, and that each time an oxygen atom of the type $=\ddot{\mathrm{O}}\!:$ or $-\ddot{\underset{\cdot\cdot}{\mathrm{O}}}-$ appears, it will have a formal charge of 0. Similarly, $-\overset{|}{\underset{|}{\mathrm{N}}}-$ will be +1, and $-\ddot{\underset{|}{\mathrm{N}}}-$ will be zero. These and other common structures are summarized in Table 1.2.

TABLE 1.2 A SUMMARY OF FORMAL CHARGES

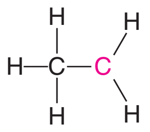
Group	Formal Charge of +1	Formal Charge of 0	Formal Charge of −1
IIIA			
IVA			
VA			
VIA			
VIIA		 (X = F, Cl, Br, or I)	

Helpful Hint

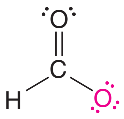
In later chapters, when you are evaluating how reactions proceed and what products form, you will find it essential to keep track of formal charges.

PRACTICE PROBLEM 1.11 Assign the proper formal charge to the colored atom in each of the following structures:

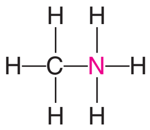
(a)



(c)

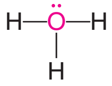


(e)

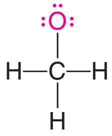


(g) $CH_3—C\equiv N:$

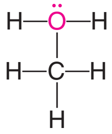
(b)



(d)



(f)



(h) $CH_3—N\equiv N:$

1.6 ISOMERS: DIFFERENT COMPOUNDS THAT HAVE THE SAME MOLECULAR FORMULA

Now that we have had an introduction to Lewis structures, it is time to discuss isomers.

- **Isomers** are compounds that have the same **molecular formula** but different structures.

We will learn about several kinds of isomers during the course of our study. For now, let us consider a type called constitutional isomers.

- **Constitutional isomers** are different compounds that have the same molecular formula but differ in the sequence in which their atoms are bonded—that is, their **connectivity**.

Acetone, used in nail polish remover and as a paint solvent, and propylene oxide, used with seaweed extracts to make food-grade thickeners and foam stabilizers for beer (among other applications) are isomers. Both of these compounds have the molecular formula C_3H_6O and therefore the same molecular weight. Yet acetone and propylene oxide have distinctly different boiling points and chemical reactivity that, as a result, lend themselves to distinctly different practical applications. Their shared molecular formula simply gives us no basis for understanding the differences between them. We must, therefore, move to a consideration of their structural formulas.

On examining the structures of acetone and propylene oxide several key aspects are clearly different (Fig. 1.2). Acetone contains a double bond between the oxygen atom and the central carbon atom. Propylene oxide does not contain a double bond, but has three atoms joined in a ring. The connectivity of the atoms is clearly different in acetone

Andy Washnik for John Wiley & Sons, Inc.

Acetone is used in some nailpolish removers.

Media Bakery

Propylene oxide alginates, made from propylene oxide and seaweed extracts, are used as food thickeners.

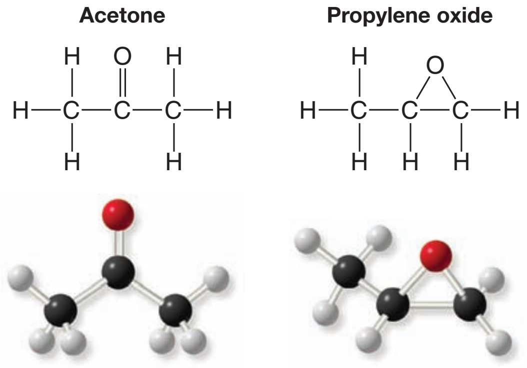


FIGURE 1.2 Ball-and-stick models and chemical formulas show the different structures of acetone and propylene oxide.

Helpful Hint

Build handheld models of these compounds and compare their structures.

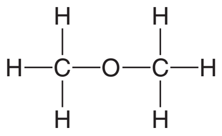
and propylene oxide. Their structures have the same molecular formula but a different constitution. They are constitutional isomers.*

- Constitutional isomers usually have different physical properties (e.g., melting point, boiling point, and density) and different chemical properties (reactivity).

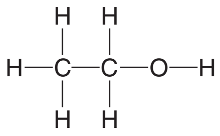
SOLVED PROBLEM 1.6

There are two constitutional isomers with the formula C_2H_6O. Write structural formulas for these isomers.

STRATEGY AND ANSWER: If we recall that carbon can form four covalent bonds, oxygen can form two, and hydrogen only one, we can arrive at the following constitutional isomers.



Dimethyl ether

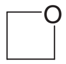


Ethanol

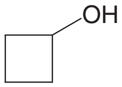
It should be noted that these two isomers are clearly different in their physical properties. At room temperature and 1 atm pressure, dimethyl ether is a gas. Ethanol is a liquid.

SOLVED PROBLEM 1.7

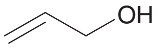
Which of the following compounds are constitutional isomers of one another?



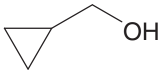
A



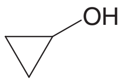
B



C



D

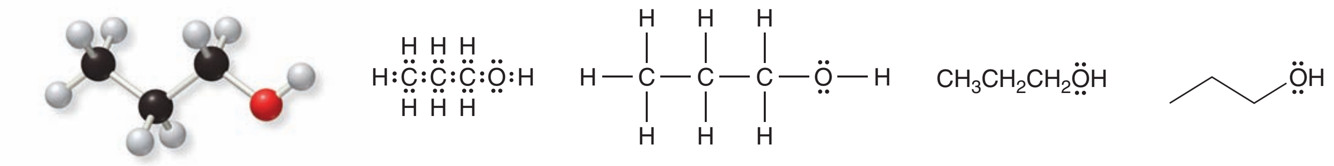


E

ANSWER: First determine the molecular formula for each compound. You will then see that **B** and **D** have the same molecular formula (C_4H_8O) but have different connectivities. They are, therefore, constitutional isomers of each other. **A**, **C**, and **E** also have the same molecular formula (C_3H_6O) and are constitutional isomers of one another.

1.7 HOW TO WRITE AND INTERPRET STRUCTURAL FORMULAS

Organic chemists use a variety of formats to write **structural formulas**. We have already used electron-dot formulas and dash formulas in previous sections. Two other important types of formulas are condensed formulas and bond-line (skeletal) formulas. Examples of these four types of structural formulas are shown in Fig. 1.3 using propyl alcohol as an example.



Ball-and-stick model (*a*) Electron-dot formula (*b*) Dash formula (*c*) Condensed formula (*d*) Bond-line formula (*e*)

FIGURE 1.3 Structural formulas for propyl alcohol.

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*An older term for isomers of this type was **structural isomers**. The International Union of Pure and Applied Chemistry (IUPAC) now recommends that use of the term "structural" when applied to constitutional isomers be abandoned.

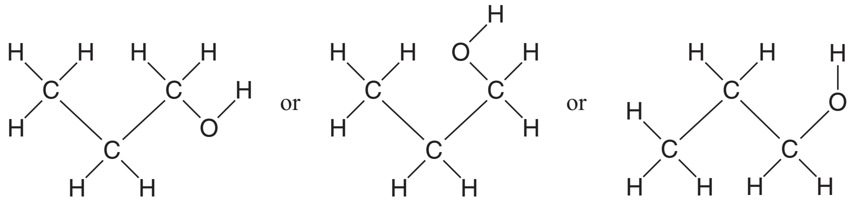
Although electron-dot formulas account explicitly for all of the valence electrons in a molecule, they are tedious and time-consuming to write. Dash, condensed, and bond-line formulas are therefore used more often.

Generally it is best to draw unshared electron pairs in chemical formulas, though sometimes they are omitted if we are not considering the chemical properties or reactivity of a compound. When we write chemical reactions, however, we shall see that it is necessary to include the unshared electron pairs when they participate in a reaction. It is a good idea, therefore, to be in the habit of writing unshared electrons pairs.

1.7A More About Dash Structural Formulas

- **Dash structural formulas** have lines that show bonding electron pairs, and include elemental symbols for all of the atoms in a molecule.

If we look at the ball-and-stick model for propyl alcohol given in Fig. 1.3*a* and compare it with the electron-dot, dash, and condensed formulas in Figs. 1.3*b–d* we find that the chain of atoms is straight in those formulas. In the model, which corresponds more accurately to the actual shape of the molecule, the chain of atoms is not at all straight. Also of importance is this: ***Atoms joined by single bonds can rotate relatively freely with respect to one another***. (We shall discuss the reason for this in Section 1.12B.) This relatively free rotation means that the chain of atoms in propyl alcohol can assume a variety of arrangements like these:



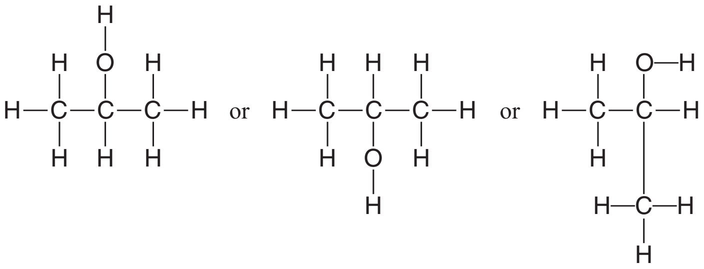
Equivalent dash formulas for propyl alcohol

Helpful Hint

It is important that you be able to recognize when a set of structural formulas has the same connectivity versus when they are constitutional isomers.

It also means that all of the structural formulas above are *equivalent* and all represent propyl alcohol. Dash structural formulas such as these indicate the way in which the atoms are attached to each other and *are not* representations of the actual shapes of the molecule. (Propyl alcohol does not have 90° **bond angles**. It has tetrahedral bond angles.) Dash structural formulas show what is called the **connectivity** of the atoms. *Constitutional isomers (Section 1.6A) have different connectivities and, therefore, must have different structural formulas.*

Consider the compound called isopropyl alcohol, whose formula we might write in a variety of ways:



Equivalent dash formulas for isopropyl alcohol

Isopropyl alcohol is a constitutional isomer (Section 1.6A) of propyl alcohol because its atoms are connected in a different order and both compounds have the same molecular formula, C_3H_8O. In isopropyl alcohol the OH group is attached to the central carbon; in propyl alcohol it is attached to an end carbon.

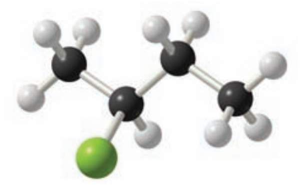
- In problems you will often be asked to write structural formulas for all the isomers that have a given molecular formula. Do not make the error of writing several equivalent formulas, like those that we have just shown, mistaking them for different constitutional isomers.

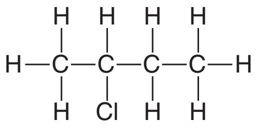
PRACTICE PROBLEM 1.12

There are actually three constitutional isomers with the molecular formula C_3H_8O. We have seen two of them in propyl alcohol and isopropyl alcohol. Write a dash formula for the third isomer.

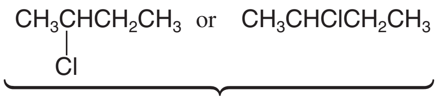
1.7B Condensed Structural Formulas

Condensed structural formulas are somewhat faster to write than dash formulas and, when we become familiar with them, they will impart all the information that is contained in the dash structure. In condensed formulas all of the hydrogen atoms that are attached to a particular carbon are usually written immediately after the carbon. In fully condensed formulas, all of the atoms that are attached to the carbon are usually written immediately after that carbon, listing hydrogens first. For example,





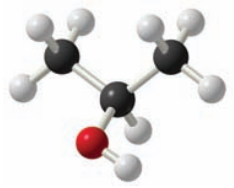
Dash formula

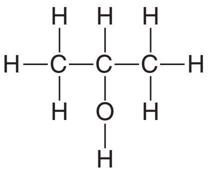


$CH_3\underset{\substack{|\\ Cl}}{C}HCH_2CH_3$ or $CH_3CHClCH_2CH_3$

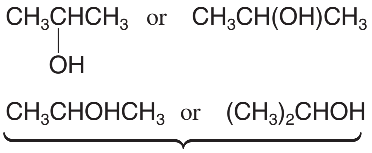
Condensed formulas

The condensed formula for isopropyl alcohol can be written in four different ways:





Dash formula



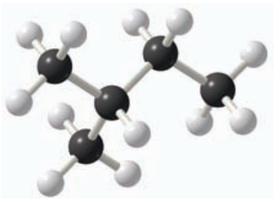
$CH_3\underset{\substack{|\\ OH}}{C}HCH_3$ or $CH_3CH(OH)CH_3$

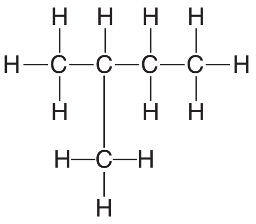
$CH_3CHOHCH_3$ or $(CH_3)_2CHOH$

Condensed formulas

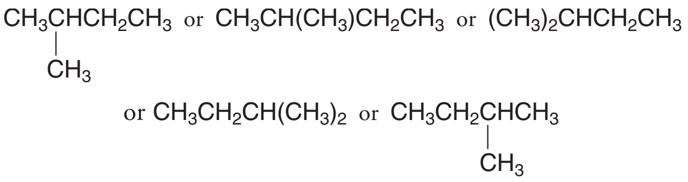
SOLVED PROBLEM 1.8

Write a condensed structural formula for the compound that follows:





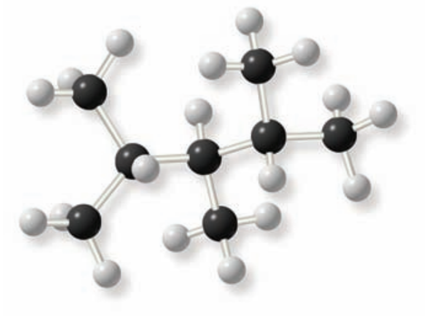
ANSWER:



$CH_3\underset{\substack{|\\ CH_3}}{C}HCH_2CH_3$ or $CH_3CH(CH_3)CH_2CH_3$ or $(CH_3)_2CHCH_2CH_3$

or $CH_3CH_2CH(CH_3)_2$ or $CH_3CH_2\underset{\substack{|\\ CH_3}}{C}HCH_3$

PRACTICE PROBLEM 1.13 Write a condensed structural formula for the following compound.



1.7C Bond-Line Formulas

The most common type of structural formula used by organic chemists, and the fastest to draw, is the **bond-line formula**. (Some chemists call these skeletal formulas.) The formula in Fig. 1.3*e* is a bond-line formula for propyl alcohol. The sooner you master the use of bond-line formulas, the more quickly you will be able to draw molecules when you take notes and work problems. And, lacking all of the symbols that are explicitly shown in dash and condensed structural formulas, bond-line formulas allow you to more quickly interpret molecular connectivity and compare one molecular formula with another.

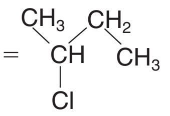
HOW TO DRAW BOND-LINE FORMULAS

We apply the following rules when we draw bond-line formulas:

- Each line represents a bond.
- Each **bend** in a line or **terminus** of a line represents a carbon atom, unless another group is shown explicitly.
- No Cs are written for carbon atoms, except optionally for CH_3 groups at the end of a chain or branch.
- No Hs are shown for hydrogen atoms, unless they are needed to give a three-dimensional perspective, in which case we use dashed or solid wedges (as explained in the next section).
- The number of hydrogen atoms bonded to each carbon is inferred by assuming that as many hydrogen atoms are present as needed to fill the valence shell of the carbon, unless a charge is indicated.
- When an atom other than carbon or hydrogen is present, the symbol for that element is written at the appropriate location (i.e., in place of a bend or at the terminus of the line leading to the atom).
- Hydrogen atoms bonded to atoms other than carbon (e.g., oxygen or nitrogen) are written explicitly.

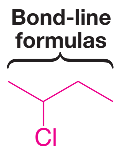
Consider the following examples of molecules depicted by bond-line formulas.

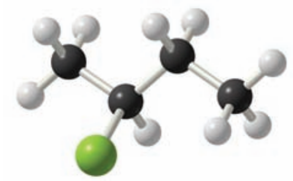
$CH_3CHClCH_2CH_3$ =



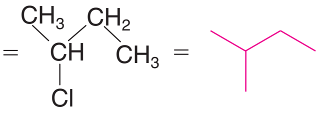
$$\underset{\displaystyle Cl}{\overset{CH_3}{CH}}-CH_2-CH_3$$

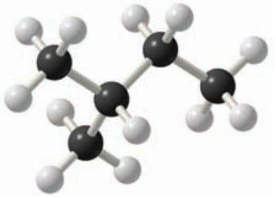
=



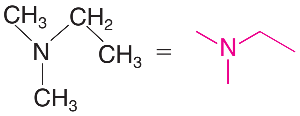


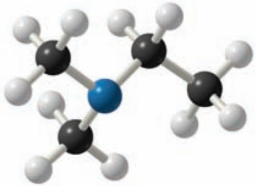
$CH_3CH(CH_3)CH_2CH_3$ =





$(CH_3)_2NCH_2CH_3$ =

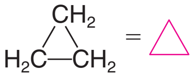


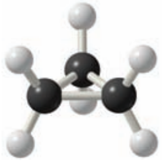


Helpful Hint

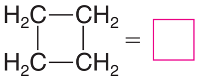
As you become more familiar with organic molecules, you will find bond-line formulas to be very useful tools for representing structures.

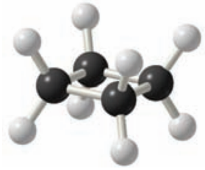
Bond-line formulas are easy to draw for molecules with multiple bonds and for cyclic molecules, as well. The following are some examples.

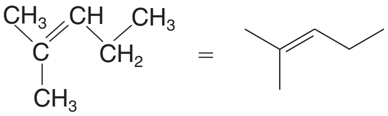


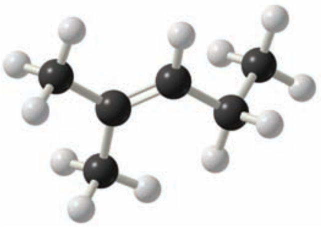


and

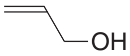


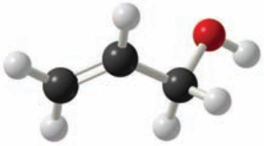


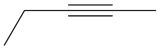


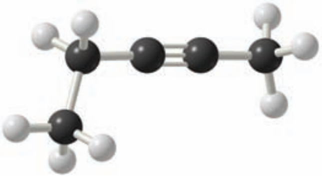


$CH_2{=}CHCH_2OH$ =



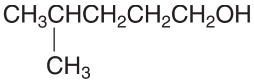






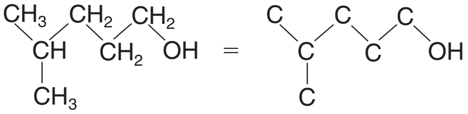
SOLVED PROBLEM 1.9

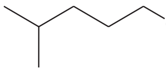
Write the bond-line formula for



$$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_2CH_2OH$$

STRATEGY AND ANSWER: First, for the sake of practice, we outline the carbon skeleton, including the OH group, as follows:



Then we write the bond-line formula as OH. As you gain experience you will likely skip the intermediate steps shown above and proceed directly to writing bond-line formulas.

PRACTICE PROBLEM 1.14 Write each of the following condensed structural formulas as a bond-line formula:

(a) $(CH_3)_2CHCH_2CH_3$

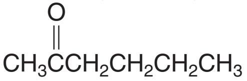
(b) $(CH_3)_2CHCH_2CH_2OH$

(c) $(CH_3)_2C{=}CHCH_2CH_3$

(d) $CH_3CH_2CH_2CH_2CH_3$

(e) $CH_3CH_2CH(OH)CH_2CH_3$

(f) $CH_2{=}C(CH_2CH_3)_2$

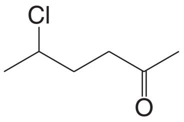
(g) 

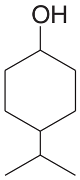
$CH_3\overset{\overset{\displaystyle O}{\|}}{C}CH_2CH_2CH_2CH_3$

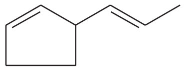
(h) $CH_3CHClCH_2CH(CH_3)_2$

PRACTICE PROBLEM 1.15 Which molecules in Practice Problem 1.14 form sets of constitutional isomers?

PRACTICE PROBLEM 1.16 Write a dash formula for each of the following bond-line formulas:

(a) 

(b) 

(c) 

1.7D Three-Dimensional Formulas

None of the formulas that we have described so far convey any information about how the atoms of a molecule are arranged in space. Molecules exist in three dimensions. We can depict three-dimensional geometry in molecules using bonds represented by dashed wedges, solid wedges, and lines.

- A dashed wedge (┅) represents a bond that projects behind the plane of the paper.
- A solid wedge (◄) represents a bond that projects out of the plane of the paper.
- An ordinary line (—) represents a bond that lies in the plane of the paper.

For example, the four C—H bonds of methane (CH_4) are oriented toward the corners of a regular tetrahedron, with the carbon in the center and an approximately 109° angle between each C—H bond, as was originally postulated by J. H. van't Hoff and L. A. Le Bel in 1874. Figure 1.4 shows the tetrahedral structure of methane.

We will discuss the physical basis for the geometries of carbon when it has only single bonds, a double bond, or a triple bond in Sections 1.12–14. For now, let us consider some guidelines for representing these bonding patterns in three dimensions using dashed and solid wedge bonds.

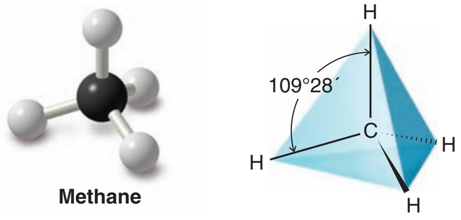


FIGURE 1.4 The tetrahedral structure of methane.

In general for carbon atoms that have only single bonds:

- A carbon atom with **four single bonds** has tetrahedral geometry (Section 1.12) and can be drawn with two bonds in the plane of the paper separated by approximately 109°, one bond behind the plane using a dashed wedge, and one bond in front of the plane using a solid wedge.
- The dashed wedge and solid wedge bonds in tetrahedral geometry nearly eclipse each other when drawn in proper three-dimensional perspective.

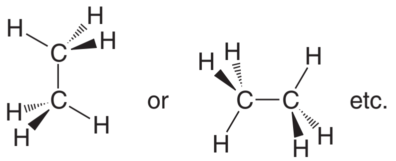
For carbon atoms with a double or a triple bond:

- A carbon atom with a **double bond** has trigonal planar geometry (Section 1.13) and can be depicted with bonds that are all in the plane of the paper and separated by 120°.
- A carbon atom with a **triple bond** has linear geometry (Section 1.14) and can be depicted with its bonds in the plane of the paper and separated by a 180° angle.

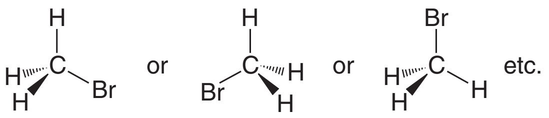
Last, when drawing three-dimensional formulas for molecules:

- Draw as many carbon atoms in the plane of the paper as possible using ordinary lines, then use dashed or solid wedge bonds for substituent groups or hydrogen atoms that are needed to show three dimensions.

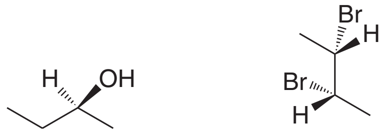
Some examples of three-dimensional formulas are shown below.



Ethane

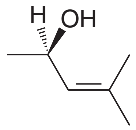


Bromomethane



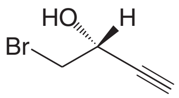
Examples of bond-line formulas that include three-dimensional representations

The carbon chains are shown in the plane of the paper. The dashed and solid wedge bonds nearly eclipse each other.



An example involving trigonal planar geometry

Bonds to the carbon with the double bond are in the plane of the paper and separated by 120°.

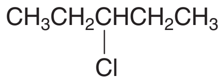


An example involving linear geometry

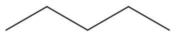
Bonds to the carbon with the triple bond are in the plane of the paper and separated by 180°.

SOLVED PROBLEM 1.10

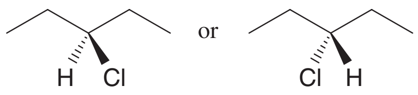
Write a bond-line formula for the following compound showing three dimensions at the carbon bearing the chlorine atom.


$$CH_3CH_2\underset{\displaystyle Cl}{\underset{|}{C}}HCH_2CH_3$$

STRATEGY AND ANSWER: First draw the carbon skeleton, placing as many carbon atoms in the plane of the paper as possible (which is all of them, in this case).



Then add the chlorine atom at the appropriate carbon using a three-dimensional representation.



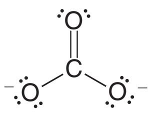
PRACTICE PROBLEM 1.17

Write three-dimensional (wedge–dashed wedge–line) representations for each of the following:

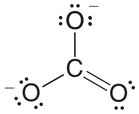
(a) CH_3Cl **(b)** CH_2Cl_2 **(c)** CH_2BrCl **(d)** CH_3CH_2Cl

1.8 RESONANCE THEORY

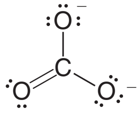
Often more than one *equivalent* Lewis structure can be written for a molecule or ion. Consider, for example, the carbonate ion (CO_3^{2-}). We can write three *different* but *equivalent* structures, **1–3**:



1



2



3

Notice two important features of these structures. First, each atom has the noble gas configuration. Second, *and this is especially important*, we can convert one structure into any other by *changing only the positions of the electrons*. We do not need to change the relative positions of the atomic nuclei. For example, if we move the electron pairs in the manner indicated by the **curved arrows** in structure **1**, we change structure **1** into structure **2**:

1 **2**

Helpful Hint

Curved arrows (Section 3.2) show movement of electron pairs, not atoms. The tail of the arrow begins at the current position of the electron pair. The *head* of the arrow points to the location where the electron pair will be in the next structure. Curved-arrow notation is one of the most important tools that you will use to understand organic reactions.

In a similar way we can change structure **2** into structure **3**:

2 **3**

Structures **1–3**, although not identical on paper, *are equivalent*. None of them alone, however, fits important data about the carbonate ion.

X-ray studies have shown that carbon–oxygen double bonds are shorter than single bonds. The same kind of study of the carbonate ion shows, however, that all of its carbon–oxygen bonds *are of equal length*. One is not shorter than the others as would be expected from representations **1**, **2**, and **3**. Clearly none of the three structures agrees with this evidence. In each structure, **1–3**, one carbon–oxygen bond is a double bond and the other two are single bonds. None of the structures, therefore, is correct. How, then, should we represent the carbonate ion?

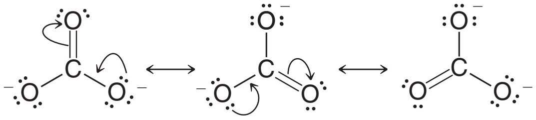
One way is through a theory called **resonance theory**. This theory states that whenever a molecule or ion can be represented by two or more Lewis structures *that differ only in the positions of the electrons*, two things will be true:

1. None of these structures, which we call **resonance structures** or **resonance contributors**, will be a realistic representation for the molecule or ion. None will be in complete accord with the physical or chemical properties of the substance.
2. The actual molecule or ion will be better represented by a *hybrid (average) of these structures*.

- ***Resonance structures, then, are not real structures for the actual molecule or ion; they exist only on paper***. As such, they can never be isolated. No single contributor adequately represents the molecule or ion. In resonance theory we view the carbonate ion, which is, of course, a real entity, as having a structure that is a **hybrid** of the three **hypothetical** resonance structures.

What would a hybrid of structures **1–3** be like? Look at the structures and look especially at a particular carbon–oxygen bond, say, the one at the top. This carbon–oxygen bond is a double bond in one structure (**1**) and a single bond in the other two (**2** and **3**). The actual carbon–oxygen bond, since it is a hybrid, must be something in between a double bond and a single bond. Because the carbon–oxygen bond is a single bond in two of the structures and a double bond in only one, it must be more like a single bond than a double bond. It must be like a one and one-third bond. We could call it a partial double bond. And, of course, what we have just said about any one carbon–oxygen bond will be equally true of the other two. Thus all of the carbon–oxygen bonds of the carbonate ion are partial double bonds, and *all are equivalent*. All of them *should be* the same length, and this is exactly what experiments tell us. The bonds are all 1.28 Å long, a distance which is intermediate between that of a carbon–oxygen single bond (1.43 Å) and that of a carbon–oxygen double bond (1.20 Å). One angstrom equals 1×10^{-10} meter.

- One other important point: by convention, when we draw resonance structures, we connect them by double-headed arrows (↔) to indicate clearly that they are hypothetical, not real. For the carbonate ion we write them this way:



We should not let these arrows, or the word "resonance," mislead us into thinking that the carbonate ion fluctuates between one structure and another. These structures individually do not represent reality and exist only on paper; therefore, the carbonate ion cannot fluctuate among them because it is a hybrid of them.

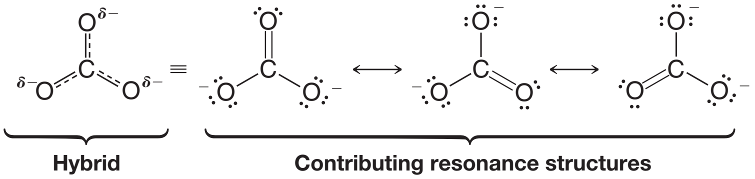
- Resonance structures do not represent an **equilibrium**.

In an equilibrium between two or more species, it is quite correct to think of different structures and moving (or fluctuating) atoms, *but not in the case of resonance* (as in the carbonate ion). Here the atoms do not move, and the "structures" exist only on paper. **An equilibrium is indicated by ⇆ and resonance by ↔.**

Helpful Hint

Each type of arrow in organic chemistry (e.g., ↷, ⇆, and ↔) has a specific meaning. It is important that you use each type of arrow only for the purpose for which it is defined.

How can we write the structure of the carbonate ion in a way that will indicate its actual structure? We may do two things: we may write all of the resonance structures as we have just done and let the reader mentally fashion the hybrid, or we may write a non-Lewis structure that attempts to represent the hybrid. For the carbonate ion we might do the following:



The bonds in the structure on the left are indicated by a combination of a solid line and a dashed line. This is to indicate that the bonds are something in between a single bond and a double bond. As a rule, we use a solid line whenever a bond appears in all structures, and a dashed line when a bond exists in one or more but not all. We also place a $\delta-$ (read partial minus) beside each oxygen to indicate that something less than a full negative charge resides on each oxygen atom. In this instance, each oxygen atom has two-thirds of a full negative charge.

Calculations from theory show the equal charge density at each oxygen in the carbonate anion. Figure 1.5 shows a calculated **electrostatic potential map** of the electron density in the carbonate ion. In an electrostatic potential map, regions of relatively more negative charge are red, while more positive regions (i.e., less negative regions) are indicated by colors trending toward blue. Equality of the bond lengths in the carbonate anion (partial double bonds as shown in the resonance hybrid above) is also evident in this model.

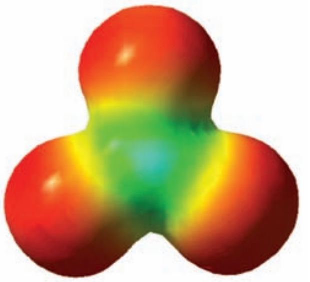


FIGURE 1.5 A calculated electrostatic potential map for the carbonate anion, showing the equal charge distribution at the three oxygen atoms. In electrostatic potential maps like this one, colors trending toward red mean increasing concentration of negative charge, while those trending toward blue mean less negative (or more positive) charge.

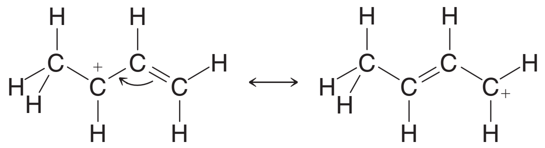
1.8A The Use of Curved Arrows: HOW TO Write Resonance Structures

As we have mentioned earlier, curved arrows are often used in writing **resonance structures**, and as we shall see in Section 3.2 they are essential in writing reaction mechanisms. Let us now point out several important things to remember about their use.

- Curved arrows are used to show the movement of both **bonding** and **unshared** electrons.
- A double-barbed curved arrow (↷) shows the movement of **two** electrons (an electron pair). [Later, we will see that a single-barbed arrow (⌒) can be used to show the movement of a single electron.]
- A curved arrow should originate precisely at the location of the relevant electrons in the initial formula and point precisely to where those electrons will be drawn in the new formula.
- A new formula should be drawn to show the result of the electron shift(s). All formulas should be proper Lewis structures and should include formal charges as appropriate. The maximum number of valence electrons should not be exceeded for any atom in a formula.

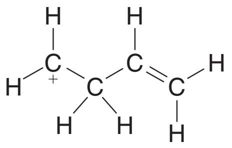
1.8B Rules for Writing Resonance Structures

1. **Resonance structures exist only on paper**. Although they have no real existence of their own, **resonance structures** are useful because they allow us to describe molecules and ions for which a single Lewis structure is inadequate. We write two or more Lewis structures, calling them resonance structures or resonance contributors. We connect these structures by double-headed arrows (⟷), and we say that the real molecule or ion is a hybrid of all of them.
2. **We are only allowed to move electrons in writing resonance structures**. The positions of the nuclei of the atoms must remain the same in all of the structures. Structure **3** is not a resonance structure of **1** or **2**, for example, because in order to form it we would have to move a hydrogen atom and this is not permitted:



1 **2**

These are resonance structures.

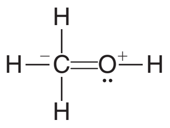


3

This is not a resonance structure of 1 or 2. It is an isomer because a hydrogen atom has been moved.

Generally speaking, when we move electrons, we move only those of **multiple bonds** (as in the example above) and those of **nonbonding electron pairs**.

3. **All of the structures must be proper Lewis structures**. We should not write structures in which carbon has five bonds, for example:

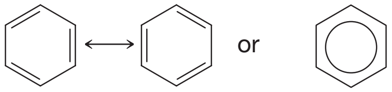


$$\mathrm{H{-}\overset{H}{\underset{H}{\overset{-}{C}}}{=}\ddot{O}^{+}{-}H}$$

This is not a proper resonance structure for methanol because carbon has five bonds. Elements of the first major row of the periodic table cannot have more than eight electrons in their valence shell.

4. **The energy of the resonance hybrid is lower than the energy of any contributing structure**. Resonance stabilizes a molecule or ion. This is especially true when the resonance structures are equivalent. Chemists call this stabilization *resonance stabilization*. **If the resonance structures are equivalent, then the resonance stabilization is large**.

In Chapter 14 we shall find that benzene is highly resonance stabilized because it is a hybrid of the two equivalent forms that follow:



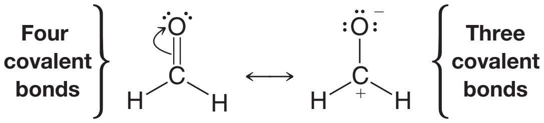
Resonance structures for benzene **Representation of hybrid**

5. **The more stable a structure is (when taken by itself), the greater is its contribution to the hybrid.**

1.8C How Do We Decide When One Resonance Structure Contributes More to the Hybrid Than Another?

The following rules will help us:

1. **The more covalent bonds a structure has, the more stable it is**. Consider the resonance structures for formaldehyde below. (Formaldehyde is a chemical used to preserve biological specimens.) Structure **A** has more covalent bonds, and therefore makes a larger contribution to the hybrid. In other words, the hybrid is more like structure **A** than structure **B**.



A **B**

More stable **Less stable**

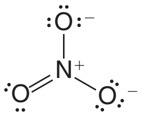
Resonance structures for formaldehyde

These structures also illustrate two other considerations:

2. **Charge separation decreases stability**. It takes energy to separate opposite charges, and therefore a structure with separated charges is less stable. Structure **B** for formaldehyde has separated plus and minus charges; therefore, on this basis, too, it is the less stable contributor and makes a smaller contribution to the hybrid.
3. **Structures in which all the atoms have a complete valence shell of electrons (i.e., the noble gas structure) are more stable**. Look again at structure **B**. The carbon atom has only six electrons around it, whereas in **A** it has eight. On this basis we can conclude that **A** is more stable and makes a larger contribution.

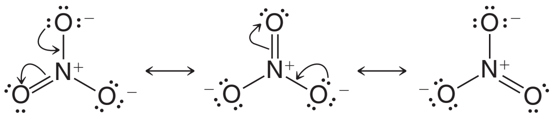
SOLVED PROBLEM 1.11

The following is one way of writing the structure of the nitrate ion:



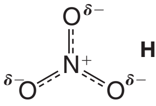
However, considerable physical evidence indicates that all three nitrogen–oxygen bonds are equivalent and that they have the same length, a bond distance between that expected for a nitrogen–oxygen single bond and a nitrogen–oxygen double bond. Explain this in terms of resonance theory.

STRATEGY AND ANSWER: We recognize that if we move the electron pairs in the following way, we can write three *different* but *equivalent* structures for the nitrate ion:



(continues on the next page)

Since these structures differ from one another *only in the positions of their electrons*, they are *resonance structures* or *resonance contributors*. As such, no single structure taken alone will adequately represent the nitrate ion. The actual molecule will be best represented by a *hybrid of these three structures*. We might write this hybrid in the following way to indicate that all of the bonds are equivalent and that they are more than single bonds and less than double bonds. We also indicate that each oxygen atom bears an equal partial negative charge. This charge distribution corresponds to what we find experimentally.

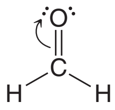


Hybrid structure for the nitrate ion

PRACTICE PROBLEM 1.18 **(a)** Write two resonance structures for the formate ion HCO_2^-. (*Note*: The hydrogen and oxygen atoms are bonded to the carbon.) **(b)** Explain what these structures predict for the carbon–oxygen bond lengths of the formate ion, and **(c)**, for the electrical charge on the oxygen atoms.

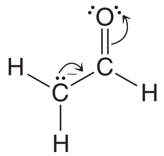
PRACTICE PROBLEM 1.19 Write the resonance structure that would result from moving the electrons as the curved arrows indicate. Be sure to include formal charges if needed.

(a)



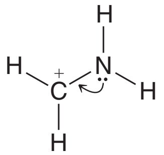
⟷ ?

(b)



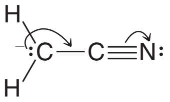
⟷ ?

(c)



⟷ ?

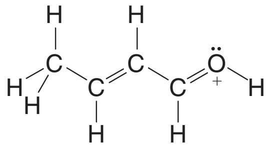
(d)



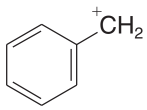
⟷ ?

PRACTICE PROBLEM 1.20 Add any missing unshared electron pairs (if any), then, using curved arrows to show the shifts in electrons, write the contributing resonance structures and resonance hybrid for each of the following:

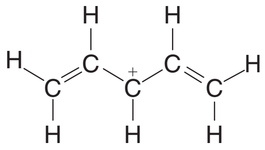
(a)



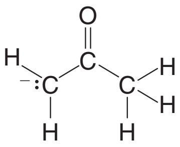
(e)



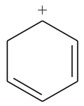
(b)



(f)

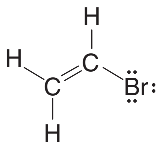


(c)



(g) $CH_3S\overset{+}{C}H_2$

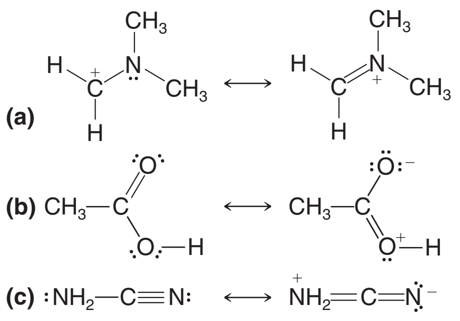
(d)



(h) CH_3NO_2

PRACTICE PROBLEM 1.21

For each set of resonance structures that follow, add a curved arrow that shows how electrons in the left formula shift to become the right formula, and designate the formula that would contribute most to the hybrid. Explain your choice:



1.9 QUANTUM MECHANICS AND ATOMIC STRUCTURE

A theory of atomic and molecular structure was advanced independently and almost simultaneously by three people in 1926: Erwin Schrödinger, Werner Heisenberg, and Paul Dirac. This theory, called **wave mechanics** by Schrödinger and **quantum mechanics** by Heisenberg, has become the basis from which we derive our modern understanding of bonding in molecules. At the heart of quantum mechanics are equations called wave functions (denoted by the Greek letter **psi**, ψ).

- Each **wave function (ψ)** corresponds to a different *energy state* for an electron.
- Each *energy state* is a sublevel where one or two electrons can reside.
- The **energy** associated with the state of an electron can be calculated from the wave function.
- The **relative probability** of finding an electron in a given region of space can be calculated from the wave function (Section 1.10).
- The solution to a wave function can be positive, negative, or zero (Fig. 1.6).
- The **phase sign** of a wave equation indicates whether the solution is positive or negative when calculated for a given point in space relative to the nucleus.

Wave functions, whether they are for sound waves, lake waves, or the energy of an electron, have the possibility of constructive interference and destructive interference.

- **Constructive interference** occurs when wave functions with the same phase sign interact. There is a *reinforcing effect* and the amplitude of the wave function increases.
- **Destructive interference** occurs when wave functions with opposite phase signs interact. There is a *subtractive effect* and the amplitude of the wave function goes to zero or changes sign.

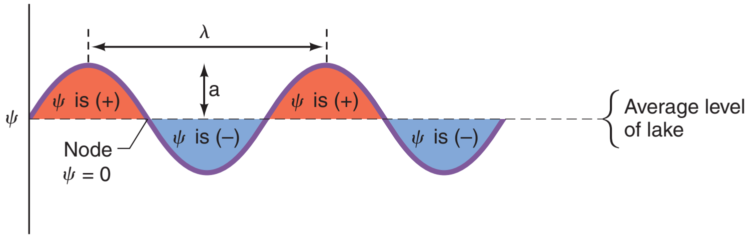
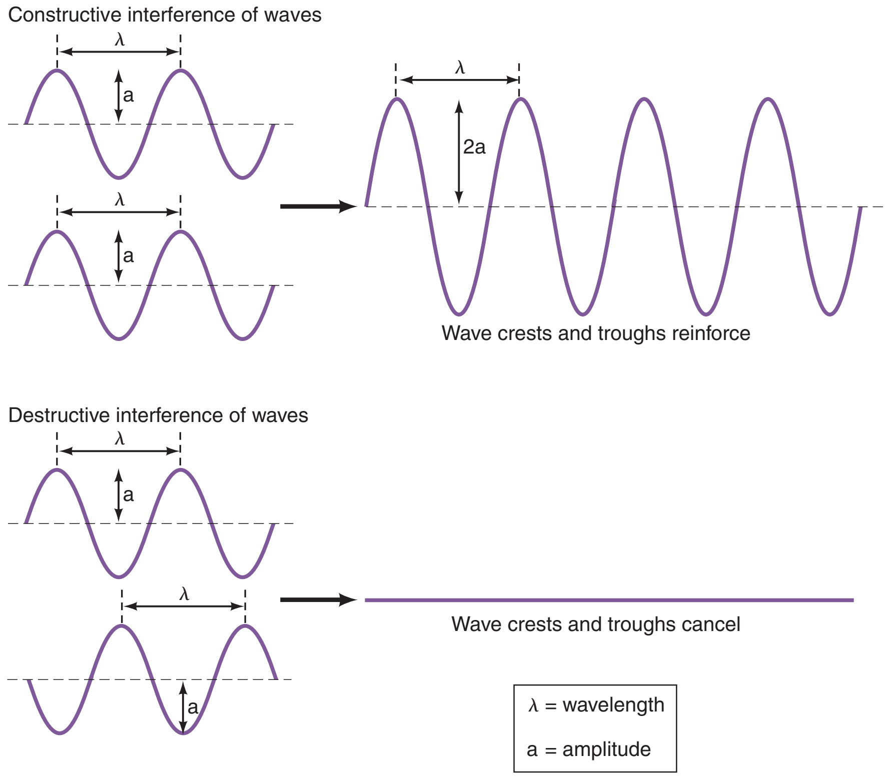


FIGURE 1.6 A wave moving across a lake is viewed along a slice through the lake. For this wave the wave function, ψ, is plus (+) in crests and minus (−) in troughs. At the average level of the lake it is zero; these places are called nodes. The magnitude of the crests and troughs is the amplitude (a) of the wave. The distance from the crest of one wave to the crest of the next is the wavelength (λ, or lambda).



Experiments have shown that electrons have properties of waves and particles, which was an idea first put forth by Louis de Broglie in 1923. Our discussion focuses on the wavelike properties of electrons, however.

1.10 ATOMIC ORBITALS AND ELECTRON CONFIGURATION

A physical interpretation related to the electron wave function was put forth by Max Born in 1926:

- The square of a wave function (ψ^2) for a particular x, y, z location expresses the probability of finding an electron at that location in space.

If the value of ψ^2 is large in a unit volume of space, the probability of finding an electron in that volume is high—we say that the **electron probability density** is large. Conversely, if ψ^2 for some other volume of space is small, the probability of finding an electron there is low.* This leads to the general definition of an orbital and, by extension, to the familiar shapes of atomic orbitals.

- An **orbital** is a region of space where the probability of finding an electron is high.
- **Atomic orbitals** are plots of ψ^2 in three dimensions. These plots generate the familiar *s*, *p*, and *d* orbital shapes.

The volumes that we show are those that would contain the electron 90–95% of the time. There is a finite, but very small, probability of finding an electron at greater distance from the nucleus than shown in the plots.

The shapes of *s* and *p* orbitals are shown in Fig. 1.7.

All ***s* orbitals** are spheres. A 1*s* orbital is a simple sphere. A 2*s* orbital is a sphere with an inner nodal surface ($\psi^2 = 0$). The inner portion of the 2*s* orbital, ψ_{2s}, has a negative phase sign.

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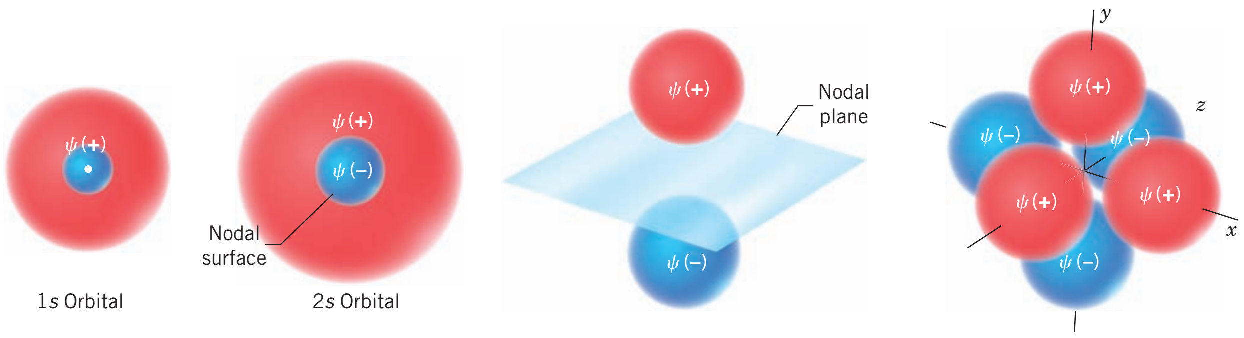
*Integration of ψ^2 over all space must equal 1; that is, the probability of finding an electron somewhere in all of space is 100%.



1*s* Orbital

2*s* Orbital

A pure (unhybridized) 2*p* orbital has two lobes.

There are three 2*p* orbitals, each with a (+) and (–) lobe, aligned symmetrically along the *x*, *y*, and *z* axes.

FIGURE 1.7 The shapes of some *s* and *p* orbitals. Pure, unhybridized *p* orbitals are almost-touching spheres. The *p* orbitals in hybridized atoms are lobe-shaped (Section 1.13).

The shape of a ***p* orbital** is like that of almost-touching spheres or lobes. The phase sign of a 2*p* wave function, ψ_{2p}, is positive in one lobe and negative in the other. A nodal plane separates the two lobes of a *p* orbital, and the three *p* orbitals of a given energy level are arranged in space along the *x*, *y*, and *z* axes in a Cartesian coordinate system.

- The + and − signs of wave functions do not imply positive or negative charge or greater or lesser probability of finding an electron.
- ψ^2 (the probability of finding an electron) is always positive, because squaring either a positive or negative solution to ψ leads to a positive value.

Thus, the probability of finding an electron in either lobe of a *p* orbital is the same. We shall see the significance of the + and − signs later when we see how atomic orbitals combine to form molecular orbitals.

1.10A Electron Configurations

The relative energies of atomic orbitals in the first and second principal shells are as follows:

- Electrons in 1*s* orbitals have the lowest energy because they are closest to the positive nucleus.
- Electrons in 2*s* orbitals are next lowest in energy.
- Electrons of the three 2*p* orbitals have equal but higher energy than the 2*s* orbital.
- Orbitals of equal energy (such as the three 2*p* orbitals) are called **degenerate orbitals**.

We can use these relative energies to arrive at the electron configuration of any atom in the first two rows of the periodic table. We need follow only a few simple rules.

1. **Aufbau principle**: Orbitals are filled so that those of lowest energy are filled first. (*Aufbau* is German for "building up.")
2. **Pauli exclusion principle**: A maximum of two electrons may be placed in each orbital *but only when the spins of the electrons are paired*. An electron spins about its own axis. For reasons that we cannot develop here, an electron is permitted only one or the other of just two possible spin orientations. We usually show these orientations by arrows, either ↿ or ⇂. Thus two spin-paired electrons would be designated ⇂↿. Unpaired electrons, which are not permitted in the same orbital, are designated ↿↿ (or ⇂⇂).
3. **Hund's rule**: When we come to orbitals of equal energy (degenerate orbitals) such as the three *p* orbitals, we add one electron to each *with their spins unpaired* until each of the degenerate orbitals contains one electron. (This allows the electrons, which repel each other, to be farther apart.) Then we begin adding a second electron to each degenerate orbital so that the spins are paired.

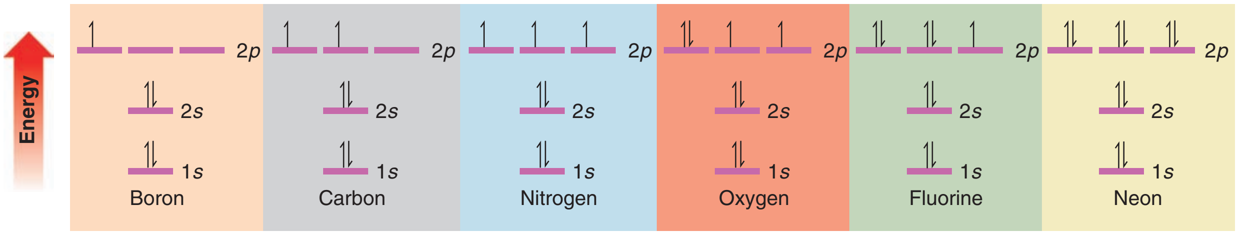


FIGURE 1.8 The ground state electron configurations of some second-row elements.

If we apply these rules to some of the second-row elements of the periodic table, we get the results shown in Fig. 1.8.

1.11 MOLECULAR ORBITALS

Atomic orbitals provide a means for understanding how atoms form covalent bonds. Let us consider a very simple case—formation of a bond between two hydrogen atoms to form a hydrogen molecule (Fig. 1.9).

When two hydrogen atoms are relatively far apart their total energy is simply that of two isolated hydrogen atoms (**I**). Formation of a covalent bond reduces the overall energy of the system, however. As the two hydrogen atoms move closer together (**II**), each nucleus increasingly attracts the other's electron. This attraction more than compensates for the repulsive force between the two nuclei (or the two electrons). The result is a covalent bond (**III**), such that the internuclear distance is an ideal balance that allows the two electrons to be shared between both atoms while at the same time avoiding repulsive interactions between their nuclei. This ideal internuclear distance between hydrogen atoms is 0.74 Å, and we call this the **bond length** in a hydrogen molecule. If the nuclei are moved closer together (**IV**) the repulsion of the two positively charged nuclei predominates, and the energy of the system rises.

Notice that each H· has a shaded area around it, indicating that its precise position is uncertain. Electrons are constantly moving.

- According to the **Heisenberg uncertainty principle**, we cannot simultaneously know the position and momentum of an electron.

These shaded areas in our diagram represent orbitals, and they result from applying the principles of quantum mechanics. Plotting the square of the wave function (ψ^2) gives us a three-dimensional region called an orbital where finding an electron is highly probable.

- An **atomic orbital** represents the region of space where one or two electrons of an isolated atom are likely to be found.

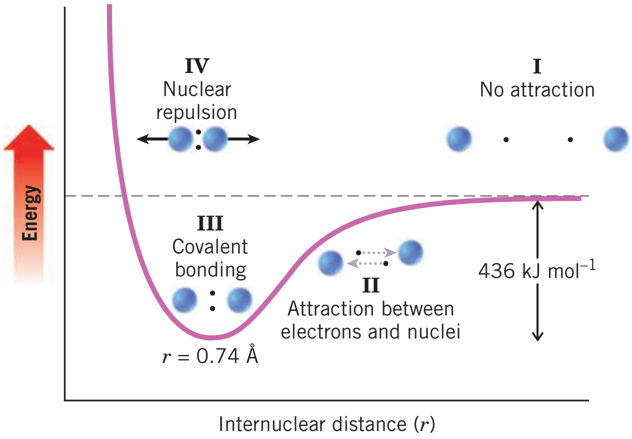


FIGURE 1.9 The potential energy of the hydrogen molecule as a function of internuclear distance.

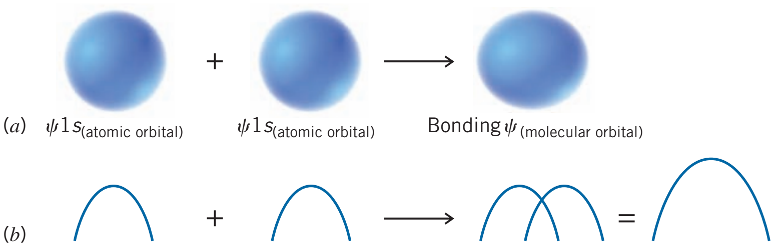


FIGURE 1.10 (*a*) The overlapping of two hydrogen 1*s* atomic orbitals with the same phase sign (indicated by their identical color) to form a bonding molecular orbital. (*b*) The analogous overlapping of two waves with the same phase, resulting in constructive interference and enhanced amplitude.

In the case of our hydrogen model above, the shaded spheres represent the 1*s* orbital of each hydrogen atom. As the two hydrogen atoms approach each other their 1*s* orbitals begin to overlap until their atomic orbitals combine to form molecular orbitals.

- A **molecular orbital (MO)** represents the region of space where one or two electrons of a molecule are likely to be found.
- An orbital (atomic or molecular) can contain a maximum of two spin-paired electrons (Pauli exclusion principle).
- When atomic orbitals combine to form molecular orbitals, **the number of molecular orbitals that result always equals the number of atomic orbitals that combine**.

Thus, in the formation of a hydrogen molecule the two ψ_{1s} atomic orbitals combine to produce two molecular orbitals. Two orbitals result because the mathematical properties of wave functions permit them to be combined by either addition or subtraction. That is, they can combine either in or out of phase.

- A **bonding molecular orbital** (ψ_{molec}) results when two orbitals of the same phase overlap (Fig. 1.10).
- An **antibonding molecular orbital** (ψ^*_{molec}) results when two orbitals of opposite phase overlap (Fig. 1.11).

The bonding molecular orbital of a hydrogen molecule in its lowest energy (ground) state contains both electrons from the individual hydrogen atoms. The value of ψ (and therefore also ψ^2) is large between the nuclei, precisely as expected since the electrons are shared by both nuclei to form the covalent bond.

The antibonding molecular orbital contains no electrons in the ground state of a hydrogen molecule. Furthermore, the value of ψ (and therefore also ψ^2) goes to zero between the nuclei, creating a node ($\psi = 0$). The antibonding orbital does not provide for electron density between the atoms, and thus it is not involved in bonding.

What we have just described has its counterpart in a mathematical treatment called the **LCAO (linear combination of atomic orbitals)** method. In the LCAO treatment, wave functions for the atomic orbitals are combined in a linear fashion (by addition or subtraction) in order to obtain new wave functions for the molecular orbitals.

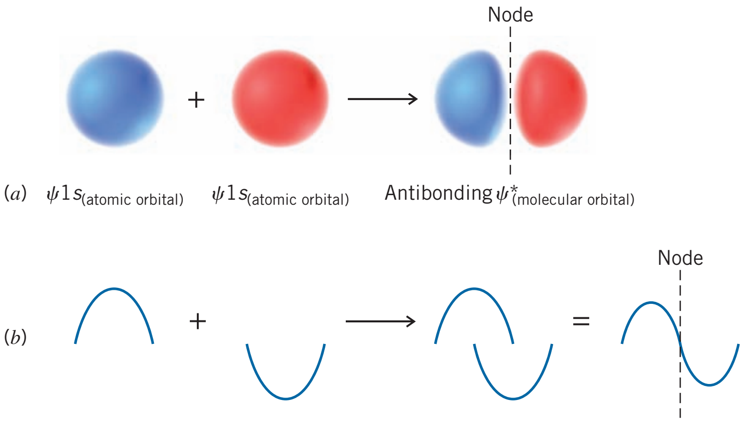
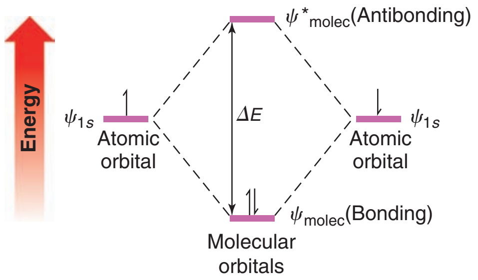


FIGURE 1.11 (*a*) The overlapping of two hydrogen 1*s* atomic orbitals with opposite phase signs (indicated by their different colors) to form an antibonding molecular orbital. (*b*) The analogous overlapping of two waves with the opposite sign, resulting in destructive interference and decreased amplitude. A node exists where complete cancellation by opposite phases makes the value of the combined wave function zero.

FIGURE 1.12 Energy diagram for the hydrogen molecule. Combination of two atomic orbitals, ψ_{1s}, gives two molecular orbitals, ψ_{molec} and ψ^*_{molec}. The energy of ψ_{molec} is lower than that of the separate atomic orbitals, and in the lowest electronic energy state of molecular hydrogen the bonding MO contains both electrons.



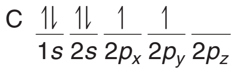
Molecular orbitals, like atomic orbitals, correspond to particular energy states for an electron. Calculations show that the relative energy of an electron in the bonding molecular orbital of the hydrogen molecule is substantially less than its energy in a ψ_{1s} atomic orbital. These calculations also show that the energy of an electron in the antibonding molecular orbital is substantially greater than its energy in a ψ_{1s} atomic orbital.

An energy diagram for the molecular orbitals of the hydrogen molecule is shown in Fig. 1.12. Notice that electrons are placed in molecular orbitals in the same way that they are in atomic orbitals. Two electrons (with their spins opposed) occupy the bonding molecular orbital, where their total energy is less than in the separate atomic orbitals. This is, as we have said, the *lowest electronic state* or *ground state* of the hydrogen molecule. An electron may occupy the antibonding molecular orbital in what is called an *excited state* for the molecule. This state forms when the molecule in the ground state (Fig. 1.12) absorbs a photon of light having the proper energy (ΔE).

1.12 THE STRUCTURE OF METHANE AND ETHANE: *sp*^{3} HYBRIDIZATION

The *s* and *p* orbitals used in the quantum mechanical description of the carbon atom, given in Section 1.10, were based on calculations for hydrogen atoms. These simple *s* and *p* orbitals do not, when taken alone, provide a satisfactory model for the *tetravalent–tetrahedral* carbon of methane (CH_4, see Practice Problem 1.22). However, a satisfactory model of methane's structure that is based on quantum mechanics *can* be obtained through an approach called **orbital hybridization**. Orbital hybridization, in its simplest terms, is nothing more than a mathematical approach that involves the combining of individual wave functions for *s* and *p* orbitals to obtain wave functions for new orbitals. The new orbitals have, *in varying proportions*, the properties of the original orbitals taken separately. These new orbitals are called **hybrid atomic orbitals**.

According to quantum mechanics, the electronic configuration of a carbon atom in its lowest energy state—called the **ground state**—is that given here:



Ground state of a carbon atom

The valence electrons of a carbon atom (those used in bonding) are those of the *outer level*, that is, the 2*s* and 2*p* electrons.

1.12A The Structure of Methane

Hybrid atomic orbitals that account for the structure of methane can be derived from carbon's second-shell *s* and *p* orbitals as follows (Fig. 1.13):

- Wave functions for the 2*s*, $2p_x$, $2p_y$, and $2p_z$ orbitals of ground state carbon are mixed to form four new and equivalent $2sp^3$ hybrid orbitals.
- The designation **sp^3** signifies that the hybrid orbital has one part *s* orbital character and three parts *p* orbital character.

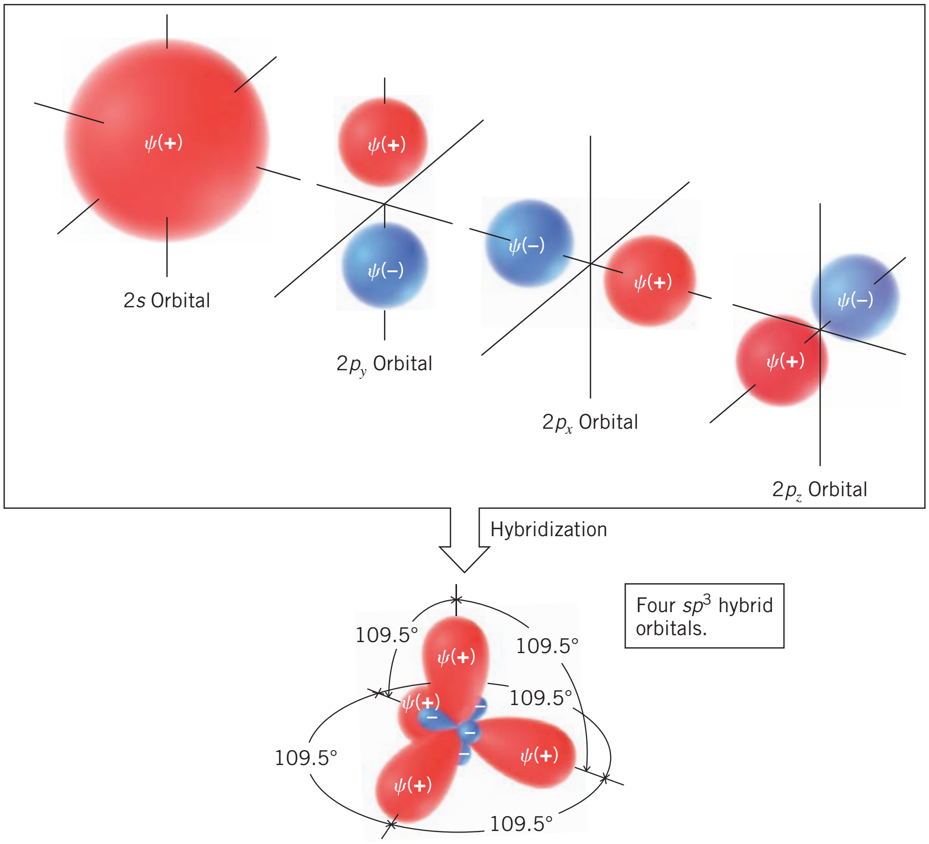
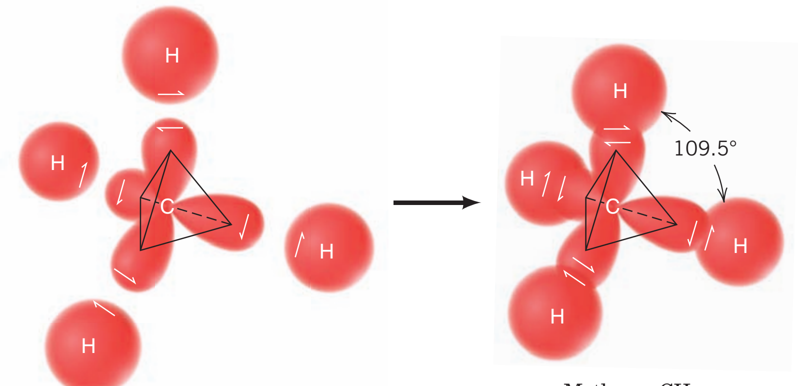


FIGURE 1.13 Hybridization of pure atomic orbitals of a carbon atom to produce sp^3 hybrid orbitals.

- The mathematical result is that the four $2sp^3$ orbitals are oriented at angles of 109.5° with respect to each other. This is precisely the orientation of the four hydrogen atoms of methane. Each H—C—H bond angle is 109.5°.

If, in our imagination, we visualize the hypothetical formation of methane from an sp^3-hybridized carbon atom and four hydrogen atoms, the process might be like that shown in Fig. 1.14. For simplicity we show only the formation of the **bonding molecular orbital** for each carbon–hydrogen bond. We see that an sp^3-hybridized carbon gives a *tetrahedral structure for methane, and one with four equivalent C—H* bonds.

In addition to accounting properly for the shape of methane, the orbital hybridization model also explains the very strong bonds that are formed between carbon and



Methane, CH_4

FIGURE 1.14 The hypothetical formation of methane from an sp^3-hybridized carbon atom and four hydrogen atoms. In orbital hybridization we combine orbitals, *not* electrons. The electrons can then be placed in the hybrid orbitals as necessary for bond formation, but always in accordance with the Pauli principle of no more than two electrons (with opposite spin) in each orbital. In this illustration we have placed one electron in each of the hybrid carbon orbitals. In addition, we have shown only the bonding molecular orbital of each C—H bond because these are the orbitals that contain the electrons in the lowest energy state of the molecule.

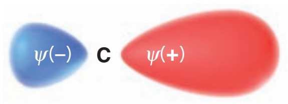


FIGURE 1.15 The shape of an sp^3 orbital.

hydrogen. To see how this is so, consider the shape of an individual sp^3 orbital shown in Fig. 1.15. Because an sp^3 orbital has the character of a *p* orbital, the positive lobe of an sp^3 orbital is large and extends relatively far from the carbon nucleus.

It is the positive lobe of an sp^3 orbital that overlaps with the positive 1*s* orbital of hydrogen to form the bonding molecular orbital of a carbon–hydrogen bond (Fig. 1.16).

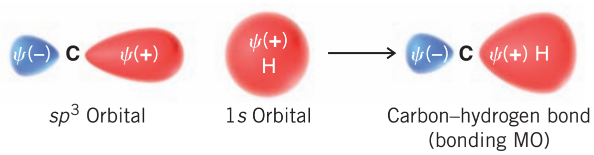


FIGURE 1.16 Formation of a C—H bond.

Because the positive lobe of the sp^3 orbital is large and is extended into space, the overlap between it and the 1*s* orbital of hydrogen is also large, and the resulting carbon–hydrogen bond is quite strong.

The bond formed from the overlap of an sp^3 orbital and a 1*s* orbital is an example of a **sigma (σ) bond** (Fig. 1.17).

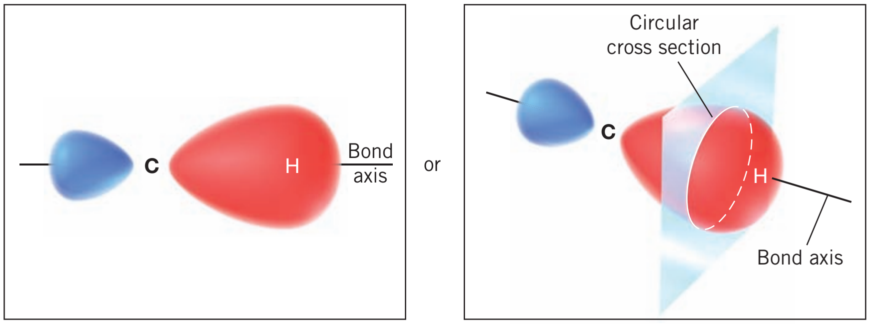


FIGURE 1.17 A σ (sigma) bond.

- A **sigma (σ) bond** has a circularly symmetrical orbital cross section when viewed along the bond between two atoms.
- All purely **single bonds** are sigma bonds.

From this point on we shall often show only the bonding molecular orbitals because they are the ones that contain the electrons when the molecule is in its lowest energy state. Consideration of antibonding orbitals is important when a molecule absorbs light and in explaining certain reactions. We shall point out these instances later.

In Fig. 1.18 we show a calculated structure for methane where the tetrahedral geometry derived from orbital hybridization is clearly apparent.

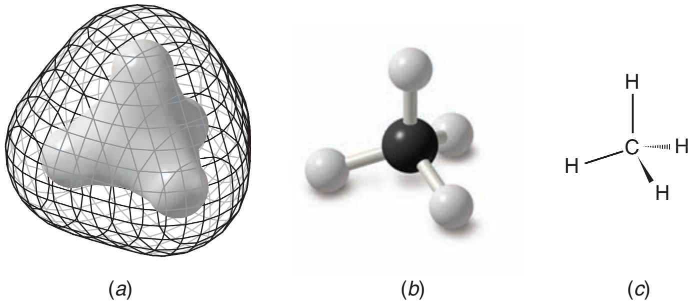


FIGURE 1.18 (*a*) In this structure of methane, based on quantum mechanical calculations, the inner solid surface represents a region of high electron density. High electron density is found in each bonding region. The outer mesh surface represents approximately the furthest extent of overall electron density for the molecule. (*b*) This ball-and-stick model of methane is like the kind you might build with a molecular model kit. (*c*) This structure is how you would draw methane. Ordinary lines are used to show the two bonds that are in the plane of the paper, a solid wedge is used to show the bond that is in front of the paper, and a dashed wedge is used to show the bond that is behind the plane of the paper.

1.12B The Structure of Ethane

The bond angles at the carbon atoms of ethane, and of all alkanes, are also tetrahedral like those in methane. A satisfactory model for ethane can be provided by sp^3-hybridized carbon atoms. Figure 1.19 shows how we might imagine the bonding molecular orbitals of an ethane molecule being constructed from two sp^3-hybridized carbon atoms and six hydrogen atoms.

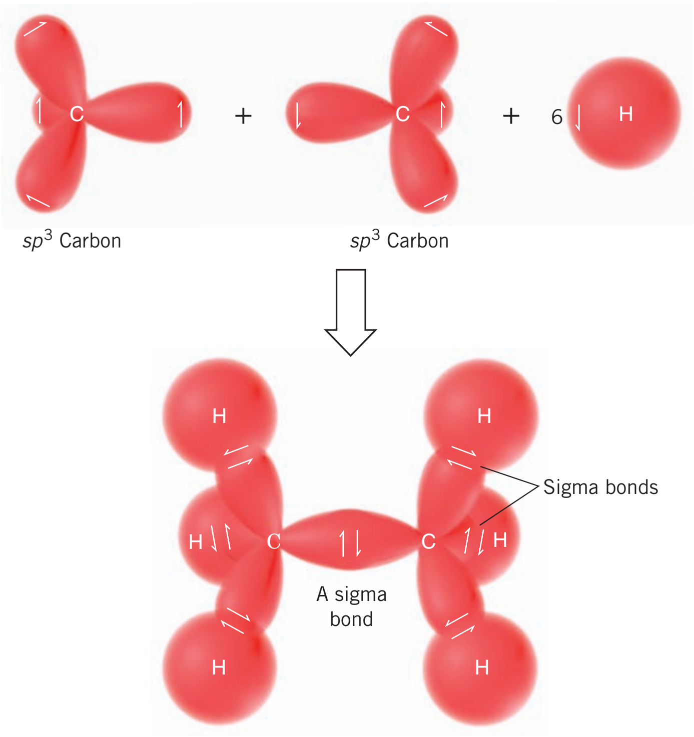


FIGURE 1.19 The hypothetical formation of the bonding molecular orbitals of ethane from two sp^3-hybridized carbon atoms and six hydrogen atoms. All of the bonds are sigma bonds. (Antibonding sigma molecular orbitals—called σ^* orbitals—are formed in each instance as well, but for simplicity these are not shown.)

The carbon–carbon bond of ethane is a *sigma bond* with cylindrical symmetry, formed by two overlapping sp^3 orbitals. (The carbon–hydrogen bonds are also sigma bonds. They are formed from overlapping carbon sp^3 orbitals and hydrogen *s* orbitals.)

- Rotation of groups joined by a single bond does not usually require a large amount of energy.

Consequently, groups joined by single bonds rotate relatively freely with respect to one another. (We discuss this point further in Section 4.8.) In Fig. 1.20 we show a calculated structure for ethane in which the tetrahedral geometry derived from orbital hybridization is clearly apparent.

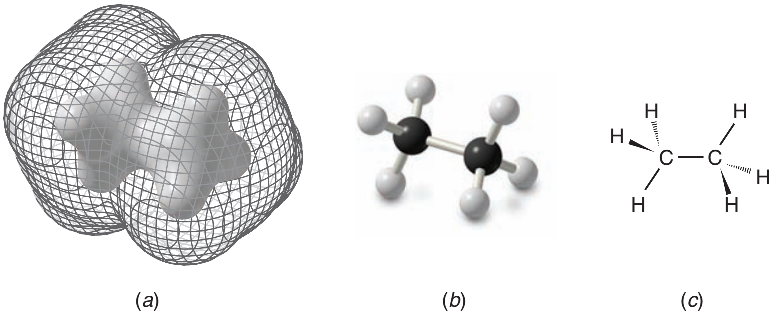
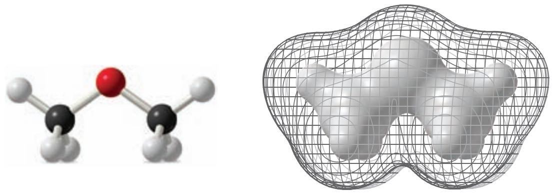


FIGURE 1.20 (*a*) In this structure of ethane, based on quantum mechanical calculations, the inner solid surface represents a region of high electron density. High electron density is found in each bonding region. The outer mesh surface represents approximately the furthest extent of overall electron density for the molecule. (*b*) A ball-and-stick model of ethane, like the kind you might build with a molecular model kit. (*c*) A structural formula for ethane as you would draw it using lines, wedges, and dashed wedges to show in three dimensions its tetrahedral geometry at each carbon.

THE CHEMISTRY OF... Calculated Molecular Models: Electron Density Surfaces

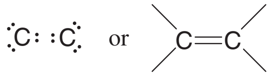
In this book we make frequent use of molecular models derived from quantum mechanical calculations. These models will help us visualize the shapes of molecules as well as understand their properties and reactivity. A useful type of model is one that shows a calculated three-dimensional surface at which a chosen value of electron density is the same all around a molecule, called an **electron density surface**. If we make a plot where the value chosen is for low electron density, the result is a van der Waals surface, the surface that represents approximately the overall shape of a molecule as determined by the furthest extent of its electron cloud. On the other hand, if we make a plot where the value of electron density is relatively high, the resulting surface is one that approximately represents the region of covalent bonding in a molecule. Surfaces of low and high electron density are shown in this box for dimethyl ether. Similar models are shown for methane and ethane in Figs. 1.18 and 1.20.



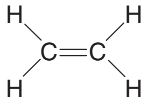
Dimethyl ether

1.13 THE STRUCTURE OF ETHENE (ETHYLENE): *sp*^{2} HYBRIDIZATION

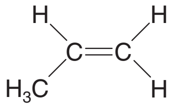
The carbon atoms of many of the molecules that we have considered so far have used their four valence electrons to form four single covalent (sigma) bonds to four other atoms. We find, however, that many important organic compounds exist in which carbon atoms share more than two electrons with another atom. In molecules of these compounds some bonds that are formed are multiple covalent bonds. When two carbon atoms share two pairs of electrons, for example, the result is a carbon–carbon double bond:



Hydrocarbons whose molecules contain a carbon–carbon double bond are called **alkenes**. Ethene (C_2H_4) and propene (C_3H_6) are both alkenes. Ethene is also called ethylene, and propene is sometimes called propylene.



Ethene



Propene

In ethene the only carbon–carbon bond is a double bond. Propene has one carbon–carbon single bond and one carbon–carbon double bond.

The spatial arrangement of the atoms of alkenes is different from that of alkanes. The six atoms of ethene are coplanar, and the arrangement of atoms around each carbon atom is triangular (Fig. 1.21).

- Carbon–carbon double bonds are comprised of *sp*^{2}-hybridized carbon atoms.

The mathematical mixing of orbitals that furnish the ***sp*^{2} orbitals** for our model can be visualized in the way shown in Fig. 1.22. The 2*s* orbital is mathematically mixed (or hybridized) with two of the 2*p* orbitals. (The hybridization procedure applies only to the

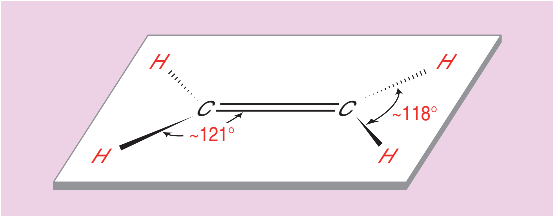


FIGURE 1.21 The structure and bond angles of ethene. The plane of the atoms is perpendicular to the paper. The dashed wedge bonds project behind the plane of the paper, and the solid wedge bonds project in front of the paper.

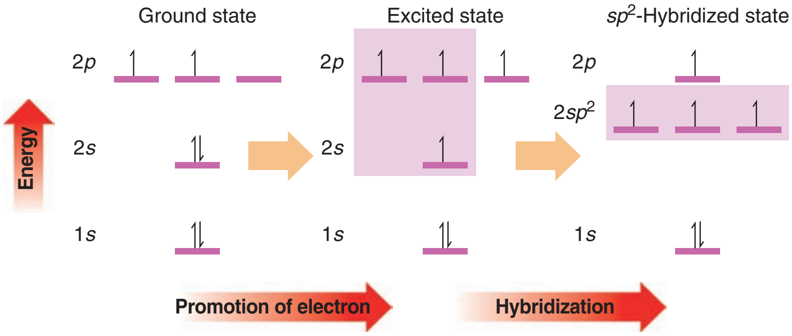


FIGURE 1.22 A process for deriving *sp*^{2}-hybridized carbon atoms.

orbitals, not to the electrons.) One 2*p* orbital is left unhybridized. One electron is then placed in each of the *sp*^{2} hybrid orbitals and one electron remains in the 2*p* orbital.

The three *sp*^{2} orbitals that result from hybridization are directed toward the corners of a regular triangle (with angles of 120° between them). The carbon *p* orbital that is not hybridized is perpendicular to the plane of the triangle formed by the hybrid *sp*^{2} orbitals (Fig. 1.23).

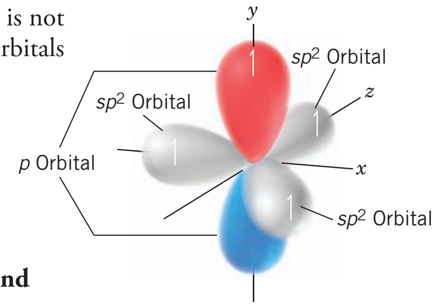


FIGURE 1.23 An *sp*^{2}-hybridized carbon atom.

In our model for ethene (Fig. 1.24) we see the following:

- Two *sp*^{2}-hybridized carbon atoms form a sigma (*σ*) bond between them by overlap of one *sp*^{2} orbital from each carbon. The remaining carbon *sp*^{2} orbitals form *σ* bonds to four hydrogens through overlap with the hydrogen 1*s* orbitals. These five *σ* bonds account for 10 of the 12 valence electrons contributed by the two carbons and four hydrogens, and comprise the ***σ*-bond framework** of the molecule.
- The remaining two bonding electrons are each located in an unhybridized *p* orbital of each carbon. Sideways overlap of these *p* orbitals and sharing of the two electrons between the carbons leads to a **pi (*π*) bond**. The overlap of these orbitals is shown schematically in Fig. 1.25.

The bond angles that we would predict on the basis of *sp*^{2}-hybridized carbon atoms (120° all around) are quite close to the bond angles that are actually found (Fig. 1.21).

We can better visualize how these *p* orbitals interact with each other if we view a structure showing calculated molecular orbitals for ethene (Fig. 1.25). We see that the parallel *p* orbitals *overlap above and below the plane of the σ framework.*

Note the difference in shape of the bonding molecular orbital of a *π* bond as contrasted to that of a *σ* bond. A *σ* bond has cylindrical symmetry about a line connecting the two bonded nuclei. A *π* bond has a nodal plane passing through the two bonded nuclei and between the *π* molecular orbital lobes.

- When two *p* atomic orbitals combine to form a *π* bond, two ***π* molecular orbital** molecular orbitals form: one is a bonding molecular orbital and the other is an **antibonding molecular orbital**.

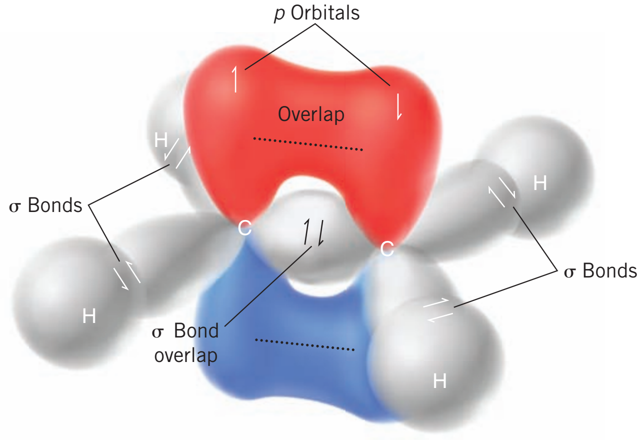


FIGURE 1.24 A model for the bonding molecular orbitals of ethene formed from two *sp*^{2}-hybridized carbon atoms and four hydrogen atoms.

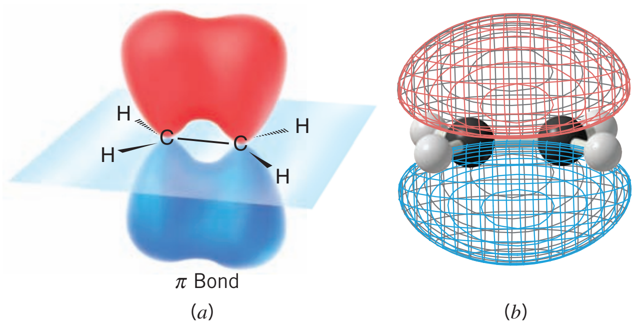


FIGURE 1.25 (*a*) A wedge–dashed wedge formula for the sigma bonds in ethene and a schematic depiction of the overlapping of adjacent *p* orbitals that form the π bond. (*b*) A calculated structure for ethene. The blue and red colors indicate opposite phase signs in each lobe of the π molecular orbital. A ball-and-stick model for the σ bonds in ethene can be seen through the mesh that indicates the π bond.

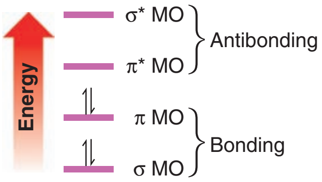
The bonding π molecular orbital results when *p*-orbital lobes of like signs overlap; the antibonding π molecular orbital results when opposite signs overlap (Fig. 1.26).

The bonding π orbital is the lower energy orbital and contains both π electrons (with opposite spins) in the ground state of the molecule. The region of greatest probability of finding the electrons in the bonding π orbital is a region generally situated above and below the plane of the σ-bond framework between the two carbon atoms. The antibonding π* orbital is of higher energy, and it is not occupied by electrons when the molecule is in the ground state. It can become occupied, however, if the molecule absorbs light of the right frequency and an electron is promoted from the lower energy level to the higher one. The antibonding π* orbital has a nodal plane between the two carbon atoms.

- To summarize, a carbon–carbon double bond consists of one σ bond and one π bond.

The σ bond results from two sp^2 orbitals overlapping end to end and is symmetrical about an axis linking the two carbon atoms. The π bond results from a sideways overlap of two *p* orbitals; it has a nodal plane like a *p* orbital. In the ground state the electrons of the π bond are located between the two carbon atoms but generally above and below the plane of the σ-bond framework.

Electrons of the π bond have greater energy than electrons of the σ bond. The relative energies of the σ and π molecular orbitals (with the electrons in the ground state) are shown in the margin diagram. The σ* orbital is the antibonding **sigma orbital**.



The relative energies of electrons involved in σ and π bonds

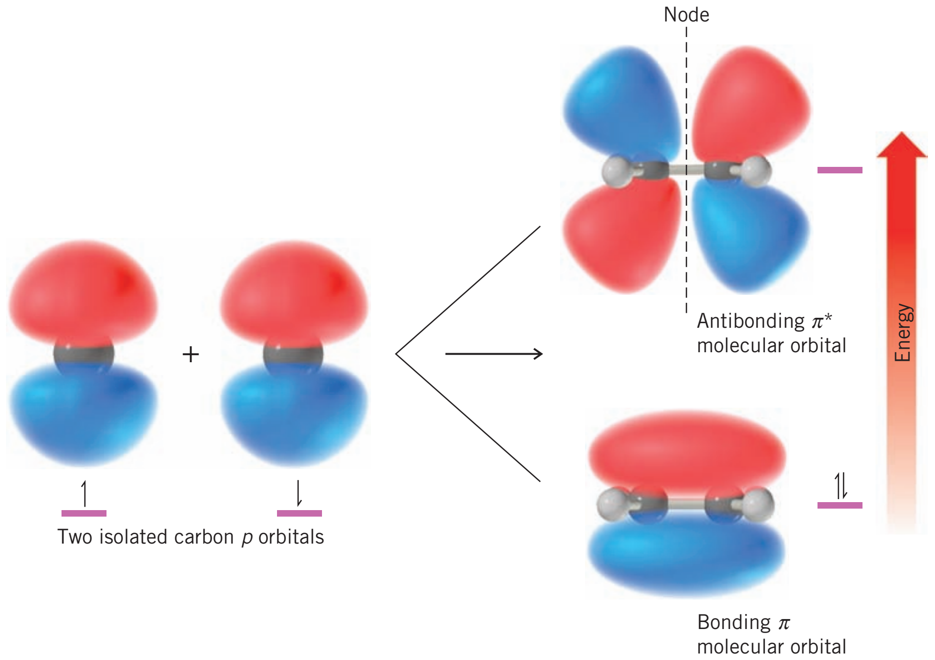


FIGURE 1.26 How two isolated carbon *p* orbitals combine to form two π (pi) molecular orbitals. The bonding MO is of lower energy. The higher energy antibonding MO contains an additional node. Both orbitals have a node in the plane containing the C and H atoms.

1.13A Restricted Rotation and the Double Bond

The σ–π model for the carbon–carbon double bond also accounts for an important property of the **double bond**:

- There is a large energy barrier to rotation associated with groups joined by a double bond.

Maximum overlap between the *p* orbitals of a π bond occurs when the axes of the *p* orbitals are exactly parallel. Rotating one carbon of the double bond 90° (Fig. 1.27) breaks the π bond, for then the axes of the *p* orbitals are perpendicular and there is no net overlap between them. Estimates based on thermochemical calculations indicate that the strength of the π bond is 264 kJ mol^{-1}. This, then, is the barrier to rotation of the double bond. It is markedly higher than the rotational barrier of groups joined by carbon–carbon single bonds (13–26 kJ mol^{-1}). While groups joined by single bonds rotate relatively freely at room temperature, those joined by double bonds do not.

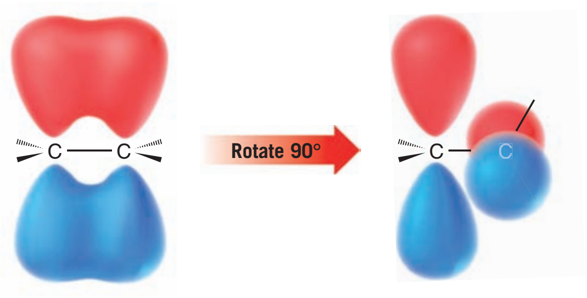
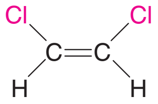


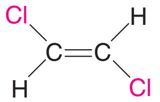
FIGURE 1.27 A stylized depiction of how rotation of a carbon atom of a double bond through an angle of 90° results in breaking of the π bond.

1.13B Cis–Trans Isomerism

Restricted rotation of groups joined by a double bond causes a new type of isomerism that we illustrate with the two dichloroethenes written as the following structures:



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



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

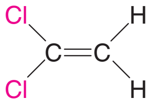
- These two compounds are isomers; they are different compounds that have the same molecular formula.

We can tell that they are different compounds by trying to place a model of one compound on a model of the other so that all parts coincide, that is, to try to **superpose** one on the other. We find that it cannot be done. Had one been **superposable** on the other, all parts of one model would correspond in three dimensions exactly with the other model. (*The notion of superposition is different from simply superimposing one thing on another*. The latter means only to lay one on the other without the necessary condition that all parts coincide.)

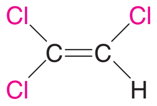
- We indicate that they are different isomers by attaching the prefix cis or trans to their names (*cis*, Latin: on this side; *trans*, Latin: across).

cis-1,2-Dichloroethene and *trans*-1,2-dichloroethene are not constitutional isomers because the connectivity of the atoms is the same in each. The two compounds ***differ only in the arrangement of their atoms in space***. Isomers of this kind are classified formally as **stereoisomers**, but often they are called simply cis–trans isomers. (We shall study stereoisomerism in detail in Chapters 4 and 5.)

The structural requirements for **cis–trans isomerism** will become clear if we consider a few additional examples. 1,1-Dichloroethene and 1,1,2-trichloroethene do not show this type of isomerism.

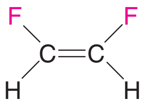


1,1-Dichloroethene
(no cis-trans isomerism)

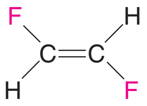


1,1,2-Trichloroethene
(no cis-trans isomerism)

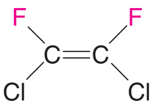
1,2-Difluoroethene and 1,2-dichloro-1,2-difluoroethene do exist as cis–trans isomers. Notice that we designate the isomer with two identical groups on the same side as being cis:



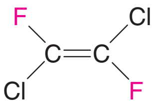
***cis*-1,2-Difluoroethene**



***trans*-1,2-Difluoroethene**



***cis*-1,2-Dichloro-1,2-difluoroethene**



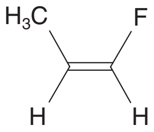
***trans*-1,2-Dichloro-1,2-difluoroethene**

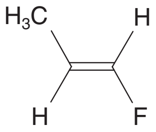
Clearly, then, ***cis–trans isomerism of this type is not possible if one carbon atom of the double bond bears two identical groups***.

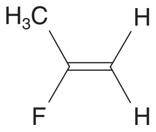
SOLVED PROBLEM 1.12

Write structures of all the isomers of C_2H_5F.

ANSWER: Taking into account cis–trans isomerism and the possibility of a ring we have the following four possibilities.







PRACTICE PROBLEM 1.22 Which of the following alkenes can exist as cis–trans isomers? Write their structures. Build hand-held models to prove that one isomer is not superposable on the other.

(a) $CH_2{=}CHCH_2CH_3$ **(c)** $CH_2{=}C(CH_3)_2$

(b) $CH_3CH{=}CHCH_3$ **(d)** $CH_3CH_2CH{=}CHCl$

1.14 THE STRUCTURE OF ETHYNE (ACETYLENE): *sp* HYBRIDIZATION

Hydrocarbons in which two carbon atoms share three pairs of electrons between them, and are thus bonded by a triple bond, are called **alkynes**. The two simplest alkynes are ethyne and propyne.

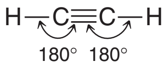
$H{-}C{\equiv}C{-}H$

Ethyne
(acetylene)
(C_2H_2)

$CH_3{-}C{\equiv}C{-}H$

Propyne
(C_3H_4)

Ethyne, a compound that is also called **acetylene**, consists of a linear arrangement of atoms. The H—C≡C bond angles of ethyne molecules are 180°:



We can account for the structure of ethyne on the basis of orbital hybridization as we did for ethane and ethene. In our model for ethane (Section 1.12B) we saw that the carbon orbitals are sp^3 hybridized, and in our model for ethene (Section 1.13) we saw that they are sp^2 hybridized. In our model for ethyne we shall see that the carbon atoms are *sp hybridized*.

The mathematical process for obtaining the *sp* hybrid orbitals of ethyne can be visualized in the following way (Fig. 1.28).

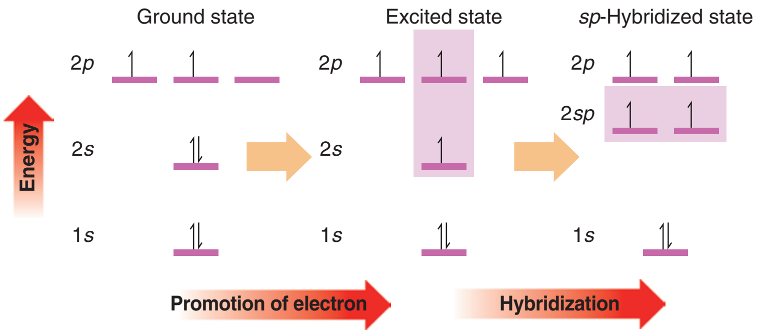


FIGURE 1.28 A process for deriving *sp*-hybridized carbon atoms.

- The 2*s* orbital and one 2*p* orbital of carbon are hybridized to form two ***sp* orbitals**.
- The remaining two 2*p* orbitals are not hybridized.

Calculations show that the *sp* hybrid orbitals have their large positive lobes oriented at an angle of 180° with respect to each other. The two 2*p* orbitals that were not hybridized are each perpendicular to the axis that passes through the center of the two *sp* orbitals (Fig. 1.29). We place one electron in each orbital.

We envision the bonding molecular orbitals of ethyne being formed in the following way (Fig. 1.30).

- Two carbon atoms overlap *sp* orbitals to form a sigma bond between them (this is one bond of the triple bond). The remaining two *sp* orbitals at each carbon atom overlap with *s* orbitals from hydrogen atoms to produce two sigma C—H bonds.

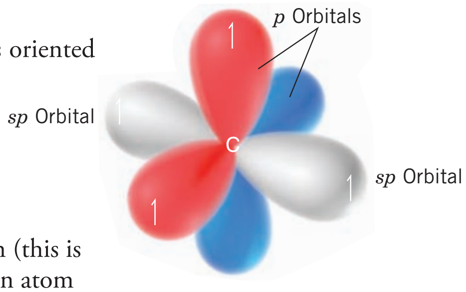


FIGURE 1.29 An *sp*-hybridized carbon atom.

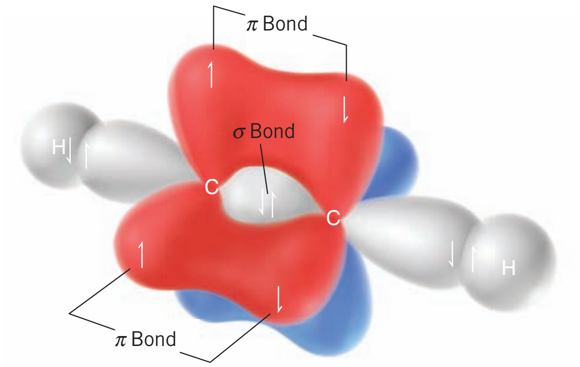
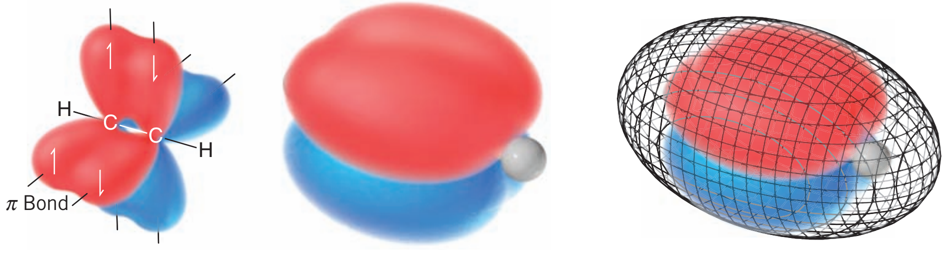


FIGURE 1.30 Formation of the bonding molecular orbitals of ethyne from two *sp*-hybridized carbon atoms and two hydrogen atoms. (Antibonding orbitals are formed as well, but these have been omitted for simplicity.)



(*a*) (*b*) (*c*)

FIGURE 1.31 (*a*) The structure of ethyne (acetylene) showing the sigma-bond framework and a schematic depiction of the two pairs of *p* orbitals that overlap to form the two π bonds in ethyne. (*b*) A structure of ethyne showing calculated π molecular orbitals. Two pairs of π molecular orbital lobes are present, one pair for each π bond. The red and blue lobes in each π bond represent opposite phase signs. The hydrogen atoms of ethyne (white spheres) can be seen at each end of the structure (the carbon atoms are hidden by the molecular orbitals). (*c*) The mesh surface in this structure represents approximately the furthest extent of overall electron density in ethyne. Note that the overall electron density (but not the π-bonding electrons) extends over both hydrogen atoms.

- The two *p* orbitals on each carbon atom also overlap side to side to form two π bonds. These are the other two bonds of the triple bond.
- The carbon–carbon triple bond consists of two π bonds and one σ bond.

Structures for ethyne based on calculated molecular orbitals and electron density are shown in Fig. 1.31. Circular symmetry exists along the length of a triple bond (Fig. 1.31*b*). As a result, there is no restriction of rotation for groups joined by a triple bond (as compared with alkenes), and if rotation would occur, no new compound would form.

1.14A Bond Lengths of Ethyne, Ethene, and Ethane

The carbon–carbon triple bond of ethyne is shorter than the carbon–carbon double bond of ethene, which in turn is shorter than the carbon–carbon single bond of ethane. The reason is that **bond lengths** are affected by the hybridization states of the carbon atoms involved.

- The greater the *s* orbital character in one or both atoms, the shorter is the bond. This is because *s* orbitals are spherical and have more electron density closer to the nucleus than do *p* orbitals.
- The greater the *p* orbital character in one or both atoms, the longer is the bond. This is because *p* orbitals are lobe-shaped with electron density extending away from the nucleus.

In terms of hybrid orbitals, an *sp* hybrid orbital has 50% *s* character and 50% *p* character. An sp^2 hybrid orbital has 33% *s* character and 67% *p* character. An sp^3 hybrid orbital has 25% *s* character and 75% *p* character. The overall trend, therefore, is as follows:

- Bonds involving *sp* hybrids are shorter than those involving sp^2 hybrids, which are shorter than those involving sp^3 hybrids. This trend holds true for both C—C and C—H bonds.

The bond lengths and bond angles of ethyne, ethene, and ethane are summarized in Fig. 1.32.

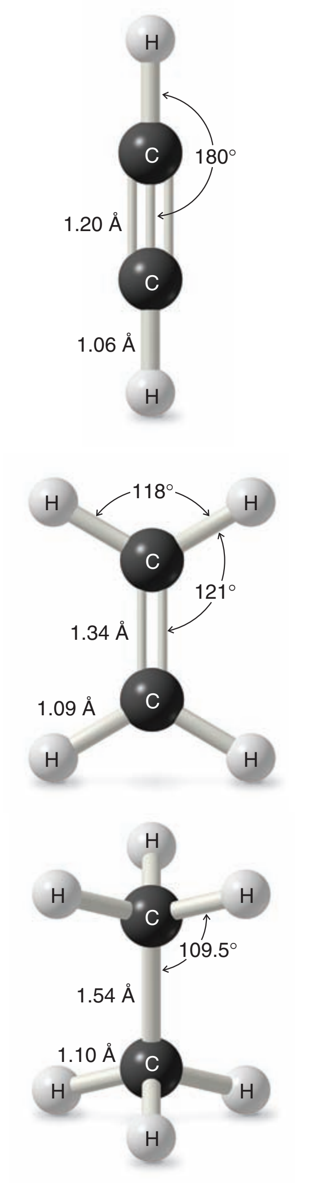
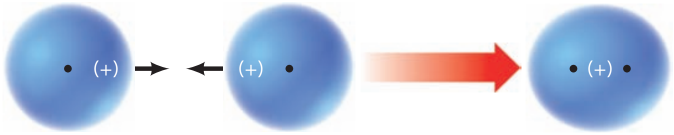


FIGURE 1.32 Bond angles and bond lengths of ethyne, ethene, and ethane.

1.15 A SUMMARY OF IMPORTANT CONCEPTS THAT COME FROM QUANTUM MECHANICS

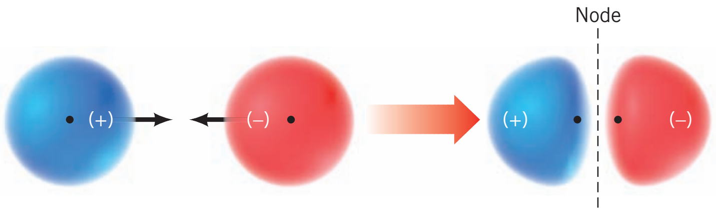
1. An **atomic orbital (AO)** corresponds to a region of space about the nucleus of a single atom where there is a high probability of finding an electron. Atomic orbitals called *s* orbitals are spherical; those called *p* orbitals are like two almost-tangent spheres. Orbitals can hold a maximum of two electrons when their spins are paired. Orbitals are described by the square of a wave function, ψ^2, and each orbital has a characteristic energy. The phase signs associated with an orbital may be + or −.
2. When atomic orbitals overlap, they combine to form **molecular orbitals (MOs)**. Molecular orbitals correspond to regions of space encompassing two (or more) nuclei where electrons are to be found. Like atomic orbitals, molecular orbitals can hold up to two electrons if their spins are paired.
3. When atomic orbitals with the same phase sign interact, they combine to form a **bonding molecular orbital**:



Bonding molecular orbital

The electron probability density of a bonding molecular orbital is large in the region of space between the two nuclei where the negative electrons hold the positive nuclei together.

4. An **antibonding molecular orbital** forms when orbitals of opposite phase sign overlap:



An antibonding orbital has higher energy than a bonding orbital. The electron probability density of the region between the nuclei is small and it contains a **node**—a region where $\psi = 0$. Thus, having electrons in an antibonding orbital does not help hold the nuclei together. The internuclear repulsions tend to make them fly apart.

5. The **energy of electrons** in a bonding *molecular* orbital is less than the energy of the electrons in their separate *atomic* orbitals. The energy of electrons in an antibonding orbital is greater than that of electrons in their separate atomic orbitals.
6. The **number of molecular orbitals** always equals the number of atomic orbitals from which they are formed. Combining two atomic orbitals will always yield two molecular orbitals—one bonding and one antibonding.
7. **Hybrid atomic orbitals** are obtained by mixing (hybridizing) the wave functions for orbitals of different types (i.e., *s* and *p* orbitals) but from the same atom.
8. Hybridizing three *p* orbitals with one *s* orbital yields four **sp^3 orbitals**. Atoms that are sp^3 hybridized direct the axes of their four sp^3 orbitals toward the corners of a tetrahedron. The carbon of methane is sp^3 hybridized and **tetrahedral**.
9. Hybridizing two *p* orbitals with one *s* orbital yields three **sp^2 orbitals**. Atoms that are sp^2 hybridized point the axes of their three sp^2 orbitals toward the corners of an equilateral triangle. The carbon atoms of ethene are sp^2 hybridized and **trigonal planar**.

Helpful Hint

A summary of sp^3, sp^2, and *sp* hybrid orbital geometries.

10. Hybridizing one *p* orbital with one *s* orbital yields two ***sp* orbitals**. Atoms that are *sp* hybridized orient the axes of their two *sp* orbitals in opposite directions (at an angle of 180°). The carbon atoms of ethyne are *sp* hybridized and ethyne is a **linear** molecule.
11. A **sigma (σ) bond** (a type of single bond) is one in which the electron density has circular symmetry when viewed along the bond axis. In general, the skeletons of organic molecules are constructed of atoms linked by sigma bonds.
12. A **pi (π) bond**, part of double and triple carbon–carbon bonds, is one in which the electron densities of two adjacent parallel *p* orbitals overlap sideways to form a bonding pi molecular orbital.

1.16 HOW TO PREDICT MOLECULAR GEOMETRY: THE VALENCE SHELL ELECTRON PAIR REPULSION MODEL

We can predict the arrangement of atoms in molecules and ions on the basis of a relatively simple idea called the **valence shell electron pair repulsion (VSEPR) model**.

We apply the **VSEPR** model in the following way:

1. We consider molecules (or ions) in which the central atom is covalently bonded to two or more atoms or groups.
2. We consider all of the valence electron pairs of the central atom—both those that are shared in covalent bonds, called **bonding pairs**, and those that are unshared, called **nonbonding pairs** or **unshared pairs** or **lone pairs**.
3. Because electron pairs repel each other, the electron pairs of the valence shell tend to stay as far apart as possible. The repulsion between nonbonding pairs is generally greater than that between bonding pairs.
4. We arrive at the *geometry* of the molecule by considering all of the electron pairs, bonding and nonbonding, but we describe the *shape* of the molecule or ion by referring to the positions of the nuclei (or atoms) and not by the positions of the electron pairs.

In the following sections we consider several examples.

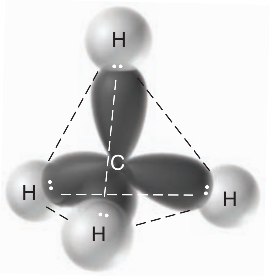


FIGURE 1.33 A tetrahedral shape for methane allows the maximum separation of the four bonding electron pairs.

1.16A Methane

The valence shell of methane contains four pairs of bonding electrons. Only a tetrahedral orientation will allow four pairs of electrons to have equal and maximum possible separation from each other (Fig. 1.33). Any other orientation, for example, a square planar arrangement, places some electron pairs closer together than others. Thus, methane has a tetrahedral shape.

The bond angles for any atom that has a regular tetrahedral structure are 109.5°. A representation of these angles in methane is shown in Fig. 1.34.

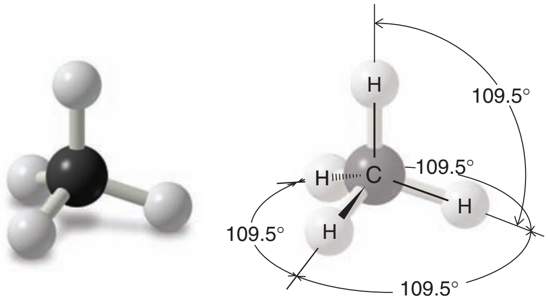


FIGURE 1.34 The bond angles of methane are 109.5°.

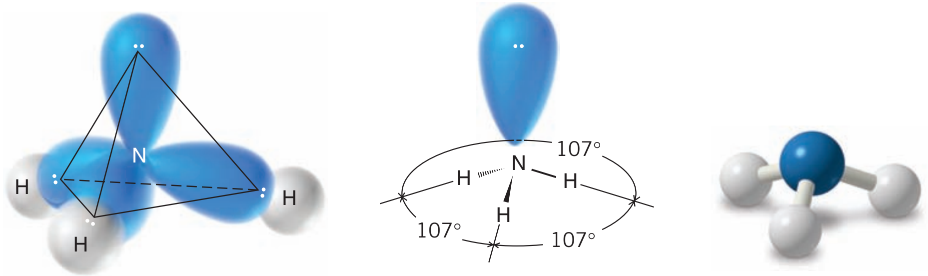


FIGURE 1.35 The tetrahedral arrangement of the electron pairs of an ammonia molecule that results when the nonbonding electron pair is considered to occupy one corner. This arrangement of electron pairs explains the trigonal pyramidal shape of the NH_3 molecule. Ball-and-stick models do not show unshared electrons.

1.16B Ammonia

The shape of a molecule of ammonia (NH_3) is a **trigonal pyramid**. There are three bonding pairs of electrons and one nonbonding pair. The bond angles in a molecule of ammonia are 107°, a value very close to the tetrahedral angle (109.5°). We can write a general tetrahedral structure for the electron pairs of ammonia by placing the nonbonding pair at one corner (Fig. 1.35). A *tetrahedral arrangement* of the electron pairs explains the *trigonal pyramidal* arrangement of the four atoms. The bond angles are 107° (not 109.5°) because the nonbonding pair occupies more space than the bonding pairs.

PRACTICE PROBLEM 1.23

What do the bond angles of ammonia suggest about the hybridization state of the nitrogen atom of ammonia?

1.16C Water

A molecule of water has an **angular** or **bent** shape. The H—O—H bond angle in a molecule of water is 104.5°, an angle that is also quite close to the 109.5° bond angles of methane.

We can write a general tetrahedral structure for the electron pairs of a molecule of water *if we place the two bonding pairs of electrons and the two nonbonding electron pairs at the corners of the tetrahedron*. Such a structure is shown in Fig. 1.36. A *tetrahedral arrangement* of the electron pairs accounts for the *angular arrangement* of the three atoms. The bond angle is less than 109.5° because the nonbonding pairs are effectively "larger" than the bonding pairs and, therefore, the structure is not perfectly tetrahedral.

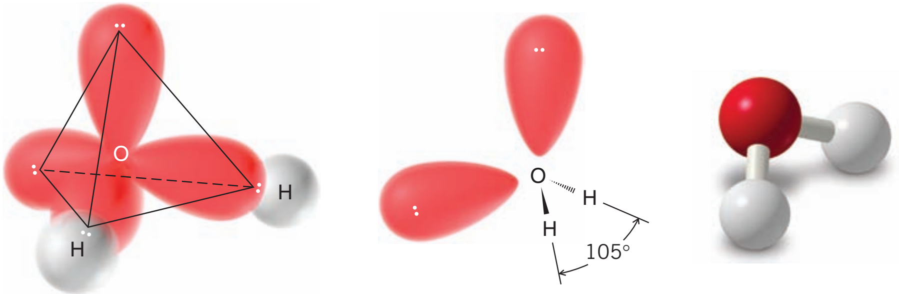


FIGURE 1.36 An approximately tetrahedral arrangement of the electron pairs of a molecule of water that results when the pairs of nonbonding electrons are considered to occupy corners. This arrangement accounts for the angular shape of the H_2O molecule.

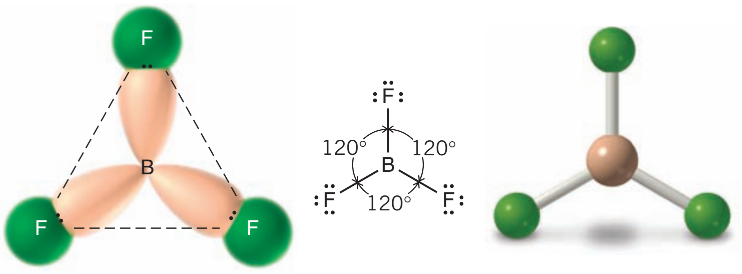
PRACTICE PROBLEM 1.24

What do the bond angles of water suggest about the hybridization state of the oxygen atom of water?

1.16D Boron Trifluoride

Boron, a group IIIA element, has only three valence electrons. In the compound boron trifluoride (BF_3) these three electrons are shared with three fluorine atoms. As a result, the boron atom in BF_3 has only six electrons (three bonding pairs) around it. Maximum separation of three bonding pairs occurs when they occupy the corners of an equilateral

FIGURE 1.37 The triangular (trigonal planar) shape of boron trifluoride maximally separates the three bonding pairs.

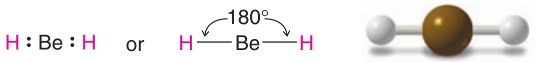


triangle. Consequently, in the boron trifluoride molecule the three fluorine atoms lie in a plane at the corners of an equilateral triangle (Fig. 1.37). Boron trifluoride is said to have a *trigonal planar structure*. The bond angles are 120°.

PRACTICE PROBLEM 1.25 What do the bond angles of boron trifluoride suggest about the hybridization state of the boron atom?

1.16E Beryllium Hydride

The central beryllium atom of BeH_2 has only two electron pairs around it; both electron pairs are bonding pairs. These two pairs are maximally separated when they are on opposite sides of the central atom, as shown in the following structures. This arrangement of the electron pairs accounts for the *linear geometry* of the BeH_2 molecule and its bond angle of 180°.



Linear geometry of BeH_2

PRACTICE PROBLEM 1.26 What do the bond angles of beryllium hydride suggest about the hybridization state of the beryllium atom?

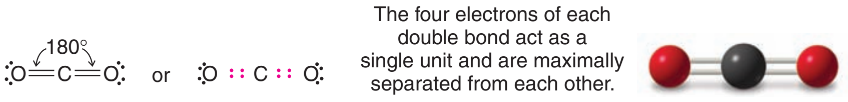
PRACTICE PROBLEM 1.27 Use VSEPR theory to predict the geometry of each of the following molecules and ions:

(a) $\overset{-}{B}H_4$
(b) BeF_2
(c) $\overset{+}{N}H_4$
(d) H_2S
(e) BH_3
(f) CF_4
(g) SiF_4
(h) $\overset{-}{:}CCl_3$

1.16F Carbon Dioxide

The VSEPR method can also be used to predict the shapes of molecules containing multiple bonds if we assume that *all of the electrons of a multiple bond act as though they were a single unit* and, therefore, are located in the region of space between the two atoms joined by a multiple bond.

This principle can be illustrated with the structure of a molecule of carbon dioxide (CO_2). The central carbon atom of carbon dioxide is bonded to each oxygen atom by a double bond. Carbon dioxide is known to have a linear shape; the bond angle is 180°.



The four electrons of each double bond act as a single unit and are maximally separated from each other.

Such a structure is consistent with a maximum separation of the two groups of four bonding electrons. The nonbonding pairs associated with the oxygen atoms have no effect on the shape.

TABLE 1.3 SHAPES OF MOLECULES AND IONS FROM VSEPR THEORY

Number of Electron Pairs at Central Atom					
Bonding	**Nonbonding**	**Total**	**Hybridization State of Central Atom**	**Shape of Molecule or Ion**[a]	**Examples**
2	0	2	*sp*	Linear	BeH_2
3	0	3	sp^2	Trigonal planar	BF_3, $\overset{+}{C}H_3$
4	0	4	sp^3	Tetrahedral	CH_4, $\overset{+}{N}H_4$
3	1	4	$\sim sp^3$	Trigonal pyramidal	NH_3, $\overset{-}{C}H_3$
2	2	4	$\sim sp^3$	Angular	H_2O

[a] Referring to positions of atoms and excluding nonbonding pairs.

PRACTICE PROBLEM 1.28

Predict the bond angles of

(a) $F_2C{=}CF_2$ **(b)** $CH_3C{\equiv}CCH_3$ **(c)** $HC{\equiv}N$

The shapes of several simple molecules and ions as predicted by VSEPR theory are shown in Table 1.3. In this table we have also included the hybridization state of the central atom.

1.17 APPLICATIONS OF BASIC PRINCIPLES

Throughout the early chapters of this book we review certain basic principles that underlie and explain much of the chemistry we shall be studying. Consider the following principles and how they apply in this chapter.

Opposite Charges Attract We see this principle operating in our explanations for covalent and ionic bonds (Section 1.3A). It is the attraction of the *positively* charged nuclei for the *negatively* charged electrons that underlies our explanation for the covalent bond. It is the attraction of the oppositely charged ions in crystals that explains the ionic bond.

Like Charges Repel It is the repulsion of the electrons in covalent bonds of the valence shell of a molecule that is central to the valence shell electron pair repulsion model for explaining molecular geometry. And, although it is not so obvious, this same factor underlies the explanations of molecular geometry that come from orbital hybridization because these repulsions are taken into account in calculating the orientations of the hybrid orbitals.

Nature Tends toward States of Lower Potential Energy This principle explains so much of the world around us. It explains why water flows downhill: the potential energy of the water at the bottom of the hill is lower than that at the top. (We say that water is in a more stable state at the bottom.) This principle underlies the aufbau principle (Section 1.10A): in its lowest energy state, the electrons of an atom occupy the lowest energy orbitals available [but Hund's rule still applies, as well as the Pauli exclusion principle (Section 1.10A), allowing only two electrons per orbital]. Similarly in molecular orbital theory (Section 1.11), electrons fill lower energy bonding molecular orbitals first because this gives the molecule lower potential energy (or greater stability). Energy has to be provided to move an electron to a higher orbital and provide an excited (less stable) state.

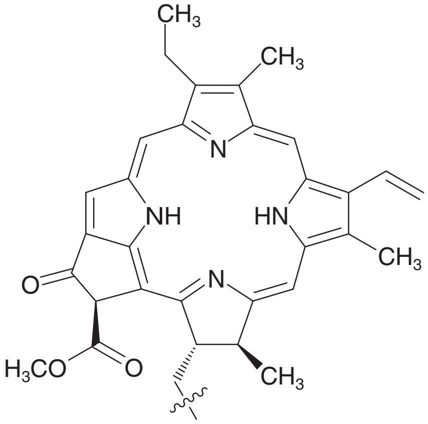
Orbital Overlap Stabilizes Molecules This principle is part of our explanation for covalent bonds. When orbitals of the same phase from different nuclei overlap, the electrons in these orbitals can be shared by both nuclei, resulting in stabilization. The result is a covalent bond.

WHY Do These Topics Matter?]

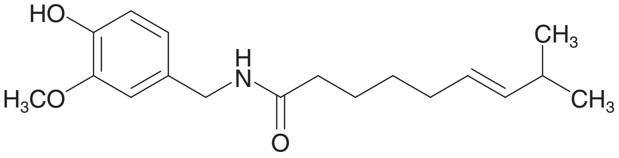
NATURAL PRODUCTS THAT CAN TREAT DISEASE

Everywhere on Earth, organisms make organic molecules comprised almost exclusively of carbon, hydrogen, nitrogen, and oxygen. Sometimes a few slightly more exotic atoms, such as halogens and sulfur, are present. Globally, these compounds aid in day-to-day functioning of these organisms and/or their survival against predators. Organic molecules include the chlorophyll in green plants, which harnesses the energy of sunlight; vitamin C is synthesized by citrus trees, protecting them against oxidative stress; capsaicin, a molecule synthesized by pepper plants (and makes peppers taste hot), serves to ward off insects and birds that might try to eat them; salicylic acid, made by willow trees, is a signaling hormone; lovastatin, found in oyster mushrooms, protects against bacterial attacks.

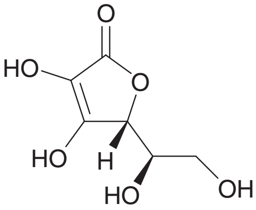
Image Source



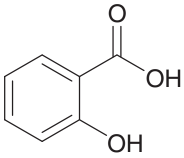
Chlorophyll core



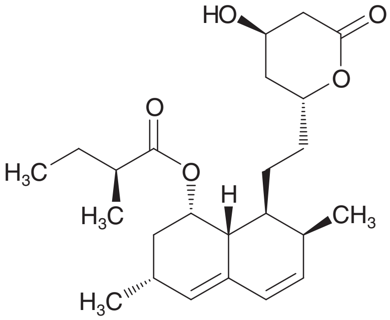
Capsaicin



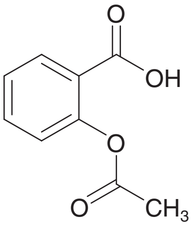
Vitamin C



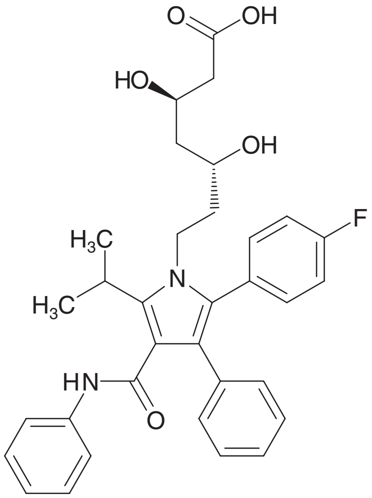
Salicylic acid



Lovastatin



Aspirin



Lipitor

These compounds are all natural products, and many advances in modern society are the result of their study and use. Capsaicin, it turns out, is an effective analgesic. It can modulate pain when applied to the skin and is currently sold under the tradename Capzacin. Salicylic acid is a painkiller as well as an anti-acne medication, while lovastatin is used as a drug to decrease levels of cholesterol in human blood. The power of modern organic chemistry lies in the ability to take such molecules, sometimes found in trace quantities in nature, and make them from readily available and inexpensive starting materials on a large scale so that all members of society can benefit from them. For instance, although we can obtain vitamin C from eating certain fruits, chemists can make large quantities in the laboratory for use in daily supplements; while some may think that "natural" vitamin C is healthier, the "synthetic" compound is equally effective since they are exactly the same chemically.

Perhaps more important, organic chemistry also provides the opportunity to change the structures of these and other natural products to make molecules with different, and potentially even more impressive, properties. For example, the addition of a few atoms to salicylic acid through a chemical reaction is what led to the discovery of aspirin (see Chapter 17), a molecule with far greater potency as a painkiller and fewer side effects than nature's compound. Similarly, scientists at Parke–Davis Warner–Lambert (now Pfizer) used the structure and activity of lovastatin as inspiration to develop Lipitor, a molecule that has saved countless lives by lowering levels of cholesterol in human serum. In fact, of the top 20 drugs based on gross sales, slightly over half are either natural products or their derivatives.

To learn more about these topics, see:

1. Nicolaou, K. C.; Montagnon, T. *Molecules that Changed the World*. Wiley-VCH: Weinheim, **2008**, p. 366.
2. Nicolaou, K. C.; Sorensen, E. J.; Winssinger, N, "The Art and Science of Organic and Natural Products Synthesis" in *J. Chem. Educ*. **1998**, *75*, 1225–1258.

SUMMARY AND REVIEW TOOLS

In Chapter 1 you have studied concepts and skills that are absolutely essential to your success in organic chemistry. You should now be able to use the periodic table to determine the number of valence electrons an atom has in its neutral state or as an ion. You should be able to use the periodic table to compare the relative electronegativity of one element with another, and determine the formal charge of an atom or ion. Electronegativity and formal charge are key concepts in organic chemistry.

You should be able to draw chemical formulas that show all of the valence electrons in a molecule (Lewis structures), using lines for bonds and dots to show unshared electrons. You should be proficient in representing structures as dash structural formulas, condensed structural formulas, and bond-line structural formulas. In particular, the more quickly you become skilled at using and interpreting bond-line formulas, the faster you will be able to process structural information in organic chemistry. You have also learned about resonance structures, the use of which will help us in understanding a variety of concepts in later chapters.

Last, you have learned to predict the three-dimensional structure of molecules using the valence shell electron pair repulsion (VSEPR) model and molecular orbital (MO) theory. An ability to predict three-dimensional structure is critical to understanding the properties and reactivity of molecules.

We encourage you to do all of the problems that your instructor has assigned. We also recommend that you use the summary and review tools in each chapter, such as the concept map that follows. Concept maps can help you see the flow of concepts in a chapter and also help remind you of key points. In fact, we encourage you to build your own concept maps for review when the opportunity arises.

Work especially hard to solidify your knowledge from this and other early chapters in the book. These chapters have everything to do with helping you learn basic tools you need for success throughout organic chemistry.

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.

ELECTRON CONFIGURATION

1.29 Which of the following ions possess the electron configuration of a noble gas?

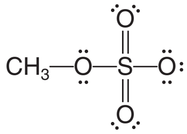
(a) Na^+ **(b)** Cl^- **(c)** F^+ **(d)** H^- **(e)** Ca^{2+} **(f)** S^{2-} **(g)** O^{2-} **(h)** Br^+

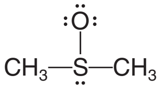
LEWIS STRUCTURES

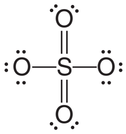
1.30 Write a Lewis structure for each of the following:

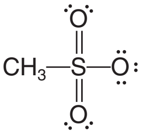
(a) $SOCl_2$ **(b)** $POCl_3$ **(c)** PCl_5 **(d)** $HONO_2$ (HNO_3)

1.31 Give the formal charge (if one exists) on each atom of the following:

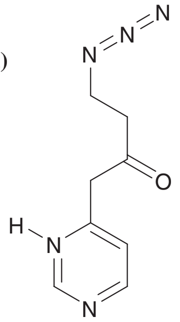
(a)

$CH_3-\underset{..}{\ddot{O}}-\overset{\overset{\ddot{O}}{\|}}{\underset{\underset{\ddot{O}}{\|}}{S}}-\underset{..}{\ddot{O}}:$

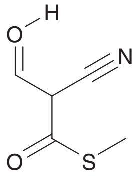
(b)

$CH_3-\overset{\overset{:\ddot{O}:}{|}}{\underset{..}{S}}-CH_3$

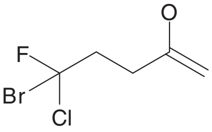
(c)

$:\underset{..}{\ddot{O}}-\overset{\overset{\ddot{O}}{\|}}{\underset{\underset{\ddot{O}}{\|}}{S}}-\underset{..}{\ddot{O}}:$

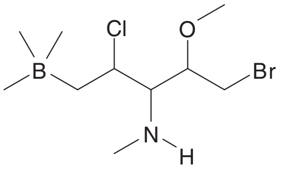
(d)

$CH_3-\overset{\overset{\ddot{O}}{\|}}{\underset{\underset{\ddot{O}}{\|}}{S}}-\underset{..}{\ddot{O}}:$

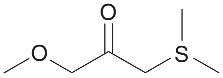
1.32 Add any unshared electrons to give each element an octet in its valence shell in the formulas below and indicate any formal charges. Note that all of the hydrogen atoms that are attached to heteroatoms have been drawn if they are present.

(a)


(b)


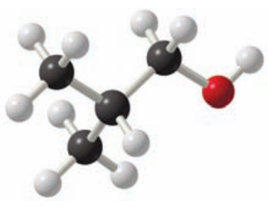
(c)


(d)


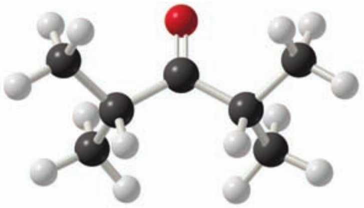
(e)


STRUCTURAL FORMULAS AND ISOMERISM

1.33 Write a condensed structural formula for each compound given here.



(a)



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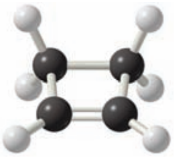
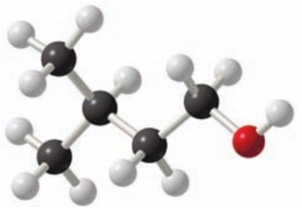


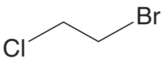
(c)

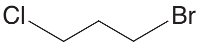


(d)

1.34 What is the molecular formula for each of the compounds given in Exercise 1.33?

1.35 Consider each pair of structural formulas that follow and state whether the two formulas represent the same compound, whether they represent different compounds that are constitutional isomers of each other, or whether they represent different compounds that are not isomeric.

(a)


and


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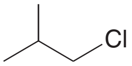
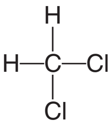
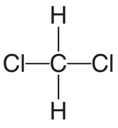
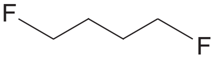
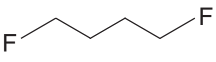
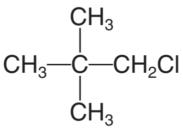
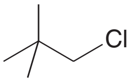


and $ClCH_2CH(CH_3)_2$

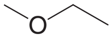
(c)

$H-\overset{\overset{H}{|}}{\underset{\underset{Cl}{|}}{C}}-Cl$
and

$Cl-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-Cl$

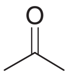
(d)


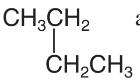
and


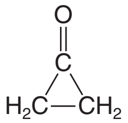
(e)

$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2Cl$
and


(f) $CH_2{=}CHCH_2CH_3$ and

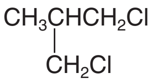

(g)


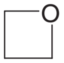
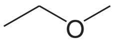
and


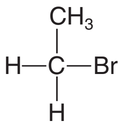
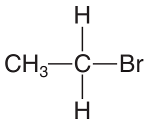
(h)

$\underset{\underset{CH_2CH_3}{|}}{CH_3CH_2}$
and

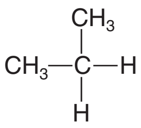
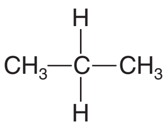

(i) $CH_3OCH_2CH_3$ and 

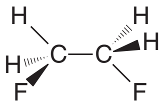
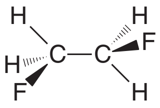
(j) $CH_2ClCHClCH_3$ and $CH_3CHClCH_2Cl$

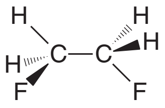
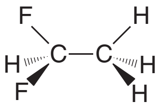
(k) $CH_3CH_2CHClCH_2Cl$ and 
$\mathrm{CH_3\underset{CH_2Cl}{CH}CH_2Cl}$

(l)  and 

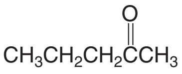
(m) 
$\mathrm{H-\overset{CH_3}{\underset{H}{C}}-Br}$
and 
$\mathrm{CH_3-\overset{H}{\underset{H}{C}}-Br}$

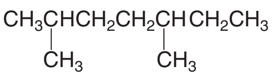
(n) 
$\mathrm{CH_3-\overset{CH_3}{\underset{H}{C}}-H}$
and 
$\mathrm{CH_3-\overset{H}{\underset{H}{C}}-CH_3}$

(o)  and 

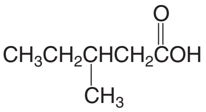
(p)  and 

1.36 Rewrite each of the following using bond-line formulas:

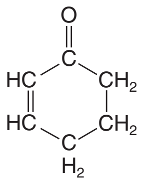
(a) 
$\mathrm{CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}CH_3}$

(b) 
$\mathrm{CH_3\underset{CH_3}{CH}CH_2CH_2\underset{CH_3}{CH}CH_2CH_3}$

(c) $(CH_3)_3CCH_2CH_2CH_2OH$

(d) 
$\mathrm{CH_3CH_2\underset{CH_3}{CH}CH_2\overset{O}{\overset{\|}{C}}OH}$

(e) $CH_2{=}CHCH_2CH_2CH{=}CHCH_3$

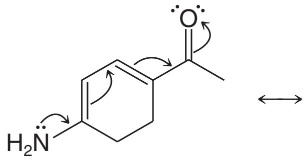
(f) 

1.37 Write bond-line formulas for all of the constitutional isomers with the molecular formula C_4H_8.

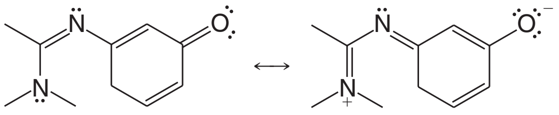
1.38 Write structural formulas for at least three constitutional isomers with the molecular formula CH_3NO_2. (In answering this question you should assign a formal charge to any atom that bears one.)

RESONANCE STRUCTURES

1.39 Write the resonance structure that would result from moving the electrons in the way indicated by the curved arrows.

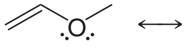


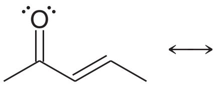
1.40 Show the curved arrows that would convert **A** into **B**.

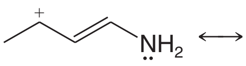


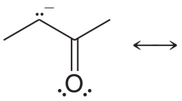
A **B**

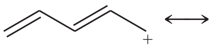
1.41 For the following write all possible resonance structures. Be sure to include formal charges where appropriate.

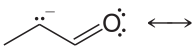
(a) 

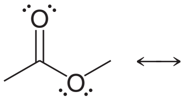
(b) 

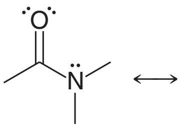
(c) 

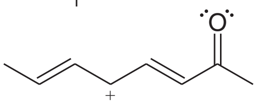
(d) 

(e) 

(f) 

(g) 

(h) 

(i) 

1.42 **(a)** Cyanic acid ($H—O—C≡N$) and isocyanic acid ($H—N=C=O$) differ in the positions of their electrons but their structures do not represent resonance structures. Explain. **(b)** Loss of a proton from cyanic acid yields the same anion as that obtained by loss of a proton from isocyanic acid. Explain.

1.43 Consider a chemical species (either a molecule or an ion) in which a carbon atom forms three single bonds to three hydrogen atoms and in which the carbon atom possesses no other valence electrons. **(a)** What formal charge would the carbon atom have? **(b)** What total charge would the species have? **(c)** What shape would you expect this species to have? **(d)** What would you expect the hybridization state of the carbon atom to be?

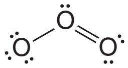
1.44 Consider a chemical species like the one in the previous problem in which a carbon atom forms three single bonds to three hydrogen atoms, but in which the carbon atom possesses an unshared electron pair. **(a)** What formal charge would the carbon atom have? **(b)** What total charge would the species have? **(c)** What shape would you expect this species to have? **(d)** What would you expect the hybridization state of the carbon atom to be?

1.45 Consider another chemical species like the ones in the previous problems in which a carbon atom forms three single bonds to three hydrogen atoms but in which the carbon atom possesses a single unpaired electron. **(a)** What formal charge would the carbon atom have? **(b)** What total charge would the species have? **(c)** Given that the shape of this species is trigonal planar, what would you expect the hybridization state of the carbon atom to be?

1.46 Draw a three-dimensional orbital representation for each of the following molecules, indicate whether each bond in it is a σ or π bond, and provide the hybridization for each non-hydrogen atom.

(a) CH_2O **(b)** $H_2C=CHCH=CH_2$ **(c)** $H_2C=C=C=CH_2$

1.47 Ozone (O_3) is found in the upper atmosphere where it absorbs highly energetic ultraviolet (UV) radiation and thereby provides the surface of Earth with a protective screen (cf. Section 10.11E). One possible resonance structure for ozone is the following:

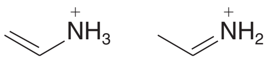


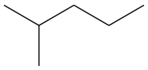
(a) Assign any necessary formal charges to the atoms in this structure. **(b)** Write another equivalent resonance structure for ozone. **(c)** What do these resonance structures predict about the relative lengths of the two oxygen–oxygen bonds of ozone? **(d)** In the structure above, and the one you have written, assume an angular shape for the ozone molecule. Is this shape consistent with VSEPR theory? Explain your answer.

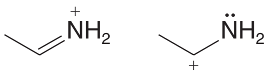
1.48 Write resonance structures for the azide ion, N_3^-. Explain how these resonance structures account for the fact that both bonds of the azide ion have the same length.

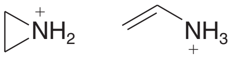
1.49 Write structural formulas of the type indicated: **(a)** bond-line formulas for seven constitutional isomers with the formula $C_4H_{10}O$; **(b)** condensed structural formulas for two constitutional isomers with the formula C_2H_7N; **(c)** condensed structural formulas for four constitutional isomers with the formula C_3H_9N; **(d)** bond-line formulas for three constitutional isomers with the formula C_5H_{12}.

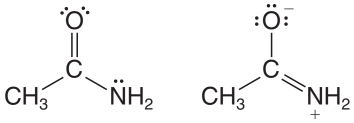
1.50 What is the relationship between the members of the following pairs? That is, are they constitutional isomers, the same, or something else (specify)?

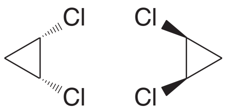
(a)


(b)

$CH_3CH_2CH_2CH(CH_3)_2$

(c)


(d)


(e)


(f)


CHALLENGE PROBLEMS

1.51 In Chapter 15 we shall learn how the nitronium ion, NO_2^+, forms when concentrated nitric and sulfuric acids are mixed. **(a)** Write a Lewis structure for the nitronium ion. **(b)** What geometry does VSEPR theory predict for the NO_2^+ ion? **(c)** Give a species that has the same number of electrons as NO_2^+.

1.52 Given the following sets of atoms, write bond-line formulas for all of the possible constitutionally isomeric compounds or ions that could be made from them. Show all unshared electron pairs and all formal charges, if any.

Set	C atoms	H atoms	Other
A	3	6	2 Br atoms
B	3	9	1 N atom and 1 O atom (not on same C)
C	3	4	1 O atom
D	2	7	1 N atom and 1 proton
E	3	7	1 extra electron

1.53 **(a)** Consider a carbon atom in its ground state. Would such an atom offer a satisfactory model for the carbon of methane? If not, why not? (*Hint:* Consider whether a ground state carbon atom could be tetravalent, and consider the bond angles that would result if it were to combine with hydrogen atoms.)

(b) Consider a carbon atom in the excited state:

$$\text{C}\ \underset{1s}{\underline{\uparrow\downarrow}}\ \underset{2s}{\underline{\uparrow}}\ \underset{2p_x}{\underline{\uparrow}}\ \underset{2p_y}{\underline{\uparrow}}\ \underset{2p_z}{\underline{\uparrow}}$$

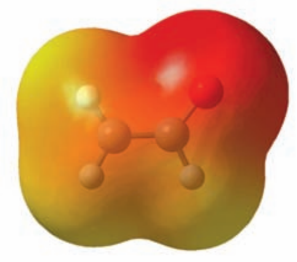
Excited state of a carbon atom

Would such an atom offer a satisfactory model for the carbon of methane? If not, why not?

1.54 Open computer molecular models for dimethyl ether, dimethylacetylene, and *cis*-1,2-dichloro-1,2-difluoroethene from the 3D Molecular Models section of the book's website. By interpreting the computer molecular model for each one, draw **(a)** a dash formula, **(b)** a bond-line formula, and **(c)** a three-dimensional dashed-wedge formula. Draw the models in whatever perspective is most convenient—generally the perspective in which the most atoms in the chain of a molecule can be in the plane of the paper.

1.55 Boron is a group IIIA element. Open the molecular model for boron trifluoride from the 3D Molecular Models section of the book's website. Near the boron atom, above and below the plane of the atoms in BF_3, are two relatively large lobes. Considering the position of boron in the periodic table and the three-dimensional and electronic structure of BF_3, what type of orbital does this lobe represent? Is it a hybridized orbital or not?

1.56 There are two contributing resonance structures for an anion called acetaldehyde enolate, whose condensed molecular formula is CH_2CHO^-. Draw the two resonance contributors and the resonance hybrid, then consider the map of electrostatic potential (MEP) shown below for this anion. Comment on whether the MEP is consistent or not with predominance of the resonance contributor you would have predicted to be represented most strongly in the hybrid.



LEARNING GROUP PROBLEMS

Consider the compound with the following condensed molecular formula:

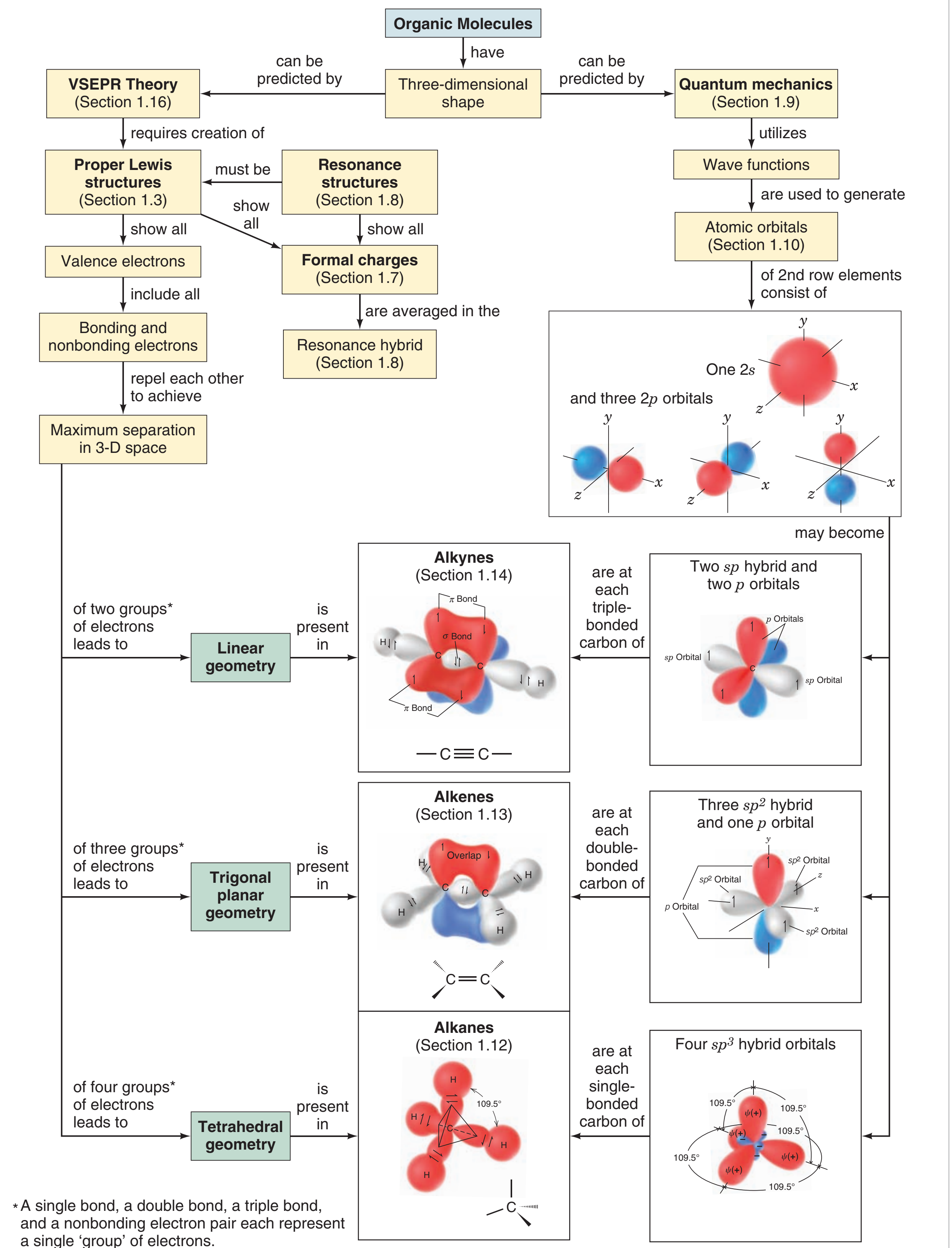
$$CH_3CHOHCH{=}CH_2$$

1. Write a full dash structural formula for the compound.
2. Show all nonbonding electron pairs on your dash structural formula.
3. Indicate any formal charges that may be present in the molecule.
4. Label the hybridization state at every carbon atom and the oxygen.
5. Draw a three-dimensional perspective representation for the compound showing approximate bond angles as clearly as possible. Use ordinary lines to indicate bonds in the plane of the paper, solid wedges for bonds in front of the paper, and dashed wedges for bonds behind the paper.
6. Label all the bond angles in your three-dimensional structure.
7. Draw a bond-line formula for the compound.
8. Devise two structures, each having two *sp*-hybridized carbons and the molecular formula C_4H_6O. Create one of these structures such that it is linear with respect to all carbon atoms. Repeat parts 1–7 above for both structures.

Helpful Hint

Your instructor will tell you how to work these problems as a Learning Group.

CONCEPT MAP



*A single bond, a double bond, a triple bond, and a nonbonding electron pair each represent a single 'group' of electrons.

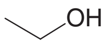
CHAPTER 2

Families of Carbon Compounds

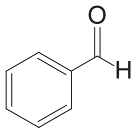
FUNCTIONAL GROUPS, INTERMOLECULAR FORCES, AND INFRARED (IR) SPECTROSCOPY

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.

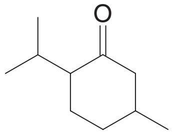
For example, all alcohols contain an —OH (hydroxyl) functional group attached to a saturated carbon bearing nothing else but carbon or hydrogen. Alcohols as simple as ethanol in alcoholic beverages and as complex as ethinyl estradiol (Section 2.1C) in birth control pills have this structural unit in 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

PHOTO CREDIT: © ValentynVolkov/iStockphoto

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

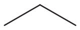
[WHY DO THESE TOPICS MATTER?] At the end of the chapter, we will see how these important concepts merge together to explain how the world's most powerful antibiotic behaves and how bacteria have evolved to escape its effects.

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.

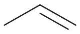
- **Hydrocarbons** are compounds that contain only carbon and hydrogen atoms.

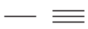
Methane (CH_4) and ethane (C_2H_6) are hydrocarbons, for example. They also belong to a subgroup of compounds called alkanes.

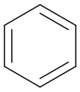

Propane (an alkane)

- **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.


Propene (an alkene)


Propyne (an alkyne)


Benzene (an aromatic compound)

- **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

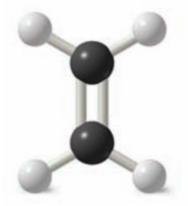

Media Bakery

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

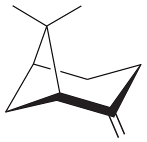


Ethene

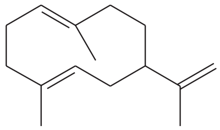
Ethene and propene, the two simplest alkenes, are among the most important industrial chemicals produced in the United States. Each year, the chemical industry produces more than 30 billion pounds of ethene and about 15 billion pounds of propene. Ethene is used as a starting material for the synthesis 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

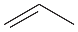
SOLVED PROBLEM 2.1

Propene, $CH_3CH{=}CH_2$, 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

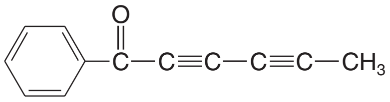
Cyclopropane has anesthetic properties.

2.1C Alkynes

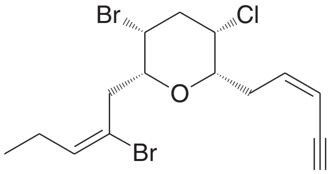
Ethyne

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

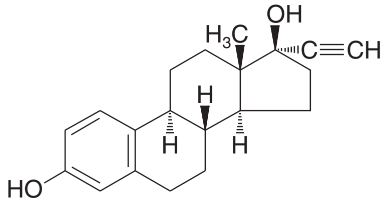
Two examples of alkynes among thousands that have a biosynthetic origin are capillin, an antifungal agent, and dactylyne, a marine natural product that is an inhibitor of pentobarbital metabolism. Ethinyl estradiol is a synthetic alkyne whose estrogen-like properties have found use in oral contraceptives.



Capillin



Dactylyne



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

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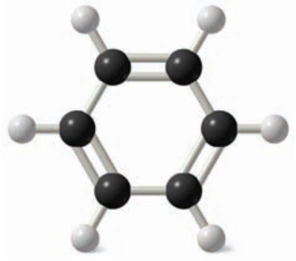
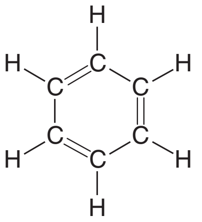
*Special Topics A–F and H are in *WileyPLUS*; Special Topic G can be found later in this volume.



Benzene

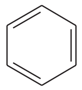
2.1D Benzene: A Representative Aromatic Hydrocarbon

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:



Kekulé structure for benzene

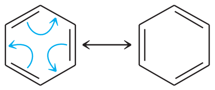
or



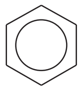
Bond-line representation of Kekulé structure

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:



Two contributing Kekulé structures for benzene

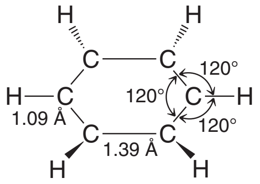


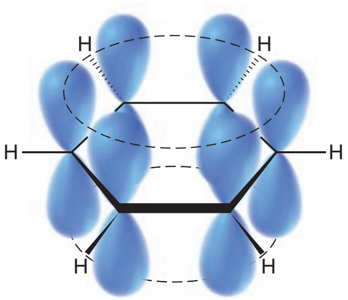
A representation of the resonance hybrid

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.

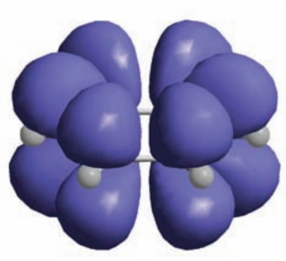
- All of the carbon–carbon bonds in benzene are one and one-half bonds, have a bond length in between that of a single bond and a double bond, and have bond angles of 120°.

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* orbitals



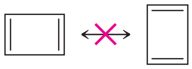
Calculated *p* orbital shapes in benzene

Calculated 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.

PRACTICE PROBLEM 2.1

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.

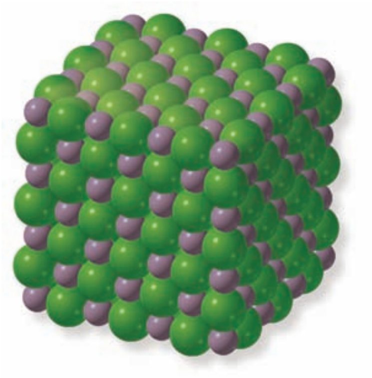


2.2 POLAR COVALENT BONDS

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**:

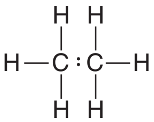
$$\mathrm{Li}^{+} \quad :\underset{\cdot\cdot}{\ddot{\mathrm{F}}}:^{-}$$

Lithium fluoride has an ionic bond.



Lithium fluoride crystal model

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.

- 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 ($\delta+$). The chlorine atom becomes somewhat electron rich and bears a *partial* negative charge ($\delta-$):

$$\overset{\delta+}{\mathrm{H}} : \overset{\delta-}{\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}}:$$

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 $+\!\!\!\longrightarrow$. The crossed end of the arrow is the positive end and the arrowhead is the negative end:

$$\text{(positive end)} +\!\!\!\longrightarrow \text{(negative end)}$$

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

$$\underset{+\!\!\!\longrightarrow}{\mathrm{H{-}Cl}}$$

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):

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

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 $1\ \mathrm{D} = 3.336 \times 10^{-30}$ 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 $\delta+$ and $\delta-$ by the appropriate atoms and draw a dipole moment vector for any of the following molecules that are polar:

(a) HF **(b)** IBr **(c)** Br_2 **(d)** F_2

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.

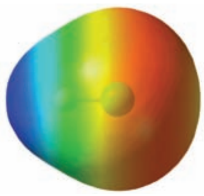


FIGURE 2.1 A calculated map of electrostatic potential for hydrogen chloride showing regions of relatively more negative charge in red and more positive charge in blue. Negative charge is clearly localized near the chlorine, resulting in a strong dipole moment for the molecule.

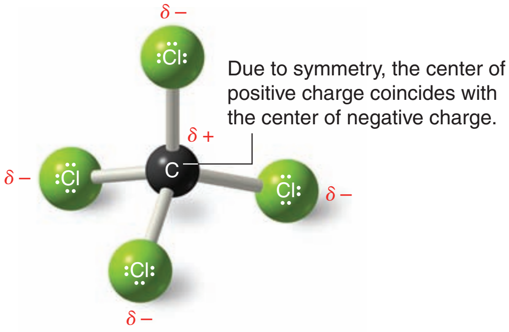
2.3 POLAR AND NONPOLAR MOLECULES

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*.



Due to symmetry, the center of positive charge coincides with the center of negative charge.

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

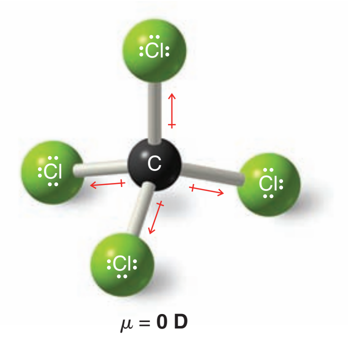


FIGURE 2.3 A tetrahedral orientation of equal bond moments causes their effects to cancel.

This result can be illustrated in a slightly different way: if we use arrows ($\longmapsto$) 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).

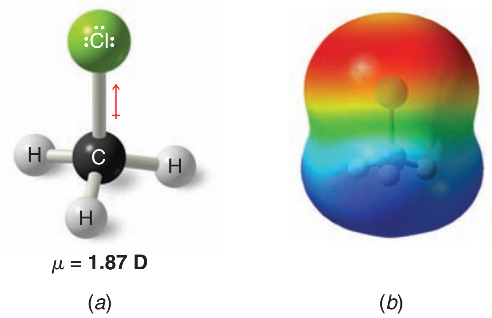
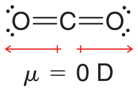


FIGURE 2.4 (*a*) The dipole moment of chloromethane arises mainly from the highly polar carbon–chlorine bond. (*b*) A map of electrostatic potential illustrates the polarity of chloromethane.

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 ($\mu = 0$ D). Explain how this observation confirms the geometry of BF_3 predicted by VSEPR theory.

PRACTICE PROBLEM 2.4 Tetrachloroethene ($CCl_2{=}CCl_2$) does not have a dipole moment. Explain this fact on the basis of the shape of $CCl_2{=}CCl_2$.

PRACTICE PROBLEM 2.5 Sulfur dioxide (SO_2) has a dipole moment ($\mu = 1.63$ D); on the other hand, carbon dioxide (see Solved Problem 2.2) has no dipole moment ($\mu = 0$ 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.)

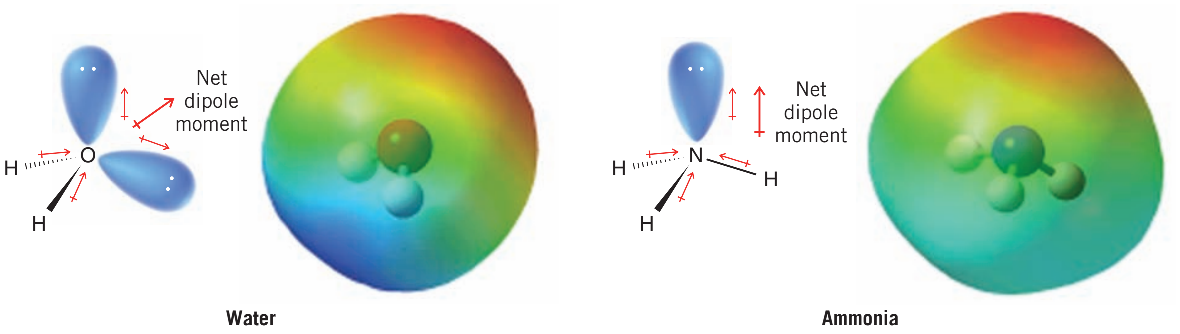


FIGURE 2.5 Bond moments and the resulting dipole moments of water and ammonia.

PRACTICE PROBLEM 2.6

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

PRACTICE PROBLEM 2.7

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.

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

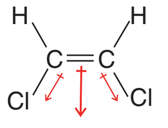
Compound	Melting Point (°C)	Boiling Point (°C)	Dipole Moment (D)
cis-1,2-Dichloroethene	−80	60	1.90
trans-1,2-Dichloroethene	−50	48	0
cis-1,2-Dibromoethene	−53	112	1.35
trans-1,2-Dibromoethene	−6	108	0

SOLVED PROBLEM 2.3

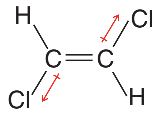
Explain why *cis*-1,2-dichloroethene (Table 2.2) has a large dipole moment whereas *trans*-1,2-dichloroethene has a dipole moment equal to zero.

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**
μ = 1.9 D



Bond moments cancel each other. Net dipole is zero.

***trans*-1,2-Dichloroethene**
μ = 0 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)** $CH_2{=}CF_2$ **(d)** $CF_2{=}CF_2$

PRACTICE PROBLEM 2.9 Write structural formulas for all of the alkenes with **(a)** the formula $C_2H_2Br_2$ and **(b)** the formula $C_2Br_2Cl_2$. In each instance designate compounds that are cis–trans isomers of each other. Predict the dipole moment of each one.

2.4 FUNCTIONAL GROUPS

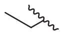
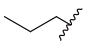
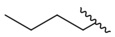
- **Functional groups** are common and specific arrangements of atoms that impart predictable reactivity and properties to a molecule.

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_3C- **Methyl**	Me-		
CH_3CH_2-H **Ethane**	CH_3CH_2- **Ethyl**	Et-		
$CH_3CH_2CH_2-H$ **Propane**	$CH_3CH_2CH_2-$ **Propyl**	Pr-		
$CH_3CH_2CH_2CH_2-H$ **Butane**	$CH_3CH_2CH_2CH_2-$ **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.

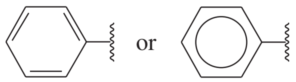
We can simplify much of our future discussion if, at this point, we introduce a symbol that is widely used in designating general structures of organic molecules: the symbol R. R ***is used as a general symbol to represent any alkyl group***. For example, R might be a methyl group, an ethyl group, a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

CH_3-	Methyl	**These and others can be designated by R.**
CH_3CH_2-	Ethyl	
$CH_3CH_2CH_2-$	Propyl	
$CH_3\underset{\vert}{C}HCH_3$	Isopropyl	

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

2.4B Phenyl and Benzyl Groups

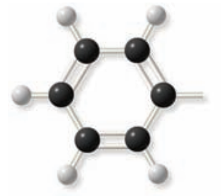
When a benzene ring is attached to some other group of atoms in a molecule, it is called a **phenyl group**, and it is represented in several ways:



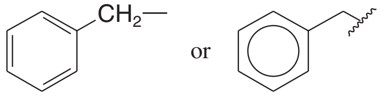
or C_6H_5- or Ph—

or $\phi-$ or Ar— (if ring substituents are present)

Ways of representing a phenyl group

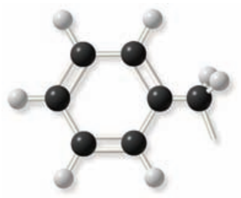


The combination of a phenyl group and a **methylene group** (—CH_2—) is called a **benzyl group**:



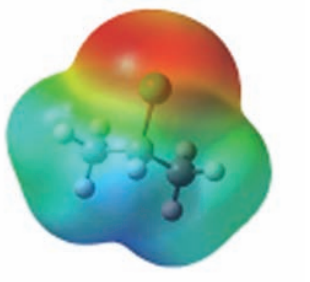
or $C_6H_5CH_2-$ or Bn—

Ways of representing a benzyl group



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, CH_3Cl and CH_3CH_2Br are alkyl halides. Alkyl halides are also called **haloalkanes**. The generic formula for an alkyl halide is $R-\ddot{\underset{\cdot\cdot}{X}}\!:$ where X = fluorine, chlorine, bromine, or iodine.



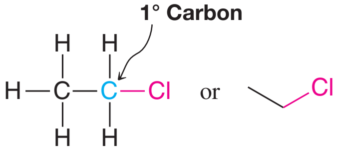
2-Chloropropane

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**

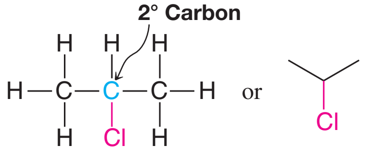
Helpful Hint

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*.

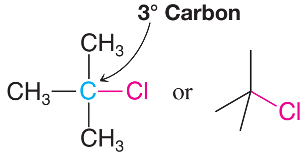
carbon and the alkyl halide is a **tertiary alkyl halide**. Examples of primary, secondary, and tertiary alkyl halides are the following:



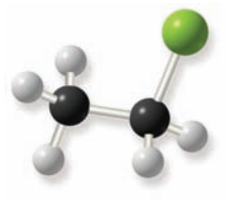
A 1° alkyl chloride

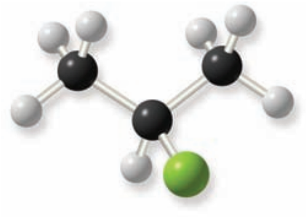


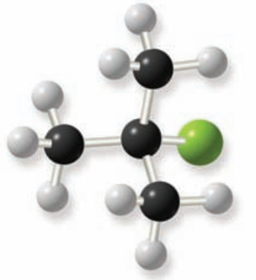
A 2° alkyl chloride



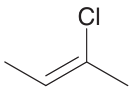
A 3° alkyl chloride



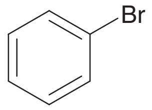




An **alkenyl halide** is a compound with a halogen atom bonded to an alkene carbon. In older nomenclature such compounds were sometimes referred to as vinyl halides. An **aryl halide** is a compound with a halogen atom bonded to an aromatic ring such as a benzene ring.



An alkenyl chloride

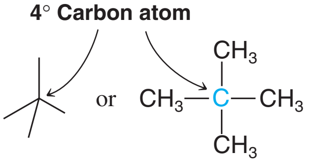


A phenyl bromide

SOLVED PROBLEM 2.4

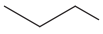
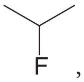
Write the structure of an alkane with the formula C_5H_{12} that has no secondary or tertiary carbon atoms. *Hint*: The compound has a quaternary (4°) carbon.

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.

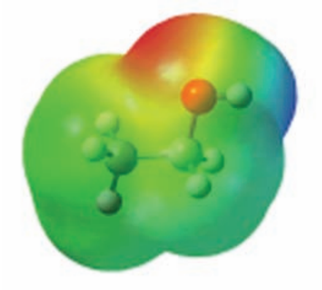


PRACTICE PROBLEM 2.10 Write bond-line structural formulas for **(a)** two constitutionally isomeric primary alkyl bromides with the formula C_4H_9Br, **(b)** a secondary alkyl bromide, and **(c)** a tertiary alkyl bromide with the same formula. Build handheld molecular models for each structure and examine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

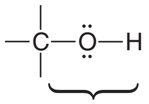
What are the names for **(c)**  Br, **(d)**  F , and **(e)** C_6H_5I?

2.6 ALCOHOLS AND PHENOLS



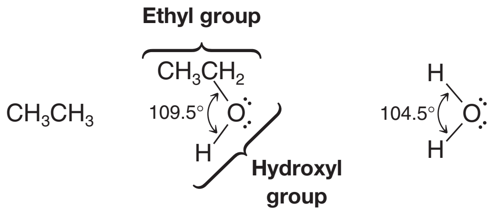
Ethanol

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 (—OH) group attached to an *sp*^{3}-hybridized carbon atom. Another example of an alcohol is ethyl alcohol, CH_3CH_2OH (also called ethanol).



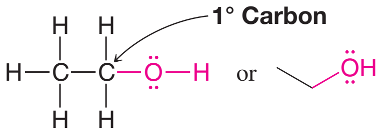
This is the functional group of an alcohol.

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:

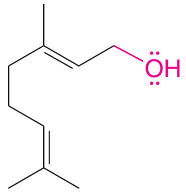


Ethane **Ethyl alcohol (ethanol)** **Water**

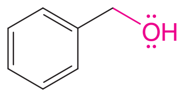
As with alkyl halides, alcohols are classified into three groups: primary (1°), secondary (2°), and tertiary (3°) alcohols. ***This classification is based on the degree of substitution of the carbon to which the hydroxyl group is directly attached***. If the carbon has only one other carbon attached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



Ethyl alcohol (a 1° alcohol)

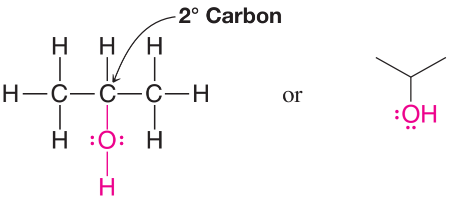


Geraniol (a 1° alcohol)

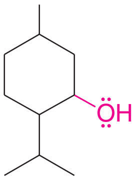


Benzyl alcohol (a 1° alcohol)

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:

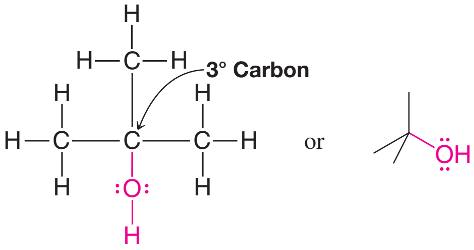


Isopropyl alcohol (a 2° alcohol)

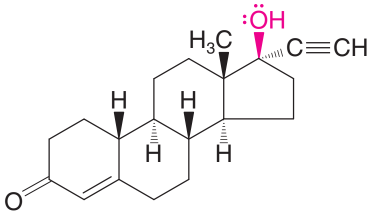


Menthol (a 2° alcohol found in peppermint oil)

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)

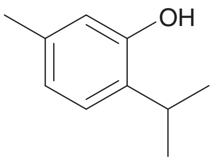
Helpful Hint

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

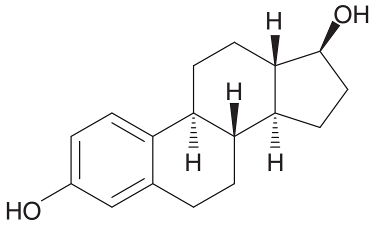
PRACTICE PROBLEM 2.12 Write bond-line structural formulas for **(a)** two primary alcohols, **(b)** a secondary alcohol, and **(c)** a tertiary alcohol—all having the molecular formula $C_4H_{10}O$.

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)

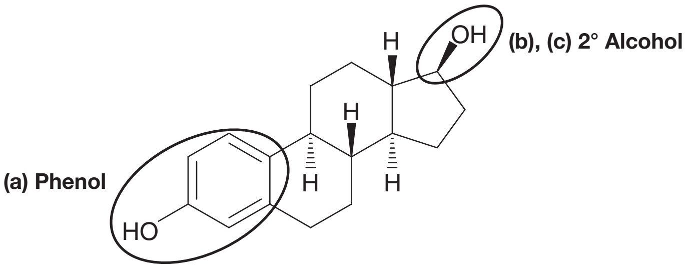


Estradiol
(a sex hormone that contains both alcohol and phenol groups)

SOLVED PROBLEM 2.5

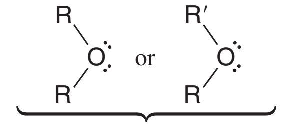
Circle the atoms that comprise **(a)** the phenol and **(b)** the alcohol functional groups in estradiol. **(c)** What is the class of the alcohol?

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.

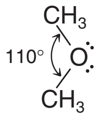


2.7 ETHERS

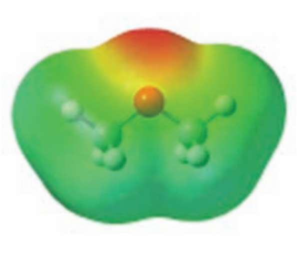
Ethers have the general formula $\mathrm{R{-}O{-}R}$ or $\mathrm{R{-}O{-}R'}$, where $\mathrm{R'}$ may be an alkyl (or phenyl) group different from R. Ethers can be thought of as derivatives of water in which both hydrogen atoms have been replaced by alkyl groups. The bond angle at the oxygen atom of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



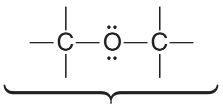
General formula for an ether



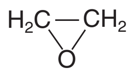
Dimethyl ether
(a typical ether)



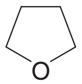
Dimethyl ether



The functional group of an ether



Ethylene oxide

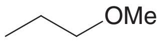


Tetrahydrofuran (THF)

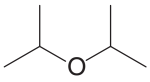
Two cyclic ethers

PRACTICE PROBLEM 2.14

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 you give to **(d)**



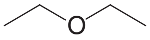
(e)



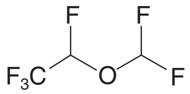
and **(f)** $\mathrm{CH_3OC_6H_5}$?

THE CHEMISTRY OF... Ethers as General Anesthetics

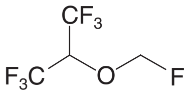
Nitrous oxide (N_2O), also called laughing gas, was first used as an anesthetic in 1799, and it is still in use today, even though when used alone it does not produce deep anesthesia. The first use of an ether, diethyl ether, to produce deep anesthesia occurred in 1842. In the years that have passed 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.



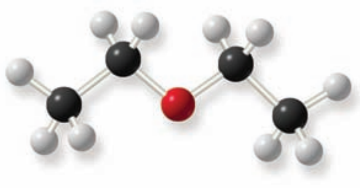
Diethyl ether

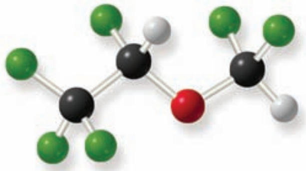


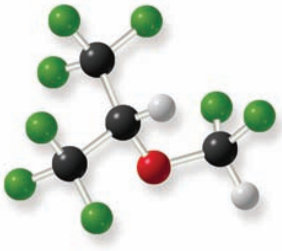
Desflurane



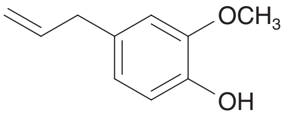
Sevoflurane





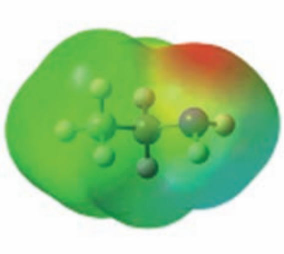


PRACTICE PROBLEM 2.15 Eugenol is the main constituent of the natural oil from cloves. Circle and label all of the functional groups in eugenol.



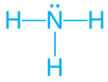
Eugenol (found in cloves)

2.8 AMINES



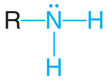
Ethylamine

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



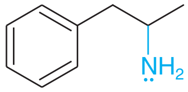
$$\begin{array}{c}\mathrm{H-\ddot{N}-H}\\ |\\ \mathrm{H}\end{array}$$

Ammonia

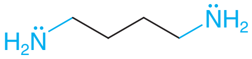


$$\begin{array}{c}\mathrm{R-\ddot{N}-H}\\ |\\ \mathrm{H}\end{array}$$

An amine

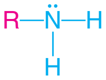


Amphetamine (a dangerous stimulant)



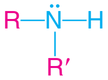
Putrescine (found in decaying meat)

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*:**



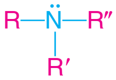
$$\begin{array}{c}\mathrm{R-\ddot{N}-H}\\ |\\ \mathrm{H}\end{array}$$

A primary (1°) amine



$$\begin{array}{c}\mathrm{R-\ddot{N}-H}\\ |\\ \mathrm{R'}\end{array}$$

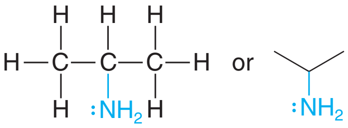
A secondary (2°) amine



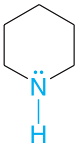
$$\begin{array}{c}\mathrm{R-\ddot{N}-R''}\\ |\\ \mathrm{R'}\end{array}$$

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 $—NH_2$ group is attached to a secondary carbon atom. It is a primary amine because only one organic group is attached to the nitrogen atom:

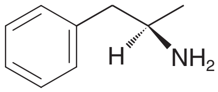


Isopropylamine (a 1° amine)

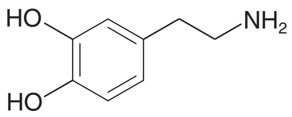


Piperidine (a cyclic 2° amine)

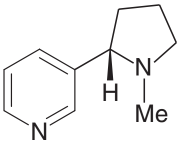
Amphetamine (below), a powerful and dangerous stimulant, is a primary amine. Dopamine, an important neurotransmitter whose depletion is associated with Parkinson's disease, is also a primary amine. Nicotine, a toxic compound found in tobacco that makes smoking addictive, has a secondary amine group and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



Amphetamine



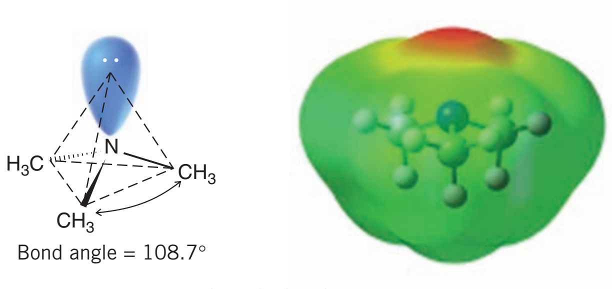
Dopamine



Nicotine

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

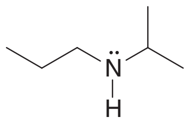
H—C—H bond angles of methane. Thus, for all practical purposes, the nitrogen atom of an amine can be considered to be sp^3 hybridized with the unshared electron pair occupying one orbital (see below). This means that the unshared pair is relatively exposed, and as we shall see this is important because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

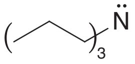


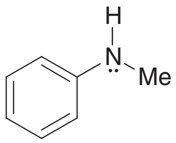
Trimethylamine

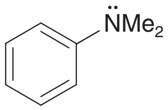
PRACTICE PROBLEM 2.16

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)**.

(a)


(b)


(c)


(d)


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

PRACTICE PROBLEM 2.17

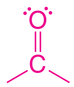
Which amines in Practice Problem 2.16 are **(a)** primary amines, **(b)** secondary amines, and **(c)** tertiary amines?

PRACTICE PROBLEM 2.18

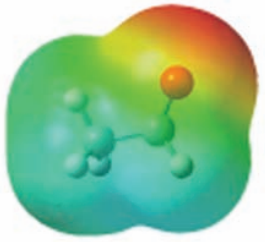
Amines are like ammonia in being weak bases. They do this by using their unshared electron pair to accept a proton. **(a)** Show the reaction that would take place between trimethyl amine and HCl. **(b)** What hybridization state would you expect for the nitrogen atom in the product of this reaction?

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

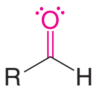


Acetaldehyde

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).

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:

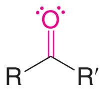
ALDEHYDES



or RCHO

(R = H in formaldehyde)

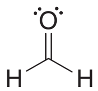
KETONES



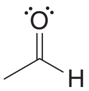
or RCOR′

(where R′ is an alkyl group that may be the same or different from R)

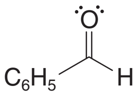
Some specific examples of aldehydes and ketones are the following:



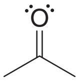
Formaldehyde



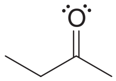
Acetaldehyde



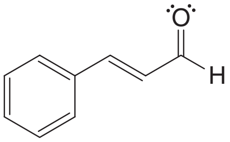
Benzaldehyde



Acetone



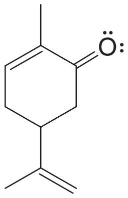
Ethyl methyl ketone



***trans*-Cinnamaldehyde (present in cinnamon)**

Erika Craddock/photo Researchers, Inc.

Cinnamon



Carvone (from spearmint)

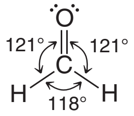
© Gilles Delacroix/Age Fotostock America, Inc.

Spearmint

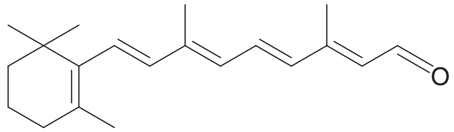
Helpful Hint

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:

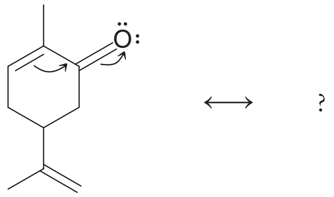


Retinal (below) is an aldehyde made from vitamin A that plays a vital role in vision. We discuss this further in Chapter 13.



Retinal

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



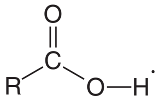
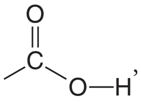
PRACTICE PROBLEM 2.20

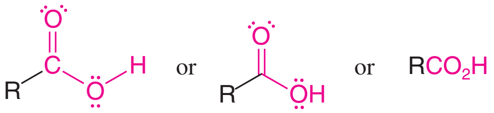
Write bond-line formulas for **(a)** four aldehydes and **(b)** three ketones that have the formula $C_5H_{10}O$.

2.10 CARBOXYLIC ACIDS, ESTERS, AND AMIDES

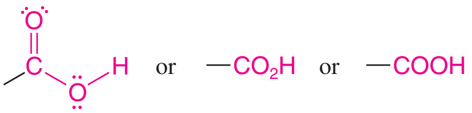
Carboxylic acids, esters, and amides all contain a carbonyl group that is bonded to an oxygen or nitrogen atom. As we shall learn in later chapters, all of these functional groups are interconvertible by appropriately chosen reactions.

2.10A Carboxylic Acids

Carboxylic acids have a carbonyl group bonded to a hydroxyl group, and they have the general formula  $R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}H$. The functional group,  $-\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}H$, is called the **carboxyl group** (**carbo**nyl + hydro**xyl**):

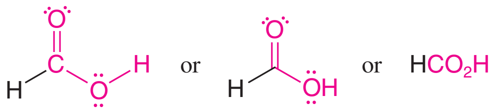


A carboxylic acid

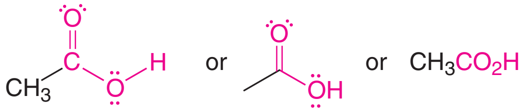


The carboxyl group

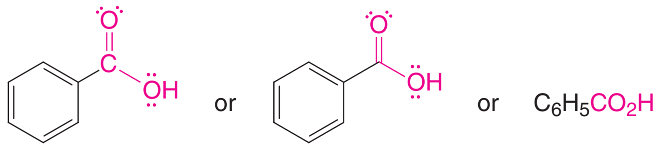
Examples of carboxylic acids are formic acid, acetic acid, and benzoic acid:



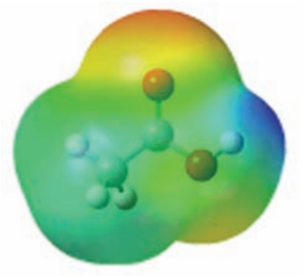
Formic acid



Acetic acid



Benzoic acid



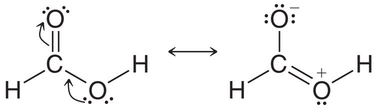
Acetic acid

Formic acid is an irritating liquid produced by ants. (The sting of the ant is caused, in part, by formic acid being injected under the skin. *Formic* is the Latin word for ant.) Acetic acid, the substance responsible for the sour taste of vinegar, is produced when certain bacteria act on the ethyl alcohol of wine and cause the ethyl alcohol to be oxidized by air.

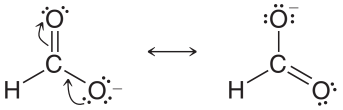
SOLVED PROBLEM 2.6

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.



Formic acid



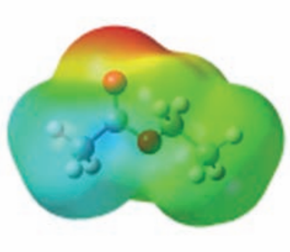
Formate ion

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

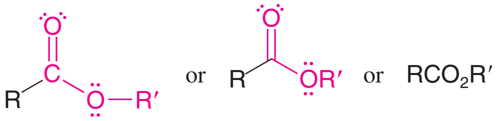
PRACTICE PROBLEM 2.21 Write bond-line formulas for four carboxylic acids with the formula $C_5H_{10}O_2$.

2.10B Esters

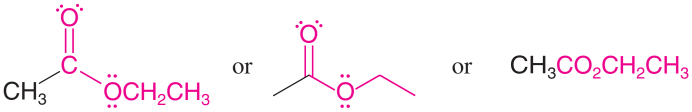
Esters have the general formula RCO_2R' (or $RCOOR'$), where a carbonyl group is bonded to an alkoxyl (—OR) group:



Ethyl acetate



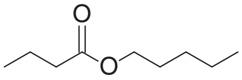
General formula for an ester



Ethyl acetate is an important solvent.

Media Bakery

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

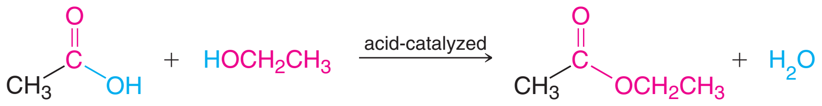


Pentyl butanoate has the odor of apricots and pears.

PRACTICE PROBLEM 2.22 Write bond-line formulas for three esters with the formula $C_5H_{10}O_2$.

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:

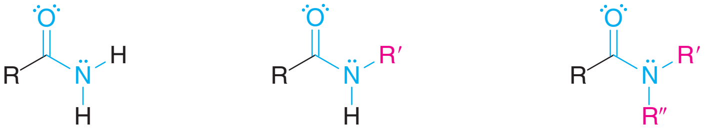


Acetic acid **Ethyl alcohol** **Ethyl acetate**

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.

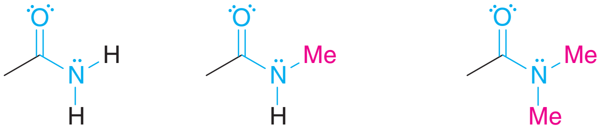
2.10C Amides

Amides have the formulas $RCONH_2$, $RCONHR'$, or $RCONR'R''$ 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 amide** **An *N*,*N*-disubstituted amide**

General formulas for amides



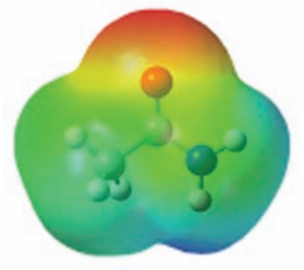
Acetamide ***N*-Methylacetamide** ***N*,*N*-Dimethylacetamide**

Specific examples of amides

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


Media Bakery

Nylon is a polymer comprised of regularly repeating amide groups.



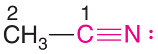
Acetamide

Write another resonance structure for acetamide.

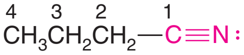
PRACTICE PROBLEM 2.24

2.11 NITRILES

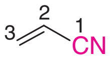
A nitrile has the formula $R{-}C{\equiv}N{:}$ (or $R{-}CN$). The carbon and the nitrogen of a nitrile are *sp* hybridized. In IUPAC systematic nomenclature, acyclic nitriles are named by adding the suffix *-nitrile* to the name of the corresponding hydrocarbon. The carbon atom of the $-C{\equiv}N$ group is assigned number 1. The name acetonitrile is an acceptable common name for CH_3CN, and acrylonitrile is an acceptable common name for $CH_2{=}CHCN$:


$$\overset{2}{CH_3}{-}\overset{1}{C}{\equiv}N{:}$$

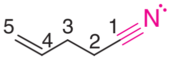
Ethanenitrile (acetonitrile)


$$\overset{4}{CH_3}\overset{3}{CH_2}\overset{2}{CH_2}{-}\overset{1}{C}{\equiv}N{:}$$

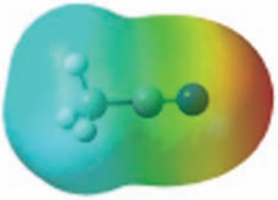
Butanenitrile



Propenenitrile (acrylonitrile)

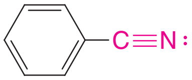


4-Pentenenitrile

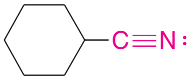


Acetonitrile

Cyclic nitriles are named by adding the suffix *-carbonitrile* to the name of the ring system to which the $-CN$ group is attached. Benzonitrile is an acceptable common name for C_6H_5CN:



Benzenecarbonitrile (benzonitrile)

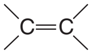
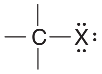
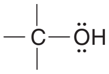
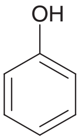
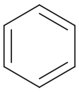
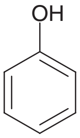
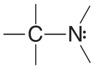
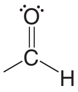
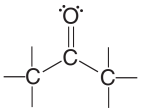
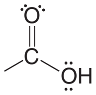
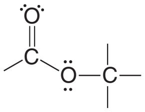
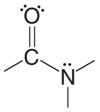
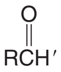
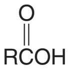
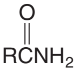
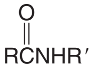
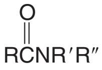
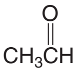
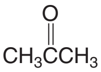
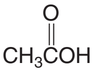
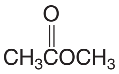
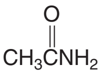


Cyclohexanecarbonitrile

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.

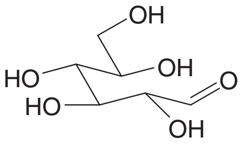
TABLE 2.3 IMPORTANT FAMILIES OF ORGANIC COMPOUNDS

	Family							
	Alkane	**Alkene**	**Alkyne**	**Aromatic**	**Haloalkane**	**Alcohol**	**Phenol**	**Ether**
Functional group	C—H and C—C bonds		—C≡C—	Aromatic ring				
General formula	RH	$RCH{=}CH_2$ $RCH{=}CHR$ $R_2C{=}CHR$ $R_2C{=}CR_2$	$RC{\equiv}CH$ $RC{\equiv}CR$	ArH	RX	ROH	ArOH	ROR
Specific example	CH_3CH_3	$CH_2{=}CH_2$	$HC{\equiv}CH$		CH_3CH_2Cl	CH_3CH_2OH		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								$—C{\equiv}N\colon$
General formula	RNH_2 R_2NH R_3N	 $R\overset{O}{\overset{\|}{C}}H$	 $R\overset{O}{\overset{\|}{C}}R'$	 $R\overset{O}{\overset{\|}{C}}OH$	 $R\overset{O}{\overset{\|}{C}}OR'$	 $R\overset{O}{\overset{\|}{C}}NH_2$  $R\overset{O}{\overset{\|}{C}}NHR'$  $R\overset{O}{\overset{\|}{C}}NR'R''$		RCN
Specific example	CH_3NH_2	 $CH_3\overset{O}{\overset{\|}{C}}H$	 $CH_3\overset{O}{\overset{\|}{C}}CH_3$	 $CH_3\overset{O}{\overset{\|}{C}}OH$	 $CH_3\overset{O}{\overset{\|}{C}}OCH_3$	 $CH_3\overset{O}{\overset{\|}{C}}NH_2$		$CH_3C{\equiv}N$
IUPAC name	Methanamine	Ethanal	Propanone	Ethanoic acid	Methyl ethanoate	Ethanamide		Ethanenitrile
Common name	Methylamine	Acetaldehyde	Acetone	Acetic acid	Methyl acetate	Acetamide		Acetonitrile

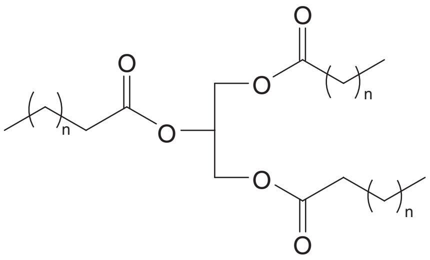
[a] These names are also accepted by the IUPAC.

2.12A Functional Groups in Biologically Important Compounds

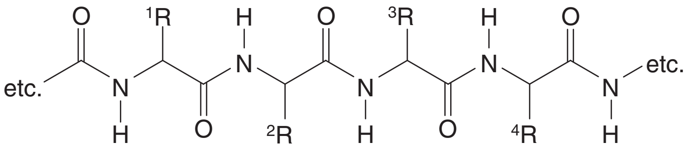
Many of the functional groups we have listed in Table 2.3 are central to the compounds of living organisms. A typical sugar, for example, is glucose. Glucose contains several alcohol hydroxyl groups (—OH) and in one of its forms contains an aldehyde group. Fats and oils contain ester groups, and proteins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



Glucose



A typical fat



Part of a protein

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.

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*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_3CH_3	−172	−88.2
Ethene	$CH_2{=}CH_2$	−169	−102
Ethyne	$HC{\equiv}CH$	−82	−84 subl
Chloromethane	CH_3Cl	−97	−23.7
Chloroethane	CH_3CH_2Cl	−138.7	13.1
Ethyl alcohol	CH_3CH_2OH	−114	78.5
Acetaldehyde	CH_3CHO	−121	20
Acetic acid	CH_3CO_2H	16.6	118
Sodium acetate	CH_3CO_2Na	324	dec
Ethylamine	$CH_3CH_2NH_2$	−80	17
Diethyl ether	$(CH_3CH_2)_2O$	−116	34.6
Ethyl acetate	$CH_3CO_2CH_2CH_3$	−84	77

[a] In 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.

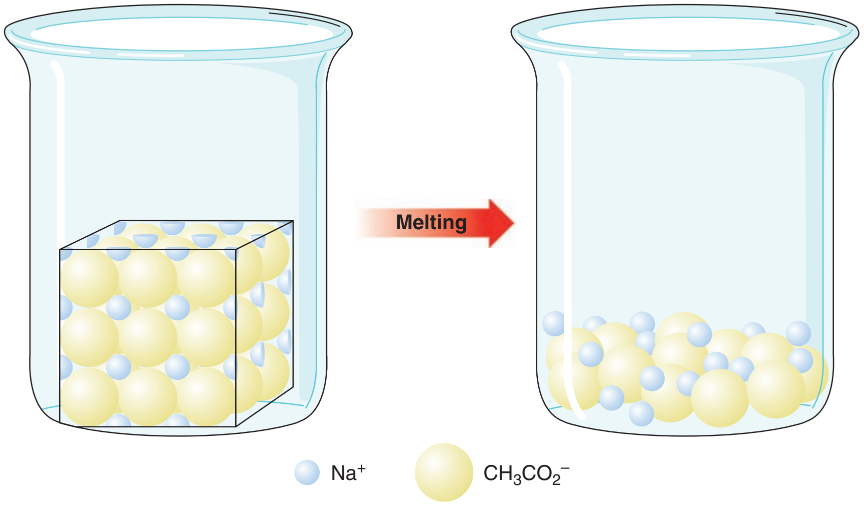


FIGURE 2.6 The melting of sodium acetate.

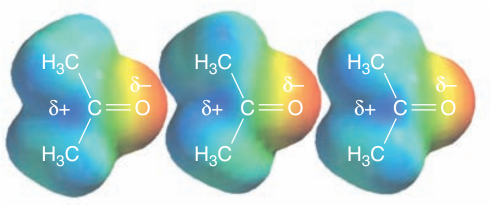


FIGURE 2.7 Electrostatic potential models for acetone molecules that show how acetone molecules might align according to attractions of their partially positive regions and partially negative regions (dipole–dipole interactions).

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

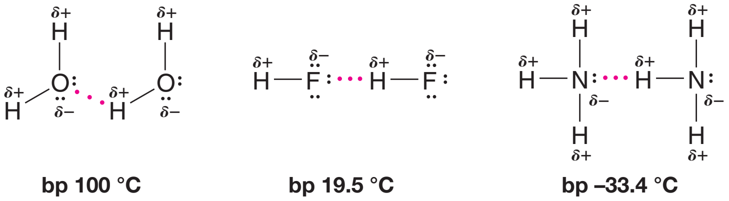
Dipole–Dipole Forces Most organic molecules are not fully ionic but have instead a *permanent dipole moment* resulting from a nonuniform distribution of the bonding electrons (Section 2.3). Acetone and acetaldehyde are examples of molecules with permanent dipoles because the carbonyl group that they 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**.

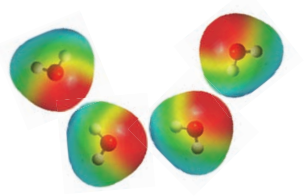
Hydrogen bonds (bond dissociation energies of about 4–38 kJ mol^{-1}) are weaker than ordinary covalent bonds but much stronger than the dipole–dipole interactions that occur above, for example, in acetone.

Hydrogen bonding explains why water, ammonia, and hydrogen fluoride all have far higher boiling points than methane (bp −161.6 °C), even though all four compounds have similar molecular weights.



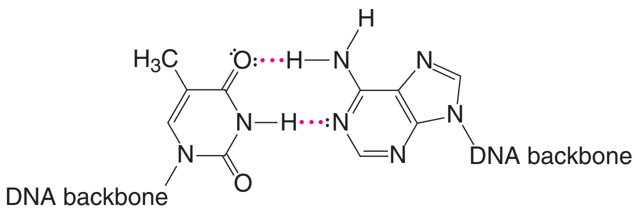
Hydrogen bonds are shown by the red dots.

One of the most important consequences of hydrogen bonding is that it causes water to be a liquid rather than a gas at 25 °C. Calculations indicate that in the absence of hydrogen bonding, water would have a boiling point near −80 °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.

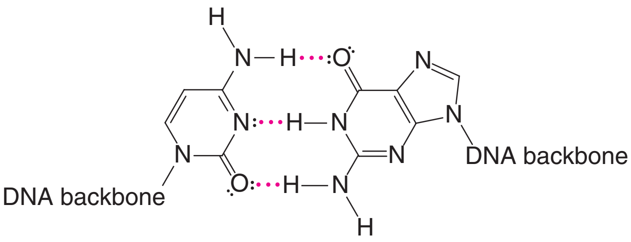


Water molecules associated by attraction of opposite partial charges.

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.

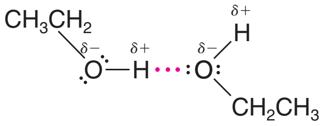


Thymine **Adenine**



Cytosine **Guanine**

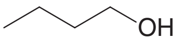
Hydrogen bonding accounts for the fact that ethyl alcohol has a much higher boiling point (78.5 °C) than dimethyl ether (24.9 °C) even though the two compounds have the same molecular weight. Molecules of ethyl alcohol, because they have a hydrogen atom covalently bonded to an oxygen atom, can form strong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



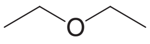
The red dots represent a hydrogen bond. Strong hydrogen bonding is limited to molecules having a hydrogen atom attached to an O, N, or F atom.

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)


or



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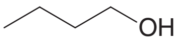

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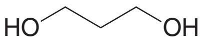
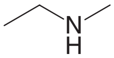
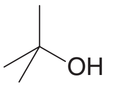


(b) $(CH_3)_3N$ or

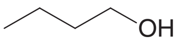


A factor (in addition to polarity and hydrogen bonding) that affects the *melting point* of many organic compounds is the compactness and rigidity of their individual molecules.

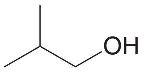
- Molecules that are symmetrical generally have abnormally high melting points. *tert*-Butyl alcohol, for example, has a much higher melting point than the other isomeric alcohols shown here:



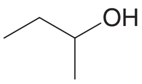
***tert*-Butyl alcohol**
(mp 25 °C)



Butyl alcohol
(mp −90 °C)



Isobutyl alcohol
(mp −108 °C)



***sec*-Butyl alcohol**
(mp −114 °C)

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 nonpolar 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

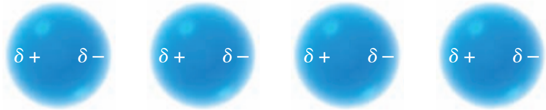


FIGURE 2.8 Temporary dipoles and induced dipoles in nonpolar molecules resulting from an uneven distribution of electrons at a given instant.

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 CI_4 are both nonpolar molecules. But if we were to consider the intermolecular forces between two CI_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.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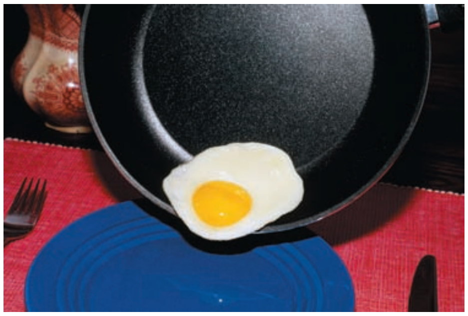
Dispersion forces are what provides a gecko's grip to smooth surfaces.

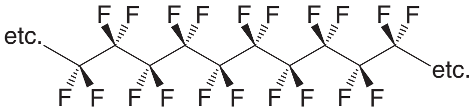
THE CHEMISTRY OF... Fluorocarbons and Teflon

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.

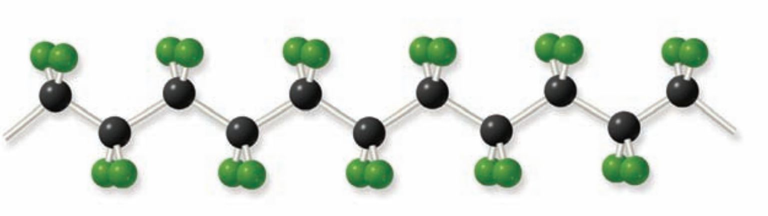


Leonard Lessin/Photo Researchers, Inc.

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.



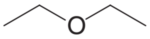
Teflon



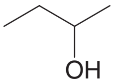
Nonpolar compounds, where the intermolecular forces are very weak, usually boil at low temperatures even at 1 atm pressure. This is not always true, however, because of other factors that we have not yet mentioned: the effects of molecular weight and molecular shape and surface area. Heavier molecules 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 °C) boils higher than methane (bp −162 °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 °C. The relationship between dispersion forces and surface area helps us understand why neopentane (2,2-dimethylpropane) has a lower boiling point (9.5 °C) than pentane (36.1 °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

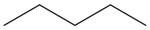
Arrange the following compounds according to their expected boiling points, with the lowest boiling point first, and explain your answer. Notice that the compounds have similar molecular weights.



Diethyl ether



***sec*-Butyl alcohol**



Pentane

STRATEGY AND ANSWER:

pentane < diethyl ether < *sec*-butyl alcohol

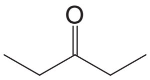
Increasing boiling point

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 —OH group that can form strong hydrogen bonds; therefore, it would have the highest boiling point.

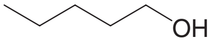
PRACTICE PROBLEM 2.27

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

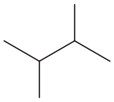
(a)



(b)



(c)



(d)

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.

Helpful Hint

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

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.

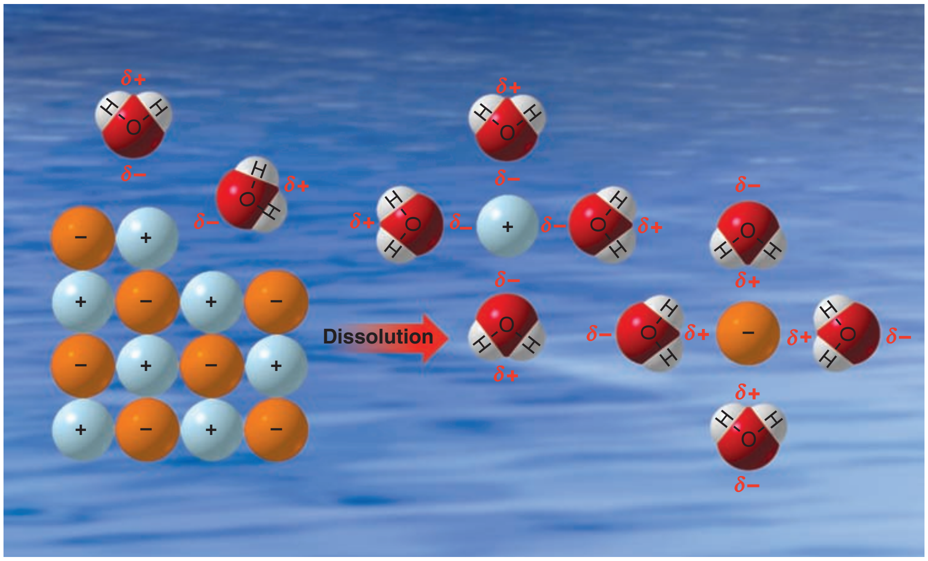
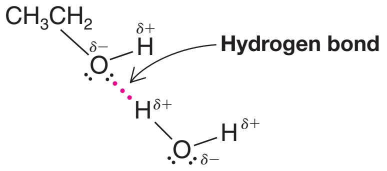


FIGURE 2.9 The dissolution of an ionic solid in water, showing the hydration of positive and negative ions by the very polar water molecules. The ions become surrounded by water molecules in all three dimensions, not just the two shown here.

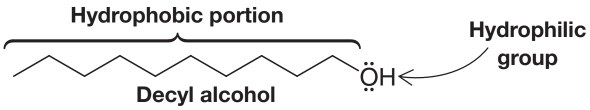
Methanol and water are miscible in all proportions; so too are mixtures of ethanol and water and mixtures of both propyl alcohols and water. In these cases the alkyl groups of the alcohols are relatively small, and the molecules therefore resemble water more than they do an alkane. Another factor in 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.

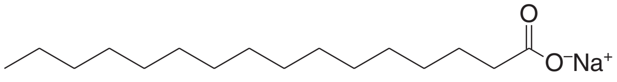
- **Hydrophobic** means incompatible with water (*hydro*, water; *phobic*, fearing or avoiding).
- **Hydrophilic** means compatible with water (*philic*, loving or seeking).

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.

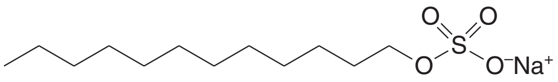


An explanation for why nonpolar groups such as long alkane chains avoid an aqueous environment—that is, for the so-called **hydrophobic effect**—is complex. The most important factor seems to involve an **unfavorable entropy change** in the water. Entropy changes (Section 3.10) have to do with changes 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

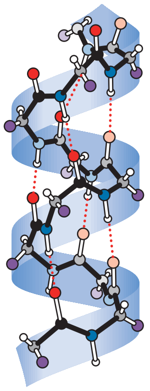
The hydrophobic long carbon chains of a soap or detergent embed themselves in the oily layer that typically surrounds the thing we want to wash away. The hydrophilic ionic groups at the ends of the chains are then left exposed on the surface and make the surface one that water molecules find attractive. 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



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

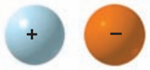
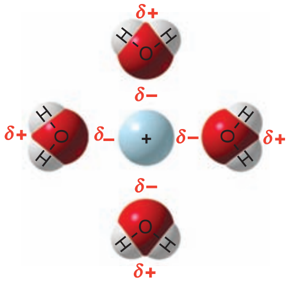
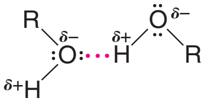
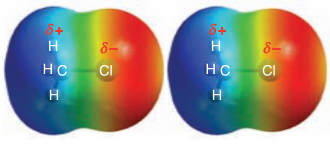
(Illustration, Irving Geis. Image from the Irving Geis Collection, HHMI. Rights owned by Howard Hughes Medical Institute. Not to be reproduced without permission.)

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.

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.

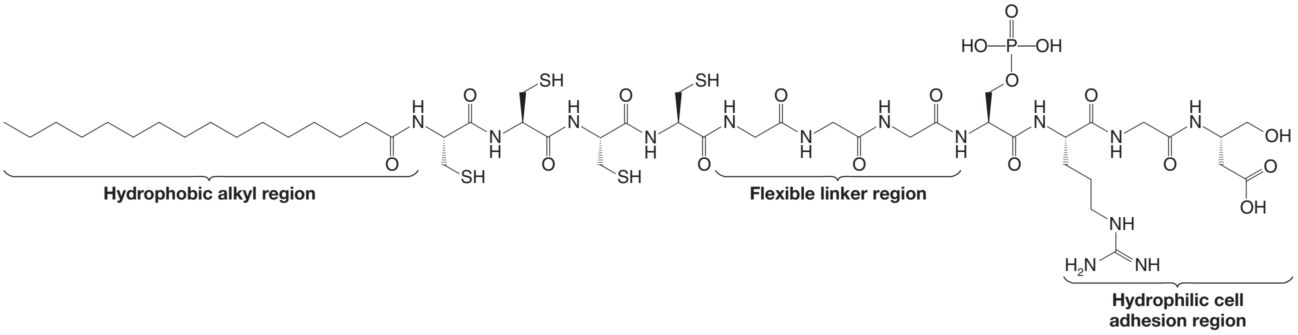
TABLE 2.5 ATTRACTIVE ELECTRIC FORCES

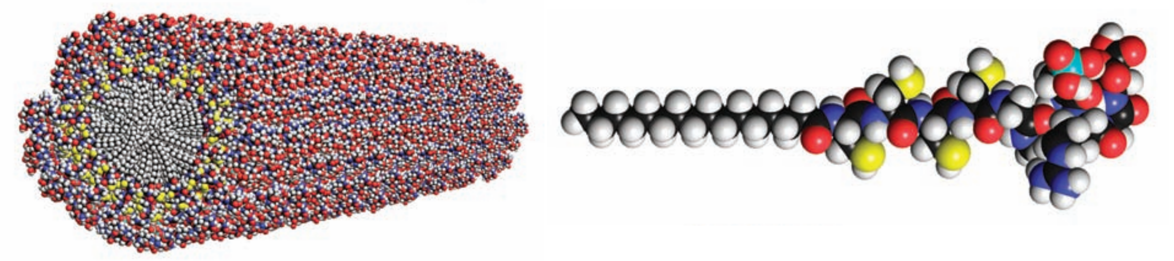
Electric Force	Relative Strength	Type	Example
Cation–anion (in a crystal)	Very strong		Sodium chloride crystal lattice
Covalent bonds	Strong (140–523 kJ mol^{-1})	Shared electron pairs	H—H (436 kJ mol^{-1}) CH_3—CH_3 (378 kJ mol^{-1}) I—I (151 kJ mol^{-1})
Ion–dipole	Moderate		Na^+ in water (see Fig. 2.9)
Hydrogen bonds	Moderate to weak (4–38 kJ mol^{-1})	$-\overset{\delta-}{Z}\!:\cdots\overset{\delta+}{H}-$	
Dipole–dipole	Weak	$\overset{\delta+}{CH_3}\overset{\delta-}{Cl}\cdots\overset{\delta+}{CH_3}\overset{\delta-}{Cl}$	
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.



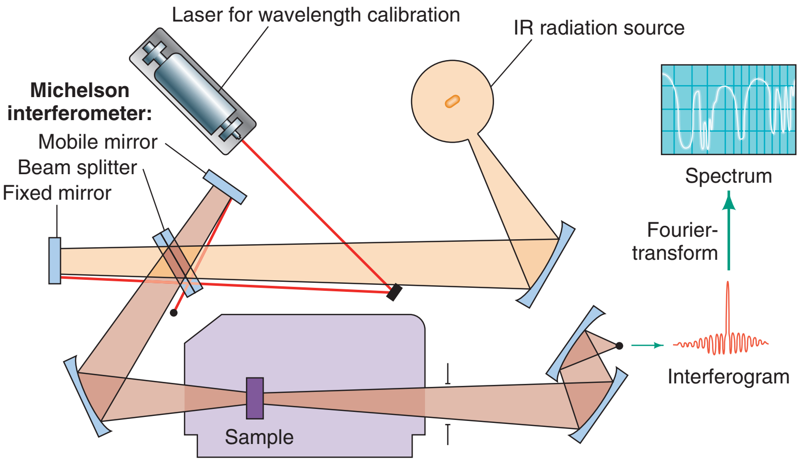


(From Hartgerink, J.D., Beniash, E. J, Stupp, S.I.:Self-assembly and Mineralization of Peptide-Amphiphile Nanofibers. SCIENCE 294:1684-1688, Figure 1 (2001). Reprinted with permission from AAAS.)

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 ($\bar{\nu}$)**.

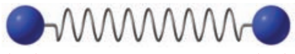
Wavenumbers are the reciprocal of wavelength when wavelength is expressed in centimeters (the unit is cm^{-1}), and therefore give the number of wave cycles per centimeter. The larger the wavenumber, the higher is the frequency of the wave, and correspondingly the higher is the frequency of the bond 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.

$$\bar{\nu} = \frac{1}{\lambda} \text{ (with } \lambda \text{ in cm)} \qquad \text{or} \qquad \bar{\nu} = \frac{10.000}{\lambda} \text{ (with } \lambda \text{ in } \mu\text{m)}$$

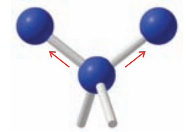
In their vibrations covalent bonds behave as if they were tiny springs connecting the atoms. When the atoms vibrate, they can do so only at certain frequencies, as if the bonds were "tuned." Because of this, covalently bonded atoms have only particular vibrational energy levels; that is, the levels are 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 $\Delta E = \frac{hc}{\lambda}$.

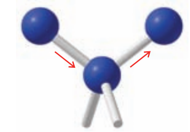
Molecules can vibrate in a variety of ways. Two atoms joined by a covalent bond can undergo a stretching vibration where the atoms move back and forth as if joined by a spring. Three atoms can also undergo a variety of stretching and bending vibrations.



A stretching vibration

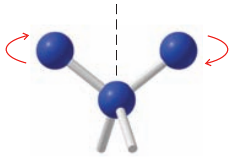


Symmetric stretching



Asymmetric stretching

An in-plane
bending vibration
(scissoring)



An out-of-plane
bending vibration
(twisting)

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≡C	2100–2260
Nitrile	C≡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

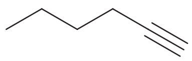
Group	Frequency Range (cm^{-1})	Intensity[a]
A. Alkyl		
C—H (stretching)	2853–2962	(m–s)
Isopropyl, $—CH(CH_3)_2$	1380–1385	(s)
	and 1365–1370	(s)
tert-Butyl, $—C(CH_3)_3$	1385–1395	(m)
	and ~1365	(s)
B. Alkenyl		
C—H (stretching)	3010–3095	(m)
C=C (stretching)	1620–1680	(v)
R—CH=CH_2 (out-of-plane C—H bendings)	985–1000	(s)
	and 905–920	(s)
R_2C=CH_2 (out-of-plane C—H bendings)	880–900	(s)
cis-RCH=CHR	675–730	(s)
trans-RCH=CHR	960–975	(s)
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)
o-Disubstituted	735–770	(s)
m-Disubstituted	680–725	(s)
	and 750–810	(very s)
p-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)

[a] Abbreviations: s = strong, m = medium, w = weak, v = variable, ~ = approximately.

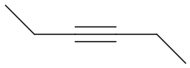
Thus, methane does not absorb IR energy for symmetric streching of the four C—H bonds; asymmetric stretching, on the other hand, does lead to an IR absorption. Symmetrical vibrations of the carbon–carbon double and triple bonds of ethene and ethyne do not result in the absorption of IR radiation, either.

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.



1-Hexyne



3-Hexyne

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

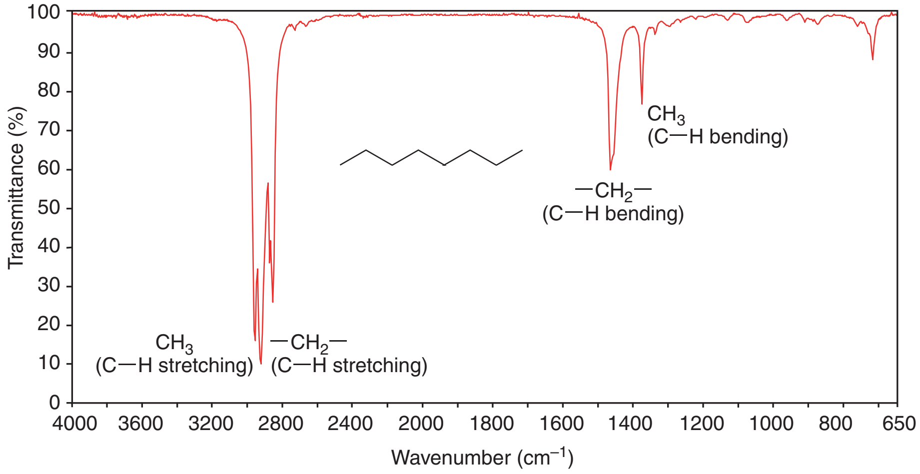


FIGURE 2.11 The IR spectrum of octane. (Notice that, in IR spectra, the peaks are usually measured in % transmittance. Thus, the peak at 2900 cm^{-1} has 10% transmittance—that is, an absorbance, *A*, of 0.90.)

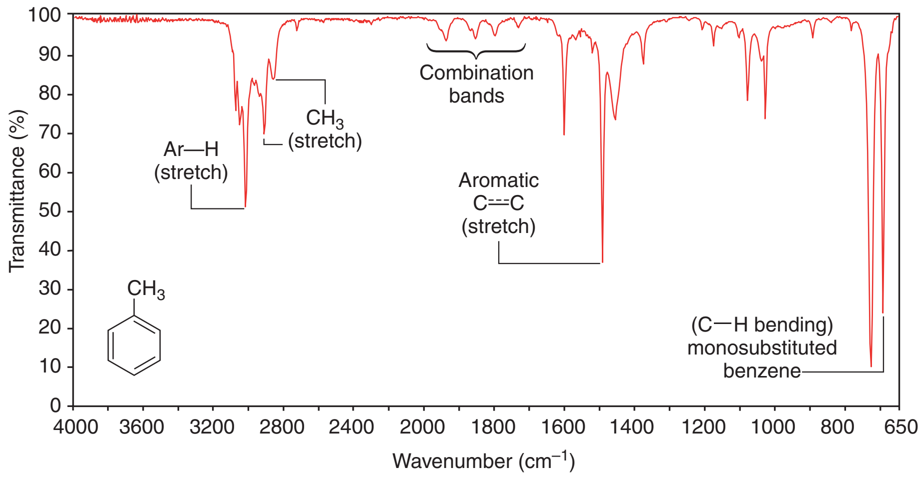


FIGURE 2.12 The IR spectrum of methylbenzene (toluene).

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 2800–3300-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 ($\equiv$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.

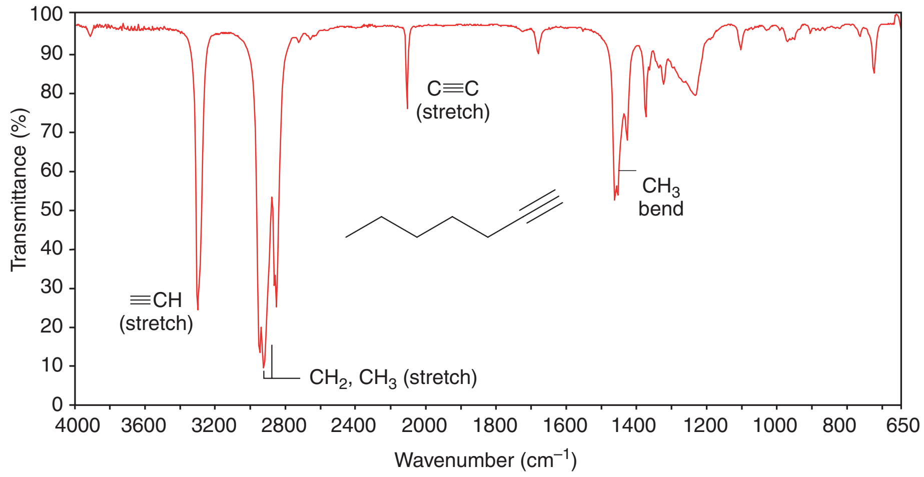
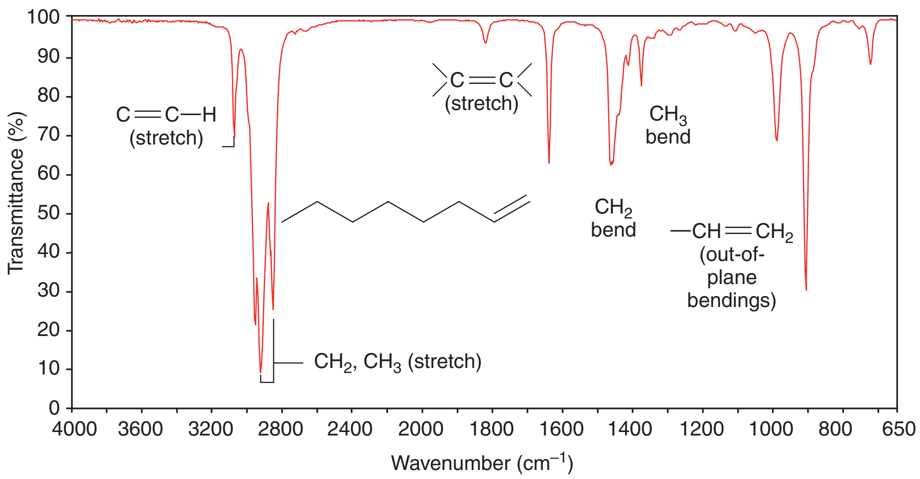


FIGURE 2.13 The IR spectrum of 1-heptyne.

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 3000–3100-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 2800–3000-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 1620–1680-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 1450–1600-cm^{-1} region.

- Absorptions arising from carbon–hydrogen bending vibrations of alkenes occur in the 600–1000-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.

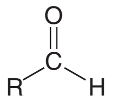
2.16B IR Spectra of Some Functional Groups Containing Heteroatoms

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

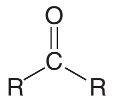
Carbonyl Functional Groups One important functional group that gives a prominent absorption peak in IR spectra is the **carbonyl group**, $\rangle C{=}O$. This group is present in aldehydes, ketones, esters, carboxylic acids, amides, and others.

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

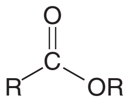
The exact location of the absorption depends on whether it arises from an aldehyde, ketone, ester, and so forth.



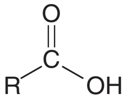
Aldehyde
1690–1740 cm^{-1}



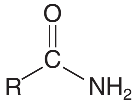
Ketone
1680–1750 cm^{-1}



Ester
1735–1750 cm^{-1}



Carboxylic acid
1710–1780 cm^{-1}

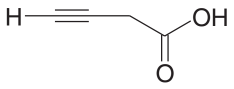


Amide
1630–1690 cm^{-1}

SOLVED PROBLEM 2.9

A compound with the molecular formula $C_4H_4O_2$ 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 CH_2 or CH_3 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.



PRACTICE PROBLEM 2.28

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?

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., CCl_4), 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.

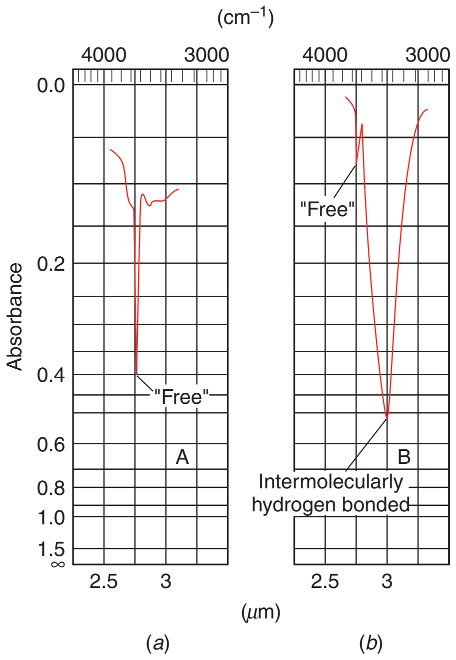


FIGURE 2.15 (*a*) The IR spectrum of an alcohol (cyclohexylcarbinol) in a dilute solution shows the sharp absorption of a "free" (non-hydrogen-bonded) hydroxyl group at 3600 cm^{-1}. (*b*) The IR spectrum of the same alcohol as a concentrated solution shows a broad hydroxyl group absorption at 3300 cm^{-1} 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 3300–3500-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.

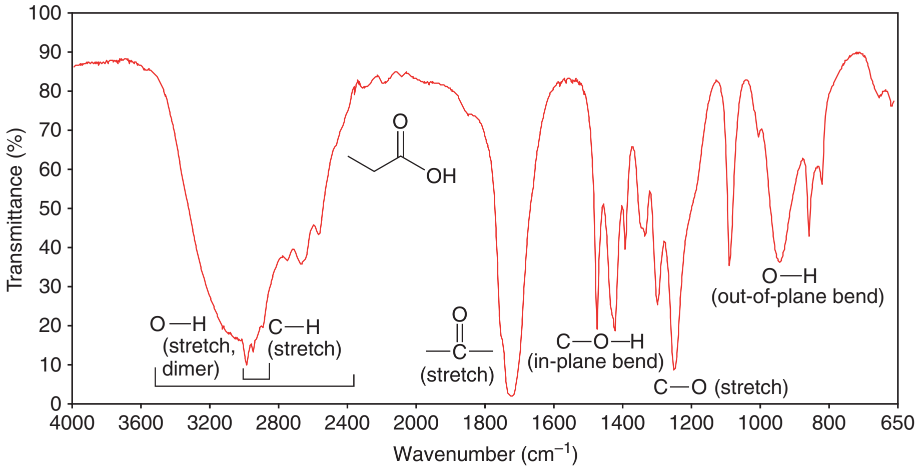


FIGURE 2.16 The IR spectrum of propanoic acid.

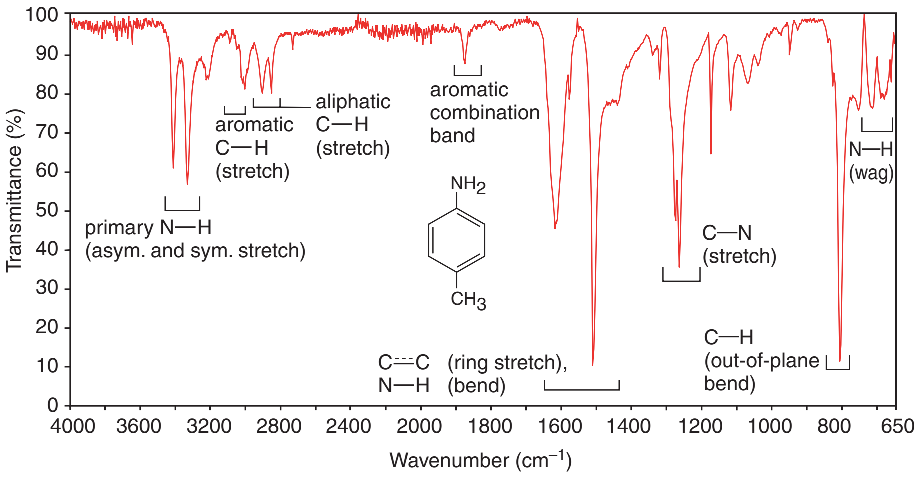
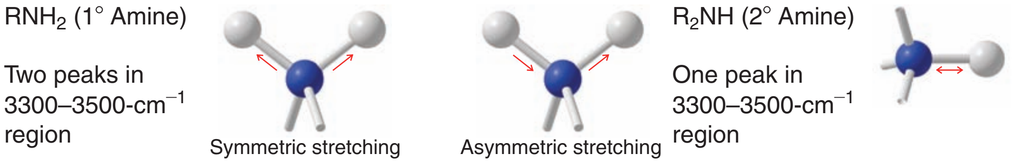


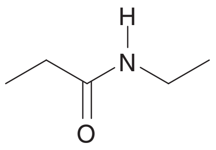
FIGURE 2.17 Annotated IR spectrum of 4-methylaniline.



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 1630–1690 cm^{-1} region arising from the carbonyl group and a single peak of moderate strength in the 3300–3500 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 2800–3000 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 1630–1780 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

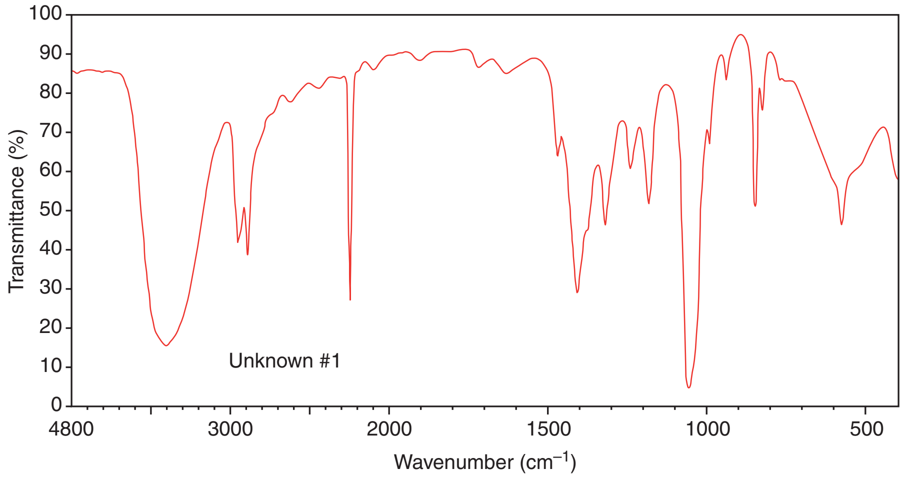


FIGURE 2.18 The IR Spectrum of Unknown 1. (SDBS, National Institute of Advanced Industrial Science and Technology)

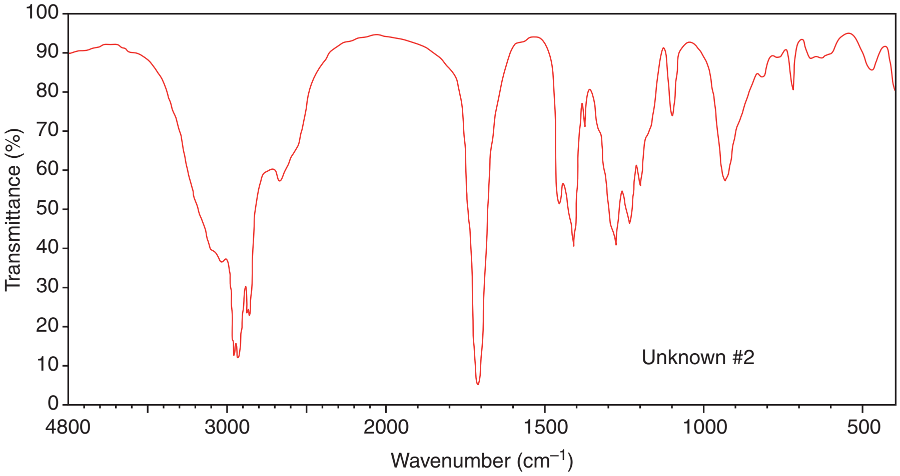


FIGURE 2.19 The IR Spectrum of Unknown 2. (SDBS, National Institute of Advanced Industrial Science and Technology)

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.

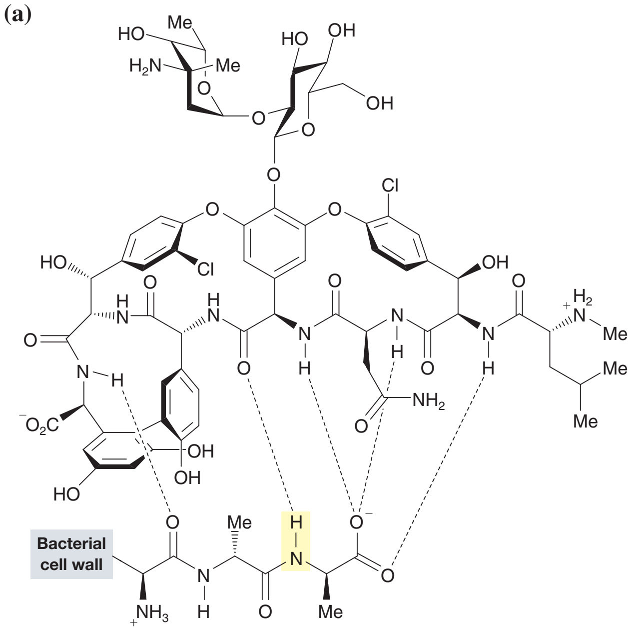
Molecular Structure Determines Properties We learned in Section 2.13 how physical properties are related to molecular structure.

[WHY Do These Topics Matter?

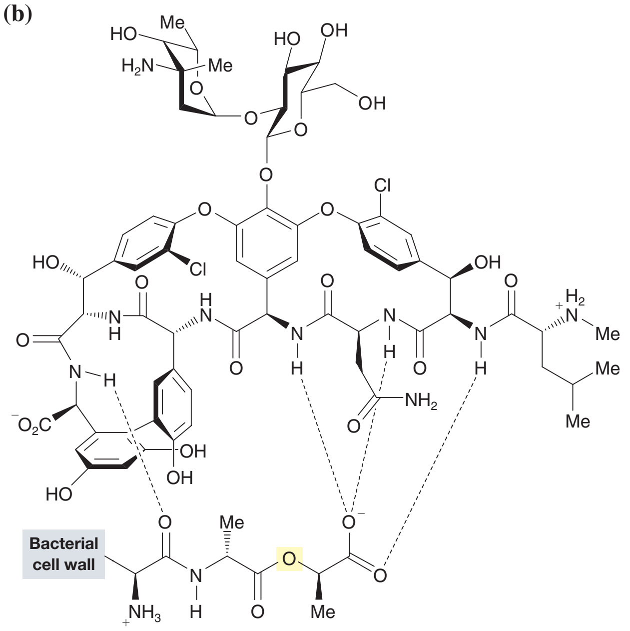
VANCOMYCIN AND ANTIBIOTIC RESISTANCE

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.



Vancomycin-susceptible bacteria



Vancomycin-resistant bacteria

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.

© WorldIllustrated/Photoshot

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 WILEY PLUS

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).

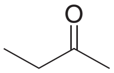
PROBLEMS WILEY PLUS

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

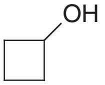
2.29 Classify each of the following compounds as an alkane, alkene, alkyne, alcohol, aldehyde, amine, and so forth.

(a)

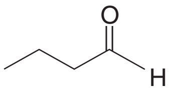


(b) $CH_3—C≡CH$

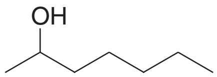
(c)



(d)

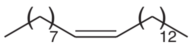


(e)



Obtained from oil of cloves

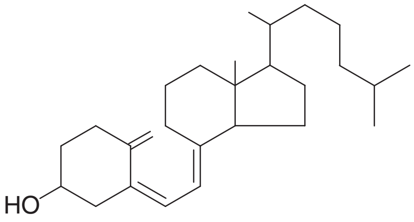
(f)



Sex attractant of the common housefly

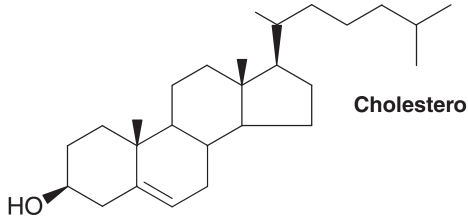
2.30 Identify all of the functional groups in each of the following compounds:

(a)



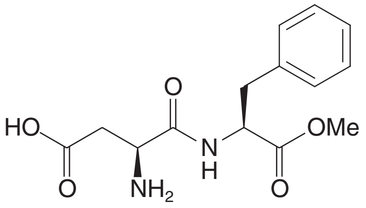
Vitamin D$_3$

(d)



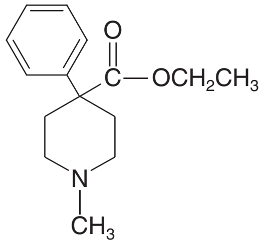
Cholesterol

(b)



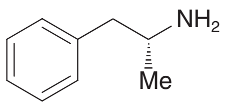
Aspartame

(e)



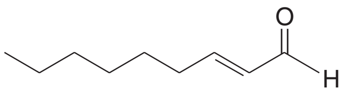
Demerol

(c)



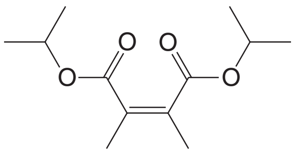
Amphetamine

(f)



A cockroach repellent found in cucumbers

(g)



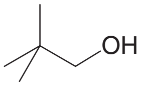
A synthetic cockroach repellent

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.

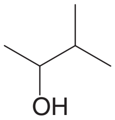
2.32 There are seven isomeric compounds with the formula $C_4H_{10}O$. Write their structures and classify each compound according to its functional group.

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

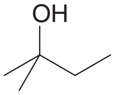
(a)



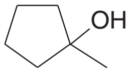
(b)



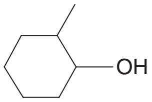
(c)



(d)

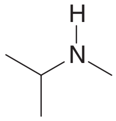


(e)

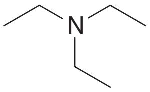


2.34 Classify the following amines as primary, secondary, or tertiary:

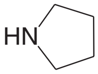
(a)



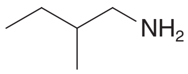
(c)



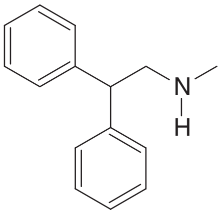
(e)



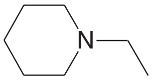
(b)



(d)



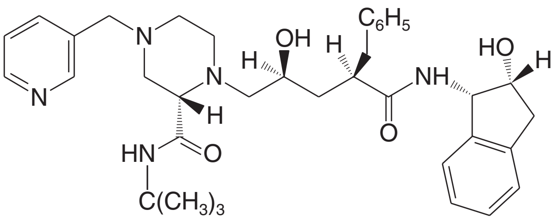
(f)



2.35 Write structural formulas for each of the following:

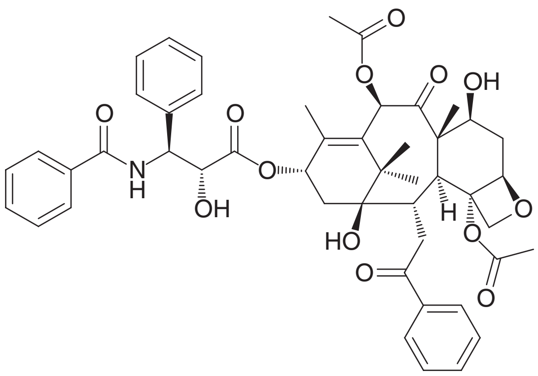
- **(a)** Three ethers with the formula $C_4H_{10}O$.
- **(b)** Three primary alcohols with the formula C_4H_8O.
- **(c)** A secondary alcohol with the formula C_3H_6O.
- **(d)** A tertiary alcohol with the formula C_4H_8O.
- **(e)** Two esters with the formula $C_3H_6O_2$.
- **(f)** Four primary alkyl 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.



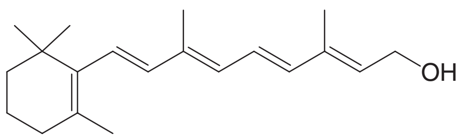
Crixivan (an HIV protease inhibitor)

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

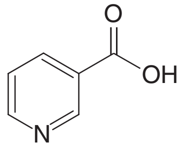


PHYSICAL PROPERTIES

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 B_3 (also called niacin).



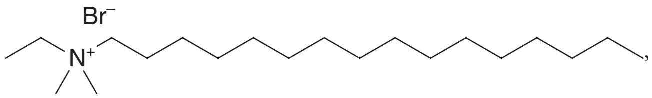
Vitamin A



Vitamin B_3 or niacin

2.39 Hydrogen fluoride has a dipole moment of 1.83 D; its boiling point is 19.34 °C. Ethyl fluoride (CH_3CH_2F) 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 Cetylethyldimethylammonium bromide is the common name for , a compound with antiseptic properties. Predict its solubility behavior in water and in diethyl ether.

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

(a) Liquid SO_2 **(b)** Liquid NH_3 **(c)** Benzene **(d)** CCl_4

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, ⟼. 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.)

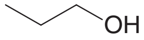
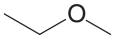
(a) CH_3F **(c)** CHF_3 **(e)** CH_2FCl **(g)** BeF_2 **(i)** CH_3OH

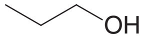
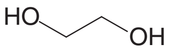
(b) CH_2F_2 **(d)** CF_4 **(f)** BCl_3 **(h)** CH_3OCH_3 **(j)** CH_2O

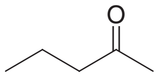
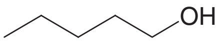
2.44 Consider each of the following molecules in turn: **(a)** dimethyl ether, $(CH_3)_2O$; **(b)** trimethylamine, $(CH_3)_3N$; **(c)** trimethylboron, $(CH_3)_3B$; and **(d)** dimethylberyllium, $(CH_3)_2Be$. Describe the hybridization state of the central atom (i.e., O, N, B, or Be) of each molecule, tell what bond angles you would expect at the central atom, and state whether the molecule would have a dipole moment.

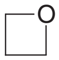
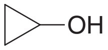
2.45 Analyze the statement: For a molecule to be polar, the presence of polar bonds is necessary, but it is not a sufficient requirement.

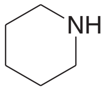
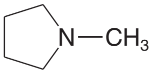
2.46 Which compound in each of the following pairs would have the higher boiling point? Explain your answers.

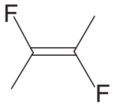
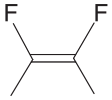
(a)  or 

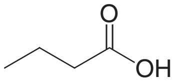
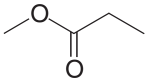
(b)  or 

(c)  or 

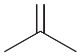
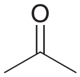
(d)  or 

(e)  or 

(f)  or 

(g)  or 

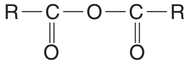
(h) Hexane, $CH_3(CH_2)_4CH_3$, or nonane, $CH_3(CH_2)_7CH_3$

(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,  $R{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}O{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}R$, 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.

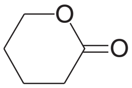
MULTICONCEPT PROBLEMS

2.50 Write structural formulas for four compounds with the formula C_3H_6O 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 C_3H_7NO. **(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 C_4H_6O that would not be expected to exhibit infrared absorption in the 3200–3550-cm^{-1} and 1620–1780-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 C_4H_6O 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 $C_5H_{10}O$, and contains two methyl groups and a 3° functional group. It has a broad infrared absorption band in the 3200–3550-cm^{-1} region and no absorption in the 1620–1680-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 $C_4H_8O_2$.

1. Write structures for at least 15 different compounds that all have the molecular formula $C_4H_8O_2$ and contain functional groups presented in this chapter.

2. 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.

3. Identify four different functional groups from among your structures. Circle and name them on the representative structures.

4. Predict approximate frequencies for IR absorptions that could be used to distinguish the four compounds representing these functional groups.

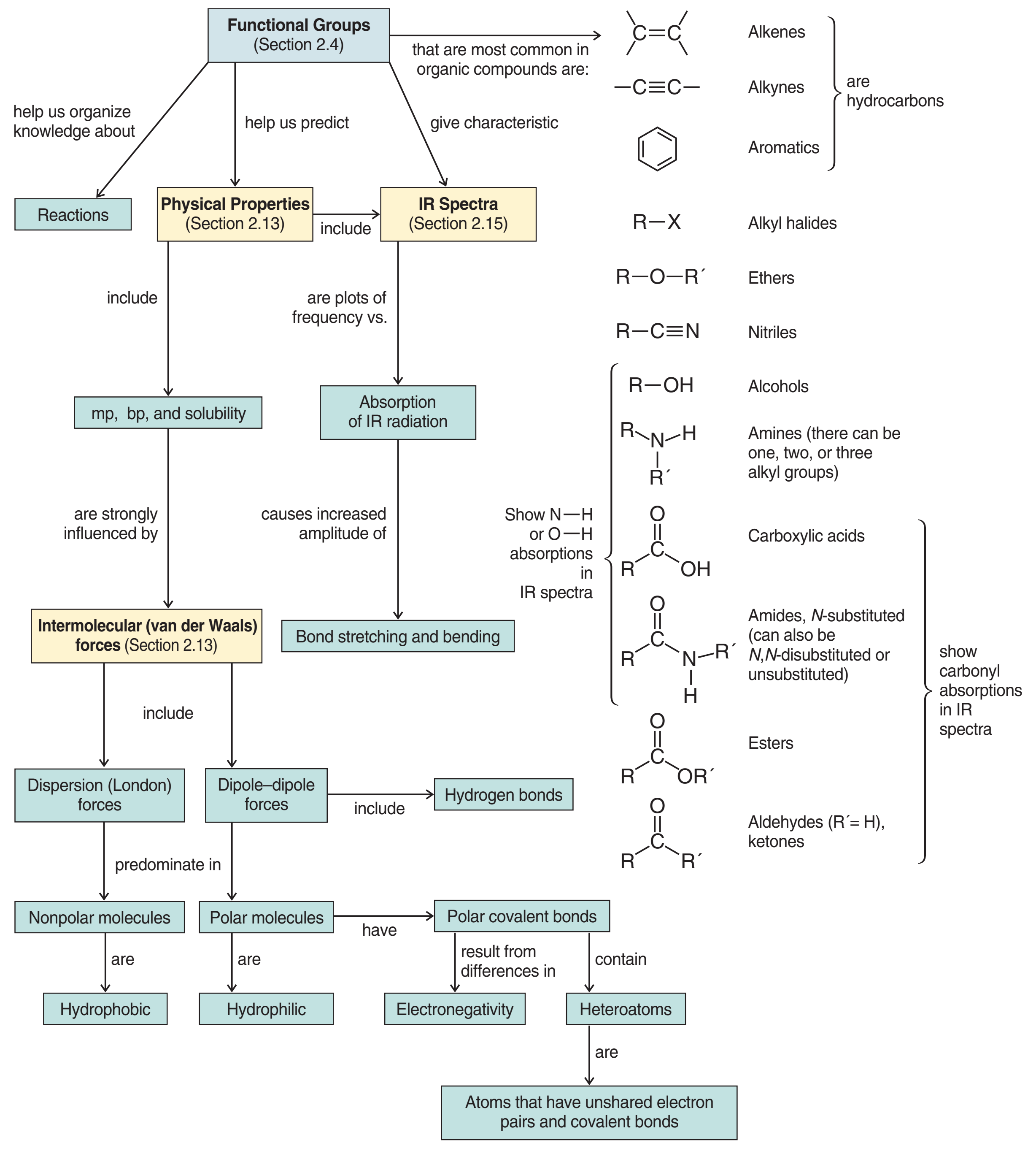
5. If any of the 15 structures you drew have atoms where the formal charge is other than zero, indicate the formal charge on the appropriate atom(s) and the overall charge for the molecule.

6. Identify which types of intermolecular forces would be possible in pure samples of all 15 compounds.

7. Pick five formulas you have drawn that represent a diversity of structures, and predict their order with respect to trend in increasing boiling point.

8. Explain your order of predicted boiling points on the basis of intermolecular forces and polarity.

CONCEPT MAP


Functional Groups (Section 2.4)
that are most common in organic compounds are:
help us organize knowledge about
help us predict
give characteristic
Reactions
Physical Properties (Section 2.13)
include
IR Spectra (Section 2.15)
include
are plots of frequency vs.
mp, bp, and solubility
Absorption of IR radiation
are strongly influenced by
causes increased amplitude of
Intermolecular (van der Waals) forces (Section 2.13)
Bond stretching and bending
include
Dispersion (London) forces
Dipole–dipole forces
include
Hydrogen bonds
predominate in
Nonpolar molecules
Polar molecules
have
Polar covalent bonds
are
are
result from differences in
contain
Hydrophobic
Hydrophilic
Electronegativity
Heteroatoms
are
Atoms that have unshared electron pairs and covalent bonds
C=C
Alkenes
—C≡C—
Alkynes
Aromatics
are hydrocarbons
R—X
Alkyl halides
R—O—R′
Ethers
R—C≡N
Nitriles
R—OH
Alcohols
R
N
H
R′
Amines (there can be one, two, or three alkyl groups)
Show N—H or O—H absorptions in IR spectra
O
C
R
OH
Carboxylic acids
O
C
R
N
R′
H
Amides, N-substituted (can also be N,N-disubstituted or unsubstituted)
O
C
R
OR′
Esters
O
C
R
R′
Aldehydes (R′= H), ketones
show carbonyl absorptions in IR spectra