

# ORGANIC CHEMISTRY

THIRD EDITION



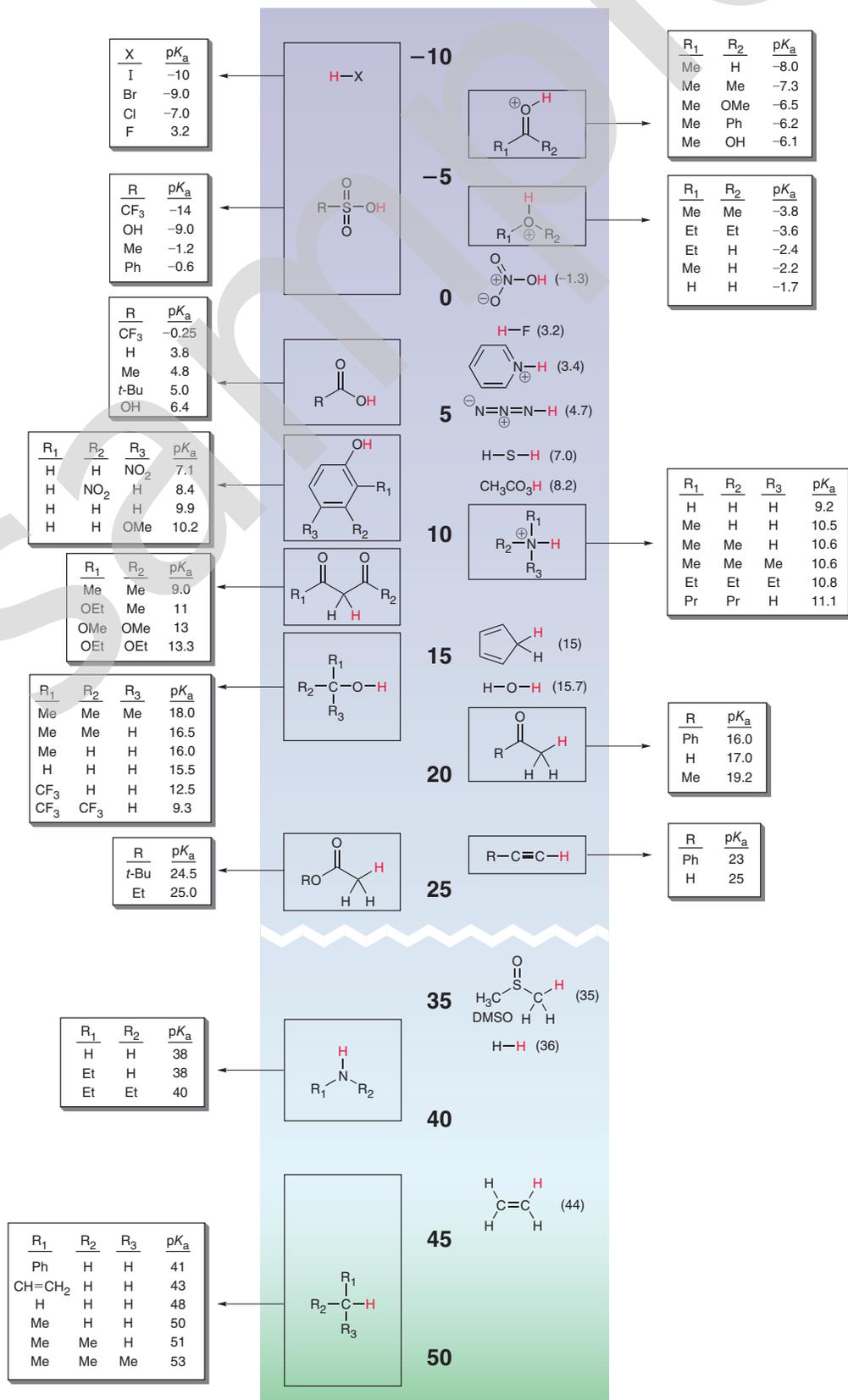
DAVID KLEIN

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# Approximate pK<sub>a</sub> Values for Commonly Encountered Structural Types



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# ORGANIC CHEMISTRY

THIRD EDITION



DAVID KLEIN

Johns Hopkins University

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# Dedication

*To my father and mother,*

*You have saved me (quite literally) on so many occasions, always steering me in the right direction. I have always cherished your guidance, which has served as a compass for me in all of my pursuits. You repeatedly urged me to work on this textbook (“write the book!”, you would say so often), with full confidence that it would be appreciated by students around the world. I will forever rely on the life lessons that you have taught me and the values that you have instilled in me. I love you.*

*To Larry,*

*By inspiring me to pursue a career in organic chemistry instruction, you served as the spark for the creation of this book. You showed me that any subject can be fascinating (even organic chemistry!) when presented by a masterful teacher. Your mentorship and friendship have profoundly shaped the course of my life, and I hope that this book will always serve as a source of pride and as a reminder of the impact you’ve had on your students.*

*To my wife, Vered,*

*This book would not have been possible without your partnership. As I worked for years in my office, you shouldered all of our life responsibilities, including taking care of all of the needs of our five amazing children. This book is our collective accomplishment and will forever serve as a testament of your constant support that I have come to depend on for everything in life. You are my rock, my partner, and my best friend. I love you.*



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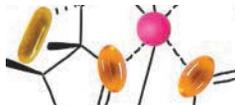
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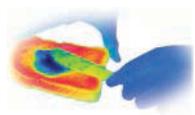
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# Preface

## WHY I WROTE THIS BOOK

Students who perform poorly on organic chemistry exams often report having invested countless hours studying. Why do many students have difficulty preparing themselves for organic chemistry exams? Certainly, there are several contributing factors, including inefficient study habits, but perhaps the most dominant factor is a fundamental *disconnect* between what students learn in the lecture hall and the tasks expected of them during an exam. To illustrate the disconnect, consider the following analogy.

Imagine that a prestigious university offers a course entitled “Bike-Riding 101.” Throughout the course, physics and engineering professors explain many concepts and principles (for example, how bicycles have been engineered to minimize air resistance). Students invest significant time studying the information that was presented, and on the last day of the course, the final exam consists of riding a bike for a distance of 100 feet. A few students may have innate talents and can accomplish the task without falling. But most students will fall several times, slowly making it to the finish line, bruised and hurt; and many students will not be able to ride for even one second without falling. Why? Because there is a *disconnect* between what the students learned and what they were expected to do for their exam.

Many years ago, I noticed that a similar disconnect exists in traditional organic chemistry instruction. That is, learning organic chemistry is much like bicycle riding; just as the students in the bike-riding analogy were expected to ride a bike after attending lectures, it is often expected that organic chemistry students will independently develop the necessary skills for solving problems. While a few students have innate talents and are able to develop the necessary skills independently, most students require guidance. This guidance was not consistently integrated within existing textbooks, prompting me to write the first edition of my textbook, *Organic Chemistry*. The main goal of my text was to employ a skills-based approach to bridge the gap between theory (concepts) and practice (problem-solving skills). The second edition further supported this goal by introducing hundreds of additional problems based on the chemical literature, thereby exposing students to exciting real-world examples of chemical research being conducted in real laboratories. The phenomenal success of the first two editions has been extremely gratifying because it provided strong evidence that my skills-based approach is indeed effective at bridging the gap described above.

I firmly believe that the scientific discipline of organic chemistry is NOT merely a compilation of principles, but rather, it is a disciplined method of thought and analysis. Students must certainly understand the concepts and principles, but more importantly, students must learn to think like organic chemists . . . that is, they must learn to become proficient at approaching new situations methodically, based on a repertoire of skills. That is the true essence of organic chemistry.

## A SKILLS-BASED APPROACH

To address the disconnect in organic chemistry instruction, I have developed a *skills-based approach* to instruction. The textbook includes all of the concepts typically covered in an organic chemistry textbook, complete with *conceptual checkpoints* that promote mastery of the concepts, but special emphasis is placed on skills development through SkillBuilders to support these concepts. Each SkillBuilder contains three parts:

**Learn the Skill:** contains a solved problem that demonstrates a particular skill.

**Practice the Skill:** includes numerous problems (similar to the solved problem in *Learn the Skill*) that give students valuable opportunities to practice and master the skill.

**Apply the Skill:** contains one or two more problems in which the student must apply the skill to solve real-world problems (as reported in the chemical literature). These problems include conceptual, cumulative, and applied problems that encourage students to think outside of the box. Sometimes problems that foreshadow concepts introduced in later chapters are also included.

At the end of each SkillBuilder, a *Need More Practice?* reference suggests end-of-chapter problems that students can work to practice the skill.

This emphasis upon skills development provides students with a greater opportunity to develop proficiency in the key skills necessary to succeed in organic chemistry. Certainly, not all necessary skills can be covered in a textbook. However, there are certain skills that are fundamental to all other skills.

As an example, resonance structures are used repeatedly throughout the course, and students must become masters of resonance structures early in the course. Therefore, a significant portion of Chapter 2 is devoted to pattern-recognition for drawing resonance structures. Rather than just providing a list of rules and then a few follow-up problems, the skills-based approach provides students with a series of skills, each of which must be mastered in sequence. Each skill is reinforced with numerous practice problems. The sequence of skills is designed to foster and develop proficiency in drawing resonance structures.

The skills-based approach to organic chemistry instruction is a unique approach. Certainly, other textbooks contain tips for problem solving, but no other textbook consistently presents skills development as the primary vehicle for instruction.

## WHAT'S NEW IN THIS EDITION

Peer review played a very strong role in the development of the first and second editions of *Organic Chemistry*. Specifically, the first edition manuscript was reviewed by nearly 500 professors and over 5,000 students, and the second edition manuscript was based on

comments received from 300 professors and 900 students. In preparing the third edition, peer review has played an equally prominent role. We have received a tremendous amount of input from the market, including surveys, class tests, diary reviews, and phone interviews. All of this input has been carefully culled and has been instrumental in identifying the focus of the third edition.

### New Features in the Third Edition

- A new chapter on organometallic reactions covers modern synthetic techniques, including Stille coupling, Suzuki coupling, Negishi coupling, the Heck reaction, and alkene metathesis.
- Substitution and elimination reactions have been combined into one chapter. This chapter (Chapter 7) also features a new section covering the preparation and reactions of alkyl tosylates, as well as a new section covering kinetic isotope effects. In addition, a new section introducing retrosynthesis has been added to the end of the chapter, so that synthesis and retrosynthesis are now introduced much earlier.
- For most SkillBuilders throughout the text, the Apply the Skill problem(s) have been replaced with moderate-level, literature-based problems. There are at least 150 of these new problems, which will expose students to exciting real-world examples of chemical research being conducted in real laboratories. Students will see that organic chemistry is a vibrant field of study, with endless possibilities for exploration and research that can benefit the world in concrete ways.
- Throughout the text, the distribution of problems has been improved by reducing the number of easy problems, and increasing the number of moderate-level, literature-based problems.
- Each chapter now includes a problem set that mimics the style of the ACS Organic Chemistry Exam.
- The section covering oxidation of alcohols (in Chapter 12, and then again in Chapter 19) has been enhanced to include modern oxidation methods, such as Swern and DMP-based oxidations.
- Coverage of Wittig reactions has been updated to include stereochemical outcomes and the Horner–Wadsworth–Emmons variation.
- Section 2.11 has been revised (Assessing the relative importance of resonance structures). The rules have been completely rewritten to focus on the importance of octets and locations of charges. The improved rules will provide students with a deeper conceptual understanding.
- In Chapter 2, a new section covers the skills necessary for drawing a resonance hybrid.
- At the end of Chapter 5 (Stereoisomerism), a new section introduces chiral compounds that lack chiral centers, including chiral allenes and chiral biphenyls.
- A new section in Chapter 11 (Synthesis) introduces “green chemistry” (atom economy, toxicology issues, etc.).
- Coverage of *E-Z* nomenclature has been moved earlier. It now appears in Chapter 5, which covers stereoisomerism.

### TEXT ORGANIZATION

The sequence of chapters and topics in *Organic Chemistry, 3e* does not differ markedly from that of other organic chemistry textbooks. Indeed, the topics are presented in the traditional order, based on functional groups (alkenes, alkynes, alcohols, ethers, aldehydes and ketones, carboxylic acid derivatives, etc.). Despite this traditional order, a strong emphasis is placed on mechanisms, with a focus on pattern recognition to illustrate the similarities between reactions that would otherwise appear unrelated. No shortcuts were taken in any of the mechanisms, and all steps are clearly illustrated, including all proton transfer steps.

Two chapters (6 and 11) are devoted almost entirely to skill development and are generally not found in other textbooks. Chapter 6, *Chemical Reactivity and Mechanisms*, emphasizes skills that are necessary for drawing mechanisms, while Chapter 11, *Synthesis*, prepares the students for proposing syntheses. These two chapters are strategically positioned within the traditional order described above and can be assigned to the students for independent study. That is, these two chapters do not need to be covered during precious lecture hours, but can be, if so desired.

The traditional order allows instructors to adopt the skills-based approach without having to change their lecture notes or methods. For this reason, the spectroscopy chapters (Chapters 14 and 15) were written to be stand-alone and portable, so that instructors can cover these chapters in any order desired. In fact, five of the chapters (Chapters 2, 3, 7, 12, and 13) that precede the spectroscopy chapters include end-of-chapter spectroscopy problems, for those students who covered spectroscopy earlier. Spectroscopy coverage also appears in subsequent functional group chapters, specifically Chapter 17 (*Aromatic Compounds*), Chapter 19 (*Aldehydes and Ketones*), Chapter 20 (*Carboxylic Acids and Their Derivatives*), Chapter 22 (*Amines*), Chapter 24 (*Carbohydrates*), and Chapter 25 (*Amino Acids, Peptides, and Proteins*).

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- **NEW Author-curated course** includes reading materials, embedded resources, practice, and problems that have been chosen specifically by the author
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**Molecular Visions™ Model Kit** To support the learning of organic chemistry concepts and allow students the tactile experience of manipulating physical models, we offer a molecular modeling kit from the Darling Company. The model kit can be bundled with the textbook or purchased stand alone.

## ADDITIONAL INSTRUCTOR RESOURCES

**Testbank** Prepared by Christine Hermann, *Radford University*.

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**PowerPoint Art Slides** Prepared by Kevin Minbiole, *Villanova University*.

**Personal Response System ("Clicker") Questions** Prepared by Dalila Kovacs, *Grand Valley State University* and Randy Winchester, *Grand Valley State University*.

## CONTRIBUTORS TO ORGANIC CHEMISTRY, 3E

I owe special thanks to my contributors for their collaboration, hard work, and creativity. Many of the new, literature-based, SkillBuilder problems were written by Laurie Starkey, *California State Polytechnic University, Pomona*; Tiffany Gierasch, *University of Maryland, Baltimore County*; Seth Elsheimer, *University of Central Florida*; and James Mackay, *Elizabethtown College*. Sections 2.11 and 19.10 were rewritten by Laurie Starkey, and Section 2.12 was written by Tiffany Gierasch. Many of the new Medically Speaking and Practically Speaking applications throughout the text were written by Ron Swisher, *Oregon Institute of Technology*.

## STUDENT RESOURCES

**Student Study Guide and Solutions Manual (ISBN 9781118700815)** Authored by David Klein. The third edition of the *Student Study Guide and Solutions Manual* to accompany *Organic Chemistry, 3e* contains:

- More detailed explanations within the solutions for every problem.

## ACKNOWLEDGMENTS

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Despite my best efforts, as well as the best efforts of the reviewers, accuracy checkers, and class testers, errors may still exist. I take full responsibility for any such errors and would encourage those using my textbook to contact me with any errors that you may find.

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# A Review of General Chemistry

ELECTRONS, BONDS, AND MOLECULAR PROPERTIES

## DID YOU EVER WONDER... what causes lightning?

**B**elieve it or not, the answer to this question is still the subject of debate (that's right... scientists have not yet figured out everything, contrary to popular belief). There are various theories that attempt to explain what causes the buildup of electric charge in clouds. One thing is clear, though—lightning involves a flow of electrons. By studying the nature of electrons and how electrons flow, it is possible to control where lightning will strike. A tall building can be protected by installing a lightning rod (a tall metal column at the top of the building) that attracts any nearby lightning bolt, thereby preventing a direct strike on the building itself. The lightning rod on the top of the Empire State Building is struck over a hundred times each year.

Just as scientists have discovered how to direct electrons in a bolt of lightning, chemists have also discovered how to direct electrons in chemical reactions. We will soon see that although organic chemistry is literally defined as the study of compounds containing carbon atoms, its true essence is actually the study of electrons, not atoms. Rather than thinking of reactions in terms of the motion of atoms, we must recognize that

*continued >*

- 1.1 Introduction to Organic Chemistry
- 1.2 The Structural Theory of Matter
- 1.3 Electrons, Bonds, and Lewis Structures
- 1.4 Identifying Formal Charges
- 1.5 Induction and Polar Covalent Bonds
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- 1.9 Hybridized Atomic Orbitals
- 1.10 Predicting Molecular Geometry: VESPR Theory
- 1.11 Dipole Moments and Molecular Polarity
- 1.12 Intermolecular Forces and Physical Properties
- 1.13 Solubility



reactions occur as a result of the motion of electrons. For example, in the following reaction the curved arrows represent the motion, or flow, of electrons. This flow of electrons causes the chemical change shown:

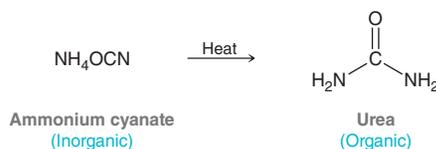


Throughout this course, we will learn how, when, and why electrons flow during reactions. We will learn about the barriers that prevent electrons from flowing, and we will learn how to overcome those barriers. In short, we will study the behavioral patterns of electrons, enabling us to predict, and even control, the outcomes of chemical reactions.

This chapter reviews some relevant concepts from your general chemistry course that should be familiar to you. Specifically, we will focus on the central role of electrons in forming bonds and influencing molecular properties.

## 1.1 Introduction to Organic Chemistry

In the early nineteenth century, scientists classified all known compounds into two categories: *Organic compounds* were derived from living organisms (plants and animals), while *inorganic compounds* were derived from nonliving sources (minerals and gases). This distinction was fueled by the observation that organic compounds seemed to possess different properties than inorganic compounds. Organic compounds were often difficult to isolate and purify, and upon heating, they decomposed more readily than inorganic compounds. To explain these curious observations, many scientists subscribed to a belief that compounds obtained from living sources possessed a special “vital force” that inorganic compounds lacked. This notion, called vitalism, stipulated that it should be impossible to convert inorganic compounds into organic compounds without the introduction of an outside vital force. Vitalism was dealt a serious blow in 1828 when German chemist Friedrich Wöhler demonstrated the conversion of ammonium cyanate (a known inorganic salt) into urea, a known organic compound found in urine:



### BY THE WAY

There are some carbon-containing compounds that are traditionally excluded from organic classification. For example, ammonium cyanate (seen on this page) is still classified as inorganic, despite the presence of a carbon atom. Other exceptions include sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) and potassium cyanide (KCN), both of which are also considered to be inorganic compounds. We will not encounter many more exceptions.

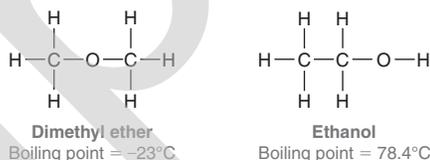
Over the decades that followed, other examples were found, and the concept of vitalism was gradually rejected. The downfall of vitalism shattered the original distinction between organic and inorganic compounds, and a new definition emerged. Specifically, organic compounds became defined as those compounds containing carbon atoms, while inorganic compounds generally were defined as those compounds lacking carbon atoms.

Organic chemistry occupies a central role in the world around us, as we are surrounded by organic compounds. The food that we eat and the clothes that we wear are comprised of organic compounds. Our ability to smell odors or see colors results from the behavior of organic compounds. Pharmaceuticals, pesticides, paints, adhesives, and plastics are all made from organic compounds. In fact, our bodies are constructed mostly from organic compounds (DNA, RNA, proteins, etc.) whose behavior and function are determined by the guiding principles of organic chemistry. The responses of our bodies to pharmaceuticals are the results of reactions guided by the principles of organic chemistry. A deep understanding of those principles enables the design of new drugs that fight disease and improve the overall quality of life and longevity. Accordingly, it is not surprising that organic chemistry is required knowledge for anyone entering the health professions.



## 1.2 The Structural Theory of Matter

In the mid-nineteenth century three individuals, working independently, laid the conceptual foundations for the structural theory of matter. August Kekulé, Archibald Scott Couper, and Alexander M. Butlerov each suggested that substances are defined by a specific arrangement of atoms. As an example, consider the following two compounds:



These compounds have the same molecular formula ( $\text{C}_2\text{H}_6\text{O}$ ), yet they differ from each other in the way the atoms are connected—that is, they differ in their constitution. As a result, they are called **constitutional isomers**. Constitutional isomers have different physical properties and different names. The first compound is a colorless gas used as an aerosol spray propellant, while the second compound is a clear liquid, commonly referred to as “alcohol,” found in alcoholic beverages.

According to the structural theory of matter, each element will generally form a predictable number of bonds. For example, carbon generally forms four bonds and is therefore said to be **tetravalent**. Nitrogen generally forms three bonds and is therefore **trivalent**. Oxygen forms two bonds and is **divalent**, while hydrogen and the halogens form one bond and are **monovalent** (Figure 1.1).

<i>Tetravalent</i>	<i>Trivalent</i>	<i>Divalent</i>	<i>Monovalent</i>
$\begin{array}{c}   \\ -\text{C}- \\   \end{array}$	$\begin{array}{c} -\text{N}- \\   \end{array}$	$-\text{O}-$	$\text{H}-\quad \text{X}-$ (where X = F, Cl, Br, or I)
Carbon generally forms <b>four</b> bonds.	Nitrogen generally forms <b>three</b> bonds.	Oxygen generally forms <b>two</b> bonds.	Hydrogen and halogens generally form <b>one</b> bond.

**FIGURE 1.1**

Valencies of some common elements encountered in organic chemistry.

## SKILLBUILDER



### 1.1 DRAWING CONSTITUTIONAL ISOMERS OF SMALL MOLECULES

#### LEARN the skill

Draw all constitutional isomers that have the molecular formula  $\text{C}_3\text{H}_8\text{O}$ .

#### STEP 1

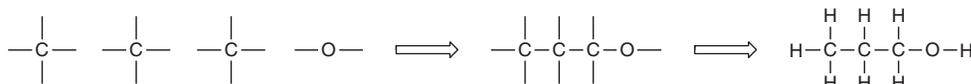
Determine the valency of each atom that appears in the molecular formula.

#### STEP 2

Connect the atoms of highest valency, and place the monovalent atoms at the periphery.

#### SOLUTION

Begin by determining the valency of each atom that appears in the molecular formula. Carbon is tetravalent, hydrogen is monovalent, and oxygen is divalent. The atoms with the highest valency are connected first. So, in this case, we draw our first isomer by connecting the three carbon atoms, as well as the oxygen atom, as shown below. The drawing is completed when the monovalent atoms (H) are placed at the periphery:



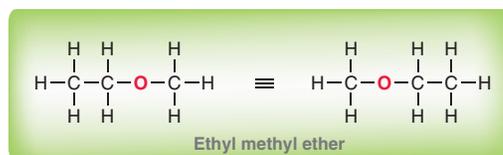
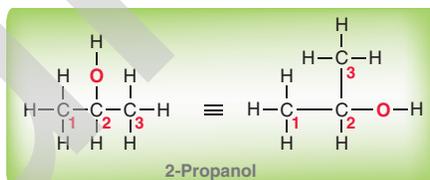
This isomer (called 1-propanol) can be drawn in many different ways, some of which are shown here:



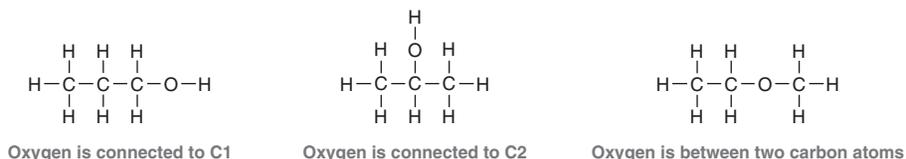
All of these drawings represent the same isomer. If we number the carbon atoms (C1, C2, and C3), with C1 being the carbon atom connected to oxygen, then all of the drawings above show the same connectivity: a three-carbon chain with an oxygen atom attached at one end of the chain.

**STEP 3**  
Consider other ways to connect the atoms.

Thus far, we have drawn just one isomer that has the molecular formula  $\text{C}_3\text{H}_8\text{O}$ . Other constitutional isomers can be drawn if we consider other possible ways of connecting the three carbon atoms and the oxygen atom. For example, the oxygen atom can be connected to C2 (rather than C1), giving a compound called 2-propanol (shown below). Alternatively, the oxygen atom can be inserted between two carbon atoms, giving a compound called ethyl methyl ether (also shown below). For each isomer, two of the many acceptable drawings are shown:



If we continue to search for alternate ways of connecting the three carbon atoms and the oxygen atom, we will not find any other ways of connecting them. So in summary, there are a total of three constitutional isomers with the molecular formula  $\text{C}_3\text{H}_8\text{O}$ , shown here:



Additional skills (not yet discussed) are required to draw constitutional isomers of compounds containing a ring, a double bond, or a triple bond. Those skills will be developed in Section 14.16.



**PRACTICE the skill** 1.1 Draw all constitutional isomers with the following molecular formula.

(a)  $\text{C}_3\text{H}_7\text{Cl}$     (b)  $\text{C}_4\text{H}_{10}$     (c)  $\text{C}_5\text{H}_{12}$     (d)  $\text{C}_4\text{H}_{10}\text{O}$     (e)  $\text{C}_3\text{H}_6\text{Cl}_2$



**APPLY the skill**

1.2 Chlorofluorocarbons (CFCs) are gases that were once widely used as refrigerants and propellants. When it was discovered that these molecules contributed to the depletion of the ozone layer, their use was banned, but CFCs continue to be detected as contaminants in the environment.<sup>1</sup> Draw all of the constitutional isomers of CFCs that have the molecular formula  $\text{C}_2\text{Cl}_3\text{F}_3$ .

need more PRACTICE? Try Problems 1.35, 1.46, 1.47, 1.54

## 1.3 Electrons, Bonds, and Lewis Structures

### What Are Bonds?

As mentioned, atoms are connected to each other by bonds. That is, bonds are the “glue” that hold atoms together. But what is this mysterious glue and how does it work? In order to answer this question, we must focus our attention on electrons.

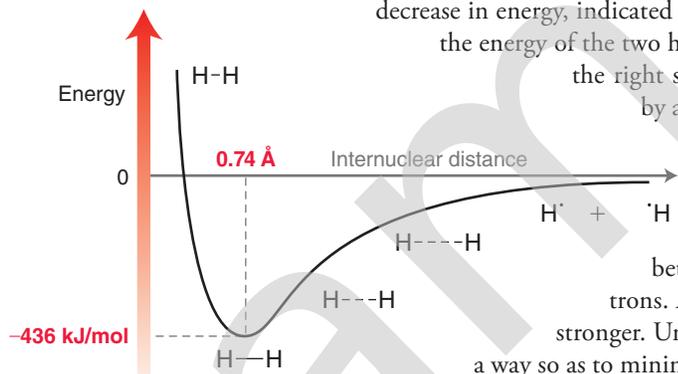
The existence of the electron was first proposed in 1874 by George Johnstone Stoney (National University of Ireland), who attempted to explain electrochemistry by suggesting the existence



of a particle bearing a unit of charge. Stoney coined the term *electron* to describe this particle. In 1897, J. J. Thomson (Cambridge University) demonstrated evidence supporting the existence of Stoney's mysterious electron and is credited with discovering the electron. In 1916, Gilbert Lewis (University of California, Berkeley) defined a **covalent bond** as the result of *two atoms sharing a pair of electrons*. As a simple example, consider the formation of a bond between two hydrogen atoms:



Each hydrogen atom has one electron. When these electrons are shared to form a bond, there is a decrease in energy, indicated by the negative value of  $\Delta H$ . The energy diagram in Figure 1.2 plots the energy of the two hydrogen atoms as a function of the distance between them. Focus on the right side of the diagram, which represents the hydrogen atoms separated by a large distance. Moving toward the left on the diagram, the hydrogen atoms approach each other, and there are several forces that must be taken into account: (1) the force of repulsion between the two negatively charged electrons, (2) the force of repulsion between the two positively charged nuclei, and (3) the forces of attraction between the positively charged nuclei and the negatively charged electrons. As the hydrogen atoms get closer to each other, all of these forces get stronger. Under these circumstances, the electrons are capable of moving in such a way so as to minimize the repulsive forces between them while maximizing their attractive forces with the nuclei. This provides for a net force of attraction, which lowers the energy of the system. As the hydrogen atoms move still closer together, the energy continues to be lowered until the nuclei achieve a separation (internuclear distance) of 0.74 angstroms ( $\text{\AA}$ ). At that point, the force of repulsion between the nuclei begins to overwhelm the forces of attraction, causing the energy of the system to increase if the atoms are brought any closer together. The lowest point on the curve represents the lowest energy (most stable) state. This state determines both the bond length (0.74  $\text{\AA}$ ) and the bond strength (436 kJ/mol).



**FIGURE 1.2**

An energy diagram showing the energy as a function of the internuclear distance between two hydrogen atoms.

#### BY THE WAY

$1 \text{ \AA} = 10^{-10}$  meters.

### Drawing the Lewis Structure of an Atom

Armed with the idea that a bond represents a pair of shared electrons, Lewis then devised a method for drawing structures. In his drawings, called **Lewis structures**, the electrons take center stage. We will begin by drawing individual atoms, and then we will draw Lewis structures for small molecules. First, we must review a few simple features of atomic structure:

- The nucleus of an atom is comprised of protons and neutrons. Each proton has a charge of +1, and each neutron is electrically neutral.
- For a neutral atom, the number of protons is balanced by an equal number of electrons, which have a charge of  $-1$  and exist in shells. The first shell, which is closest to the nucleus, can contain two electrons, and the second shell can contain up to eight electrons.
- The electrons in the outermost shell of an atom are called the valence electrons. The number of valence electrons in an atom is identified by its group number in the periodic table (Figure 1.3).

1A	2A		3A	4A	5A	6A	7A	8A
H	He		B	C	N	O	F	Ne
Li	Be		Al	Si	P	S	Cl	Ar
Na	Mg		Ga	Ge	As	Se	Br	Kr
K	Ca	Transition Metal Elements	In	Sn	Sb	Te	I	Xe
Rb	Sr		Tl	Pb	Bi	Po	At	Rn
Cs	Ba							

**FIGURE 1.3**

A periodic table showing group numbers.

The Lewis dot structure of an individual atom indicates the number of valence electrons, which are placed as dots around the periodic symbol of the atom (C for carbon, O for oxygen, etc.). The placement of these dots is illustrated in the following SkillBuilder.

## SKILLBUILDER



## 1.2 DRAWING THE LEWIS DOT STRUCTURE OF AN ATOM

## LEARN the skill

Draw the Lewis dot structure of (a) a boron atom and (b) a nitrogen atom.

## STEP 1

Determine the number of valence electrons.

## STEP 2

Place one valence electron by itself on each side of the atom.

## STEP 3

If the atom has more than four valence electrons, the remaining electrons are paired with the electrons already drawn.

## SOLUTION

(a) In a Lewis dot structure, only valence electrons are drawn, so we must first determine the number of valence electrons. Boron belongs to group 3A on the periodic table, and it therefore has three valence electrons. The periodic symbol for boron (B) is drawn, and each electron is placed by itself (unpaired) around the B, like this:



(b) Nitrogen belongs to group 5A on the periodic table, and it therefore has five valence electrons. The periodic symbol for nitrogen (N) is drawn, and each electron is placed by itself (unpaired) on a side of the N until all four sides are occupied:



Any remaining electrons must be paired up with the electrons already drawn. In the case of nitrogen, there is only one more electron to place, so we pair it up with one of the four unpaired electrons (it doesn't matter which one we choose):



## PRACTICE the skill

1.3 Draw a Lewis dot structure for each of the following atoms:

- (a) Carbon      (b) Oxygen      (c) Fluorine      (d) Hydrogen  
 (e) Bromine      (f) Sulfur      (g) Chlorine      (h) Iodine

1.4 Compare the Lewis dot structure of nitrogen and phosphorus and explain why you might expect these two atoms to exhibit similar bonding properties.

1.5 Name one element that you would expect to exhibit bonding properties similar to boron. Explain.

1.6 Draw a Lewis structure of a carbon atom that is missing one valence electron (and therefore bears a positive charge). Which second-row element does this carbon atom resemble in terms of the number of valence electrons?

## APPLY the skill

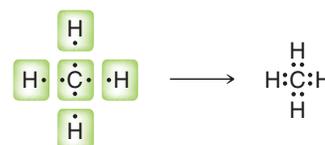
1.7 Lithium salts have been used for decades to treat mental illnesses, including depression and bipolar disorder. Although the treatment is effective, researchers are still trying to determine how lithium salts behave as mood stabilizers.<sup>2</sup>

(a) Draw a Lewis structure of an uncharged lithium atom, Li.

(b) Lithium salts contain a lithium atom that is missing one valence electron (and therefore bears a positive charge). Draw a Lewis structure of the lithium cation.

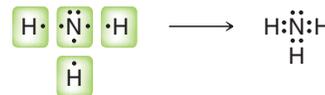
## Drawing the Lewis Structure of a Small Molecule

The Lewis dot structures of individual atoms are combined to produce Lewis dot structures of small molecules. These drawings are constructed based on the observation that atoms tend to bond in such a way so as to achieve the electron configuration of a noble gas. For example, hydrogen will form one bond to achieve the electron configuration of helium (two valence electrons), while second-row elements (C, N, O, and F) will form the necessary number of bonds so as to achieve the electron configuration of neon (eight valence electrons).





This observation, called the **octet rule**, explains why carbon is tetravalent. As just shown, it can achieve an octet of electrons by using each of its four valence electrons to form a bond. The octet rule also explains why nitrogen is trivalent. Specifically, it has five valence electrons and requires three bonds in order to achieve an octet of electrons. Notice that the nitrogen atom contains one pair of unshared, or nonbonding, electrons, called a **lone pair**.



In the next chapter, we will discuss the octet rule in more detail; in particular, we will explore when it can be violated and when it cannot be violated. For now, let's practice drawing Lewis structures.

## SKILLBUILDER



### 1.3 DRAWING THE LEWIS STRUCTURE OF A SMALL MOLECULE

#### LEARN the skill

Draw the Lewis structure of  $\text{CH}_2\text{O}$ .

#### SOLUTION

There are four discrete steps when drawing a Lewis structure: First determine the number of valence electrons for each atom.

##### STEP 1

Draw all individual atoms.



##### STEP 2

Connect atoms that form more than one bond.

Then, connect any atoms that form more than one bond. Hydrogen atoms only form one bond each, so we will save those for last. In this case, we connect the C and the O.



##### STEP 3

Connect the hydrogen atoms.

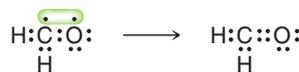
Next, connect all hydrogen atoms. We place the hydrogen atoms next to carbon, because carbon has more unpaired electrons than oxygen.



##### STEP 4

Pair any unpaired electrons so that each atom achieves an octet.

Finally, check to see if each atom (except hydrogen) has an octet. In fact, neither the carbon nor the oxygen has an octet, so in a situation like this, the unpaired electrons are shared as a double bond between carbon and oxygen.



Now all atoms have achieved an octet. When drawing Lewis structures, remember that you cannot simply add more electrons to the drawing. For each atom to achieve an octet, the existing electrons must be shared. The total number of valence electrons should be correct when you are finished. In this example, there was one carbon atom, two hydrogen atoms, and one oxygen atom, giving a total of 12 valence electrons ( $4 + 2 + 6$ ). The drawing above **MUST** have 12 valence electrons, no more and no less.

#### PRACTICE the skill

1.8 Draw a Lewis structure for each of the following compounds:

- (a)  $\text{C}_2\text{H}_6$    (b)  $\text{C}_2\text{H}_4$    (c)  $\text{C}_2\text{H}_2$    (d)  $\text{C}_3\text{H}_8$    (e)  $\text{C}_3\text{H}_6$    (f)  $\text{CH}_3\text{OH}$

1.9 Borane ( $\text{BH}_3$ ) is very unstable and quite reactive. Draw a Lewis structure of borane and explain the source of the instability.

1.10 There are four constitutional isomers with the molecular formula  $\text{C}_3\text{H}_9\text{N}$ . Draw a Lewis structure for each isomer and determine the number of lone pairs on the nitrogen atom in each case.

1.11 Smoking tobacco with a water pipe, or hookah, is often perceived as being less dangerous than smoking cigarettes, but hookah smoke has been found to contain the same



variety of toxins and carcinogens (cancer-causing compounds) as cigarette smoke.<sup>3</sup> Draw a Lewis structure for each of the following dangerous compounds found in tobacco smoke:

- (a) HCN (hydrogen cyanide)      (b) CH<sub>2</sub>CHCHCH<sub>2</sub> (1,3-butadiene)

→ need more **PRACTICE?** Try Problem 1.39

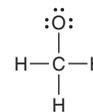
## 1.4 Identifying Formal Charges

A **formal charge** is associated with any atom that does not exhibit the appropriate number of valence electrons. When such an atom is present in a Lewis structure, the formal charge must be drawn. Identifying a formal charge requires two discrete tasks:

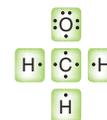
1. Determine the appropriate number of valence electrons for an atom.
2. Determine whether the atom exhibits the appropriate number of electrons.

The first task can be accomplished by inspecting the periodic table. As mentioned earlier, the group number indicates the appropriate number of valence electrons for each atom. For example, carbon is in group 4A and therefore has four valence electrons. Oxygen is in group 6A and has six valence electrons.

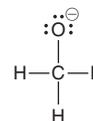
After identifying the appropriate number of electrons for each atom in a Lewis structure, the next task is to determine if any of the atoms exhibit an unexpected number of electrons. For example, consider the following structure.



Each line represents two shared electrons (a bond). For our purposes, we must split each bond apart equally, and then count the number of electrons on each atom.



Each hydrogen atom has one valence electron, as expected. The carbon atom also has the appropriate number of valence electrons (four), but the oxygen atom does not. The oxygen atom in this structure exhibits seven valence electrons, but it should only have six. In this case, the oxygen atom has one extra electron, and it must therefore bear a negative formal charge, which is indicated like this.



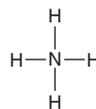
## SKILLBUILDER



### 1.4 CALCULATING FORMAL CHARGE

#### LEARN the skill

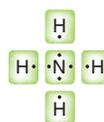
Consider the nitrogen atom in the structure below and determine if it has a formal charge:



#### SOLUTION

We begin by determining the appropriate number of valence electrons for a nitrogen atom. Nitrogen is in group 5A of the periodic table, and it should therefore have five valence electrons.

Next, we count how many valence electrons are exhibited by the nitrogen atom in this particular example.



#### STEP 1

Determine the appropriate number of valence electrons.

#### STEP 2

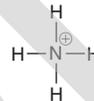
Determine the actual number of valence electrons in this case.



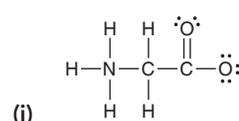
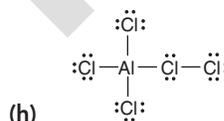
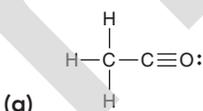
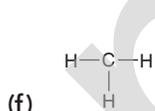
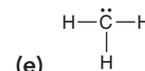
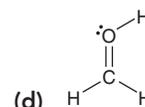
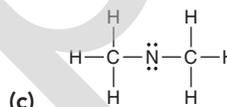
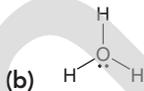
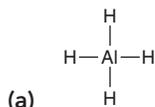


**STEP 3**  
Assign a formal charge.

In this case, the nitrogen atom exhibits only four valence electrons. It is missing one electron, so it must bear a positive charge, which is shown like this:



**PRACTICE the skill** 1.12 Identify any formal charges in the structures below:

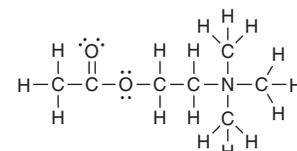


1.13 Draw a structure for each of the following ions; in each case, indicate which atom possesses the formal charge:



**APPLY the skill**

1.14 If you are having trouble paying attention during a long lecture, your levels of acetylcholine (a neurotransmitter) may be to blame.<sup>4</sup> Identify any formal charges in acetylcholine.



Acetylcholine

need more PRACTICE? Try Problem 1.41

## 1.5 Induction and Polar Covalent Bonds

Chemists classify bonds into three categories: (1) covalent, (2) polar covalent, and (3) ionic. These categories emerge from the electronegativity values of the atoms sharing a bond. Electronegativity is a measure of the ability of an atom to attract electrons. Table 1.1 gives the electronegativity values for elements commonly encountered in organic chemistry.

TABLE 1.1 ELECTRONEGATIVITY VALUES OF SOME COMMON 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	
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	

↑ Increasing electronegativity

When two atoms form a bond, one critical consideration allows us to classify the bond: What is the difference in the electronegativity values of the two atoms? Below are some rough guidelines:

*If the difference in electronegativity is less than 0.5*, the electrons are considered to be equally shared between the two atoms, resulting in a covalent bond. Examples include C—C and C—H:



The C—C bond is clearly covalent, because there is no difference in electronegativity between the two atoms forming the bond. Even a C—H bond is considered to be covalent, because the difference in electronegativity between C and H is less than 0.5.

*If the difference in electronegativity is between 0.5 and 1.7*, the electrons are not shared equally between the atoms, resulting in a **polar covalent bond**. For example, consider a bond between carbon and oxygen (C—O). Oxygen is significantly more electronegative (3.5) than carbon (2.5), and therefore oxygen will more strongly attract the electrons of the bond. The withdrawal of electrons toward oxygen is called **induction**, which is often indicated with an arrow like this.



Induction causes the formation of partial positive and partial negative charges, symbolized by the Greek symbol delta ( $\delta$ ). The partial charges that result from induction will be very important in upcoming chapters.

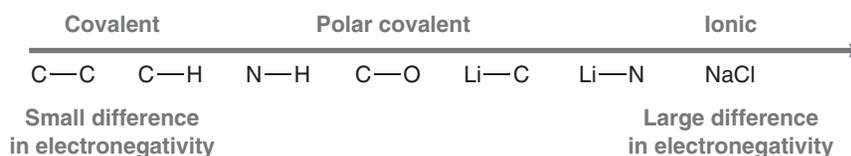


*If the difference in electronegativity is greater than 1.7*, the electrons are not shared at all. For example, consider the bond between sodium and oxygen in sodium hydroxide (NaOH).



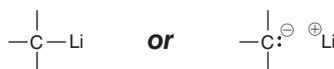
The difference in electronegativity between O and Na is so great that both electrons of the bond are possessed solely by the oxygen atom, rendering the oxygen negatively charged and the sodium positively charged. The bond between oxygen and sodium, called an **ionic bond**, is the result of the force of attraction between the two oppositely charged ions.

The cutoff numbers (0.5 and 1.7) should be thought of as rough guidelines. Rather than viewing them as absolute, we must view the various types of bonds as belonging to a spectrum without clear cutoffs (Figure 1.4).



**FIGURE 1.4**  
The nature of various bonds commonly encountered in organic chemistry.

This spectrum has two extremes: covalent bonds on the left and ionic bonds on the right. Between these two extremes are the polar covalent bonds. Some bonds fit clearly into one category, such as C—C bonds (covalent), C—O bonds (polar covalent), or NaCl bonds (ionic). However, there are many cases that are not so clear-cut. For example, a C—Li bond has a difference in electronegativity of 1.5, and this bond is often drawn either as polar covalent or as ionic. Both drawings are acceptable:



Another reason to avoid absolute cutoff numbers when comparing electronegativity values is that the electronegativity values shown above are obtained via one particular method developed by Linus Pauling. However, there are at least seven other methods for calculating electronegativity values, each of which provides slightly different values. Strict adherence to the Pauling scale would suggest that C—Br and C—I bonds are covalent, but these bonds will be treated as polar covalent throughout this course.

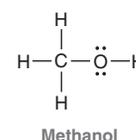
## SKILLBUILDER



### 1.5 LOCATING PARTIAL CHARGES RESULTING FROM INDUCTION

#### LEARN the skill

Consider the structure of methanol. Identify all polar covalent bonds and show any partial charges that result from inductive effects:



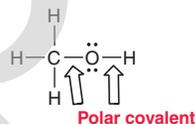


### SOLUTION

First identify all polar covalent bonds. The C—H bonds are considered to be covalent because the electronegativity values for C and H are fairly close. It is true that carbon is more electronegative than hydrogen, and therefore, there is a small inductive effect for each C—H bond. However, we will generally consider this effect to be negligible for C—H bonds.

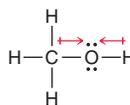
The C—O bond and the O—H bond are both polar covalent bonds:

**STEP 1**  
Identify all polar covalent bonds.



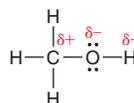
Now determine the direction of the inductive effects. Oxygen is more electronegative than C or H, so the inductive effects are shown like this:

**STEP 2**  
Determine the direction of each dipole.

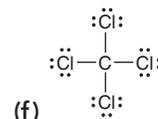
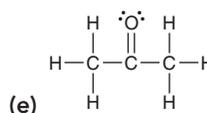
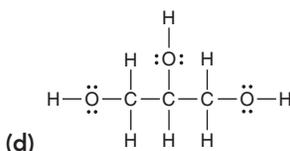
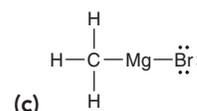
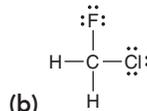
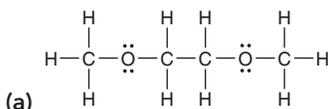


These inductive effects dictate the locations of the partial charges:

**STEP 3**  
Indicate the location of partial charges.

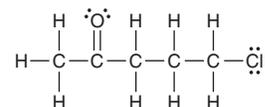


**PRACTICE the skill** 1.15 For each of the following compounds, identify any polar covalent bonds by drawing  $\delta+$  and  $\delta-$  symbols in the appropriate locations:

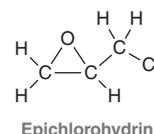


**APPLY the skill**

1.16 The regions of  $\delta+$  in a compound are the regions most likely to be attacked by an anion, such as hydroxide ( $\text{HO}^-$ ). In the compound shown, identify the two carbon atoms that are most likely to be attacked by a hydroxide ion.



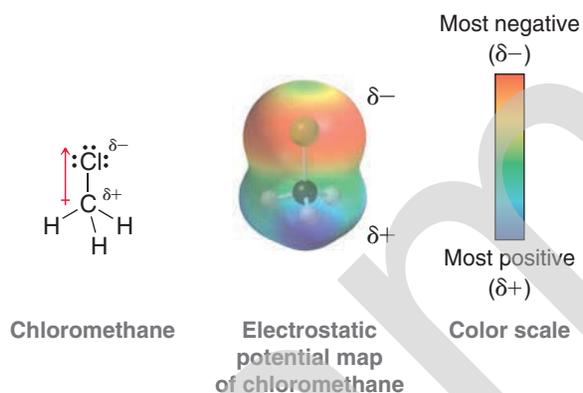
1.17 Plastics and synthetic fibers are examples of the many materials made from repeating subunits of carbon-containing molecules called polymers. Although most synthetic polymers are prepared from fossil fuel sources, many researchers are exploring ways to make polymers from renewable sources instead. One example is the synthesis of an epoxy resin polymer using a by-product from cashew nut processing, another compound isolated from corn cobs, and epichlorohydrin, shown here.<sup>5</sup> Identify any polar covalent bonds in epichlorohydrin by drawing  $\delta+$  and  $\delta-$  symbols in the appropriate locations.



need more PRACTICE? Try Problems 1.37, 1.38, 1.48, 1.57

## Practically Speaking | Electrostatic Potential Maps

Partial charges can be visualized with three-dimensional, rainbow-like images called **electrostatic potential maps**. As an example, consider the following electrostatic potential map of chloromethane:



In the image, a color scale is used to represent areas of  $\delta^-$  and  $\delta^+$ . As indicated, red represents a region that is  $\delta^-$ , while blue

represents a region that is  $\delta^+$ . In reality, electrostatic potential maps are rarely used by practicing organic chemists when they communicate with each other; however, these illustrations can often be helpful to students who are learning organic chemistry. Electrostatic potential maps are generated by performing a series of calculations. Specifically, an imaginary point positive charge is positioned at various locations, and for each location, we calculate the potential energy associated with the attraction between the point positive charge and the surrounding electrons. A large attraction indicates a position of  $\delta^-$ , while a small attraction indicates a position of  $\delta^+$ . The results are then illustrated using colors, as shown.

A comparison of any two electrostatic potential maps is only valid if both maps were prepared using the same color scale. Throughout this book, care has been taken to use the same color scale whenever two maps are directly compared to each other. However, it will not be useful to compare two maps from different pages of this book (or any other book), as the exact color scales are likely to be different.

## 1.6 Atomic Orbitals

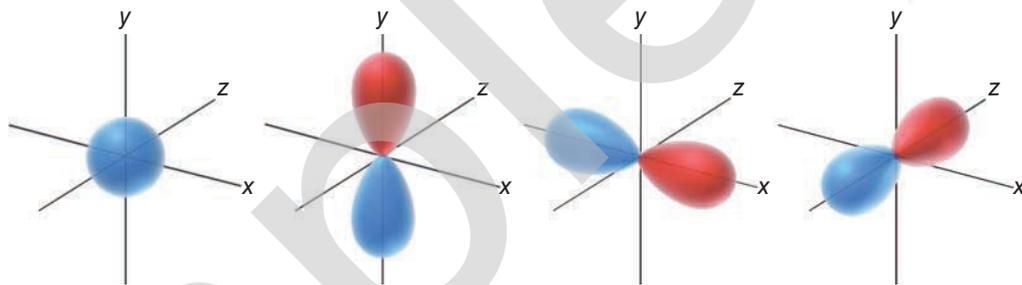
### Quantum Mechanics

By the 1920s, vitalism had been discarded. Chemists were aware of constitutional isomerism and had developed the structural theory of matter. The electron had been discovered and identified as the source of bonding, and Lewis structures were used to keep track of shared and unshared electrons. But the understanding of electrons was about to change dramatically.

In 1924, French physicist Louis de Broglie suggested that electrons, heretofore considered as particles, also exhibited wavelike properties. Based on this assertion, a new theory of matter was born. In 1926, Erwin Schrödinger, Werner Heisenberg, and Paul Dirac independently proposed a mathematical description of the electron that incorporated its wavelike properties. This new theory, called *wave mechanics*, or **quantum mechanics**, radically changed the way we viewed the nature of matter and laid the foundation for our current understanding of electrons and bonds.

Quantum mechanics is deeply rooted in mathematics and represents an entire subject by itself. The mathematics involved is beyond the scope of our course, and we will not discuss it here. However, in order to understand the nature of electrons, it is critical to understand a few simple highlights from quantum mechanics:

- An equation is constructed to describe the total energy of a hydrogen atom (i.e., one proton plus one electron). This equation, called the wave equation, takes into account the wavelike behavior of an electron that is in the electric field of a proton.
- The wave equation is then solved to give a series of solutions called wavefunctions. The Greek symbol psi ( $\psi$ ) is used to denote each wavefunction ( $\psi_1$ ,  $\psi_2$ ,  $\psi_3$ , etc.). Each of these wavefunctions corresponds to an allowed energy level for the electron. This result is incredibly important because it suggests that an electron, when contained in an atom, can only exist at discrete energy levels ( $\psi_1$ ,  $\psi_2$ ,  $\psi_3$ , etc.). In other words, the energy of the electron is *quantized*.
- Each wavefunction is a function of spatial location. It provides information that allows us to assign a numerical value for each location in three-dimensional space relative to the nucleus. The square of that value ( $\psi^2$  for any particular location) has a special meaning. It indicates the probability of finding the electron in that location. Therefore, a three-dimensional plot of  $\psi^2$  will generate an image of an atomic orbital (Figure 1.5).



**FIGURE 1.5**  
Illustrations of an  $s$  orbital  
and three  $p$  orbitals.

### Electron Density and Atomic Orbitals

An *orbital* is a region of space that can be occupied by an electron. But care must be taken when trying to visualize this. There is a statement from the previous section that must be clarified because it is potentially misleading: “ $\psi^2$  represents the probability of finding an electron in a particular location.” This statement seems to treat an electron as if it were a particle flying around within a specific region of space. But remember that an electron is not purely a particle—it has wavelike properties as well. Therefore, we must construct a mental image that captures both of these properties. That is not easy to do, but the following analogy might help. We will treat an occupied orbital as if it is a cloud—similar to a cloud in the sky. No analogy is perfect, and there are certainly features of clouds that are very different from orbitals. However, focusing on some of these differences between electron clouds (occupied orbitals) and real clouds makes it possible to construct a better mental model of an electron in an orbital:

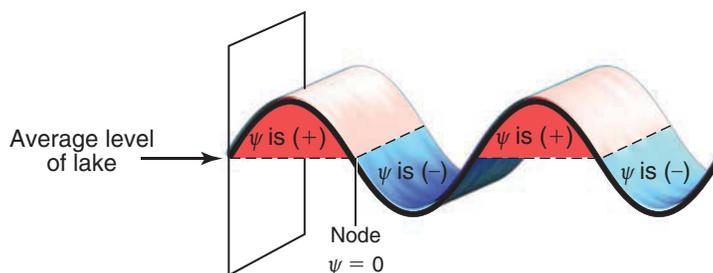
- Clouds in the sky can come in any shape or size. However, electron clouds have specific shapes and sizes (as defined by the orbitals).
- A cloud in the sky is comprised of billions of individual water molecules. An electron cloud is not comprised of billions of particles. We must think of an electron cloud as a single entity, even though it can be thicker in some places and thinner in other places. This concept is critical and will be used extensively throughout the course in explaining reactions.
- A cloud in the sky has edges, and it is possible to define a region of space that contains 100% of the cloud. In contrast, an electron cloud does not have defined edges. We frequently use the term **electron density**, which is associated with the probability of finding an electron in a particular region of space. The “shape” of an orbital refers to a region of space that contains 90–95% of the electron density. Beyond this region, the remaining 5–10% of the electron density tapers off but never ends. In fact, if we want to consider the region of space that contains 100% of the electron density, we must consider the entire universe.

In summary, we must think of an orbital as a region of space that can be occupied by electron density. An occupied orbital must be treated as a *cloud of electron density*. This region of space is called an **atomic orbital** (AO), because it is a region of space defined with respect to the nucleus of a single atom. Examples of atomic orbitals are the  $s$ ,  $p$ ,  $d$ , and  $f$  orbitals that were discussed in your general chemistry textbook.

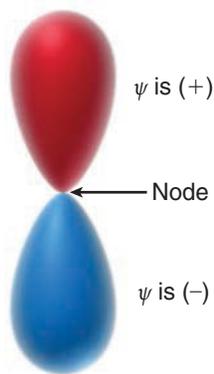
### Phases of Atomic Orbitals

Our discussion of electrons and orbitals has been based on the premise that electrons have wavelike properties. As a result, it will be necessary to explore some of the characteristics of simple waves in order to understand some of the characteristics of orbitals.

Consider a wave that moves across the surface of a lake (Figure 1.6). The wavefunction ( $\psi$ ) mathematically describes the wave, and the value of the wavefunction is dependent on location. Locations



**FIGURE 1.6**  
Phases of a wave moving  
across the surface of a lake.



**FIGURE 1.7**  
The phases of a  $p$  orbital.

above the average level of the lake have a positive value for  $\psi$  (indicated in red), and locations below the average level of the lake have a negative value for  $\psi$  (indicated in blue). Locations where the value of  $\psi$  is zero are called **nodes**.

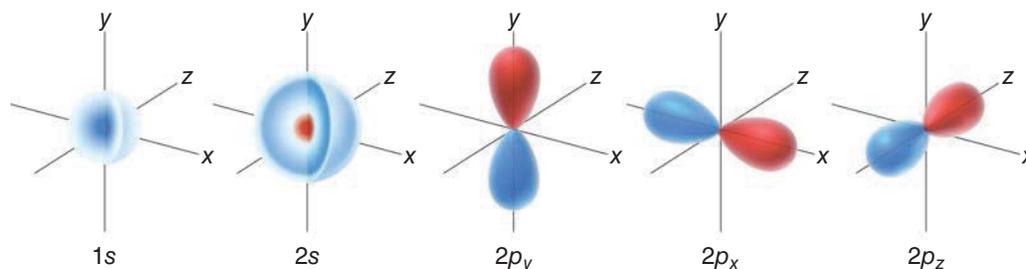
Similarly, orbitals can have regions where the value of  $\psi$  is positive, negative, or zero. For example, consider a  $p$  orbital (Figure 1.7). Notice that the  $p$  orbital has two lobes: The top lobe is a region of space where the values of  $\psi$  are positive, while the bottom lobe is a region where the values of  $\psi$  are negative. Between the two lobes is a location where  $\psi = 0$ . This location represents a node.

Be careful not to confuse the sign of  $\psi$  (+ or -) with electrical charge. A positive value for  $\psi$  does not imply a positive charge. The value of  $\psi$  (+ or -) is a mathematical convention that refers to the *phase* of the wave (just like in the lake). Although  $\psi$  can have positive or negative values, nevertheless  $\psi^2$  (which describes the electron density as a function of location) will always be a positive number. At a node, where  $\psi = 0$ , the electron density ( $\psi^2$ ) will also be zero. This means that there is no electron density located at a node.

From this point forward, we will draw the lobes of an orbital with colors (red and blue) to indicate the phase of  $\psi$  for each region of space.

### Filling Atomic Orbitals with Electrons

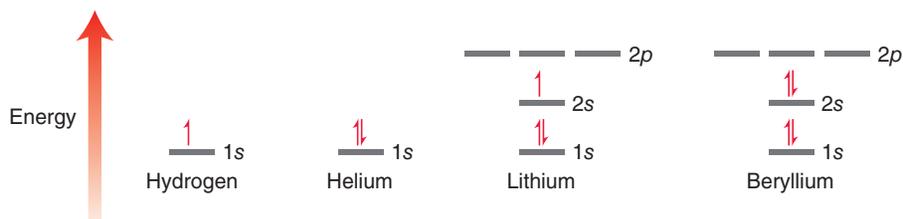
The energy of an electron depends on the type of orbital that it occupies. Most of the organic compounds that we will encounter will be composed of first- and second-row elements (H, C, N, and O). These elements utilize the  $1s$  orbital, the  $2s$  orbital, and the three  $2p$  orbitals. Our discussions will therefore focus primarily on these orbitals (Figure 1.8). Electrons are lowest in energy when they occupy a  $1s$  orbital, because the  $1s$  orbital is closest to the nucleus and it has no nodes (the more nodes that an orbital has, the greater its energy). The  $2s$  orbital has one node and is farther away from the nucleus; it is therefore higher in energy than the  $1s$  orbital. After the  $2s$  orbital, there are three  $2p$  orbitals that are all equivalent in energy to one another. Orbitals with the same energy level are called **degenerate orbitals**.



**FIGURE 1.8**  
Illustrations of  $s$  orbitals and three  $p$  orbitals.

As we move across the periodic table, starting with hydrogen, each element has one more electron than the element before it (Figure 1.9). The order in which the orbitals are filled by electrons is determined by just three simple principles:

1. The **Aufbau principle**. The lowest energy orbital is filled first.
2. The **Pauli exclusion principle**. Each orbital can accommodate a maximum of two electrons that have opposite spin. To understand what “spin” means, we can imagine an electron spinning in space (although this is an oversimplified explanation of the term “spin”). For reasons that are beyond the scope of this course, electrons only have two possible spin states (designated by  $\downarrow$  or  $\uparrow$ ). In order for the orbital to accommodate two electrons, the electrons must have opposite spin states.

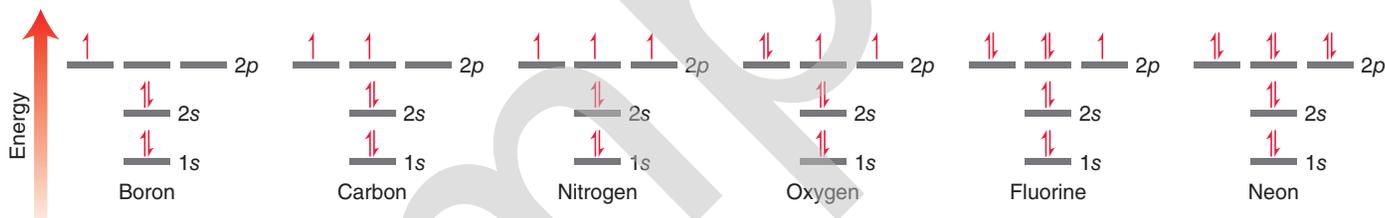


**FIGURE 1.9**  
Energy diagrams showing the electron configurations for H, He, Li, and Be.



3. **Hund's rule.** When dealing with degenerate orbitals, such as  $p$  orbitals, one electron is placed in each degenerate orbital first, before electrons are paired up.

The application of the first two principles can be seen in the electron configurations shown in Figure 1.9 (H, He, Li, and Be). The application of the third principle can be seen in the electron configurations for the remaining second-row elements (Figure 1.10).



**FIGURE 1.10** Energy diagrams showing the electron configurations for B, C, N, O, F, and Ne.

## SKILLBUILDER



### 1.6 IDENTIFYING ELECTRON CONFIGURATIONS

#### LEARN the skill

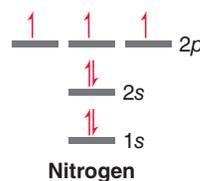
Identify the electron configuration of a nitrogen atom.

#### STEP 1

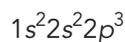
Place the valence electrons in atomic orbitals using the Aufbau principle, the Pauli exclusion principle, and Hund's rule.

#### SOLUTION

The electron configuration indicates which atomic orbitals are occupied by electrons. Nitrogen has a total of seven electrons. These electrons occupy atomic orbitals of increasing energy, with a maximum of two electrons in each orbital:



Two electrons occupy the 1s orbital, two electrons occupy the 2s orbital, and three electrons occupy the 2p orbitals. This is summarized using the following notation:



**STEP 2**  
Identify the number of valence electrons in each atomic orbital.

#### PRACTICE the skill

**1.18** Identify the electron configuration for each of the following atoms:

- (a) Carbon (b) Oxygen (c) Boron (d) Fluorine (e) Sodium (f) Aluminum

**1.19** Identify the electron configuration for each of the following ions:

- (a) A carbon atom with a negative charge (c) A nitrogen atom with a positive charge  
(b) A carbon atom with a positive charge (d) An oxygen atom with a negative charge

#### APPLY the skill

**1.20** Silicon is the second most abundant element in the Earth's crust, and its compounds can be as ordinary as beach sand. However, silicon also plays an indispensable role in modern devices such as computers, cell phones, semiconductors, and solar panels. A recent technology incorporates silicon in nanometer-sized particles called quantum dots that act as luminescent labels for pancreatic cancer cells.<sup>6</sup> Identify the electron configuration of a silicon atom.

need more PRACTICE? Try Problem 1.44

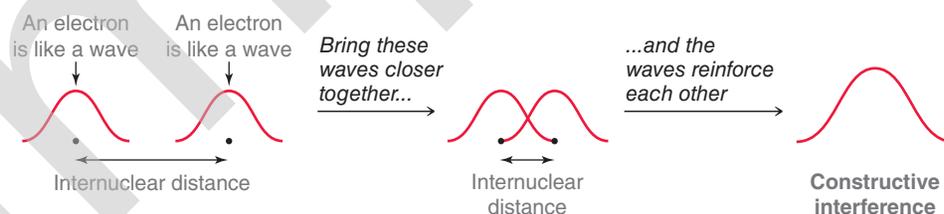
## 1.7 Valence Bond Theory

With the understanding that electrons occupy regions of space called orbitals, we can now turn our attention to a deeper understanding of covalent bonds. Specifically, a covalent bond is formed from the overlap of atomic orbitals. There are two commonly used theories for describing the nature of atomic orbital overlap: valence bond theory and molecular orbital (MO) theory. The valence bond approach is more simplistic in its treatment of bonds, and therefore we will begin our discussion with valence bond theory.

If we are going to treat electrons as waves, then we must quickly review what happens when two waves interact with each other. Two waves that approach each other can interfere in one of two possible ways—constructively or destructively. Similarly, when atomic orbitals overlap, they can interfere either constructively (Figure 1.11) or destructively (Figure 1.12).

**FIGURE 1.11**

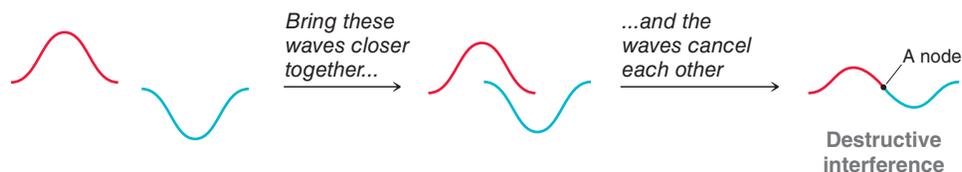
Constructive interference resulting from the interaction of two electrons.



**Constructive interference** produces a wave with larger amplitude. In contrast, destructive interference results in waves canceling each other, which produces a node (Figure 1.12).

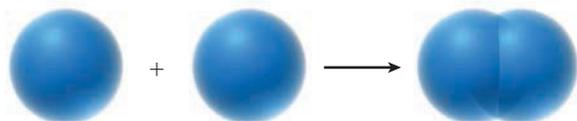
**FIGURE 1.12**

Destructive interference resulting from the interaction of two electrons.



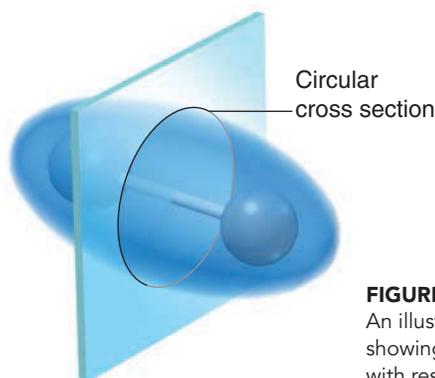
According to **valence bond theory**, a bond is simply the sharing of electron density between two atoms as a result of the constructive interference of their atomic orbitals. Consider, for example, the bond that is formed between the two hydrogen atoms in molecular hydrogen ( $\text{H}_2$ ). This bond is formed from the overlap of the  $1s$  orbitals of each hydrogen atom (Figure 1.13).

The electron density of this bond is primarily located on the bond axis (the line that can be drawn between the two hydrogen atoms). This type of bond is called a **sigma ( $\sigma$ ) bond** and is characterized by circular symmetry with respect to the bond axis. To visualize what this means, imagine a plane that is drawn perpendicular to the bond axis. This plane will carve out a circle (Figure 1.14). This is the defining feature of  $\sigma$  bonds and will be true of all purely single bonds. Therefore, *all single bonds are  $\sigma$  bonds*.



**FIGURE 1.13**

The overlap of the  $1s$  atomic orbitals of two hydrogen atoms, forming molecular hydrogen ( $\text{H}_2$ ).



**FIGURE 1.14**

An illustration of a sigma bond, showing the circular symmetry with respect to the bond axis.



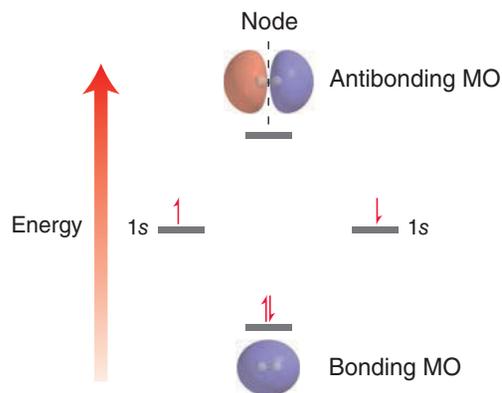
## 1.8 Molecular Orbital Theory

In most situations, valence bond theory will be sufficient for our purposes. However, there will be cases in the upcoming chapters where valence bond theory will be inadequate to describe the observations. In such cases, we will utilize molecular orbital theory, a more sophisticated approach to viewing the nature of bonds.

**Molecular orbital (MO) theory** uses mathematics as a tool to explore the consequences of atomic orbital overlap. The mathematical method is called the linear combination of atomic orbitals (LCAO). According to this theory, atomic orbitals are mathematically combined to produce new orbitals, called **molecular orbitals**.

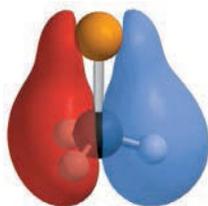
It is important to understand the distinction between atomic orbitals and molecular orbitals. Both types of orbitals are used to accommodate electrons, but an atomic orbital is a region of space associated with an individual atom, while a molecular orbital is associated with an entire molecule. That is, the molecule is considered to be a single entity held together by many electron clouds, some of which can actually span the entire length of the molecule. These molecular orbitals are filled with electrons in a particular order in much the same way that atomic orbitals are filled. Specifically, electrons first occupy the lowest energy orbitals, with a maximum of two electrons per orbital. In order to visualize what it means for an orbital to be associated with an entire molecule, we will explore two molecules: molecular hydrogen ( $H_2$ ) and bromomethane ( $CH_3Br$ ).

Consider the bond formed between the two hydrogen atoms in molecular hydrogen. This bond is the result of the overlap of two atomic orbitals ( $s$  orbitals), each of which is occupied by one electron. According to MO theory, when two atomic orbitals overlap, they cease to exist. Instead, they are replaced by two molecular orbitals, each of which is associated with the entire molecule (Figure 1.15).



**FIGURE 1.15**

An energy diagram showing the relative energy levels of bonding and antibonding molecular orbitals.

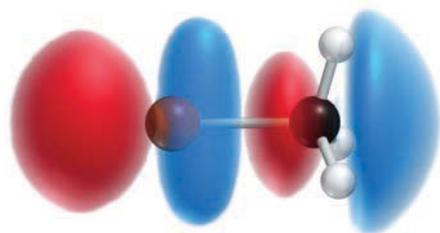


**FIGURE 1.16**

A low-energy molecular orbital of  $CH_3Br$ . Red and blue regions indicate the different phases, as described in Section 1.6. Notice that this molecular orbital is associated with the entire molecule, rather than being associated with two specific atoms.

In the energy diagram shown in Figure 1.15, the individual atomic orbitals are represented on the right and left, with each atomic orbital having one electron. These atomic orbitals are combined mathematically (using the LCAO method) to produce two molecular orbitals. The lower energy molecular orbital, or **bonding MO**, is the result of constructive interference of the original two atomic orbitals. The higher energy molecular orbital, or **antibonding MO**, is the result of destructive interference. Notice that the antibonding MO has one node, which explains why it is higher in energy. Both electrons occupy the bonding MO in order to achieve a lower energy state. This lowering in energy is the essence of the bond. For an  $H-H$  bond, the lowering in energy is equivalent to  $436 \text{ kJ/mol}$ . This energy corresponds with the bond strength of an  $H-H$  bond (as shown in Figure 1.2).

Now let's consider a molecule such as  $CH_3Br$ , which contains more than just one bond. Valence bond theory continues to view each bond separately, with each bond being formed from two overlapping atomic orbitals. In contrast, MO theory treats the bonding electrons as being associated with the entire molecule. The molecule has many molecular orbitals, each of which can be occupied by two electrons. Figure 1.16 illustrates one of the many molecular



**FIGURE 1.17**  
The LUMO of  $\text{CH}_3\text{Br}$ .

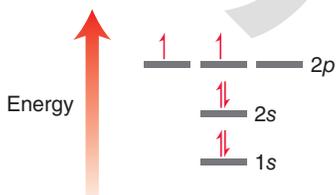
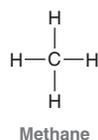
orbitals of  $\text{CH}_3\text{Br}$ . This molecular orbital is capable of accommodating up to two electrons. Red and blue regions indicate the different phases, as described in Section 1.6. As we saw with molecular hydrogen, not all molecular orbitals will be occupied. The bonding electrons will occupy the lower energy molecular orbitals (such as the one shown in Figure 1.16), while the higher energy molecular orbitals remain unoccupied. For every molecule, two of its molecular orbitals will be of particular interest: (1) the highest energy orbital from among the occupied orbitals is called the **highest occupied molecular orbital**, or **HOMO**, and (2) the lowest energy orbital from among the unoccupied orbitals is called the **lowest unoccupied molecular orbital**, or **LUMO**. For example, in Chapter 7, we will explore a reaction in which  $\text{CH}_3\text{Br}$  is attacked by a hydroxide ion ( $\text{HO}^-$ ). In order for this process to occur, the hydroxide ion must transfer its electron density into the lowest energy, empty molecular orbital, or LUMO, of  $\text{CH}_3\text{Br}$  (Figure 1.17). The nature of the LUMO (i.e., number of nodes, location of nodes, etc.) will be useful in explaining the preferred direction from which the hydroxide ion will attack.

We will use MO theory several times in the chapters that follow. Most notably, in Chapter 16, we will investigate the structure of compounds containing several double bonds. For those compounds, valence bond theory will be inadequate, and MO theory will provide a more meaningful understanding of the bonding structure. Throughout this textbook, we will continue to develop both valence bond theory and MO theory.

## 1.9 Hybridized Atomic Orbitals

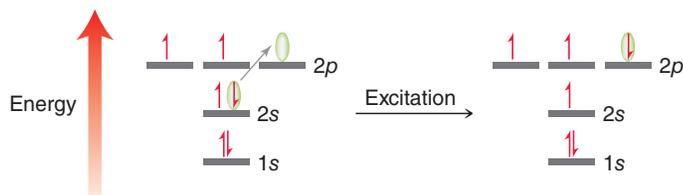
### Methane and $sp^3$ Hybridization

Let us now apply valence bond theory to the bonds in methane:

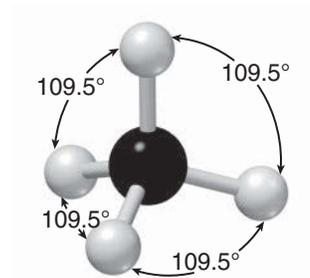


**FIGURE 1.18**  
An energy diagram showing the electron configuration of carbon.

Recall the electron configuration of carbon (Figure 1.18). This electron configuration cannot satisfactorily describe the bonding structure of methane ( $\text{CH}_4$ ), in which the carbon atom has four separate C—H bonds, because the electron configuration shows only two atomic orbitals capable of forming bonds (each of these orbitals has one unpaired electron). This would imply that the carbon atom will form only two bonds, but we know that it forms four bonds. We can solve this problem by imagining an excited state of carbon (Figure 1.19): a state in which a  $2s$  electron has been promoted to a



**FIGURE 1.19**  
An energy diagram showing the electronic excitation of an electron in a carbon atom.

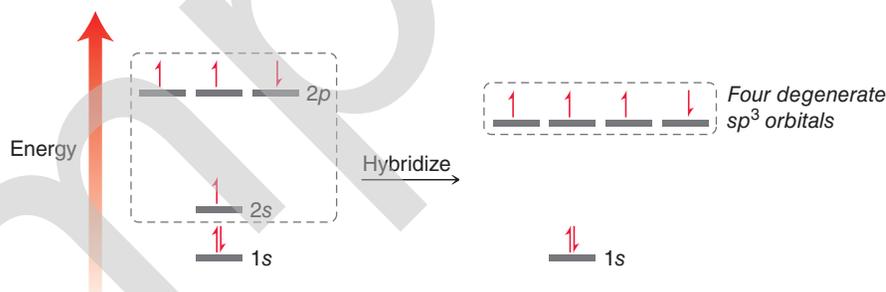


**FIGURE 1.20**  
The tetrahedral geometry of methane. All bond angles are  $109.5^\circ$ .

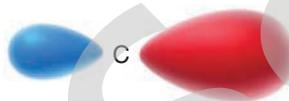
higher energy  $2p$  orbital. Now the carbon atom has four atomic orbitals capable of forming bonds, but there is yet another problem here. The geometry of the  $2s$  and three  $2p$  orbitals does not satisfactorily explain the observed three-dimensional geometry of methane (Figure 1.20). All bond angles are  $109.5^\circ$ , and the four bonds point away from each other in a perfect tetrahedron. This geometry cannot be explained by an excited state of carbon because the  $s$  orbital and the three  $p$  orbitals do not occupy a tetrahedral geometry. The  $p$  orbitals are separated from each other by only  $90^\circ$  (as seen in Figure 1.5) rather than  $109.5^\circ$ .



This problem was solved in 1931 by Linus Pauling, who suggested that the electronic configuration of the carbon atom in methane does not necessarily have to be the same as the electronic configuration of a free carbon atom. Specifically, Pauling mathematically averaged, or *hybridized*, the  $2s$  orbital and the three  $2p$  orbitals, giving four degenerate hybridized atomic orbitals (Figure 1.21). The hybridization process in Figure 1.21 does not represent a real physical process that the orbitals undergo.



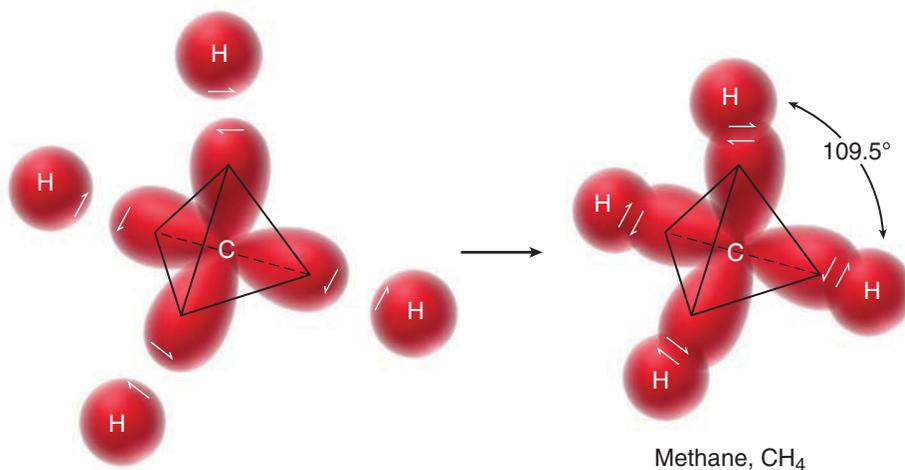
**FIGURE 1.21**  
An energy diagram showing four degenerate hybridized atomic orbitals.



**FIGURE 1.22**  
An illustration of an  $sp^3$ -hybridized atomic orbital.

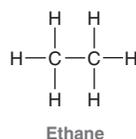
Rather, it is a mathematical procedure that is used to arrive at a satisfactory description of the observed bonding. This procedure gives us four orbitals that were produced by averaging one  $s$  orbital and three  $p$  orbitals, and therefore we refer to these atomic orbitals as  $sp^3$ -hybridized orbitals. Figure 1.22 shows an  $sp^3$ -hybridized orbital. If we use these hybridized atomic orbitals to describe the bonding of methane, we can successfully explain the observed geometry of the bonds. The four  $sp^3$ -hybridized orbitals are equivalent in energy (degenerate) and will therefore position themselves as far apart from each other as possible, achieving a tetrahedral geometry. Also notice that hybridized atomic orbitals are unsymmetrical. That is, hybridized atomic orbitals have a larger front lobe (shown in red in Figure 1.22) and a smaller back lobe (shown in blue). The larger front lobe enables hybridized atomic orbitals to be more efficient than  $p$  orbitals in their ability to form bonds.

Using valence bond theory, each of the four bonds in methane is represented by the overlap between an  $sp^3$ -hybridized atomic orbital from the carbon atom and an  $s$  orbital from a hydrogen atom (Figure 1.23). For purposes of clarity the back lobes (blue) have been omitted from the images in Figure 1.23.

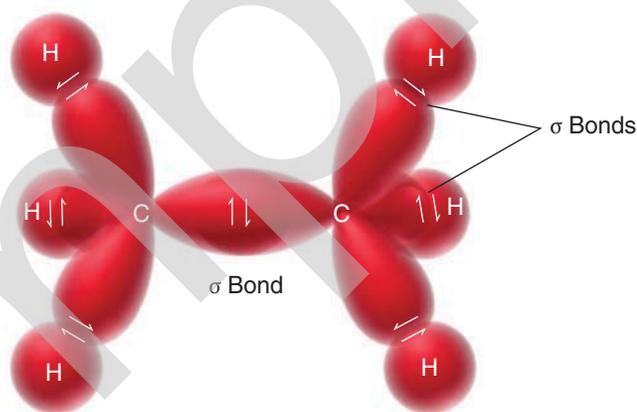


**FIGURE 1.23**  
A tetrahedral carbon atom using each of its four  $sp^3$ -hybridized orbitals to form a bond.

The bonding in ethane is treated in much the same way:



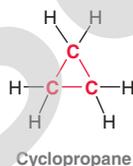
All bonds in this compound are single bonds, and therefore they are all  $\sigma$  bonds. Using the valence bond approach, each of the bonds in ethane can be treated individually and is represented by the overlap of atomic orbitals (Figure 1.24).



**FIGURE 1.24**  
A valence bond picture of the bonding in ethane.

### CONCEPTUAL CHECKPOINT

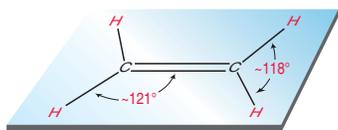
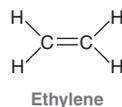
**1.21** Cyclopropane is a compound in which the carbon atoms form a three-membered ring:



Each of the carbon atoms in cyclopropane is  $sp^3$  hybridized. Cyclopropane is more reactive than other cyclic compounds (four-membered rings, five-membered rings, etc.). Analyze the bond angles in cyclopropane and explain why cyclopropane is so reactive.

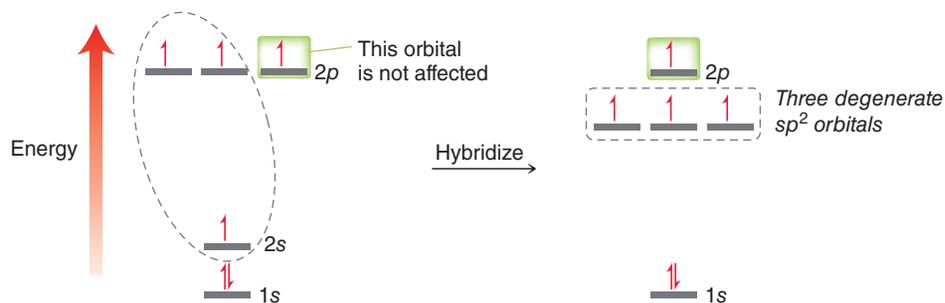
### Double Bonds and $sp^2$ Hybridization

Now let's consider the structure of a compound bearing a double bond. The simplest example is ethylene.

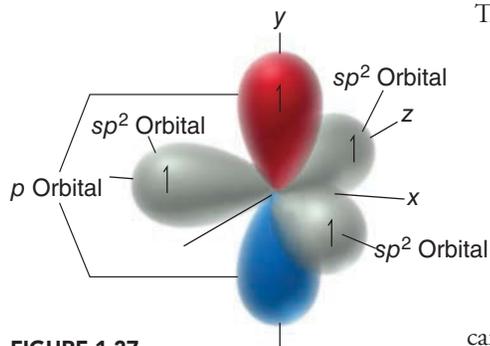


**FIGURE 1.25**  
All six atoms of ethylene are in one plane.

Ethylene exhibits a planar geometry (Figure 1.25). A satisfactory model for explaining this geometry can be achieved by the mathematical maneuver of hybridizing the  $s$  and  $p$  orbitals of the carbon atom to obtain hybridized atomic orbitals. When we did this procedure earlier to explain the bonding in methane, we hybridized the  $s$  orbital and all three  $p$  orbitals to produce four equivalent  $sp^3$ -hybridized orbitals. However, in the case of ethylene, each carbon atom only needs to form bonds with three atoms, not four. Therefore, each carbon atom only needs three hybridized orbitals. So in this case we will mathematically average the  $s$  orbital with only two of the three  $p$  orbitals (Figure 1.26). The remaining  $p$  orbital will remain unaffected by our mathematical procedure.



**FIGURE 1.26**  
An energy diagram showing three degenerate  $sp^2$ -hybridized atomic orbitals.

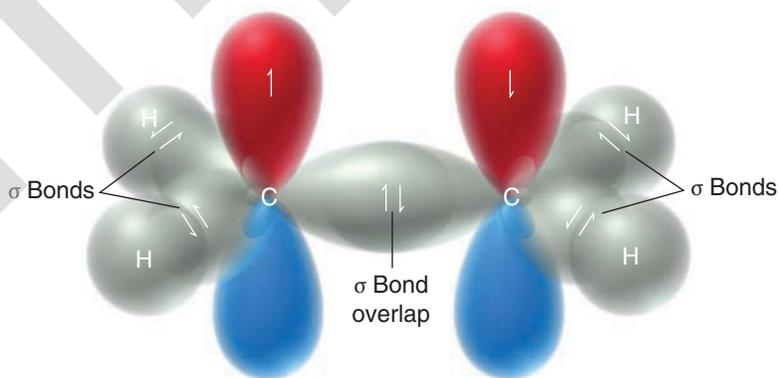


**FIGURE 1.27**  
An illustration of an  $sp^2$ -hybridized carbon atom.

The result of this mathematical operation is a carbon atom with one  $p$  orbital and three  $sp^2$ -hybridized orbitals (Figure 1.27). In Figure 1.27 the  $p$  orbital is shown in red and blue, and the hybridized orbitals are shown in gray (for clarity, only the front lobe of each hybridized orbital is shown). They are called  $sp^2$ -hybridized orbitals to indicate that they were obtained by averaging one  $s$  orbital and two  $p$  orbitals. As shown in Figure 1.27, each of the carbon atoms in ethylene is  $sp^2$  hybridized, and we can use this hybridization state to explain the bonding structure of ethylene.

Each carbon atom in ethylene has three  $sp^2$ -hybridized orbitals available to form  $\sigma$  bonds (Figure 1.28). One  $\sigma$  bond forms between the two carbon atoms, and then each carbon atom also forms a  $\sigma$  bond with each of its neighboring hydrogen atoms.

In addition, each carbon atom has one  $p$  orbital (shown in Figure 1.28 with blue and red lobes).

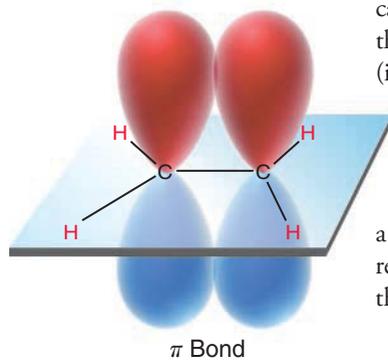


**FIGURE 1.28**  
An illustration of the  $\sigma$  bonds in ethylene.

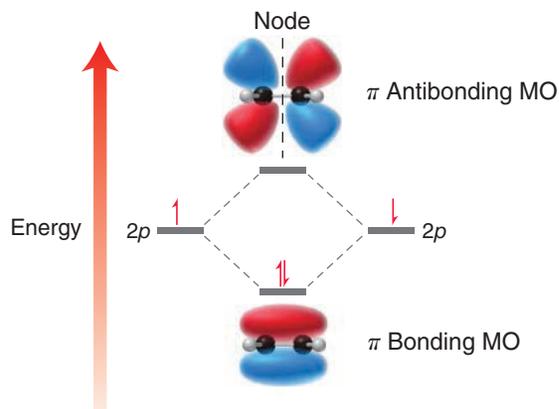
These  $p$  orbitals actually overlap with each other as well, which is a separate bonding interaction called a **pi ( $\pi$ ) bond** (Figure 1.29). Do not be confused by the nature of this type of bond. It is true that the  $\pi$  overlap occurs in two places—above the plane of the molecule (in red) and below the plane (in blue). Nevertheless, these two regions of overlap represent only one interaction called a  $\pi$  bond.

The image of the  $\pi$  bond in Figure 1.29 is based on the valence bond approach (the  $p$  orbitals are simply drawn overlapping each other). Molecular orbital theory provides a fairly similar image of a  $\pi$  bond. Compare Figure 1.29 with the bonding MO in Figure 1.30.

To summarize, we have seen that the carbon atoms of ethylene are connected via a  $\sigma$  bond and a  $\pi$  bond. The  $\sigma$  bond results from the overlap of  $sp^2$ -hybridized atomic orbitals, while the  $\pi$  bond results from the overlap of  $p$  orbitals. These two separate bonding interactions ( $\sigma$  and  $\pi$ ) comprise the double bond of ethylene.



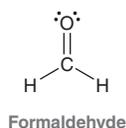
**FIGURE 1.29**  
An illustration of the  $\pi$  bond in ethylene.



**FIGURE 1.30**  
An energy diagram showing images of bonding and antibonding MOs in ethylene.

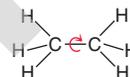
## CONCEPTUAL CHECKPOINT

1.22 Consider the structure of formaldehyde:



- Identify the type of bonds that form the C=O double bond.
- Identify the atomic orbitals that form each C—H bond.
- What type of atomic orbitals do the lone pairs occupy?

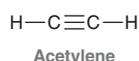
1.23 Sigma bonds experience free rotation at room temperature:



In contrast,  $\pi$  bonds do not experience free rotation. Explain. (Hint: Compare Figures 1.24 and 1.29, focusing on the orbitals used in forming a  $\sigma$  bond and the orbitals used in forming a  $\pi$  bond. In each case, what happens to the orbital overlap during bond rotation?)

## Triple Bonds and $sp$ Hybridization

Now let's consider the bonding structure of a compound bearing a triple bond, such as acetylene:



A triple bond is formed by  **$sp$ -hybridized** carbon atoms. To achieve  $sp$  hybridization, one  $s$  orbital is mathematically averaged with only one  $p$  orbital (Figure 1.31). This leaves two  $p$  orbitals

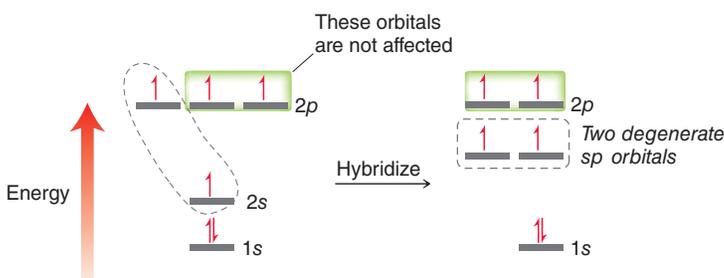


FIGURE 1.31

An energy diagram showing two degenerate  $sp$ -hybridized atomic orbitals.

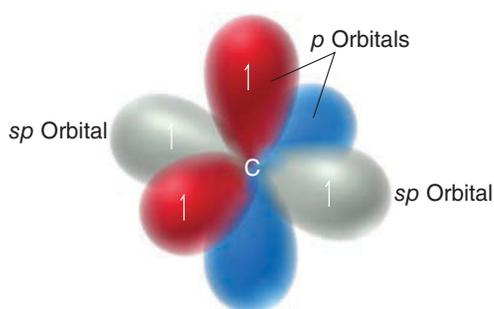


FIGURE 1.32

An illustration of an  $sp$ -hybridized carbon atom. The  $sp$ -hybridized orbitals are shown in gray.

unaffected by the mathematical operation. As a result, an  $sp$ -hybridized carbon atom has two  $sp$  orbitals and two  $p$  orbitals (Figure 1.32).

The two  $sp$ -hybridized orbitals are available to form  $\sigma$  bonds (one on either side), and the two  $p$  orbitals are available to form  $\pi$  bonds, giving the bonding structure for acetylene shown in Figure 1.33. A triple bond between two carbon atoms is therefore the result of three separate bonding interactions: one  $\sigma$  bond and two  $\pi$  bonds. The  $\sigma$  bond results from the overlap of  $sp$  orbitals, while each of the two  $\pi$  bonds result from overlapping  $p$  orbitals. As shown in Figure 1.33, the geometry of the triple bond is linear.

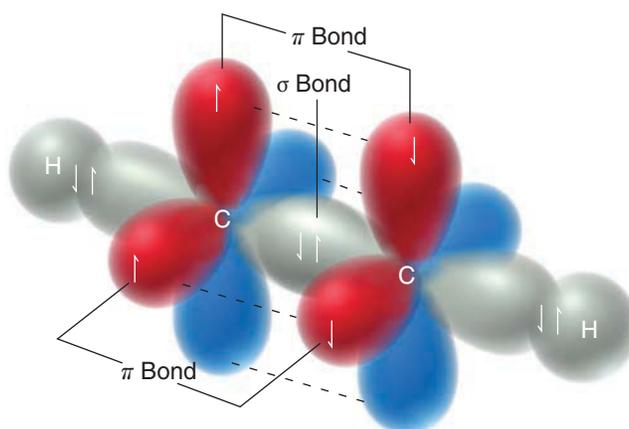


FIGURE 1.33

An illustration of the  $\sigma$  bonds and  $\pi$  bonds in acetylene.

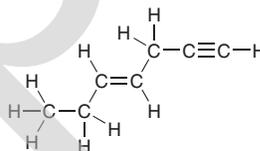
## SKILLBUILDER



## 1.7 IDENTIFYING HYBRIDIZATION STATES

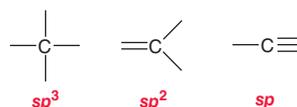
## LEARN the skill

Identify the hybridization state of each carbon atom in the following compound:



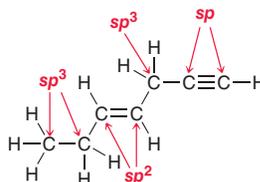
## SOLUTION

To determine the hybridization state of an uncharged carbon atom, simply count the number of  $\sigma$  bonds and  $\pi$  bonds:

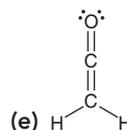
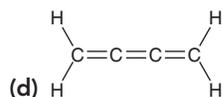
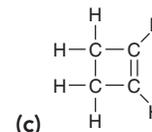
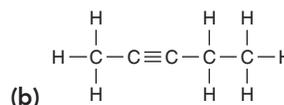
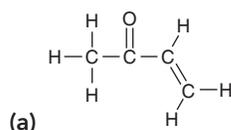


A carbon atom with four single bonds (four  $\sigma$  bonds) will be  $sp^3$  hybridized. A carbon atom with three  $\sigma$  bonds and one  $\pi$  bond will be  $sp^2$  hybridized. A carbon atom with two  $\sigma$  bonds and two  $\pi$  bonds will be  $sp$  hybridized. Carbon atoms bearing a positive or negative charge will be discussed in more detail in the upcoming chapter.

Using the simple scheme above, the hybridization state of most carbon atoms can be determined instantly:

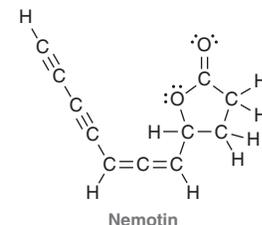


## PRACTICE the skill 1.24 Determine the hybridization state of each carbon atom in the following compounds.



## APPLY the skill

1.25 Nemotin is a compound that was first isolated from the fungi *Poria tenuis* and *Poria corticola* in the 1940s and was shown to possess potent antibacterial activity. However, its structure was not verified until it was made in the laboratory much more recently.<sup>7</sup> Determine the hybridization state of each carbon atom in nemotin.

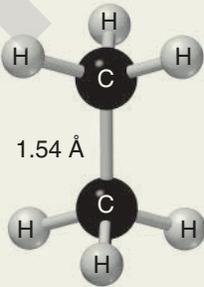
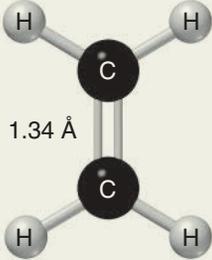
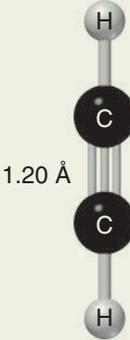


need more PRACTICE? Try Problems 1.55, 1.56

## Bond Strength and Bond Length

The information we have seen in this section allows us to compare single bonds, double bonds, and triple bonds. A single bond has only one bonding interaction (a  $\sigma$  bond), a double bond has two bonding interactions (one  $\sigma$  bond and one  $\pi$  bond), and a triple bond has three bonding interactions (one  $\sigma$  bond and two  $\pi$  bonds). Therefore, it is not surprising that a triple bond is stronger than a double bond, which in turn is stronger than a single bond. Compare the strengths and lengths of the C—C bonds in ethane, ethylene, and acetylene (Table 1.2).

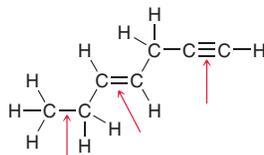
**TABLE 1.2** COMPARISON OF BOND LENGTHS AND BOND ENERGIES FOR ETHANE, ETHYLENE, AND ACETYLENE

	ETHANE	ETHYLENE	ACETYLENE
Structure			
C—C bond length	1.54 Å	1.34 Å	1.20 Å
Bond energy	368 kJ/mol	632 kJ/mol	820 kJ/mol



### CONCEPTUAL CHECKPOINT

1.26 Rank the indicated bonds in terms of increasing bond length:



## 1.10 Predicting Molecular Geometry: VSEPR Theory

The shapes of small molecules can often be predicted if we presume that all electron pairs (whether bonding or nonbonding) repel each other, and as such, they arrange themselves in three-dimensional space so as to achieve maximal distance from each other. This approach, called **valence shell electron pair repulsion (VSEPR)** theory, enables us to make quick predictions about molecular geometry. In this section, we will encounter several different molecular shapes for small molecules, all of which are predicted accurately using the VSEPR model.

### Tetrahedral Geometry

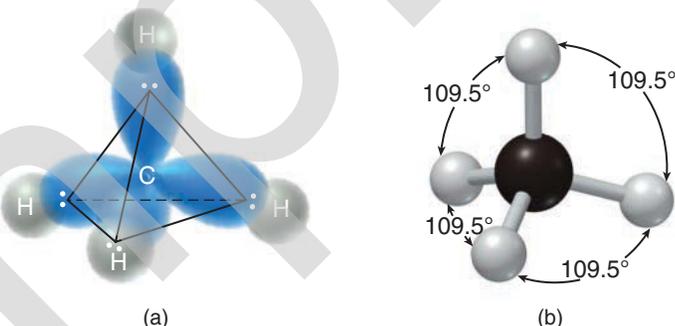
We begin our analysis with methane ( $\text{CH}_4$ ), in which the carbon atom has four  $\sigma$  bonds and no lone pairs. VSEPR theory presumes that all four electron pairs will be positioned so as to achieve maximal distance from each other, suggesting a **tetrahedral** arrangement. That is, the VSEPR model



predicts that the four hydrogen atoms should be positioned at the four corners of a tetrahedron (Figure 1.34a). This prediction is consistent with  $sp^3$  hybridization, as described by valence bond theory (Section 1.9), and it is also consistent with the observed bond angles of  $109.5^\circ$  (Figure 1.34b).

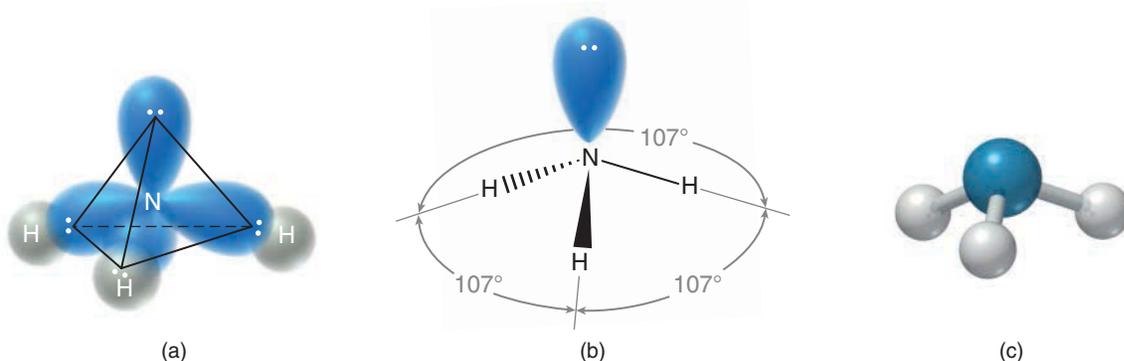
**FIGURE 1.34**

(a) The tetrahedral arrangement of electron pairs in  $\text{CH}_4$ .  
 (b) All bond angles in  $\text{CH}_4$  are  $109.5^\circ$ .



### Trigonal Pyramidal Geometry

Now let's apply the VSEPR model to ammonia ( $\text{NH}_3$ ), in which the nitrogen atom has three  $\sigma$  bonds and one lone pair. The total number of electron pairs, also called the **steric number**, is four in this case (as it was in the previous case as well). VSEPR theory presumes that all four electron pairs will be positioned so as to achieve maximal distance from each other, suggesting once again a tetrahedral arrangement (Figure 1.35a). However, in this case, a lone pair is positioned at one corner of the tetrahedron. This predicted arrangement is observed to be accurate, and it is consistent with the valence bond approach, in which the nitrogen atom is  $sp^3$  hybridized, and the lone pair occupies an  $sp^3$ -hybridized orbital.



**FIGURE 1.35**

(a) The tetrahedral arrangement of electron pairs in  $\text{NH}_3$ .  
 (b) All bond angles in  $\text{NH}_3$  are approximately  $107^\circ$ .  
 (c)  $\text{NH}_3$  has trigonal pyramidal geometry.

As illustrated in Figure 1.36b, the bond angles for ammonia are observed to be  $107^\circ$ , rather than  $109.5^\circ$ . This shorter bond angle can be justified by VSEPR theory if we presume that lone pairs repel more strongly than  $\sigma$  bonds (lone pairs are not bound by another nucleus, so they occupy more space than bonding electron pairs). As such, the lone pair in ammonia repels the three bonds more strongly, causing the  $\text{H}-\text{N}-\text{H}$  bond angle to be less than  $109.5^\circ$ .

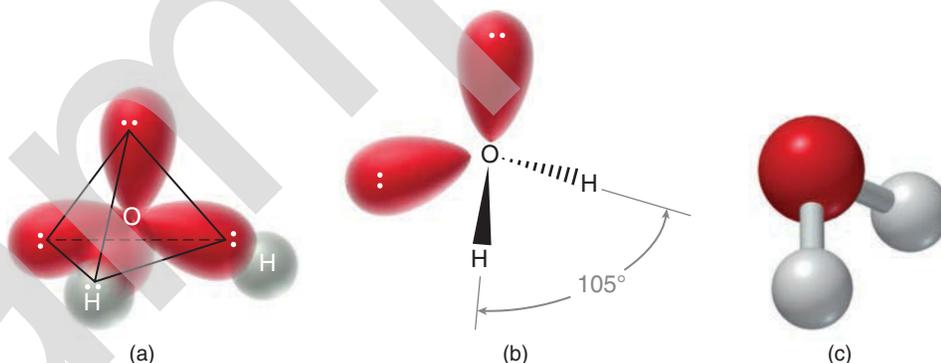
When we describe the geometry (or shape) of a molecule, we are generally referring to the arrangement of atoms. When we focus only on the positions of the atoms (ignoring the lone pair), the shape of ammonia is **trigonal pyramidal** (Figure 1.35c). “Trigonal” indicates the nitrogen atom is connected to three other atoms, and “pyramidal” indicates the compound is shaped like a pyramid, with the nitrogen atom sitting at the top of the pyramid.

### Bent Geometry

Now let's apply the VSEPR model to water ( $\text{H}_2\text{O}$ ), in which the oxygen atom has two  $\sigma$  bonds and two lone pairs. With a total of four electron pairs to consider (steric number = 4), VSEPR theory presumes that all four electron pairs will be positioned so as to achieve maximal distance from each other, suggesting once again a tetrahedral arrangement (Figure 1.36a). Notice that the VSEPR model predicts that the lone pairs should be positioned at two corners of the tetrahedral arrangement.

FIGURE 1.36

(a) The tetrahedral arrangement of electron pairs in  $\text{H}_2\text{O}$ , as predicted by VSEPR.  
 (b) The bond angle in  $\text{H}_2\text{O}$  is approximately  $105^\circ$ .  
 (c)  $\text{H}_2\text{O}$  has bent geometry.



Once again, VSEPR theory can explain the observed bond angle ( $105^\circ$ ) by considering the effect of two lone pairs (Figure 1.36b). Specifically, the lone pairs repel each other more strongly than  $\sigma$  bonds, causing the  $\text{H}-\text{O}-\text{H}$  bond angle to be even smaller than the bond angles in ammonia. In order to describe the geometry of  $\text{H}_2\text{O}$ , we focus on the arrangement of atoms, which gives a **bent** geometry (Figure 1.36c).

This analysis demonstrates that the VSEPR model correctly predicts the bent geometry of water, and the observed bond angle is even justified. However, VSEPR theory also predicts that the two lone pairs of  $\text{H}_2\text{O}$  should be degenerate (the same energy), and this has proven to be false. Experiments conducted over 30 years ago have revealed that the lone pairs of  $\text{H}_2\text{O}$  are indeed different (one lone pair is significantly higher in energy than the other). These observations strongly suggest that at least one lone pair occupies a  $p$  orbital, while the other lone pair occupies a lower-energy, hybridized orbital. Since one lone pair occupies a  $p$  orbital, the oxygen atom cannot be  $sp^3$  hybridized, as we might expect from a classical interpretation of valence bond theory and VSEPR theory. In this case, the VSEPR model fails to explain why the lone pairs are different in hybridization, energy, and orientation. Indeed, this is compelling evidence that the VSEPR model does not take all of the relevant factors into account when predicting geometry. The VSEPR model assumes that steric repulsion of electrons is the only factor that determines electronic and molecular structures, but there are often additional relevant factors. In the case of  $\text{H}_2\text{O}$ , the lone pairs do NOT occupy the two corners of a tetrahedron, as predicted. Although VSEPR theory has correctly predicted the bent geometry of  $\text{H}_2\text{O}$ , it appears to have done so for the wrong reasons. This example illustrates that VSEPR is just a first approximation. It is just a model, incomplete and flawed (as most simple models are), but it is nevertheless useful, because it can be used to predict the geometry for most small molecules with reasonable accuracy.

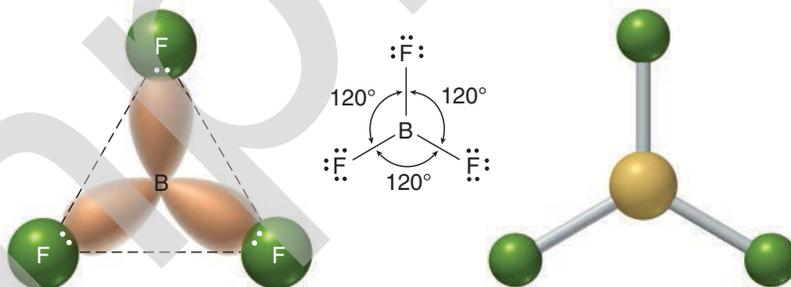
Thus far, we have seen three different molecular shapes: tetrahedral, trigonal pyramidal, and bent. We will now explore other common molecular shapes that are accurately predicted with VSEPR theory.

### Trigonal Planar Geometry

Consider the structure of  $\text{BF}_3$ . Boron has three valence electrons, each of which is used to form a  $\sigma$  bond. Therefore, the boron atom requires the use of three hybridized orbitals (rather than four, as we have seen in previous examples). Applying valence bond theory, we expect the boron atom to be  $sp^2$  hybridized (with three equivalent  $sp^2$ -hybridized orbitals and one empty  $p$  orbital). As we saw in



Section 1.9,  $sp^2$  hybridization is associated with **trigonal planar** geometry, in which all bond angles are  $120^\circ$  (Figure 1.37). The term “trigonal” indicates that the boron atom is connected to three other atoms, and the term “planar” indicates that all atoms lie in the same plane.



**FIGURE 1.37**  
 $\text{BF}_3$  has trigonal planar geometry, with bond angles of  $120^\circ$ .

Once again, the VSEPR model correctly predicts the trigonal planar geometry of  $\text{BF}_3$ . There are three electron pairs that are repelling each other (steric number = 3), and they are expected to position themselves in space so as to achieve maximal separation. This is only accomplished in a trigonal planar arrangement, with bond angles of  $120^\circ$ , exactly as observed.

### Linear Geometry

Consider the structure of  $\text{BeH}_2$ . Beryllium has two valence electrons, each of which is used to form a  $\sigma$  bond. The beryllium atom therefore requires only two hybridized orbitals, and must be  $sp$  hybridized. Recall (Section 1.9) that  $sp$  hybridization is associated with **linear** geometry (Figure 1.38):



**FIGURE 1.38**  
 $\text{BeH}_2$  has linear geometry, with a bond angle of  $180^\circ$ .

Once again, the VSEPR model correctly predicts the linear geometry of  $\text{BeH}_2$ . There are two electron pairs that are repelling each other (steric number = 2), and they are expected to position themselves in space so as to achieve maximal separation. This is only accomplished in a linear arrangement, with a bond angle of  $180^\circ$ .

In summary, we have encountered five different molecular shapes, all of which are listed in Table 1.3.

**TABLE 1.3** COMMON MOLECULAR SHAPES THAT CAN BE PREDICTED WITH VSEPR THEORY

EXAMPLE	BONDING ELECTRON PAIRS (BONDS)	NONBONDING ELECTRON PAIRS (LONE PAIRS)	STERIC NUMBER	PREDICTED ARRANGEMENT OF ELECTRON PAIRS	PREDICTED MOLECULAR GEOMETRY
$\text{CH}_4$	4	0	4	Tetrahedral	Tetrahedral
$\text{NH}_3$	3	1	4	Tetrahedral	Trigonal Pyramidal
$\text{H}_2\text{O}$	2	2	4	Tetrahedral	Bent
$\text{BF}_3$	3	0	3	Trigonal Planar	Trigonal Planar
$\text{BeH}_2$	2	0	2	Linear	Linear

## SKILLBUILDER



## 1.8 PREDICTING GEOMETRY

## LEARN the skill

Using VSEPR theory, predict the geometry of a hydronium ion ( $\text{H}_3\text{O}^+$ ):



## STEP 1

Determine the steric number.

## STEP 2

Identify the arrangement of electron pairs.

## STEP 3

Identify the geometry.

## SOLUTION

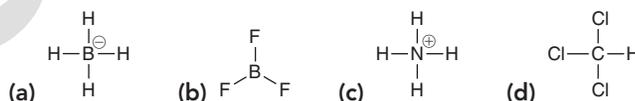
We begin by counting the number of electron pairs (bonding and nonbonding) on the oxygen atom. There are three sigma bonds and one lone pair, giving a total of four electron pairs (steric number = 4).

Next, identify the arrangement of the electron pairs in 3D space. According to VSEPR theory, we presume that all electron pairs will be positioned so as to achieve maximal distance from one another. Since there are four electron pairs, VSEPR theory predicts a tetrahedral arrangement of electron pairs.

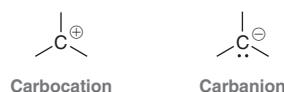
In this case, a lone pair is predicted to occupy one corner of the tetrahedron, giving rise to trigonal pyramidal geometry (just like  $\text{NH}_3$ ).

## PRACTICE the skill

1.27 Use VSEPR theory to predict the geometry for each of the following structures:



1.28 Compare the structures of a carbocation and a carbanion:



In one of these ions, the central carbon atom is trigonal planar, while the other is trigonal pyramidal. Using VSEPR theory, assign the correct geometry to each ion.

1.29 Ammonia ( $\text{NH}_3$ ) will react with a strong acid, such as hydronium ( $\text{H}_3\text{O}^+$ ), to give an ammonium ion, as shown below. This type of process is an acid-base reaction, which will be the topic of Chapter 3. Using VSEPR theory, determine whether you expect a change in bond angles when ammonia is converted into an ammonium ion. Explain.



## APPLY the skill

1.30 When sand is coated with a layer of trimethylhydroxysilane,  $(\text{CH}_3)_3\text{SiOH}$ , it repels water and can no longer get wet. Hydrophobic sand (aka, magic sand) is fun to play with, but it can also have useful applications in agriculture to reduce water consumption.<sup>8</sup> Predict the geometry for the silicon atom in trimethylhydroxysilane.

need more PRACTICE? Try Problems 1.40, 1.41, 1.50, 1.55, 1.56, 1.58

## 1.11 Dipole Moments and Molecular Polarity

Recall that induction is caused by the presence of an electronegative atom, as we saw earlier in the case of chloromethane. In Figure 1.39a the arrow shows the inductive effect of the chlorine atom. Figure 1.39b is a map of the electron density, revealing that the molecule is polarized. Chloromethane is



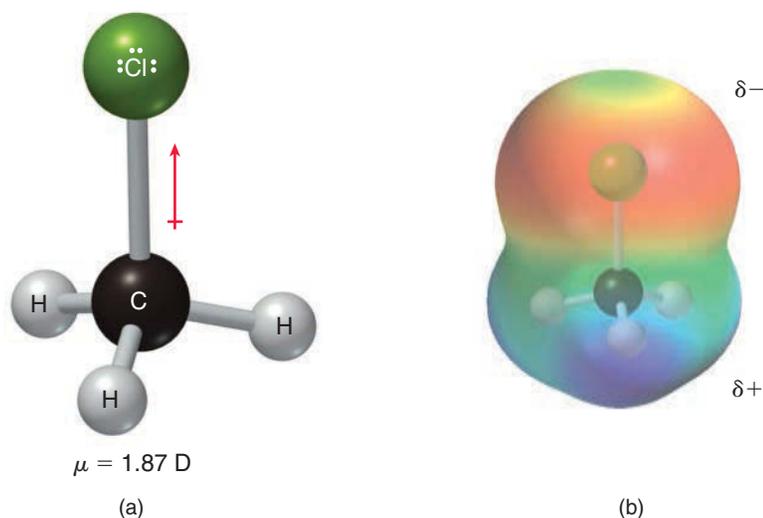
said to exhibit a dipole moment, because *the center of negative charge and the center of positive charge are separated from one another by a certain distance*. The **dipole moment** ( $\mu$ ) is used as an indicator of polarity, where  $\mu$  is defined as the amount of partial charge ( $\delta$ ) on either end of the dipole multiplied by the distance of separation ( $d$ ):

$$\mu = \delta \times d$$

Partial charges ( $\delta^+$  and  $\delta^-$ ) are generally on the order of  $10^{-10}$  esu (electrostatic units) and the distances are generally on the order of  $10^{-8}$  cm. Therefore, for a polar compound, the dipole moment ( $\mu$ ) will generally have an order of magnitude of around  $10^{-18}$  esu  $\cdot$  cm. The dipole moment of chloromethane, for example, is  $1.87 \times 10^{-18}$  esu  $\cdot$  cm. Since most compounds will have a dipole moment on this order of magnitude ( $10^{-18}$ ), it is more convenient to report dipole moments with a new unit, called a **debye (D)**, where

$$1 \text{ debye} = 10^{-18} \text{ esu} \cdot \text{cm}$$

Using these units, the dipole moment of chloromethane is reported as 1.87 D. The debye unit is named after Dutch scientist Peter Debye, whose contributions to the fields of chemistry and physics earned him a Nobel Prize in 1936.



**FIGURE 1.39**

(a) Ball-and-stick model of chloromethane showing the dipole moment.  
(b) An electrostatic potential map of chloromethane.

Measuring the dipole moment of a particular bond allows us to calculate the percent ionic character of that bond. As an example, let's analyze a C—Cl bond. This bond has a bond length of  $1.772 \times 10^{-8}$  cm, and an electron has a charge of  $4.80 \times 10^{-10}$  esu. If the bond were 100% ionic, then the dipole moment would be

$$\begin{aligned} \mu &= e \times d \\ &= (4.80 \times 10^{-10} \text{ esu}) \times (1.772 \times 10^{-8} \text{ cm}) \\ &= 8.51 \times 10^{-18} \text{ esu} \cdot \text{cm} \end{aligned}$$

or 8.51 D. In reality, the bond is not 100% ionic. The experimentally observed dipole moment is measured at 1.87 D, and we can use this value to calculate the percent ionic character of a C—Cl bond:

$$\frac{1.87 \text{ D}}{8.51 \text{ D}} \times 100\% = 22\%$$

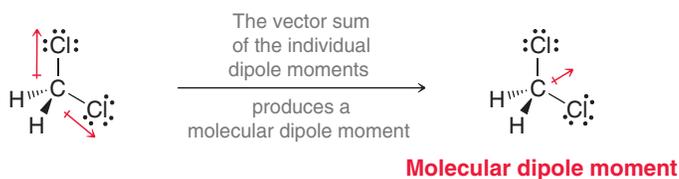
Table 1.4 shows the percent ionic character for a few of the bonds that we will frequently encounter in this text. Take special notice of the C=O bond. It has considerable ionic character, rendering it extremely reactive. Chapters 19–21 are devoted exclusively to the reactivity of compounds containing C=O bonds.

TABLE 1.4 PERCENT IONIC CHARACTER FOR SEVERAL BONDS			
BOND	BOND LENGTH ( $\times 10^{-8}$ cm)	OBSERVED $\mu$ (D)	PERCENT IONIC CHARACTER
C—O	1.41	0.7 D	$\frac{(0.7 \times 10^{-18} \text{ esu} \cdot \text{cm})}{(4.80 \times 10^{-10} \text{ esu})(1.41 \times 10^{-8} \text{ cm})} \times 100\% = 10\%$
O—H	0.96	1.5 D	$\frac{(1.5 \times 10^{-18} \text{ esu} \cdot \text{cm})}{(4.80 \times 10^{-10} \text{ esu})(0.96 \times 10^{-8} \text{ cm})} \times 100\% = 33\%$
C=O	1.227	2.4 D	$\frac{(2.4 \times 10^{-18} \text{ esu} \cdot \text{cm})}{(4.80 \times 10^{-10} \text{ esu})(1.23 \times 10^{-8} \text{ cm})} \times 100\% = 41\%$

Chloromethane was a simple example, because it has only one polar bond. When dealing with a compound that has more than one polar bond, it is necessary to take the vector sum of the individual dipole moments. The vector sum is called the **molecular dipole moment**, and it takes into account both the magnitude and the direction of each individual dipole moment. For example, consider the structure of dichloromethane (Figure 1.40). The individual dipole moments partially cancel, but not completely. The vector sum produces a dipole moment of 1.14 D, which is significantly smaller than the dipole moment of chloromethane because the two dipole moments here partially cancel each other.

FIGURE 1.40

The molecular dipole moment of dichloromethane is the net sum of all dipole moments in the compound.



The presence of a lone pair has a significant effect on the molecular dipole moment. The two electrons of a lone pair are balanced by two positive charges in the nucleus, but the lone pair is separated from the nucleus by some distance. There is, therefore, a dipole moment associated with every lone pair. A common example is ammonia (Figure 1.41). In this way, the lone pair contributes significantly to the magnitude of the molecular dipole moment, although its direction is not altered. That is, the direction of the molecular dipole moment would be the same with or without the contribution of the lone pair.

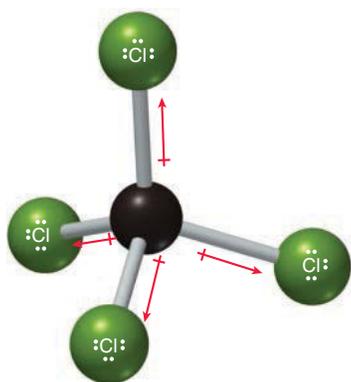


FIGURE 1.42

A ball-and-stick model of carbon tetrachloride. The individual dipole moments cancel to give a zero net dipole moment.



FIGURE 1.41

The net dipole moment of ammonia.

Table 1.5 shows experimentally observed molecular dipole moments for several common solvents. Notice that carbon tetrachloride ( $\text{CCl}_4$ ) has no molecular dipole moment. In this case, the individual dipole moments cancel each other completely to give the molecule a zero net dipole moment ( $\mu = 0$ ). This example (Figure 1.42) demonstrates that we must take geometry into account when assessing molecular dipole moments.



TABLE 1.5 DIPOLE MOMENTS FOR SOME COMMON SOLVENTS (AT 20°C)

COMPOUND	STRUCTURE	DIPOLE MOMENT	COMPOUND	STRUCTURE	DIPOLE MOMENT
Acetone	$\begin{array}{c} \cdot\cdot \\ \text{O} \\ \parallel \\ \text{H}_3\text{C}-\text{C}-\text{CH}_3 \end{array}$	2.69 D	Ammonia	NH <sub>3</sub>	1.47 D
Chloromethane	CH <sub>3</sub> Cl	1.87 D	Diethyl ether	$\begin{array}{c} \text{H} \quad \text{H} \quad \quad \text{H} \quad \text{H} \\   \quad   \quad \quad   \quad   \\ \text{H}-\text{C}-\text{C}-\ddot{\text{O}}-\text{C}-\text{C}-\text{H} \\   \quad   \quad \quad   \quad   \\ \text{H} \quad \text{H} \quad \quad \text{H} \quad \text{H} \end{array}$	1.15 D
Water	H <sub>2</sub> O	1.85 D	Methylene chloride	CH <sub>2</sub> Cl <sub>2</sub>	1.14 D
Methanol	CH <sub>3</sub> OH	1.69 D	Pentane	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\   \quad   \quad   \quad   \quad   \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\   \quad   \quad   \quad   \quad   \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$	0 D
Ethanol	$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ \text{H}-\text{C}-\text{C}-\ddot{\text{O}}-\text{H} \\   \quad   \\ \text{H} \quad \text{H} \end{array}$	1.66 D	Carbon tetrachloride	CCl <sub>4</sub>	0 D

## SKILLBUILDER



## 1.9 IDENTIFYING THE PRESENCE OF MOLECULAR DIPOLE MOMENTS

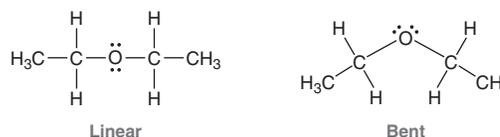
## LEARN the skill

Identify whether each of the following compounds exhibits a molecular dipole moment. If so, indicate the direction of the net molecular dipole moment:

- (a) CH
- <sub>3</sub>
- CH
- <sub>2</sub>
- OCH
- <sub>2</sub>
- CH
- <sub>3</sub>
- (b) CO
- <sub>2</sub>

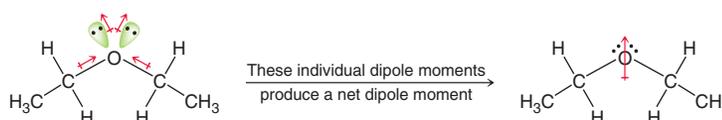
## SOLUTION

(a) In order to determine whether the individual dipole moments cancel each other completely, we must first predict the molecular geometry. Specifically, we need to know if the geometry around the oxygen atom is linear or bent:



To make this determination, we use the method described in the previous SkillBuilder. The oxygen atom has two  $\sigma$  bonds and two lone pairs, so the steric number is 4. Since there are two lone pairs, VSEPR theory predicts bent geometry.

After determining the molecular geometry, now draw all dipole moments and determine whether they cancel each other. In this case, they do not fully cancel each other:



This compound does in fact have a net molecular dipole moment, and the direction of the moment is shown above.

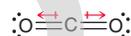
**STEP 1**  
Predict the molecular geometry.

**STEP 2**  
Identify the direction of all dipole moments.

**STEP 3**  
Draw the net dipole moment.

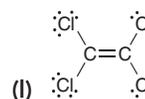
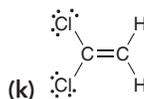
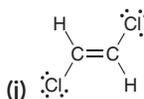
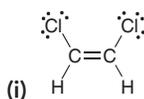
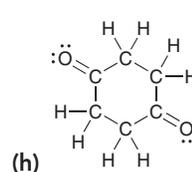
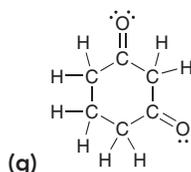
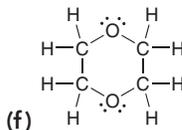
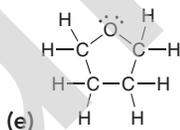
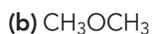


(b) Carbon dioxide (CO<sub>2</sub>) has two C=O bonds, each of which exhibits a dipole moment. In order to determine whether the individual dipole moments cancel each other completely, we must first predict the molecular geometry. Once again, we use the method described in the previous SkillBuilder. The carbon atom has two  $\sigma$  bonds and no lone pairs, so the steric number is two. Accordingly, VSEPR theory predicts linear geometry. Therefore, we expect the dipole moments to fully cancel each other:



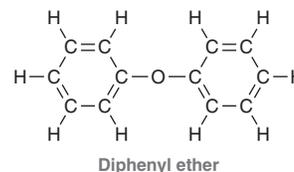
In a similar way, the dipole moments associated with the lone pairs also cancel each other, and therefore CO<sub>2</sub> does not have a net molecular dipole moment.

**PRACTICE the skill** 1.31 Identify whether each of the following compounds exhibits a molecular dipole moment. For compounds that do, indicate the direction of the net molecular dipole moment:



**APPLY the skill**

1.32 Volatile organic compounds (VOCs) contribute to the aroma of plants and can also be used for communication between plants. Diphenyl ether was identified as a minor VOC found in tomato plants.<sup>9</sup> Identify whether diphenyl ether exhibits a molecular dipole moment. If so, indicate the direction of the net molecular dipole moment.



need more PRACTICE? Try Problems 1.38, 1.40, 1.43, 1.61, 1.62, 1.63, 1.64

## 1.12 Intermolecular Forces and Physical Properties

The physical properties of a compound are determined by the attractive forces between the individual molecules, called **intermolecular forces**. It is often difficult to use the molecular structure alone to predict a precise melting point or boiling point for a compound. However, a few simple trends will allow us to compare compounds to each other in a relative way, for example, to predict which compound will boil at a higher temperature.

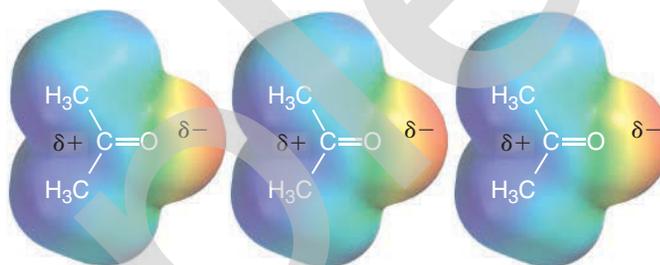
All intermolecular forces are *electrostatic*—that is, these forces occur as a result of the attraction between opposite charges. The electrostatic interactions for neutral molecules (with no formal charges) are often classified as (1) **dipole-dipole interactions**, (2) hydrogen bonding, and (3) fleeting dipole-dipole interactions.

### Dipole-Dipole Interactions

Compounds with net dipole moments can either attract each other or repel each other, depending on how they approach each other in space. In the solid phase, the molecules align so as to attract each other (Figure 1.43).

FIGURE 1.43

In solids, molecules align themselves so that their dipole moments experience attractive forces.



In the liquid phase, the molecules are free to tumble in space, but they do tend to move in such a way so as to attract each other more often than they repel each other. The resulting net attraction between the molecules results in an elevated melting point and boiling point. To illustrate this, compare the physical properties of isobutylene and acetone:



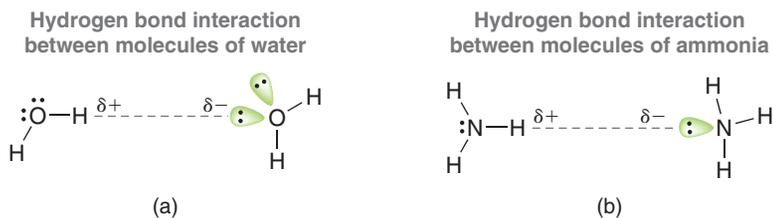
Isobutylene lacks a significant dipole moment, but acetone does have a strong net dipole moment. Therefore, acetone molecules will experience greater attractive interactions than isobutylene molecules. As a result, acetone has a higher melting point and higher boiling point than isobutylene.

### Hydrogen Bonding

The term **hydrogen bonding** is misleading. A hydrogen bond is not actually a “bond” but is just a specific type of dipole-dipole interaction. When a hydrogen atom is connected to an electronegative atom (usually O or N), the hydrogen atom will bear a partial positive charge ( $\delta+$ ) as a result of induction. This  $\delta+$  can then interact with a lone pair from an electronegative atom of another molecule. This can be illustrated with water or ammonia (Figure 1.44). This attractive interaction

FIGURE 1.44

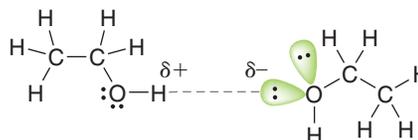
- (a) Hydrogen bonding between molecules of water.  
 (b) Hydrogen bonding between molecules of ammonia.



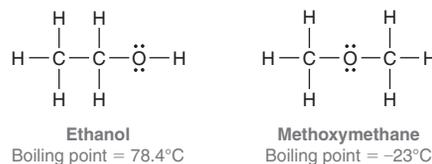
can occur with any compound that has an O—H bond or an N—H bond. For example, ethanol has an O—H bond, so it exhibits the same kind of attractive interaction (Figure 1.45).

FIGURE 1.45

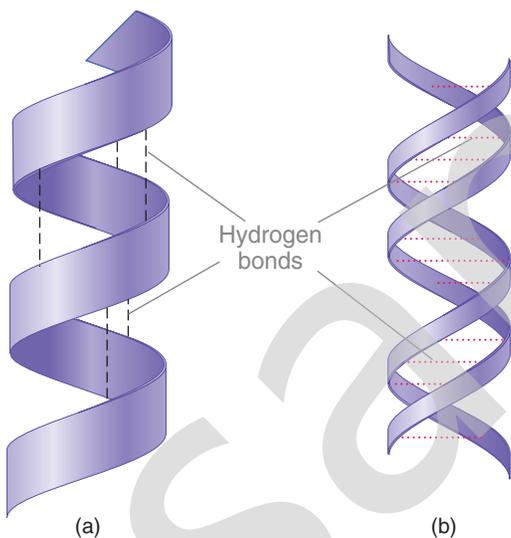
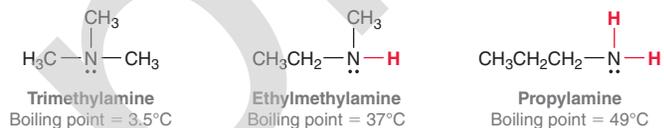
Hydrogen bonding between molecules of ethanol.



This type of interaction is quite strong because hydrogen is a relatively small atom, and as a result, the partial charges can get very close to each other. In fact, the effect of hydrogen bonding on physical properties is quite dramatic. At the beginning of this chapter, we briefly mentioned the difference in properties between the following two constitutional isomers:



These compounds have the same molecular formula, but they have very different boiling points. Ethanol experiences intermolecular hydrogen bonding, giving rise to a very high boiling point. Methoxymethane does not experience intermolecular hydrogen bonding, giving rise to a relatively lower boiling point. A similar trend can be seen in a comparison of the following amines:



**FIGURE 1.46**  
(a) An alpha helix of a protein.  
(b) The double helix in DNA.

### LOOKING AHEAD

The structure of DNA is explored in more detail in Section 24.9.

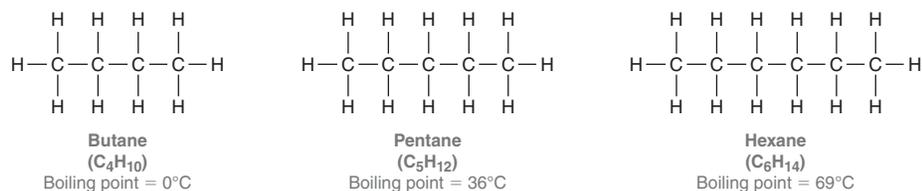
Once again, all three compounds have the same molecular formula ( $C_3H_9N$ ), but they have very different properties as a result of the extent of hydrogen bonding. Trimethylamine does not exhibit any hydrogen bonding and has a relatively low boiling point. Ethylmethylamine does exhibit hydrogen bonding and therefore has a higher boiling point. Finally, propylamine, which has the highest boiling point of the three compounds, has two  $N-H$  bonds and therefore exhibits even more hydrogen-bonding interactions.

Hydrogen bonding is incredibly important in determining the shapes and interactions of biologically important compounds. Chapter 25 will focus on proteins, which are long molecules that coil up into specific shapes under the influence of hydrogen bonding (Figure 1.46a). These shapes ultimately determine their biological function. Similarly, hydrogen bonds hold together individual strands of DNA to form the familiar double-helix structure.

As mentioned earlier, hydrogen “bonds” are not really bonds. To illustrate this, compare the energy of a real bond with the energy of a hydrogen-bonding interaction. A typical single bond ( $C-H$ ,  $N-H$ ,  $O-H$ ) has a bond strength of approximately 400 kJ/mol. In contrast, a hydrogen-bonding interaction has an average strength of approximately 20 kJ/mol. This leaves us with the obvious question: Why do we call them hydrogen *bonds* instead of just hydrogen *interactions*? To answer this question, consider the double-helix structure of DNA (Figure 1.46b). The two strands are joined by hydrogen-bonding interactions that function like rungs of a very long, twisted ladder. The net sum of these interactions is a significant factor that contributes to the structure of the double helix, in which the hydrogen-bonding interactions appear *as if* they were actually bonds. Nevertheless, it is relatively easy to “unzip” the double helix and retrieve the individual strands.

### Fleeting Dipole-Dipole Interactions

Some compounds have no permanent dipole moments, and yet analysis of boiling points indicates that they must have fairly strong intermolecular attractions. To illustrate this point, consider the following compounds:



### LOOKING AHEAD

Hydrocarbons will be discussed in more detail in Chapters 4, 16, and 17.

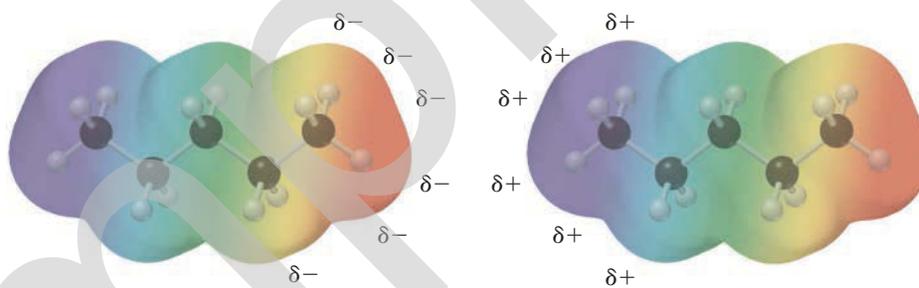
These three compounds are hydrocarbons, compounds that contain only carbon and hydrogen atoms. If we compare the properties of the hydrocarbons above, an important trend becomes apparent. Specifically, the boiling point appears to increase with increasing molecular weight. This trend can be justified by considering the fleeting, or transient, dipole moments that are more prevalent in larger hydrocarbons. To understand the source of these temporary dipole moments, we consider the electrons to be in constant motion, and therefore, the center of negative charge is also constantly moving around within the molecule. On average, the center of negative charge coincides with the center of positive charge, resulting in a zero dipole moment. However, at any given instant, the center of negative charge and the center of positive charge might not coincide. The resulting transient dipole moment can then induce a separate transient dipole moment in a neighboring molecule, initiating a fleeting attraction



between the two molecules (Figure 1.47). These attractive forces are called **London dispersion forces**, named after German-American physicist Fritz London. Large hydrocarbons have more surface area than smaller hydrocarbons and therefore experience these attractive forces to a larger extent.

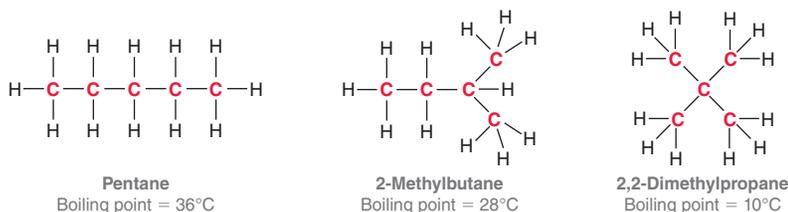
**FIGURE 1.47**

The fleeting attractive forces between two molecules of pentane.



London dispersion forces are stronger for higher molecular weight hydrocarbons because these compounds have larger surface areas that can accommodate more interactions. As a result, compounds of higher molecular weight will generally boil at higher temperatures. Table 1.6 illustrates this trend.

A branched hydrocarbon generally has a smaller surface area than its corresponding straight-chain isomer, and therefore, branching causes a decrease in boiling point. This trend can be seen by comparing the following constitutional isomers of  $C_5H_{12}$ :



## Practically Speaking | Biomimicry and Gecko Feet

The term biomimicry describes the notion that scientists often draw creative inspiration from studying nature. By investigating some of nature's processes, it is possible to mimic those processes and to develop new technology. One such example is based on the way that geckos can scurry up walls and along ceilings. Until recently, scientists were baffled by the curious ability of geckos to walk upside down, even on very smooth surfaces such as polished glass.

As it turns out, geckos do not use any chemical adhesives, nor do they use suction. Instead, their abilities arise from the intermolecular forces of attraction between the molecules in their feet and the molecules in the surface on which they are walking. When you place your hand on a surface, there are certainly intermolecular forces of attraction between the molecules of your hand and the surface, but the microscopic topography of your hand is quite bumpy. As a result, your hand only makes contact with the surface at perhaps a few thousand points. In contrast, the foot of a gecko has approximately half a million microscopic flexible hairs, called *setae*, each of which has even smaller hairs.

When a gecko places its foot on a surface, the flexible hairs allow the gecko to make extraordinary contact with the surface, and the resulting London dispersion forces are collectively strong enough to support the gecko.

In the last decade, many research teams have drawn inspiration from geckos and have created materials with densely packed microscopic hairs. For example, some scientists are

developing adhesive bandages that could be used in the healing of surgical wounds, while other scientists are developing special gloves and boots that would enable people to climb up walls (and perhaps walk upside down on ceilings). Imagine the possibility of one day being able to walk on walls and ceilings like Spiderman.

There are still many challenges that we must overcome before these materials will show their true potential. It is a technical challenge to design microscopic hairs that are strong enough to prevent the hairs from becoming tangled but flexible enough to allow the hairs to stick to any surface. Many researchers believe that these challenges can be overcome, and if they are right, we might have the opportunity to see the world turned literally upside down within the next decade.

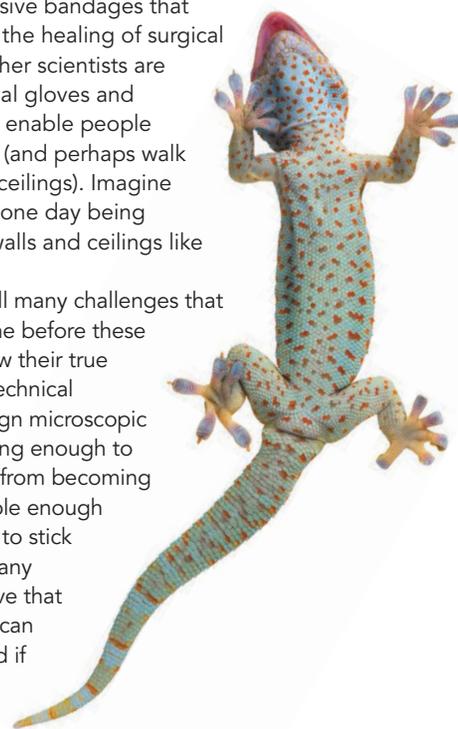


TABLE 1.6 BOILING POINTS FOR HYDROCARBONS OF INCREASING MOLECULAR WEIGHT

STRUCTURE	BOILING POINT (°C)	STRUCTURE	BOILING POINT (°C)
$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}-\text{H} \\   \\ \text{H} \end{array}$	-164	$\begin{array}{cccccc} \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} \\   &   &   &   &   &   \\ \text{H}-\text{C} & -\text{C} & -\text{C} & -\text{C} & -\text{C} & -\text{C}-\text{H} \\   &   &   &   &   &   \\ \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} \end{array}$	69
$\begin{array}{cc} \text{H} & \text{H} \\   &   \\ \text{H}-\text{C} & -\text{C}-\text{H} \\   &   \\ \text{H} & \text{H} \end{array}$	-89	$\begin{array}{cccccc} \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} \\   &   &   &   &   &   \\ \text{H}-\text{C} & -\text{C} & -\text{C} & -\text{C} & -\text{C} & -\text{C}-\text{H} \\   &   &   &   &   &   \\ \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} \end{array}$	98
$\begin{array}{ccc} \text{H} & \text{H} & \text{H} \\   &   &   \\ \text{H}-\text{C} & -\text{C} & -\text{C}-\text{H} \\   &   &   \\ \text{H} & \text{H} & \text{H} \end{array}$	-42	$\begin{array}{cccccc} \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} \\   &   &   &   &   &   &   \\ \text{H}-\text{C} & -\text{C} & -\text{C} & -\text{C} & -\text{C} & -\text{C} & -\text{C}-\text{H} \\   &   &   &   &   &   &   \\ \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} \end{array}$	126
$\begin{array}{cccc} \text{H} & \text{H} & \text{H} & \text{H} \\   &   &   &   \\ \text{H}-\text{C} & -\text{C} & -\text{C} & -\text{C}-\text{H} \\   &   &   &   \\ \text{H} & \text{H} & \text{H} & \text{H} \end{array}$	0	$\begin{array}{cccccc} \text{H} & \text{H} \\   &   &   &   &   &   &   &   \\ \text{H}-\text{C} & -\text{C} & -\text{C} & -\text{C} & -\text{C} & -\text{C} & -\text{C} & -\text{C}-\text{H} \\   &   &   &   &   &   &   &   \\ \text{H} & \text{H} \end{array}$	151
$\begin{array}{ccccc} \text{H} & \text{H} & \text{H} & \text{H} & \text{H} \\   &   &   &   &   \\ \text{H}-\text{C} & -\text{C} & -\text{C} & -\text{C} & -\text{C}-\text{H} \\   &   &   &   &   \\ \text{H} & \text{H} & \text{H} & \text{H} & \text{H} \end{array}$	36	$\begin{array}{cccccc} \text{H} & \text{H} \\   &   &   &   &   &   &   &   \\ \text{H}-\text{C} & -\text{C} & -\text{C} & -\text{C} & -\text{C} & -\text{C} & -\text{C} & -\text{C}-\text{H} \\   &   &   &   &   &   &   &   \\ \text{H} & \text{H} \end{array}$	174

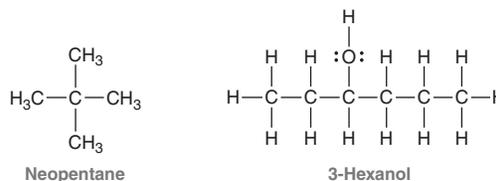
## SKILLBUILDER



## 1.10 PREDICTING PHYSICAL PROPERTIES OF COMPOUNDS BASED ON THEIR MOLECULAR STRUCTURE

## LEARN the skill

Determine which compound has the higher boiling point, neopentane or 3-hexanol:



## SOLUTION

When comparing boiling points of compounds, we look for the following factors:

1. Are there any dipole-dipole interactions in either compound?
2. Will either compound form hydrogen bonds?
- 3a. How many carbon atoms are in each compound?
- 3b. How much branching is in each compound?

The second compound above (3-hexanol) is the winner in all of these categories. It has a dipole moment, while neopentane does not. It will experience hydrogen bonding, while neopentane will not. It has six carbon atoms, while neopentane only has five. And, finally, it has a straight chain, while neopentane is highly branched. Each of these factors alone would suggest that 3-hexanol should have a higher boiling point. When we consider all of these factors together, we expect that the boiling point of 3-hexanol will be significantly higher than neopentane.

## STEP 1

Identify all dipole-dipole interactions in both compounds.

## STEP 2

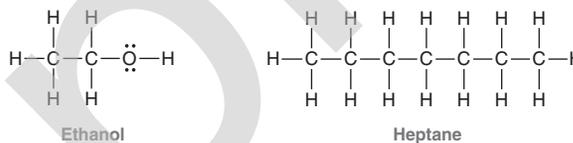
Identify all H-bonding interactions in both compounds.



**STEP 3**

Identify the number of carbon atoms and extent of branching in both compounds.

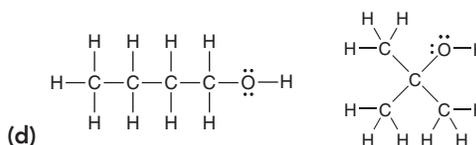
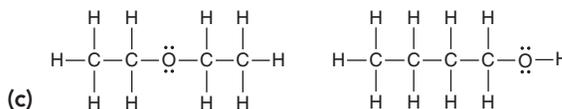
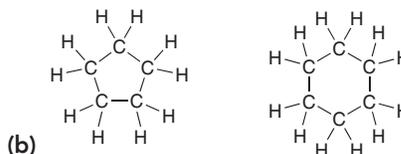
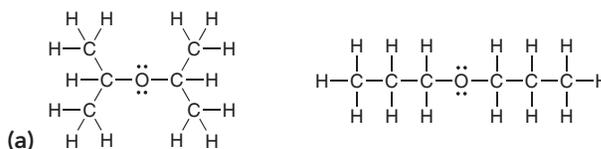
When comparing two compounds, it is important to consider all four factors. However, it is not always possible to make a clear prediction because in some cases there may be competing factors. For example, compare ethanol and heptane:



Ethanol will exhibit hydrogen bonding, but heptane has many more carbon atoms. Which factor dominates? It is not easy to predict. In this case, heptane has the higher boiling point, which is perhaps not what we would have guessed. In order to use the trends to make a prediction, there must be a clear winner.

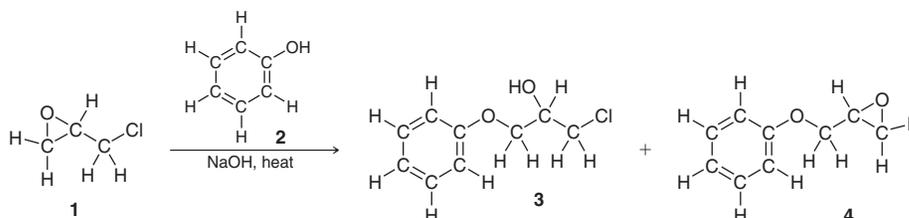


**PRACTICE the skill** 1.33 For each of the following pairs of compounds, identify the higher boiling compound and justify your choice:



**APPLY the skill**

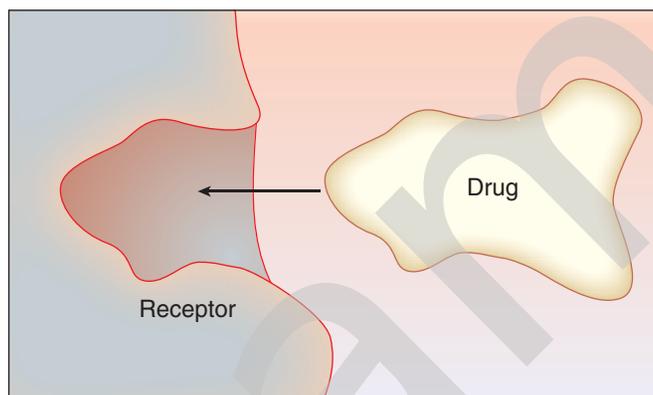
1.34 Epichlorohydrin (**1**) is an epoxide used in the production of plastic, epoxy glues, and resins (reactions of epoxides will be discussed in Chapter 13). When epichlorohydrin is treated with phenol (**2**), two products are formed (**3** and **4**).<sup>10</sup> These two products can be separated from each other via distillation, a process which exploits the difference in their boiling points. Which product (**3** or **4**) is expected to have the lower boiling point?



## Medically Speaking | Drug-Receptor Interactions

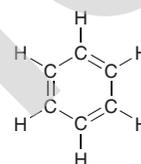


In most situations, the physiological response produced by a drug is attributed to the interaction between the drug and a biological receptor site. A receptor is a region within a biological macromolecule that can serve as a pouch in which the drug molecule can fit:



Initially, this mechanism was considered to work much like a lock and key. That is, a drug molecule would function as a key, either fitting or not fitting into a particular receptor. Extensive research on drug-receptor interactions has forced us to modify this simple lock-and-key model. It is now understood that both the drug and the receptor are flexible, constantly changing their shapes. As such, drugs can bind to receptors with various levels of efficiency, with some drugs binding more strongly and other drugs binding more weakly.

How does a drug bind to a receptor? In some cases, the drug molecule forms covalent bonds with the receptor. In such cases, the binding is indeed very strong (approximately 400 kJ/mol for each covalent bond) and therefore irreversible. We will see an example of irreversible binding when we explore a class of anticancer agents called nitrogen mustards (Chapter 7). For most drugs, however, the desired physiological response is meant to be temporary, which can only be accomplished if a drug can bind *reversibly* with its target receptor. This requires a weaker interaction between the drug and the receptor (at least weaker than a covalent bond). Examples of weak interactions include hydrogen-bonding interactions (20 kJ/mol) and London dispersion forces (approximately 4 kJ/mol for each carbon atom participating in the interaction). As an example, consider the structure of a benzene ring, which is incorporated as a structural subunit in many drugs:

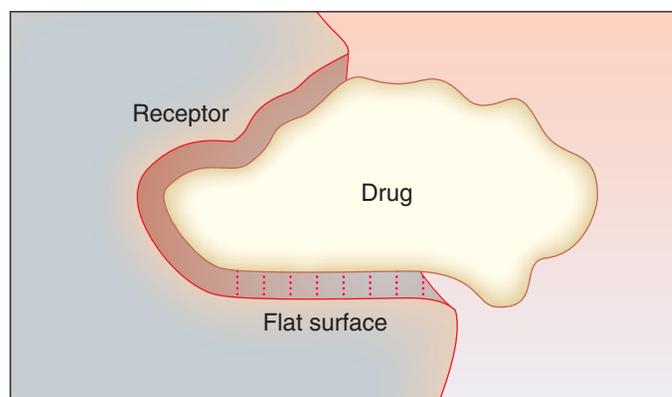


Benzene

In the benzene ring, each carbon is  $sp^2$  hybridized and therefore trigonal planar. As a result, a benzene ring represents a flat surface:



If the receptor also has a flat surface, the resulting London dispersion forces can contribute to the reversible binding of the drug to the receptor site:



This interaction is roughly equivalent to the strength of a single hydrogen-bonding interaction. The binding of a drug to a receptor is the result of the sum of the intermolecular forces of attraction between a portion of the drug molecule and the receptor site. We will have more to say about drugs and receptors in the upcoming chapters. In particular, we will see how drugs make their journey to the receptor, and we will explore how drugs flex and bend when interacting with a receptor site.

## 1.13 Solubility

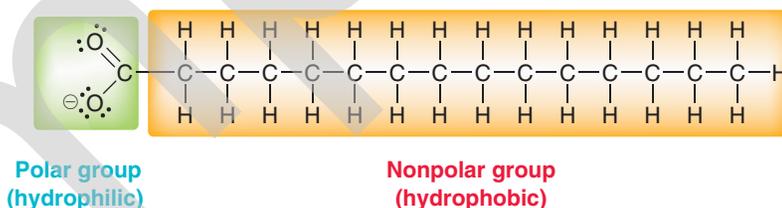
Solubility is based on the principle that “like dissolves like.” In other words, polar compounds are soluble in polar solvents, while nonpolar compounds are soluble in nonpolar solvents. Why is this so? A polar compound experiences dipole-dipole interactions with the molecules of a polar solvent, allowing the compound to dissolve in the solvent. Similarly, a nonpolar compound experiences London dispersion forces with the molecules of a nonpolar solvent. Therefore, if an article of clothing



is stained with a polar compound, the stain can generally be washed away with water (like dissolves like). However, water will be insufficient for cleaning clothing stained with nonpolar compounds, such as oil or grease. In a situation like this, the clothes can be cleaned with soap or by dry cleaning.

## Soap

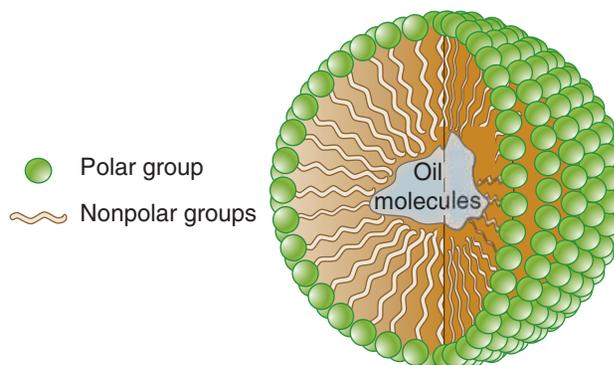
Soaps are compounds that have a polar group on one end of the molecule and a nonpolar group on the other end (Figure 1.48).



**FIGURE 1.48**

The hydrophilic and hydrophobic ends of a soap molecule.

The polar group represents the **hydrophilic** region of the molecule (literally, “loves water”), while the nonpolar group represents the **hydrophobic** region of the molecule (literally, “afraid of water”). Oil molecules are surrounded by the hydrophobic tails of the soap molecules, forming a **micelle** (Figure 1.49).



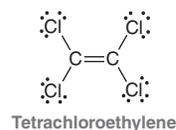
**FIGURE 1.49**

A micelle is formed when the hydrophobic tails of soap molecules surround the nonpolar oil molecules.

The surface of the micelle is comprised of all of the polar groups, rendering the micelle water soluble. This is a clever way to dissolve the oil in water, but this technique only works for clothing that can be subjected to water and soap. Some clothes will be damaged in soapy water, and in those situations, dry cleaning is the preferred method.

## Dry Cleaning

Rather than surrounding the nonpolar compound with a micelle so that it will be water soluble, it is actually conceptually simpler to use a nonpolar solvent. This is just another application of the principle of “like dissolves like.” Dry cleaning utilizes a nonpolar solvent, such as tetrachloroethylene, to dissolve the nonpolar compounds. This compound is nonflammable, making it an ideal choice as a solvent. Dry cleaning allows clothes to be cleaned without coming into contact with water or soap.

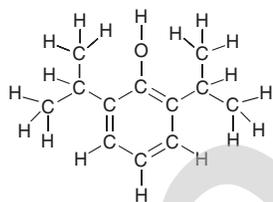


## Medically Speaking Propofol: The Importance of Drug Solubility

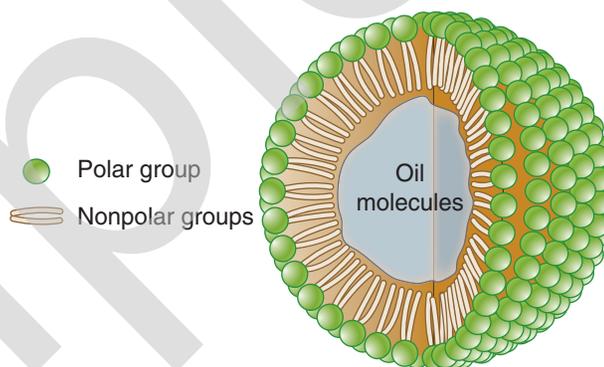


The drug propofol received a lot of publicity in 2009 as one of the drugs implicated in the death of Michael Jackson:

Propofol is normally used for initiating and maintaining anesthesia during surgery. It is readily soluble in the hydrophobic membranes of the brain, where it inhibits the firing (or excitation) of brain neurons. To be effective, propofol must be administered through intravenous injection, yet this poses a solubility problem. Specifically, the hydrophobic region of the drug is much larger than the hydrophilic region, and consequently, the drug does not readily dissolve in water (or in blood). Propofol *does* dissolve very well in soybean oil (a complex mixture of hydrophobic compounds, discussed in Section 26.3), but injecting a dose of soybean oil into the bloodstream would result in an oil globule, which could be fatal. To overcome this problem, a group of compounds called lecithins (discussed in Section 26.5) are added to the mixture. Lecithins are compounds that exhibit hydrophobic regions as well as a hydrophilic region. As such, lecithins form micelles, analogous to soap (as described in Section 1.13), which encapsulate the mixture of propofol and soybean oil. This solution of micelles can then be injected into the bloodstream. The propofol readily passes out of the micelles, crosses the hydrophobic membranes of the brain, and reaches the target neurons.



Propofol



The high concentration of micelles results in a solution that looks very much like milk, and ampules of propofol are sometimes referred to as “milk of amnesia.”



## REVIEW OF CONCEPTS AND VOCABULARY

### SECTION 1.1

- Organic compounds contain carbon atoms.

### SECTION 1.2

- Constitutional isomers** share the same molecular formula but have different connectivity of atoms and different physical properties.
- Each element will generally form a predictable number of bonds. Carbon is generally **tetravalent**, nitrogen **trivalent**, oxygen **divalent**, and hydrogen and the halogens **monovalent**.

### SECTION 1.3

- A **covalent bond** results when two atoms share a pair of electrons.
- Covalent bonds are illustrated using **Lewis structures**, in which electrons are represented by dots.
- Second-row elements generally obey the **octet rule**, bonding to achieve noble gas electron configuration.
- A pair of unshared electrons is called a **lone pair**.

### SECTION 1.4

- A **formal charge** occurs when atoms do not exhibit the appropriate number of valence electrons; formal charges must be drawn in Lewis structures.

### SECTION 1.5

- Bonds are classified as (1) **covalent**, (2) **polar covalent**, or (3) **ionic**.
- Polar covalent bonds exhibit **induction**, causing the formation of **partial positive charges** ( $\delta^+$ ) and **partial negative charges** ( $\delta^-$ ). **Electrostatic potential maps** present a visual illustration of partial charges.

### SECTION 1.6

- Quantum mechanics** describes electrons in terms of their wavelike properties.
- A **wave equation** describes the total energy of an electron when in the vicinity of a proton. Solutions to wave equations are called **wavefunctions** ( $\psi$ ), where  $\psi^2$  represents the probability of finding an electron in a particular location.



- **Atomic orbitals** are represented visually by generating three-dimensional plots of  $\psi^2$ ; nodes indicate that the value of  $\psi$  is zero.
- An occupied orbital can be thought of as a cloud of **electron density**.
- Electrons fill orbitals following three principles: (1) the **Aufbau principle**, (2) the **Pauli exclusion principle**, and (3) **Hund's rule**. Orbitals with the same energy level are called degenerate orbitals.

### SECTION 1.7

- **Valence bond theory** treats every bond as the sharing of electron density between two atoms as a result of the constructive interference of their atomic orbitals. **Sigma ( $\sigma$ ) bonds** are formed when the electron density is located primarily on the bond axis.

### SECTION 1.8

- **Molecular orbital theory** uses a mathematical method called the **linear combination of atomic orbitals (LCAO)** to form molecular orbitals. Each molecular orbital is associated with the entire molecule, rather than just two atoms.
- The bonding MO of molecular hydrogen results from constructive interference between its two atomic orbitals. The antibonding MO results from destructive interference.
- An **atomic orbital** is a region of space associated with an individual atom, while a molecular orbital is associated with an entire molecule.
- Two molecular orbitals are the most important to consider: (1) the **highest occupied molecular orbital**, or HOMO, and (2) the **lowest unoccupied molecular orbital**, or LUMO.

### SECTION 1.9

- Methane's tetrahedral geometry can be explained using four degenerate  **$sp^3$ -hybridized orbitals** to achieve its four single bonds.
- Ethylene's planar geometry can be explained using three degenerate  **$sp^2$ -hybridized orbitals**. The remaining  $p$  orbitals overlap to form a separate bonding interaction, called a pi ( $\pi$ ) bond. The carbon atoms of ethylene are connected via a  $\sigma$  bond, resulting from the overlap of  $sp^2$ -hybridized atomic orbitals, and via a  $\pi$  bond, resulting from the overlap of  $p$  orbitals, both of which comprise the double bond of ethylene.
- Acetylene's linear geometry is achieved via  **$sp$ -hybridized** carbon atoms in which a triple bond is created from the bonding interactions of one  $\sigma$  bond, resulting from overlapping  $sp$  orbitals, and two  $\pi$  bonds, resulting from overlapping  $p$  orbitals.

- Triple bonds are stronger and shorter than double bonds, which are stronger and shorter than single bonds.

### SECTION 1.10

- The geometry of small compounds can be predicted using valence shell electron pair repulsion (**VSEPR**) theory, which focuses on the number of  $\sigma$  bonds and lone pairs exhibited by each atom. The total, called the steric number, indicates the number of electron pairs that repel each other.
- A compound's geometry depends on the number of lone pairs and can be tetrahedral, trigonal pyramidal, bent, trigonal planar, or linear.

### SECTION 1.11

- **Dipole moments ( $\mu$ )** occur when the center of negative charge and the center of positive charge are separated from one another by a certain distance; the dipole moment is used as an indicator of polarity (measured in **debyes**).
- The percent ionic character of a bond is determined by measuring its dipole moment. The vector sum of individual dipole moments in a compound determines the **molecular dipole moment**.

### SECTION 1.12

- The physical properties of compounds are determined by intermolecular forces, the attractive forces between molecules.
- **Dipole-dipole interactions** occur between two molecules that possess permanent dipole moments. Hydrogen bonding, a special type of dipole-dipole interaction, occurs when the lone pairs of an electronegative atom interact with an electron-poor hydrogen atom. Compounds that exhibit hydrogen bonding have higher boiling points than similar compounds that lack hydrogen bonding.
- **London dispersion forces** result from the interaction between transient dipole moments and are stronger for larger alkanes due to their larger surface area and ability to accommodate more interactions.

### SECTION 1.13

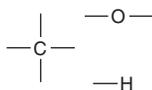
- Polar compounds are soluble in polar solvents; nonpolar compounds are soluble in nonpolar solvents.
- Soaps are compounds that contain both **hydrophilic** and **hydrophobic** regions. The hydrophobic tails surround nonpolar compounds, forming a water-soluble micelle.

## SKILLBUILDER REVIEW

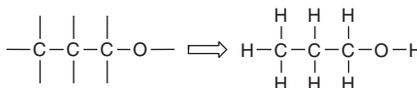
### 1.1 DRAWING CONSTITUTIONAL ISOMERS OF SMALL MOLECULES

**EXAMPLE**  
Draw all constitutional isomers that have the molecular formula  $C_3H_8O$ .

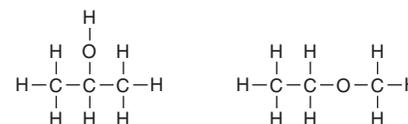
**STEP 1** Determine the valency of each atom.



**STEP 2** Connect the atoms of highest valency, and place the monovalent atoms at the periphery.



**STEP 3** Consider other ways to connect the atoms.



## 1.2 DRAWING THE LEWIS DOT STRUCTURE OF AN ATOM

**STEP 1** Determine the number of valence electrons.



**STEP 2** Place one electron by itself on each side of the atom.



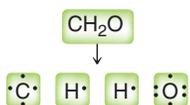
**STEP 3** If the atom has more than four valence electrons, the remaining electrons are paired with the electrons already drawn.



Try Problems 1.3–1.7

## 1.3 DRAWING THE LEWIS STRUCTURE OF A SMALL MOLECULE

**STEP 1** Draw all individual atoms.



**STEP 2** Connect atoms that form more than one bond.



**STEP 3** Connect hydrogen atoms.



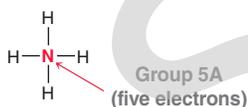
**STEP 4** Pair any unpaired electrons, so that each atom achieves an octet.



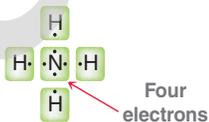
Try Problems 1.8–1.11, 1.39

## 1.4 CALCULATING FORMAL CHARGE

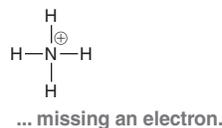
**STEP 1** Determine appropriate number of valence electrons.



**STEP 2** Determine the number of valence electrons in this case.



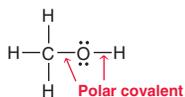
**STEP 3** Assign a formal charge.



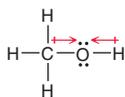
Try Problems 1.12–1.14, 1.41

## 1.5 LOCATING PARTIAL CHARGES

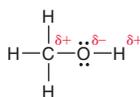
**STEP 1** Identify all polar covalent bonds.



**STEP 2** Determine the direction of each dipole.



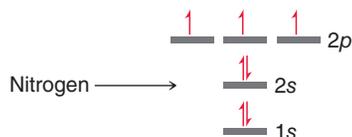
**STEP 3** Indicate location of partial charges.



Try Problems 1.15–1.17, 1.37, 1.38, 1.48, 1.57

## 1.6 IDENTIFYING ELECTRON CONFIGURATIONS

**STEP 1** Fill orbitals using the Aufbau principle, the Pauli exclusion principle, and Hund's rule.



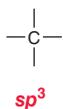
**STEP 2** Summarize using the following notation:



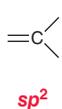
Try Problems 1.18–1.20, 1.44

## 1.7 IDENTIFYING HYBRIDIZATION STATES

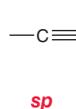
Four single bonds



A double bond



A triple bond



Try Problems 1.24–1.25, 1.55, 1.56



## 1.8 PREDICTING GEOMETRY

**STEP 1** Determine the steric number by adding the number of  $\sigma$  bonds and lone pairs.



# of  $\sigma$  bonds = 3

# of lone pairs = 1

Steric number = 4

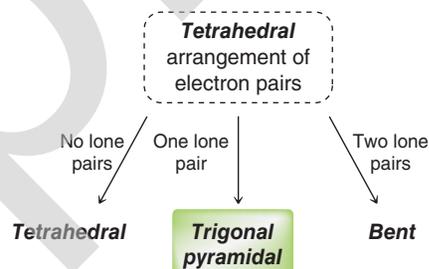
**STEP 2** Use steric number to identify the arrangement of electron pairs.

4  $\longrightarrow$  Tetrahedral

3  $\longrightarrow$  Trigonal planar

2  $\longrightarrow$  Linear

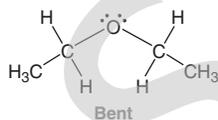
**STEP 3** Identify the geometry.



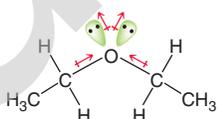
Try Problems 1.27–1.30, 1.40, 1.41, 1.50, 1.55, 1.56, 1.58

## 1.9 IDENTIFYING MOLECULAR DIPOLE MOMENTS

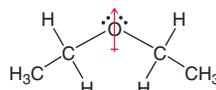
**STEP 1** Predict geometry.



**STEP 2** Identify direction of all dipole moments.



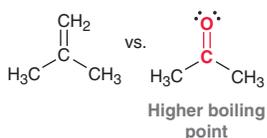
**STEP 3** Draw net dipole moment.



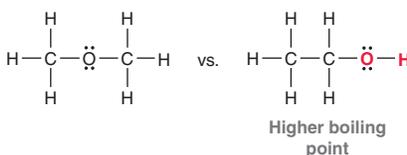
Try Problems 1.31, 1.32, 1.38, 1.40, 1.43, 1.61, 1.62, 1.63, 1.64

## 1.10 PREDICTING PHYSICAL PROPERTIES

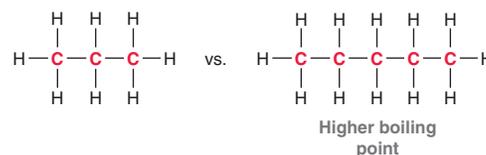
**STEP 1** Identify dipole-dipole interactions.



**STEP 2** Identify H-bonding interactions.



**STEP 3** Identify number of carbon atoms and extent of branching.



Try Problems 1.33, 1.34, 1.52, 1.53, 1.60, 1.65

## PRACTICE PROBLEMS

Note: Most of the Problems are available within **WileyPLUS**, an online teaching and learning solution.

**1.35** Draw structures for all constitutional isomers with the following molecular formulas:

- (a)  $\text{C}_6\text{H}_{14}$       (b)  $\text{C}_2\text{H}_5\text{Cl}$       (c)  $\text{C}_2\text{H}_4\text{Cl}_2$       (d)  $\text{C}_2\text{H}_3\text{Cl}_3$

**1.36** Draw structures for all constitutional isomers with the molecular formula  $\text{C}_4\text{H}_8$  that have:

- (a) Only single bonds      (b) One double bond

**1.37** For each compound below, identify any polar covalent bonds and indicate the direction of the dipole moment using the symbols  $\delta^+$  and  $\delta^-$ :

- (a) HBr      (b) HCl      (c)  $\text{H}_2\text{O}$       (d)  $\text{CH}_4\text{O}$

**1.38** For each pair of compounds below, identify the one that would be expected to have more ionic character. Explain your choice.

- (a) NaBr or HBr      (b) BrCl or FCl

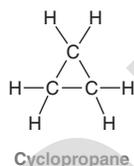
**1.39** Draw a Lewis dot structure for each of the following compounds:

- (a)  $\text{CH}_3\text{CH}_2\text{OH}$  (b)  $\text{CH}_3\text{CN}$

**1.40** Draw a Lewis structure for a compound with the molecular formula  $\text{C}_4\text{H}_{11}\text{N}$  in which three of the carbon atoms are bonded to the nitrogen atom. What is the geometry of the nitrogen atom in this compound? Does this compound exhibit a molecular dipole moment? If so, indicate the direction of the dipole moment.

**1.41** Draw a Lewis structure of the anion  $\text{AlBr}_4^-$  and determine its geometry.

**1.42** Draw the structure for the only constitutional isomer of cyclopropane:



**1.43** Determine whether each compound below exhibits a molecular dipole moment:

- (a)  $\text{CH}_4$  (b)  $\text{NH}_3$  (c)  $\text{H}_2\text{O}$   
 (d)  $\text{CO}_2$  (e)  $\text{CCl}_4$  (f)  $\text{CH}_2\text{Br}_2$

**1.44** Identify the neutral element that corresponds with each of the following electron configurations:

- (a)  $1s^2 2s^2 2p^4$  (b)  $1s^2 2s^2 2p^5$  (c)  $1s^2 2s^2 2p^2$   
 (d)  $1s^2 2s^2 2p^3$  (e)  $1s^2 2s^2 2p^6 3s^2 3p^5$

**1.45** In the compounds below, classify each bond as covalent, polar covalent, or ionic:

- (a)  $\text{NaBr}$  (b)  $\text{NaOH}$  (c)  $\text{NaOCH}_3$   
 (d)  $\text{CH}_3\text{OH}$  (e)  $\text{CH}_2\text{O}$

**1.46** Draw structures for all constitutional isomers with the following molecular formulas:

- (a)  $\text{C}_2\text{H}_6\text{O}$  (b)  $\text{C}_2\text{H}_6\text{O}_2$  (c)  $\text{C}_2\text{H}_4\text{Br}_2$

**1.47** Draw structures for any five constitutional isomers with the molecular formula  $\text{C}_2\text{H}_6\text{O}_3$ .

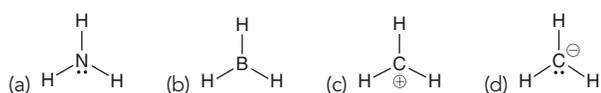
**1.48** For each type of bond below, determine the direction of the expected dipole moment:

- (a)  $\text{C}-\text{O}$  (b)  $\text{C}-\text{Mg}$  (c)  $\text{C}-\text{N}$  (d)  $\text{C}-\text{Li}$   
 (e)  $\text{C}-\text{Cl}$  (f)  $\text{C}-\text{H}$  (g)  $\text{O}-\text{H}$  (h)  $\text{N}-\text{H}$

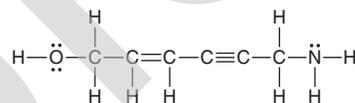
**1.49** Predict the bond angles for all bonds in the following compounds:

- (a)  $\text{CH}_3\text{CH}_2\text{OH}$  (b)  $\text{CH}_2\text{O}$  (c)  $\text{C}_2\text{H}_4$  (d)  $\text{C}_2\text{H}_2$   
 (e)  $\text{CH}_3\text{OCH}_3$  (f)  $\text{CH}_3\text{NH}_2$  (g)  $\text{C}_3\text{H}_8$  (h)  $\text{CH}_3\text{CN}$

**1.50** Identify the expected hybridization state and geometry for the central atom in each of the following compounds:

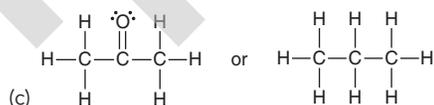


**1.51** Count the total number of  $\sigma$  bonds and  $\pi$  bonds in the compound below:



**1.52** For each pair of compounds below, predict which compound will have the higher boiling point and explain your choice:

- (a)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OCH}_3$  or  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$   
 (b)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$  or  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$



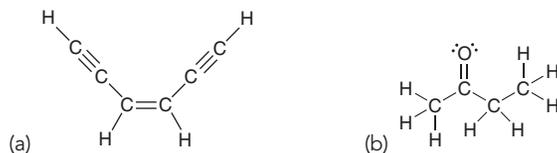
**1.53** Which of the following pure compounds will exhibit hydrogen bonding?

- (a)  $\text{CH}_3\text{CH}_2\text{OH}$  (b)  $\text{CH}_2\text{O}$  (c)  $\text{C}_2\text{H}_4$  (d)  $\text{C}_2\text{H}_2$   
 (e)  $\text{CH}_3\text{OCH}_3$  (f)  $\text{CH}_3\text{NH}_2$  (g)  $\text{C}_3\text{H}_8$  (h)  $\text{NH}_3$

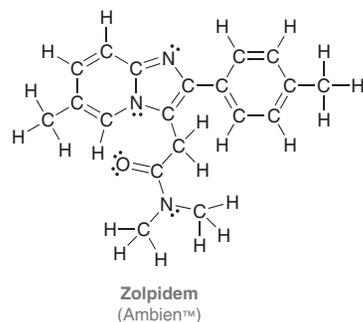
**1.54** For each case below, identify the most likely value for x:

- (a)  $\text{BH}_x$  (b)  $\text{CH}_x$  (c)  $\text{NH}_x$  (d)  $\text{CH}_2\text{Cl}_x$

**1.55** Identify the hybridization state and geometry of each carbon atom in the following compounds:



**1.56** Ambien™ is a sedative used in the treatment of insomnia. It was discovered in 1982 and brought to market in 1992 (it takes a long time for new drugs to undergo the extensive testing required to receive approval from the Food and Drug Administration). Identify the hybridization state and geometry of each carbon atom in the structure of this compound:

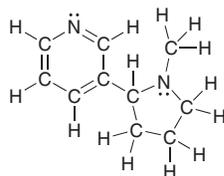


**1.57** Identify the most electronegative element in each of the following compounds:

- (a)  $\text{CH}_3\text{OCH}_2\text{CH}_2\text{NH}_2$  (b)  $\text{CH}_2\text{ClCH}_2\text{F}$  (c)  $\text{CH}_3\text{Li}$

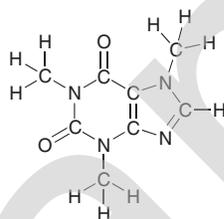


**1.58** Nicotine is an addictive substance found in tobacco. Identify the hybridization state and geometry of each of the nitrogen atoms in nicotine:



Nicotine

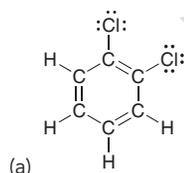
**1.59** Below is the structure of caffeine, but its lone pairs are not shown. Identify the location of all lone pairs in this compound:



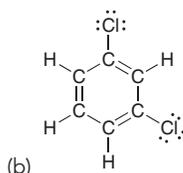
Caffeine

**1.60** There are two different compounds with the molecular formula  $C_2H_6O$ . One of these isomers has a much higher boiling point than the other. Explain why.

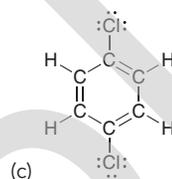
**1.61** Identify which compounds below possess a molecular dipole moment and indicate the direction of that dipole moment:



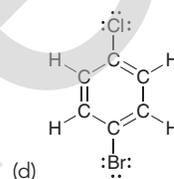
(a)



(b)



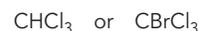
(c)



(d)

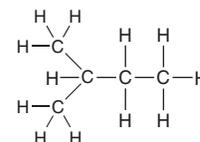
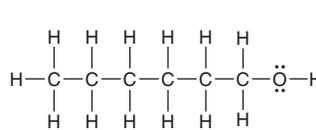
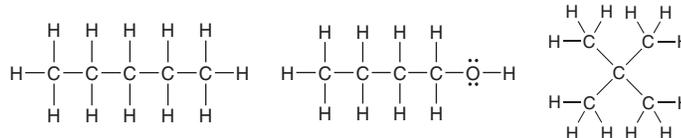
**1.62** Methylene chloride ( $CH_2Cl_2$ ) has fewer chlorine atoms than chloroform ( $CHCl_3$ ). Nevertheless, methylene chloride has a larger molecular dipole moment than chloroform. Explain.

**1.63** Which of the following compounds has the larger dipole moment? Explain your choice:



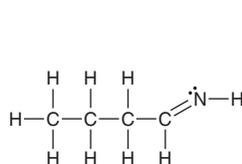
**1.64** Bonds between carbon and oxygen ( $C-O$ ) are more polar than bonds between sulfur and oxygen ( $S-O$ ). Nevertheless, sulfur dioxide ( $SO_2$ ) exhibits a dipole moment while carbon dioxide ( $CO_2$ ) does not. Explain this apparent anomaly.

**1.65** Arrange the following compounds in order of increasing boiling point:

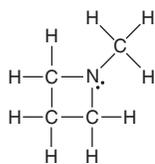


## INTEGRATED PROBLEMS

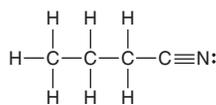
**1.66** Consider the three compounds shown below and then answer the questions that follow:



Compound A



Compound B



Compound C

- Which two compounds are constitutional isomers?
- Which compound contains a nitrogen atom with trigonal pyramidal geometry?
- Identify the compound with the greatest number of  $\sigma$  bonds.
- Identify the compound with the fewest number of  $\sigma$  bonds.
- Which compound contains more than one  $\pi$  bond?

- Which compound contains an  $sp^2$ -hybridized carbon atom?
- Which compound contains only  $sp^3$ -hybridized atoms (in addition to hydrogen atoms)?
- Which compound do you predict will have the highest boiling point? Explain.

**1.67** Propose at least two different structures for a compound with six carbon atoms that exhibits the following features:

- All six carbon atoms are  $sp^2$  hybridized.
- Only one carbon atom is  $sp$  hybridized, and the remaining five carbon atoms are all  $sp^3$  hybridized (remember that your compound can have elements other than carbon and hydrogen).
- There is a ring, and all of the carbon atoms are  $sp^3$  hybridized.
- All six carbon atoms are  $sp$  hybridized, and the compound contains no hydrogen atoms (remember that a triple bond is linear and therefore cannot be incorporated into a ring of six carbon atoms).

**1.68** Draw all constitutional isomers with the molecular formula  $C_5H_{10}$  that possess one  $\pi$  bond.

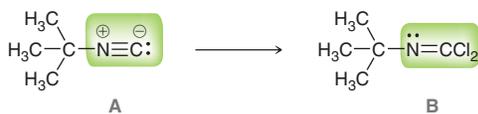
**1.69** With current spectroscopic techniques (discussed in Chapters 14–16), chemists are generally able to determine the structure of an unknown organic compound in just one day. These techniques have only been available for the last several decades. In the first half of the twentieth century, structure determination was a very slow and painful process in which the compound under investigation would be subjected to a variety of chemical reactions. The results of those reactions would provide chemists with clues about the structure of the compound. With enough clues, it was sometimes (but not always) possible to determine the structure. As an example, try to determine the structure of an unknown compound, using the following clues:

- The molecular formula is  $C_4H_{10}N_2$ .
- There are no  $\pi$  bonds in the structure.
- The compound has no net dipole moment.
- The compound exhibits very strong hydrogen bonding.

You should find that there are at least two constitutional isomers that are consistent with the information above. (**Hint:** Consider incorporating a ring in your structure.)

**1.70** A compound with the molecular formula  $C_5H_{11}N$  has no  $\pi$  bonds. Every carbon atom is connected to exactly two hydrogen atoms. Determine the structure of the compound.

**1.71** Isonitriles (**A**) are an important class of compounds because of the versatile reactivity of the functional group, enabling the preparation of numerous new compounds and natural products. Isonitriles can be converted to isonitrile dihalides (**B**), which represents a useful procedure for temporarily hiding the reactivity of an isonitrile.<sup>11</sup>



- Identify the hybridization state for each highlighted atom in **A**.
- One of the carbon atoms in **A** exhibits a lone pair. In what type of atomic orbital does this lone pair reside?
- Predict the C—N—C bond angle in compound **A**.
- Identify the hybridization state for each highlighted atom in **B**.
- The nitrogen atom in **B** exhibits a lone pair. In what type of atomic orbital does this lone pair reside?
- Predict the C—N—C bond angle in compound **B**.

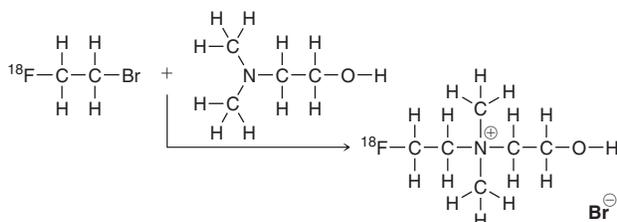
**1.72** Consider the following table that provides bond lengths for a variety of C—X bonds (measured in Å).

	X = F	X = Cl	X = Br	X = I
	1.40	1.79	1.97	2.16
	1.34		1.88	2.10
	1.27	1.63	1.79	

Two trends emerge when we compare these data. First, notice that the bond length increases as the size of the halogen increases. This should make sense, since the valence electrons in iodine are farther away from

the nucleus than the valence electrons in Br, so a C—I bond is longer than a C—Br bond. For the same reason, a C—Br bond is longer than a C—Cl bond, which in turn is longer than a C—F bond. Notice also that bond length decreases as the hybridization state goes from  $sp^3$  to  $sp^2$  to  $sp$ . This should also make sense, because  $sp$ -hybridized atoms hold their valence electrons closer to the nucleus (as seen in Table 1.2), and therefore form shorter bonds. These two trends are in conflict with each other when we compare a  $C_{sp^2}$ —Cl bond with a  $C_{sp}$ —I bond. The former bond is expected to be shorter because of the first trend (size of halogen), while the latter bond is expected to be shorter because of the second trend (hybridization state). Use the data provided to determine which bond is actually shorter, and explain your choice.

**1.73** Positron emission tomography (PET) is a medical imaging technique that produces a three-dimensional picture of functional processes in the body, such as the brain uptake of glucose. PET imaging requires the introduction of [ $^{18}F$ ]-fluorine (a radioactive isotope of fluorine) into molecules and can be achieved by several routes, such as the following:<sup>12</sup>



(a) Identify the hybridization for all atoms except for C, H, and O in the three compounds. Note: Throughout this chapter, all lone pairs were drawn. We will soon see (Chapter 2) that lone pairs are often omitted from structural drawings, because they can be inferred by the presence or absence of formal charges. In this problem, none of the lone pairs have been drawn.

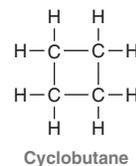
(b) Predict the bond angle of each C—N—C bond in the product.

**Problems 1.74–1.77 follow the style of the ACS organic chemistry exam. For each of these problems, there will be one correct answer and three distractors.**

**1.74** Which is the correct hybridization state and geometry for the carbon atom in HCN?

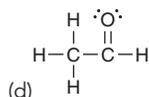
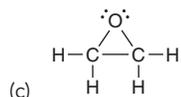
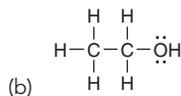
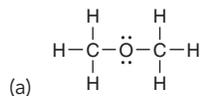
- $sp$ , linear
- $sp^2$ , trigonal planar
- $sp^3$ , tetrahedral
- None of the above

**1.75** Which of the following is a constitutional isomer of cyclobutane?

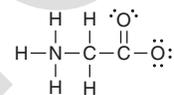


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1.76 Which of the following is expected to have the highest boiling point?



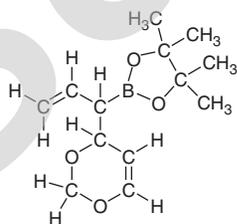
1.77 The following structure has been drawn without formal charges. Which statement describes the missing formal charge(s)?



- (a) This structure has one positive charge and one negative charge.  
 (b) This structure has one positive charge but no negative charges.  
 (c) This structure has one negative charge but no positive charges.  
 (d) This structure has no formal charges.

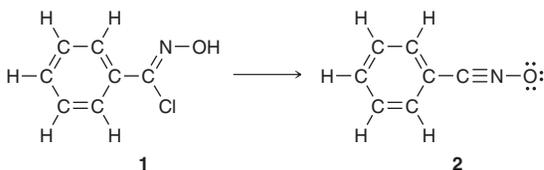
## CHALLENGE PROBLEMS

1.78 Phenalamide A<sub>2</sub> belongs to a class of natural products that are of interest because of their antibiotic, antifungal, and antiviral activity. In the first total synthesis of this compound, the following boronate ester was utilized:<sup>13</sup>



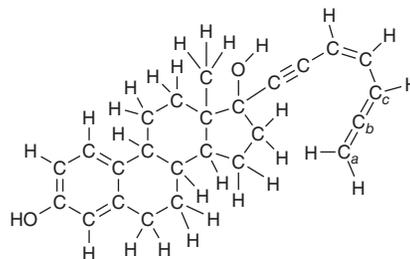
- (a) Determine the hybridization state of the boron atom.  
 (b) Predict the O—B—O bond angle and then suggest a reason why the actual bond angle might deviate from the predicted value in this case.  
 (c) The lone pairs have not been drawn. Draw all of them. (Hint: Note that the structure has no formal charges.)

1.79 The formation of a variety of compounds called oxazolidinones is important for the synthesis of many different natural products and other compounds that have potential use as future medicines. One method<sup>14</sup> for preparing oxazolidinones involves the conversion of a hydroximoyl chloride, such as compound **1**, into a nitrile oxide, such as compound **2**:



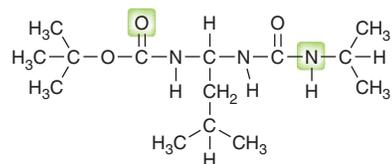
- (a) Identify any formal charges that are missing from the structures of **1** and **2**.  
 (b) Determine which compound is expected to be more soluble in a polar solvent, and justify your choice.  
 (c) Determine the amount by which the C—C—N bond angle increases as a result of the conversion from **1** to **2**.

1.80 The following compound belongs to a class of compounds, called estradiol derivatives, which show promise in the treatment of breast cancer:<sup>15</sup>



- (a) Determine the hybridization state of C<sub>a</sub>, C<sub>b</sub>, and C<sub>c</sub>.  
 (b) Determine the H—C<sub>a</sub>—C<sub>b</sub> bond angle.  
 (c) Determine the C<sub>a</sub>—C<sub>b</sub>—C<sub>c</sub> bond angle.  
 (d) C<sub>b</sub> exhibits two π bonds: one to C<sub>a</sub>, and the other to C<sub>c</sub>. Draw a picture of C<sub>a</sub>, C<sub>b</sub>, and C<sub>c</sub> that shows the relative orientation of the two different p orbitals that C<sub>b</sub> is utilizing to form its two π bonds. Also show the p orbitals on C<sub>a</sub> and C<sub>c</sub> that are being used by each of those atoms. Describe the relative orientation of the p orbitals on C<sub>a</sub> and C<sub>c</sub>.

1.81 The following structure shows promise for studying how enzymes (nature's catalysts) coil up into very discrete shapes that endow them with catalytic function:<sup>16</sup>



- (a) This compound has two N—C—N units, with differing bond angles. Predict the difference in bond angles between these two units and explain the source of the difference.  
 (b) When this compound was prepared and investigated, it demonstrated a preference for adopting a three-dimensional shape in which the two highlighted regions were in close proximity. Describe the interaction that occurs and create a drawing that illustrates this interaction.

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15. *Tetrahedron Lett.* **2001**, 42, 8579–8582.
16. *Org. Lett.* **2001**, 3, 3843–3846.

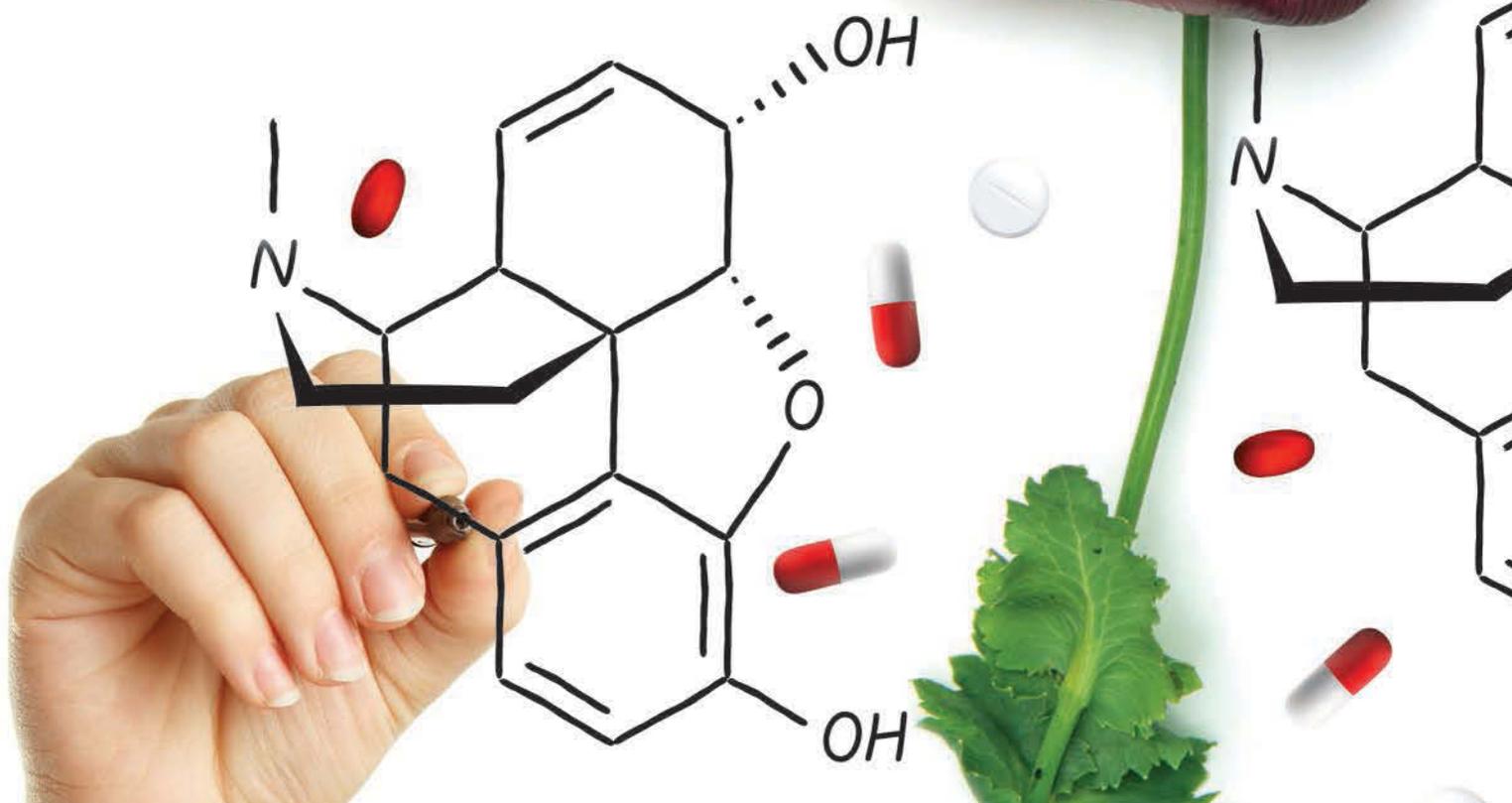
# Molecular Representations

**DID YOU EVER WONDER...**  
how new drugs are designed?

Scientists employ many techniques in the design of new drugs. One such technique, called lead modification, enables scientists to identify the portion of a compound responsible for its medicinal properties and then to design similar compounds with better properties. We will see an example of this technique, specifically, where the discovery of morphine led to the development of a whole family of potent analgesics (codeine, heroin, methadone, and many others).

In order to compare the structures of the compounds being discussed, we will need a more efficient way to draw the structures of organic compounds. Lewis structures are only efficient for small molecules, such as those we considered in the previous chapter. The goal of this chapter is to master the skills necessary to use and interpret the drawing method most often utilized by organic chemists and biochemists. These drawings, called bond-line structures, are fast to draw and easy to read, and they focus our attention on the reactive centers in a compound. In the second half of this chapter, we will see that bond-line structures are inadequate in some circumstances, and we will explore the technique that chemists employ to deal with the inadequacy of bond-line structures.

- 2.1 Molecular Representations
- 2.2 Bond-Line Structures
- 2.3 Identifying Functional Groups
- 2.4 Carbon Atoms with Formal Charges
- 2.5 Identifying Lone Pairs
- 2.6 Three-Dimensional Bond-Line Structures
- 2.7 Introduction to Resonance
- 2.8 Curved Arrows
- 2.9 Formal Charges in Resonance Structures
- 2.10 Drawing Resonance Structures via Pattern Recognition
- 2.11 Assessing the Relative Importance of Resonance Structures
- 2.12 The Resonance Hybrid
- 2.13 Delocalized and Localized Lone Pairs



## DO YOU REMEMBER?

Before you go on, be sure you understand the following topics.

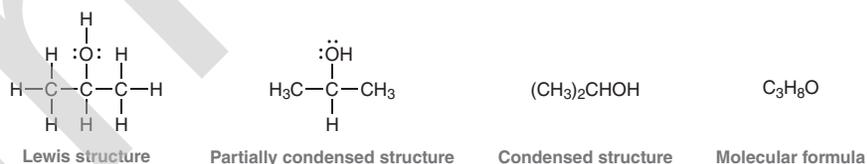
If necessary, review the suggested sections to prepare for this chapter:

- Electrons, Bonds, and Lewis Structures (Section 1.3)
- Molecular Orbital Theory (Section 1.8)
- Identifying Formal Charges (Section 1.4)

Take the **DO YOU REMEMBER?** QUIZ in **WileyPLUS** to check your understanding.

## 2.1 Molecular Representations

Chemists use many different styles to draw molecules. Let's consider the structure of isopropanol, also called isopropyl rubbing alcohol, which is used as a disinfectant in sterilizing pads. The structure of this compound is shown below in a variety of drawing styles:

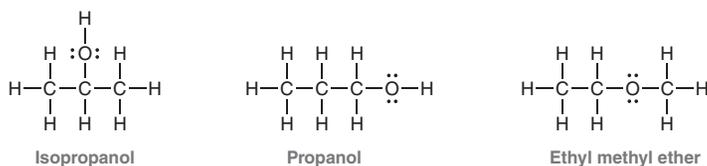


Lewis structures were discussed in the previous chapter. The advantage of Lewis structures is that all atoms and bonds are explicitly drawn. However, Lewis structures are only practical for very small molecules. For larger molecules, it becomes extremely burdensome to draw out every bond and every atom.

In **partially condensed structures**, the C—H bonds are not all drawn explicitly. In the example above,  $\text{CH}_3$  refers to a carbon atom with bonds to three hydrogen atoms. Once again, this drawing style is only practical for small molecules.

In **condensed structures**, single bonds are not drawn. Instead, groups of atoms are clustered together, when possible. For example, isopropanol has two  $\text{CH}_3$  groups, both of which are connected to the central carbon atom, shown like this:  $(\text{CH}_3)_2\text{CHOH}$ . Once again, this drawing style is only practical for small molecules with simple structures.

The molecular formula of a compound simply shows the number of each type of atom in the compound ( $\text{C}_3\text{H}_8\text{O}$ ). No structural information is provided. There are actually three constitutional isomers with the molecular formula  $\text{C}_3\text{H}_8\text{O}$ :



In reviewing some of the different styles for drawing molecules, we see that none are convenient for larger molecules. Molecular formulas do not provide enough information, Lewis structures take too long to draw, and partially condensed and condensed drawings are only suitable for relatively simple molecules. In upcoming sections, we will learn the rules for drawing bond-line structures, which are most commonly used by organic chemists. For now, let's practice the drawing styles above, which will be used for small molecules throughout the course.

## SKILLBUILDER



## 2.1 CONVERTING BETWEEN DIFFERENT DRAWING STYLES

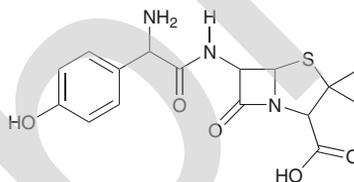
## LEARN the skill

Draw a Lewis structure for the following compound:





molecules very quickly. **Bond-line structures** not only simplify the drawing process but also are easier to read. The following is a bond-line structure of amoxicillin.

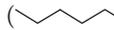


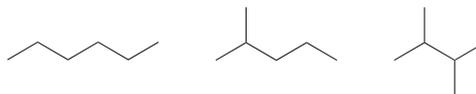
Most of the atoms are not drawn, but with practice, these drawings will become very user-friendly. Throughout the rest of this textbook, most compounds will be drawn in bond-line format, and therefore, it is absolutely critical to master this drawing technique. The following sections are designed to develop this mastery.

### BY THE WAY

You may find it worthwhile to purchase or borrow a molecular model set. There are several different kinds of molecular model sets on the market, and most of them are comprised of plastic pieces that can be connected to generate models of small molecules. Any one of these model sets will help you to visualize the relationship between molecular structures and the drawings used to represent them.

### How to Read Bond-Line Structures

Bond-line structures are drawn in a zigzag format () , where each corner or endpoint represents a carbon atom. For example, each of the following compounds has six carbon atoms (count them!):



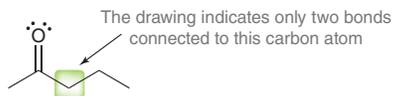
Double bonds are shown with two lines, and triple bonds are shown with three lines:



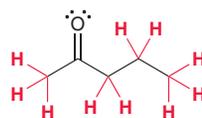
Notice that triple bonds are drawn in a linear fashion rather than in a zigzag format, because triple bonds involve *sp*-hybridized carbon atoms, which have linear geometry (Section 1.9). The two carbon atoms of a triple bond and the two carbon atoms connected to them are drawn in a straight line. All other bonds are drawn in a zigzag format; for example, the following compound has eight carbon atoms:



Hydrogen atoms bonded to carbon are also not shown in bond-line structures, because it is assumed that each carbon atom will possess enough hydrogen atoms so as to achieve a total of four bonds. For example, the following highlighted carbon atom appears to have only two bonds:



Therefore, we can infer that there must be two more bonds to hydrogen atoms that have not been drawn (to give a total of four bonds). In this way, all hydrogen atoms are inferred by the drawing:



With a bit of practice, it will no longer be necessary to count bonds. Familiarity with bond-line structures will allow you to “see” all of the hydrogen atoms even though they are not drawn. This level of familiarity is absolutely essential, so let’s get some practice.

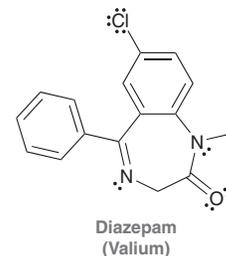


## SKILLBUILDER

### 2.2 READING BOND-LINE STRUCTURES

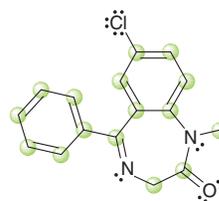
#### LEARN the skill

Consider the structure of diazepam, first marketed by the Hoffmann-La Roche Company under the trade name Valium. Diazepam is a sedative and muscle relaxant used in the treatment of anxiety, insomnia, and seizures. Identify the number of carbon atoms in diazepam, then fill in all the missing hydrogen atoms that are inferred by the drawing.

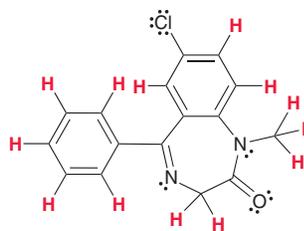


#### SOLUTION

Remember that each corner and each endpoint represents a carbon atom. This compound therefore has 16 carbon atoms, highlighted here.



Each carbon atom should have four bonds. We therefore draw enough hydrogen atoms in order to give each carbon atom a total of four bonds. Any carbon atoms that already have four bonds will not have any hydrogen atoms:



#### STEP 1

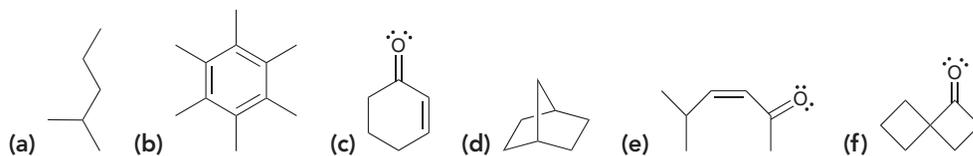
Count the carbon atoms, which are represented by corners or endpoints.

#### STEP 2

Count the hydrogen atoms. Each carbon atom will have enough hydrogen atoms to have exactly four bonds.

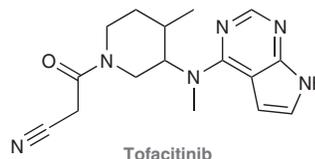
#### PRACTICE the skill

2.3 For each of the following molecules, determine the number of carbon atoms present and then determine the number of hydrogen atoms connected to each carbon atom:



#### APPLY the skill

2.4 Initially approved to treat psoriasis (a skin disorder) and rheumatoid arthritis, the drug tofacitinib has recently been found to also promote hair growth and restore hair loss.<sup>2</sup> Identify the number of carbon atoms in tofacitinib, and then fill in all of the missing hydrogen atoms that are inferred by the drawing.



need more PRACTICE? Try Problems 2.34, 2.48, 2.50

## How to Draw Bond-Line Structures

It is certainly important to be able to read bond-line structures fluently, but it is equally important to be able to draw them proficiently. When drawing bond-line structures, the following rules should be observed:

### WATCH OUT

Notice that the first structure includes atom labels for each carbon (C) and hydrogen (H), while the second structure does not show any atom labels for carbon and hydrogen. Both structures are valid drawings, but it is incorrect to label the carbon atoms without also labeling the hydrogen atoms (for example: C—C—C—C). Either draw every C and every H, as in the first structure, or don't draw any of those labels, as in the second structure.

1. Carbon atoms in a straight chain should be drawn in a zigzag format:



2. When drawing double bonds, draw all bonds as far apart as possible:



3. When drawing single bonds, the direction in which the bonds are drawn is irrelevant:



These two drawings do not represent constitutional isomers—they are just two drawings of the same compound. Both are perfectly acceptable.

4. All *heteroatoms* (atoms other than carbon and hydrogen) must be drawn, and any hydrogen atoms attached to a heteroatom must also be drawn. For example:



5. Never draw a carbon atom with more than four bonds. Carbon only has four orbitals in its valence shell, and therefore carbon atoms can form a maximum of four bonds.

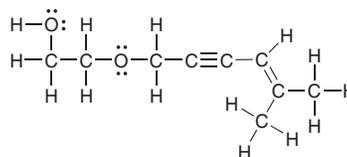
## SKILLBUILDER



### 2.3 DRAWING BOND-LINE STRUCTURES

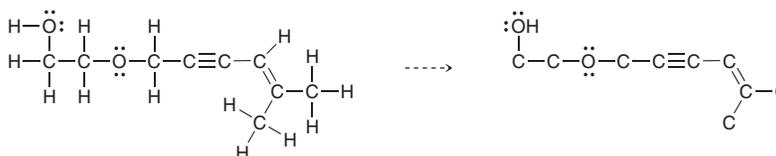
#### LEARN the skill

Draw a bond-line structure for the following compound:



#### SOLUTION

Drawing a bond-line structure requires just a few conceptual steps. First, delete all hydrogen atoms except for those connected to heteroatoms:



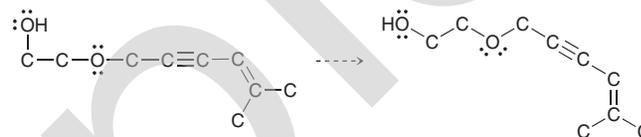
#### STEP 1

Delete hydrogen atoms, except for those connected to heteroatoms.



Then, place the carbon skeleton in a zigzag arrangement, making sure that any triple bonds are drawn as linear:

**STEP 2**  
Draw in zigzag format,  
keeping triple bonds  
linear.

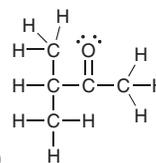
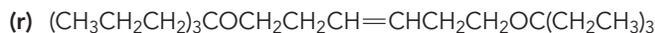
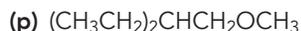
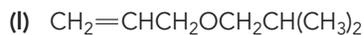
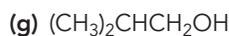
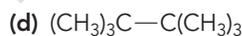
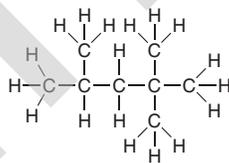


Finally, delete all carbon atoms:

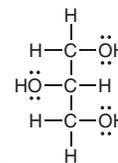
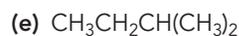
**STEP 3**  
Delete carbon atoms.



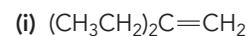
**PRACTICE the skill** 2.5 Draw a bond-line structure for each of the following compounds:



(b)

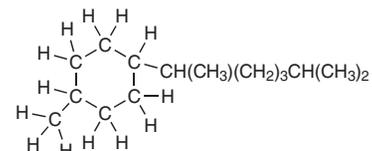


(c)



**APPLY the skill**

2.6 Certain compounds that are alternatives to fossil fuels can be produced by engineered microbes. Bisabolane, an example of a renewable biofuel, is a synthetic alternative to diesel fuel.<sup>3</sup> Draw a bond-line structure for bisabolane:

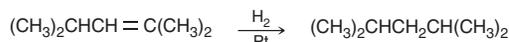


Bisabolane

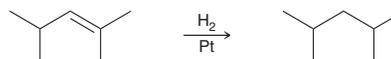
need more **PRACTICE?** Try Problems 2.35, 2.36, 2.42, 2.51, 2.55

## 2.3 Identifying Functional Groups

Bond-line drawings are the preferred drawing style used by practicing organic chemists. In addition to being more efficient, bond-line drawings are also easier to read. As an example, consider the following reaction:



When the reaction is presented in this way, it is somewhat difficult to see what is happening. It takes time to digest the information being presented. However, when we redraw the same reaction using bond-line structures, it becomes very easy to identify the transformation taking place:



It is immediately apparent that a double bond is being converted into a single bond. With bond-line drawings, it is easier to identify the functional group and its location. A **functional group** is

a characteristic group of atoms/bonds that possess a predictable chemical behavior. In each of the reactions below, the starting material has a carbon-carbon double bond, which is a functional group. Compounds with carbon-carbon double bonds typically react with molecular hydrogen ( $H_2$ ) in the presence of a catalyst (such as Pt). Both of the starting materials below have a carbon-carbon double bond, and consequently, they exhibit similar chemical behavior.



The chemistry of every organic compound is determined by the functional groups present in the compound. Therefore, the classification of organic compounds is based on their functional groups. For example, an *alkene* is a compound that exhibits a carbon-carbon double bond, while an *alcohol* is a compound that exhibits an OH group. Many of the chapters in this book are organized by functional group. Table 2.1 provides a list of common functional groups and the corresponding chapters in which they appear.

TABLE 2.1 EXAMPLES OF COMMON FUNCTIONAL GROUPS

FUNCTIONAL GROUP*	CLASSIFICATION	EXAMPLE	CHAPTER	FUNCTIONAL GROUP*	CLASSIFICATION	EXAMPLE	CHAPTER
$R-\ddot{X}:$ (X=Cl, Br, or I)	Alkyl halide	$n$ -Propyl chloride	7	$R-\overset{\cdot\cdot}{O}=\overset{\cdot\cdot}{C}-R$	Ketone	2-Butanone	19
$R-\overset{\cdot\cdot}{C}=\overset{\cdot\cdot}{C}-R$	Alkene	1-Butene	7, 8	$R-\overset{\cdot\cdot}{O}=\overset{\cdot\cdot}{C}-H$	Aldehyde	Butanal	19
$R-C\equiv C-R$	Alkyne	1-Butyne	9	$R-\overset{\cdot\cdot}{O}=\overset{\cdot\cdot}{C}-\overset{\cdot\cdot}{O}-H$	Carboxylic acid	Pentanoic acid	20
$R-\ddot{O}H$	Alcohol	1-Butanol	12	$R-\overset{\cdot\cdot}{O}=\overset{\cdot\cdot}{C}-\ddot{X}:$	Acyl halide	Acetyl chloride	20
$R-\ddot{O}-R$	Ether	Diethyl ether	13	$R-\overset{\cdot\cdot}{O}=\overset{\cdot\cdot}{C}-\overset{\cdot\cdot}{O}-\overset{\cdot\cdot}{C}-R$	Anhydride	Acetic anhydride	20
$R-\ddot{S}H$	Thiol	1-Butanethiol	13	$R-\overset{\cdot\cdot}{O}=\overset{\cdot\cdot}{C}-\overset{\cdot\cdot}{O}-R$	Ester	Ethyl acetate	20
$R-\ddot{S}-R$	Sulfide	Diethyl sulfide	13	$R-\overset{\cdot\cdot}{O}=\overset{\cdot\cdot}{C}-\overset{\cdot\cdot}{N}(R)-R$	Amide	Butanamide	20
	Aromatic (or arene)	Methylbenzene	17, 18	$R-\overset{\cdot\cdot}{N}(R)-R$	Amine	Diethylamine	22

\* The "R" refers to the remainder of the compound, usually carbon and hydrogen atoms.



## Medically Speaking | Marine Natural Products



The field of marine natural products (MNP) continues to expand rapidly as researchers explore the ocean's rich biodiversity in search of new pharmaceuticals. It is a subdiscipline of natural product chemistry and has recently seen some success stories of new drugs. In the early days before the dawn of SCUBA, marine drug discovery efforts were aimed primarily at easily accessible marine life like red algae, sponges, and soft corals that were not far from the ocean's shoreline.

Since then, more emphasis was placed on the previously overlooked deep sea organisms as well as marine microbes associated with ocean sediments and macroorganisms. These sources have yielded both structurally diverse and bioactive compounds. Moreover, the marine microbes are thought to be the real producers of marine natural products (MNP) that were previously isolated from their macroorganism hosts like mollusks, sponges, and tunicates.

The early stage of MNP drug discovery was met with supply issues due to limited marine samples that yielded small quantities of the bioactive natural products. This demand was addressed with innovative methods such as aquaculture (farming of aquatic organisms), total synthesis, and biosynthesis. The use of genomics (DNA sequencing of organisms) and proteomics (study of protein structure and function), for example, has provided new insights into the production and distribution of these natural products.

Of all the MNP and MNP-derived drug candidates identified to date, seven have been approved by the Food and Drug Administration (FDA) for public use, with at least 13 others at various stages of clinical trials. Examples of FDA approved drugs are: eribulin mesylate (E7389), omega-3-acid ethyl ester, and trabectedin (ET-743). See structures below.

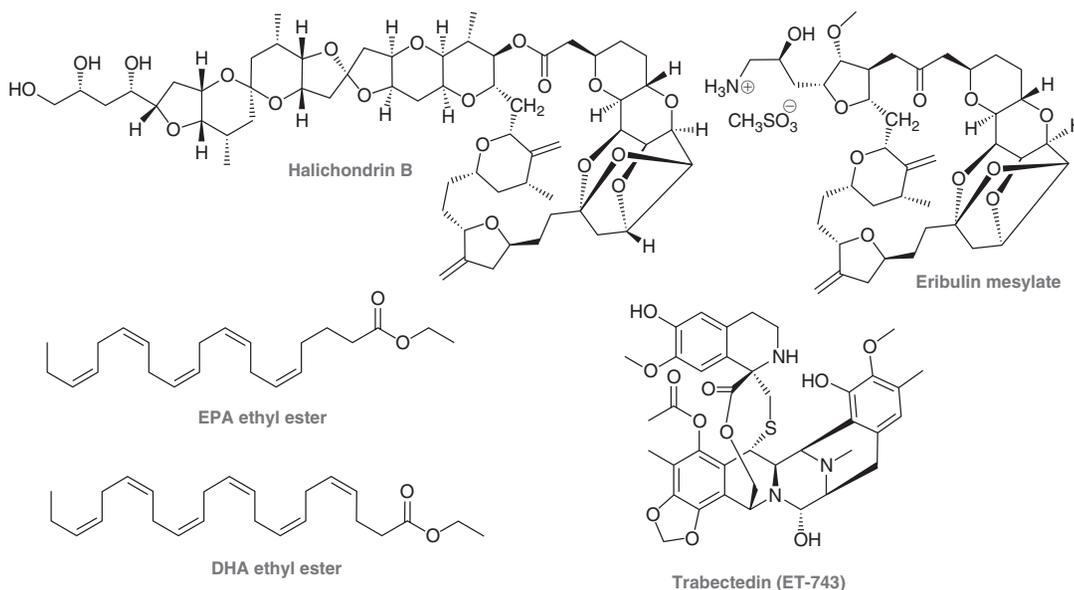
Eribulin mesylate is a synthetic analogue of the marine natural product halichondrin B which was isolated from the black sponge *Halichondria okadai*. It is a polyether analogue that is used in the treatment of cancer which spreads from the breast to other body organs. It acts by blocking cellular growth, which results in the death of the cancer cells.



The second drug, omega-3-acid ethyl ester, contains derivatives of long-chain, unsaturated carboxylic acids (omega-3 fatty acids) that were isolated from fish oil. They consist primarily of ethyl esters of eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA). The drug is used to treat persons with high levels of fat (lipid) in their bloodstream as this condition can lead to heart disease and stroke.

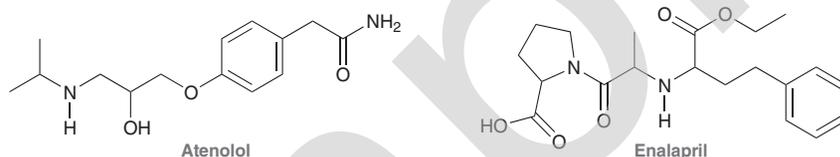
The third therapeutic agent, trabectedin (ET-743), was isolated from the marine tunicate *Ecteinascidia turbinata*. It is used to treat patients with soft tissue sarcoma (STS) and those with recurring ovarian cancer. Trabectedin binds to DNA and causes cell death.

The future of marine natural products is indeed bright. With the increasing technological advances in high-throughput screening (HTS), compound libraries, mass spectrometry (MS), nuclear magnetic resonance (NMR) spectroscopy, genomics, compound biosynthesis, and more, scientists will continue to push the envelope in the hopes of finding those important marine natural products that will serve as future drug candidates.




**CONCEPTUAL CHECKPOINT**

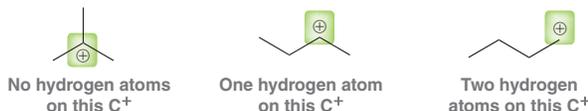
**2.7** Atenolol and enalapril are drugs used in the treatment of heart disease. Both of these drugs lower blood pressure (albeit in different ways) and reduce the risk of heart attack. Using Table 2.1, identify and label all functional groups in these two compounds:



## 2.4 Carbon Atoms with Formal Charges

We have seen that carbon generally has four bonds, which allows us to “see” all of the hydrogen atoms even though they are not explicitly shown in bond-line structures. Now we must modify that rule: *A carbon atom will generally have four bonds only when it does not have a formal charge.* When a carbon atom bears a formal charge, either positive or negative, it will have three bonds rather than four. To understand why, let’s first consider  $C^+$ , and then we will consider  $C^-$ .

Recall that the appropriate number of valence electrons for a carbon atom is four. In order to have a positive formal charge, a carbon atom must be missing an electron. In other words, it must have only three valence electrons. Such a carbon atom can only form three bonds. This must be taken into account when counting hydrogen atoms:



Now let’s focus on negatively charged carbon atoms. In order to have a negative formal charge, a carbon atom must have one extra electron. In other words, it must have five valence electrons. Two of those electrons will form a lone pair, and the other three electrons will be used to form bonds.



In summary, both  $C^+$  and  $C^-$  will have only three bonds. The difference between them is the nature of the fourth orbital. In the case of  $C^+$ , the fourth orbital is empty. In the case of  $C^-$ , the fourth orbital is occupied by a lone pair of electrons.

## 2.5 Identifying Lone Pairs

### WATCH OUT

Formal charges must always be drawn and can never be omitted, unlike lone pairs, which may be omitted from a bond-line structure.

In bond-line drawings, formal charges must always be drawn. If a formal charge is present and not drawn, then the resulting bond-line structure is incorrect and therefore useless. In contrast, lone pairs do not have to be drawn in a bond-line drawing (and indeed, they are often omitted), because the locations of the lone pairs can be inferred from the drawing. So we need to get some practice identifying lone pairs when they are not drawn. The following example will demonstrate the thought process:



In order to determine the number of lone pairs on the oxygen atom, we simply use the same two-step process described in Section 1.4 for calculating formal charges:

1. *Determine the appropriate number of valence electrons for the atom.* Oxygen is in group 6A of the periodic table, and therefore, it should have six valence electrons.
2. *Determine if the atom actually exhibits the appropriate number of electrons.* This oxygen atom has a negative formal charge, which means it must have one extra electron. Therefore, this oxygen



atom must have  $6 + 1 = 7$  valence electrons. One of those electrons is being used to form the C—O bond, which leaves six electrons for lone pairs. This oxygen atom must therefore have three lone pairs:



The process above represents an important skill; however, it is even more important to become familiar enough with atoms that the process becomes unnecessary. There is just a handful of patterns to recognize. Let's go through them methodically, starting with oxygen. Table 2.2 summarizes the important patterns that you will encounter for oxygen atoms.

- A negative charge corresponds with one bond and three lone pairs.
- The absence of charge corresponds with two bonds and two lone pairs.
- A positive charge corresponds with three bonds and one lone pair.

**TABLE 2.2 FORMAL CHARGE ON AN OXYGEN ATOM ASSOCIATED WITH A PARTICULAR NUMBER OF BONDS AND LONE PAIRS**

 1 bond + 3 lone pairs	 2 bonds + 2 lone pairs	 3 bonds + 1 lone pair
<p><b>Examples:</b></p>	<p><b>Examples:</b></p>	<p><b>Examples:</b></p>

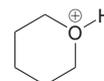
## SKILLBUILDER



### 2.4 IDENTIFYING LONE PAIRS ON OXYGEN ATOMS

#### LEARN the skill

Draw all of the lone pairs in the following structure:



#### STEP 1

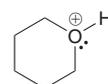
Determine the appropriate number of valence electrons.

#### STEP 2

Analyze the formal charge and determine the actual number of valence electrons.

#### SOLUTION

The oxygen atom above has a positive formal charge and three bonds. It is preferable to recognize the pattern—that a positive charge and three bonds must mean that the oxygen atom has just one lone pair:



Alternatively, and less preferably, it is possible to calculate the number of lone pairs using the following two steps. First, determine the appropriate number of valence electrons

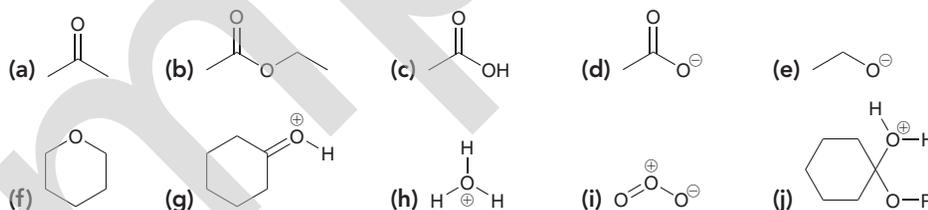
**STEP 3**

Count the number of bonds and determine how many of the actual valence electrons must be lone pairs.

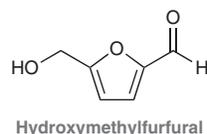
**PRACTICE the skill**

for the atom. Oxygen is in group 6A of the periodic table, and therefore, it should have six valence electrons. Then, determine if the atom actually exhibits the appropriate number of electrons. This oxygen atom has a positive charge, which means it is missing an electron:  $6 - 1 = 5$  valence electrons. Three of these five electrons are being used to form bonds, which leaves just two electrons for a lone pair. This oxygen atom has only one lone pair.

**2.8** Draw all lone pairs on each of the oxygen atoms in the following structures. Before doing this, review Table 2.2 and then come back to these problems. Try to identify all lone pairs without having to count. Then, count to see if you were correct.

**APPLY the skill**

**2.9** The rich and varied flavors of toasted bread, roasted coffee, and seared meat are a result of a process known as the Maillard reaction. This reaction creates hundreds of new flavorful compounds, including hydroxymethylfurfural (HMF). By measuring levels of HMF in foods such as puffed cereals, production processes can be evaluated.<sup>4</sup> Identify all of the missing lone pairs of electrons in hydroxymethylfurfural.



need more **PRACTICE?** Try Problems 2.38, 2.39

Now let's explore nitrogen atoms. Table 2.3 shows the important patterns that you will encounter with nitrogen atoms. In summary:

- A negative charge corresponds with two bonds and two lone pairs.
- The absence of charge corresponds with three bonds and one lone pair.
- A positive charge corresponds with four bonds and no lone pairs.

**TABLE 2.3** FORMAL CHARGE ON A NITROGEN ATOM ASSOCIATED WITH A PARTICULAR NUMBER OF BONDS AND LONE PAIRS

 2 bonds + 2 lone pairs	No Charge  3 bonds + 1 lone pair	 4 bonds + 0 lone pairs
<b>Examples:</b>   	<b>Examples:</b>   	<b>Examples:</b> has no lone pairs has no lone pairs has no lone pairs

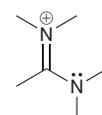
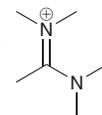


## SKILLBUILDER

### 2.5 IDENTIFYING LONE PAIRS ON NITROGEN ATOMS

#### LEARN the skill

Draw any lone pairs associated with the nitrogen atoms in the following structure:



#### STEP 1

Determine the appropriate number of valence electrons.

#### STEP 2

Analyze the formal charge and determine the actual number of valence electrons.

#### STEP 3

Count the number of bonds and determine how many of the actual valence electrons must be lone pairs.

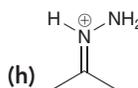
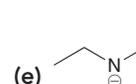
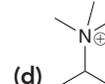
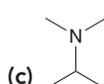
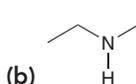
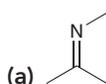
#### SOLUTION

The top nitrogen atom has a positive formal charge and four bonds. The bottom nitrogen has three bonds and no formal charge. It is preferable to simply recognize that the top nitrogen atom must have no lone pairs and the bottom nitrogen atom must have one lone pair:

Alternatively, and less preferably, it is possible to calculate the number of lone pairs using the following two steps. First, determine the appropriate number of valence electrons for the atom. Each nitrogen atom should have five valence electrons. Next, determine if each atom actually exhibits the appropriate number of electrons. The top nitrogen atom has a positive charge, which means it is missing an electron. This nitrogen atom actually has only four valence electrons. Since the nitrogen atom has four bonds, it is using each of its four electrons to form a bond. This nitrogen atom does not possess a lone pair. The bottom nitrogen atom has no formal charge, so this nitrogen atom must be using five valence electrons. It has three bonds, which means that there are two electrons left over, forming one lone pair.

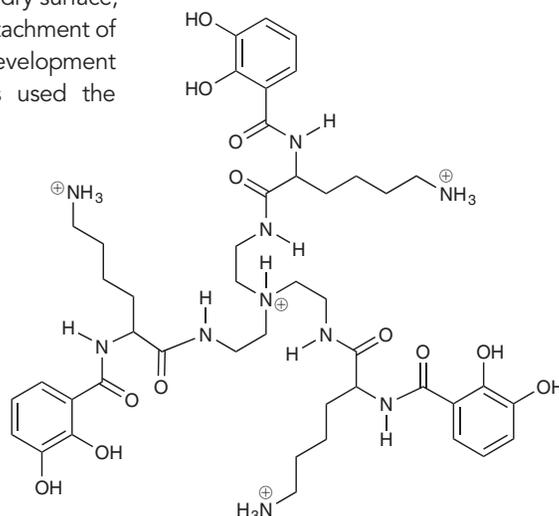
#### PRACTICE the skill

**2.10** Draw all lone pairs on each of the nitrogen atoms in the following structures. First, review Table 2.3 and then come back to these problems. Try to identify all lone pairs *without* having to count. Then, count to see if you were correct.



#### APPLY the skill

**2.11** Glue adhesion usually requires a dry surface, so studying the chemistry behind the attachment of mussels to wet rocks can lead to the development of new adhesive materials. Chemists used the compound shown to model the mussel foot proteins involved in the adhesion process.<sup>5</sup> Some of the nitrogen atoms in this structure are believed to play a critical role in achieving the strong binding. Draw all lone pairs associated with the nitrogen atoms of this compound.



need more PRACTICE? Try Problems 2.34, 2.45

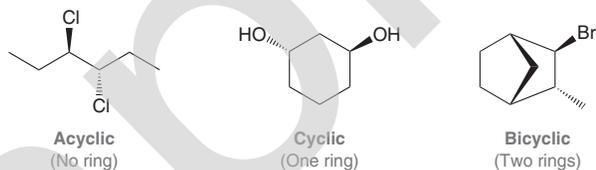
## 2.6 Three-Dimensional Bond-Line Structures

Throughout this book, we will use many different kinds of drawings to represent the three-dimensional geometry of molecules. The most common method is a bond-line structure that includes **wedges** and **dashes** to indicate three dimensionality. These structures are used for all types of compounds,

including acyclic, cyclic, and bicyclic compounds (Figure 2.1). In the drawings in Figure 2.1, a wedge represents a group coming out of the page, and a dash represents a group going behind the page. We will use wedges and dashes extensively in Chapter 5 and thereafter.

FIGURE 2.1

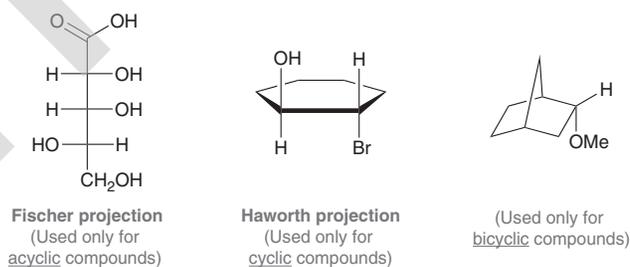
Bond-line structures with wedges and dashes to indicate three dimensionality.



In certain circumstances, there are other types of drawings that can be used, all of which also indicate three-dimensional geometry (Figure 2.2).

FIGURE 2.2

Common drawing styles that show three dimensionality for acyclic, cyclic, and bicyclic compounds.



**Fischer projections** are used for acyclic compounds while **Haworth projections** are used exclusively for cyclic compounds. Each of these drawing styles will be used several times throughout this book, particularly in Chapters 5, 7, and 24.

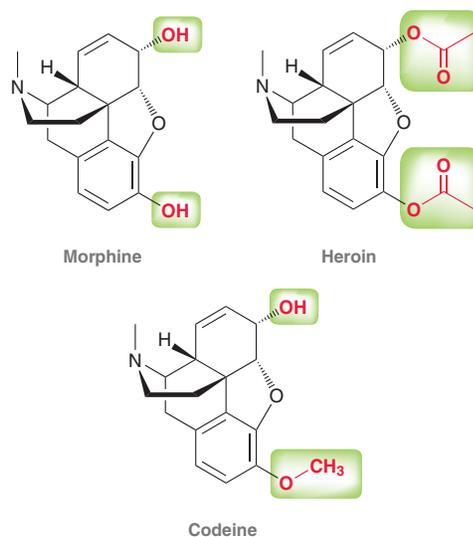
## Medically Speaking | Identifying the Pharmacophore



As mentioned in the chapter opener, there are many techniques that scientists employ in the design of new drugs. One such technique is called *lead modification*, which involves modifying the structure of a compound known to exhibit desirable medicinal properties. The known compound “leads” the way to the development of other similar compounds and is therefore called the *lead compound*. The story of morphine provides a good example of this process.

Morphine is a very potent analgesic (pain reliever) that is known to act on the central nervous system as a depressant (causing sedation and slower respiratory function), and it is also known to relieve symptoms of anxiety and cause an overall state of euphoria. Because morphine is addictive, it is primarily used for the short-term treatment of acute pain and for terminally ill patients suffering from extreme pain. The analgesic properties of morphine have been exploited for over a millennium. It is the major component of opium, obtained from the unripe seed pods of the poppy plant, *Papaver somniferum*. Morphine was first isolated from opium in 1803, and by the mid-1800s, it was used heavily to control pain during and after surgical procedures. By the end of the 1800s, the addictive properties of morphine became apparent, which fueled the search for nonaddictive analgesics.

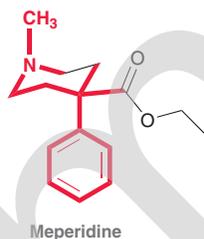
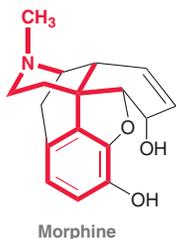
In 1925, the structure of morphine was correctly determined. This structure functioned as a lead compound and was modified to produce other compounds with analgesic properties. Early modifications focused on replacing the hydroxyl (OH) groups with other functional groups. Examples include heroin and codeine:



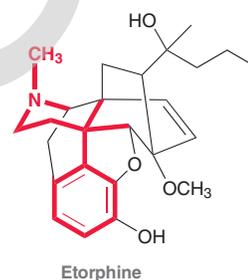
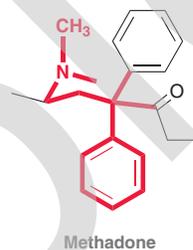
Heroin exhibits stronger activity than morphine and is extremely addictive. Codeine shows less activity than morphine and is less addictive. Codeine is currently used as an analgesic and cough suppressant.

In 1938, the analgesic properties of meperidine, also known as Demerol, were fortuitously discovered. As the story goes, meperidine was originally prepared to function as an antispasmodic agent (to suppress muscle spasms). When administered to mice, it curiously caused the tails of the mice to

become erect. It was already known that morphine and related compounds produced a similar effect in mice, so meperidine was further tested and found to exhibit analgesic properties. This discovery generated much interest by providing new insights in the search for other analgesics. By comparing the structures of morphine, meperidine, and their derivatives, scientists were able to determine which structural features are essential for analgesic activity, shown in red:

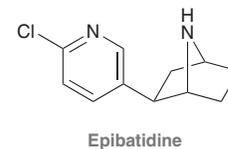


When morphine is drawn in this way, its structural similarity to meperidine becomes more apparent. Specifically, the bonds indicated in red represent the portion of each compound responsible for the analgesic activity. This part of the compound is called the *pharmacophore*. If any part of the pharmacophore is removed or changed, the resulting compound will not be capable of binding effectively to the appropriate biological receptor, and the compound will not exhibit analgesic properties. The term *auxophore* refers to the rest of the compound (the bonds shown in black). Removing any of these bonds may or may not affect the strength with which the pharmacophore binds to the receptor, thereby affecting the compound's analgesic potency. When modifying a lead compound, the auxophoric regions are the portions targeted for modification. For example, the auxophoric regions of morphine were modified to develop methadone and etorphine.



Methadone, developed in Germany during World War II, is used to treat heroin addicts suffering from withdrawal symptoms. Methadone binds to the same receptor as heroin, but it has a longer retention time in the body, thereby enabling the body to cope with the decreasing levels of drug that normally cause withdrawal symptoms. Etorphine is over 3000 times more potent than morphine and is used exclusively in veterinary medicine to immobilize elephants and other large mammals.

Scientists are constantly searching for new lead compounds. In 1992, researchers at NIH (National Institutes of Health) in Bethesda, Maryland, isolated epibatidine from the skin of the Ecuadorian frog, *Epipedobates tricolor*. Epibatidine was found to be an analgesic that is 200 times more potent than morphine. Further studies indicated that epibatidine and morphine bind to different receptors. This discovery was very exciting, because it meant that epibatidine could possibly serve as a new lead compound. Although this compound is too toxic for clinical use, a significant number of researchers have been working to identify the pharmacophore of epibatidine and to develop nontoxic derivatives.



## 2.7 Introduction to Resonance

### The Inadequacy of Bond-Line Structures

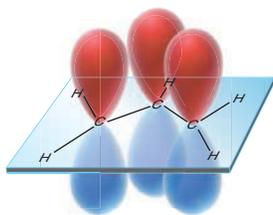
We have seen that bond-line structures are generally the most efficient and preferred way to draw the structure of an organic compound. Nevertheless, bond-line structures suffer from one major defect. Specifically, a pair of bonding electrons is always represented as a line that is drawn between two atoms, which implies that the bonding electrons are confined to a region of space directly in between two atoms. In some cases, this assertion is acceptable, as in the following structure:



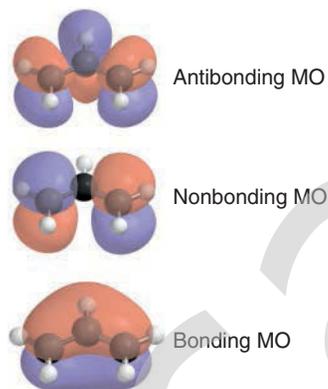
In this case, the  $\pi$  electrons are in fact located where they are drawn, in between the two central carbon atoms. But in other cases, the electron density is spread out over a larger region of the molecule. For example, consider the following ion, called an *allyl carbocation*:



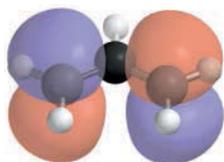
It might seem from the drawing above that there are two  $\pi$  electrons on the left side and a positive charge on the right side. But this is not the entire picture, and the drawing above is inadequate. Let's take a closer look and first analyze the hybridization states. Each of the three carbon atoms above is  $sp^2$  hybridized. Why? The two carbon atoms on the left side are each  $sp^2$  hybridized because each of



**FIGURE 2.3**  
The overlapping  $p$  orbitals of an allyl carbocation.



**FIGURE 2.4**  
The molecular orbitals associated with the  $\pi$  electrons of an allylic system.



**FIGURE 2.5**  
The nonbonding molecular orbital associated with the  $\pi$  electrons of an allylic system.

those carbon atoms is utilizing a  $p$  orbital to form the  $\pi$  bond (Section 1.9). The third carbon atom, bearing the positive charge, is also  $sp^2$  hybridized because it has an empty  $p$  orbital. Figure 2.3 shows the three  $p$  orbitals associated with an allyl carbocation. This image focuses our attention on the continuous system of  $p$  orbitals, which functions as a “conduit,” allowing the two  $\pi$  electrons to be associated with all three carbon atoms. Valence bond theory is inadequate for analysis of this system because it treats the electrons as if they were confined between only two atoms. A more appropriate analysis of the allyl cation requires the use of molecular orbital (MO) theory (Section 1.8), in which electrons are associated with the molecule as a whole, rather than individual atoms. Specifically, in MO theory, the entire molecule is treated as one entity, and all of the electrons in the entire molecule occupy regions of space called molecular orbitals. Two electrons are placed in each orbital, starting with the lowest energy orbital, until all electrons occupy orbitals.

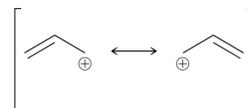
According to MO theory, the three  $p$  orbitals shown in Figure 2.3 no longer exist. Instead, they have been replaced by three MOs, illustrated in Figure 2.4 in order of increasing energy. Notice that the lowest energy MO, called the *bonding molecular orbital*, has no vertical nodes. The next higher energy MO, called the *nonbonding molecular orbital*, has one vertical node. The highest energy MO, called the *antibonding molecular orbital*, has two vertical nodes. The  $\pi$  electrons of the allyl system will fill these MOs, starting with the lowest energy MO. How many  $\pi$  electrons will occupy these MOs? The allyl carbocation has only two  $\pi$  electrons, rather than three, because one of the carbon atoms bears a positive formal charge indicating that one electron is missing. The two  $\pi$  electrons of the allyl system will occupy the lowest energy MO (the bonding MO). If the missing electron were to return, it would occupy the next higher energy MO, which is the nonbonding MO. Focus your attention on the nonbonding MO (shown again in Figure 2.5).

There should be an electron occupying this nonbonding MO, but the electron is missing. Therefore, the colored lobes are empty and represent regions of space that are electron deficient. In conclusion, MO theory suggests that the positive charge of the allyl carbocation is associated with the two ends of the system, rather than just one end.

In a situation like this, any individual bond-line structure that we draw will be inadequate. How can we draw a positive charge that is spread out over two locations, and how can we draw two  $\pi$  electrons that are associated with three carbon atoms?

## Resonance

The approach that chemists use to deal with the inadequacy of bond-line structures is called **resonance**. According to this approach, we draw more than one bond-line structure and then mentally meld them together:



These drawings are called **resonance structures**, and they show that the positive charge is spread over two locations (and the  $\pi$  electrons are spread over all three carbon atoms). Notice that we separate resonance structures with a straight, two-headed arrow, and we place brackets around the structures. The arrow and brackets indicate that the drawings are resonance structures of *one entity*. This one entity, called a **resonance hybrid**, is *not* flipping back and forth between the different resonance structures. To better understand this, consider the following analogy: A person who has never before seen a nectarine asks a farmer to describe a nectarine. The farmer answers:

Picture a *peach* in your mind, and now picture a *plum* in your mind. Well, a *nectarine* has features of both fruits: the inside tastes like a peach, the outside is smooth like a plum, and the color is somewhere in between the color of a peach and the color of a plum. So take your image of a peach together with your image of a plum and *meld them together* in your mind into one image. That's a nectarine.

Here is the important feature of the analogy: The nectarine does not vibrate back and forth every second between being a peach and being a plum. A nectarine is a nectarine all of the time. The image of a peach by itself is not adequate to describe a nectarine. Neither is the image of a plum. But by combining certain characteristics of a peach with certain characteristics of a plum, it is possible to imagine the features of a nectarine. Similarly, with resonance structures, no single drawing adequately describes the nature of the electron density spread out over the molecule. To deal with this problem, we draw several drawings and then meld them together in our minds to obtain one image, or hybrid, just as we did to obtain an image for a nectarine.

Don't be confused by this important point: The term “resonance” does not describe any real process that is actually happening. Rather, chemists draw multiple resonance structures as a bookkeeping method to overcome the inadequacy of bond-line drawings.



## Resonance Stabilization

We developed the concept of resonance using the allyl cation as an example, and we saw that the two  $\pi$  electrons are spread out over the three carbon atoms of the allylic system. This spreading of electrons, called **delocalization**, is a stabilizing factor. That is, *molecules and ions are stabilized by the delocalization of electrons*. This stabilization is often referred to as **resonance stabilization**, and the allyl cation is said to be *resonance stabilized*. Resonance stabilization plays a major role in the outcome of many reactions, and we will invoke the concept of resonance in almost every chapter of this textbook. The study of organic chemistry therefore requires a thorough mastery of drawing resonance structures, and the following sections are designed to foster the necessary skills.

## 2.8 Curved Arrows

In this section, we will focus on **curved arrows**, which are the tools necessary to draw resonance structures properly. Every curved arrow has a *tail* and *head*:



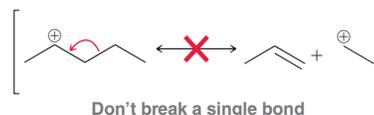
Curved arrows used for drawing resonance structures do not represent the motion of electrons—they are simply tools that allow us to draw resonance structures with ease. These tools treat the electrons *as if* they were moving, even though the electrons are actually not moving at all. In Chapter 3, we will encounter curved arrows that actually do represent the flow of electrons. For now, keep in mind that all curved arrows in this chapter are just tools and do not represent a flow of electrons.

It is essential that the tail and head of every arrow be drawn in precisely the proper location. The tail shows where the electrons are coming from, and the head shows where the electrons are going (remember, the electrons aren't really going anywhere, but we treat them as if they were for the purpose of drawing the resonance structures). We will soon learn patterns for drawing proper curved arrows. But, first, we must learn where not to draw curved arrows. There are two rules that must be followed when drawing curved arrows for resonance structures:

1. *Avoid breaking a single bond.*
2. *Never exceed an octet for second-row elements.*

Let's explore each of these rules:

1. *Avoid breaking a single bond when drawing resonance structures.* By definition, resonance structures must have all the same atoms connected in the same order. Breaking a single bond would change this—hence the first rule:



There are very few exceptions to this rule, and we will only violate it two times in this textbook (both in Chapter 8). Each time, we will explain why it is permissible in that case. In all other cases, the tail of an arrow should never be placed on a single bond.

2. *Never exceed an octet for second-row elements.* Elements in the second row (C, N, O, F) have only four orbitals in their valence shell. Each orbital can either form a bond or hold a lone pair. Therefore, for second-row elements the total of the number of bonds plus the number of lone pairs can never be more than four. They can never have five or six bonds; the most is four. Similarly, they can never have four bonds and a lone pair, because this would also require five orbitals. For the same reason, they can never have three bonds and two lone pairs. Let's see some examples of curved arrows that violate this second rule. In each of these drawings, the central atom cannot form another bond because it does not have a fifth orbital that can be used.

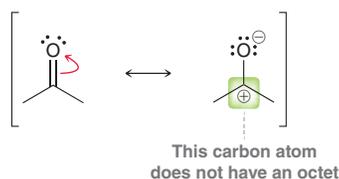


The violation in each of these examples is clear, but with bond-line structures, it can be more difficult to see the violation because the hydrogen atoms are not drawn (and, very often, neither are the lone pairs). Care must be taken to “see” the hydrogen atoms even when they are not drawn:



At first it is difficult to see that the curved arrow on the left structure is violating the second rule. But when we count the hydrogen atoms, it becomes clear that the curved arrow above would create a carbon atom with five bonds.

From now on, we will refer to the second rule as the *octet rule*. But be careful—for purposes of drawing resonance structures, it is only considered a violation if a second-row element has *more* than an octet of electrons. However, it is not a violation if a second-row element has *less* than an octet of electrons. For example:



This second drawing above is acceptable, even though the central carbon atom has only six electrons surrounding it. For our purposes, we will only consider the octet rule to be violated if we exceed an octet.

Our two rules (avoid breaking a single bond and never exceed an octet for a second-row element) reflect the two features of a curved arrow: the tail and the head. A poorly placed arrow tail violates the first rule, and a poorly directed arrow head violates the second rule.

## SKILLBUILDER



### 2.6 IDENTIFYING VALID RESONANCE ARROWS

#### LEARN the skill

Inspect the arrow drawn on the following structure and determine whether it violates either of the two rules for drawing curved arrows:



#### STEP 1

Make sure that the tail of the curved arrow is not located on a single bond.

#### STEP 2

Make sure that the head of the curved arrow does not violate the octet rule.

#### SOLUTION

In order to determine if either rule has been broken, we must look carefully at the tail and the head of the curved arrow. The tail is placed on a double bond, and therefore, this curved arrow does not break a single bond. So the first rule is not violated.

Next, we look at the head of the arrow: Has the octet rule been violated? Is there a fifth bond being formed here? Remember that a carbocation ( $C^+$ ) only has three bonds, not four. Two of the bonds are shown, which means that the  $C^+$  has only one bond to a hydrogen atom:



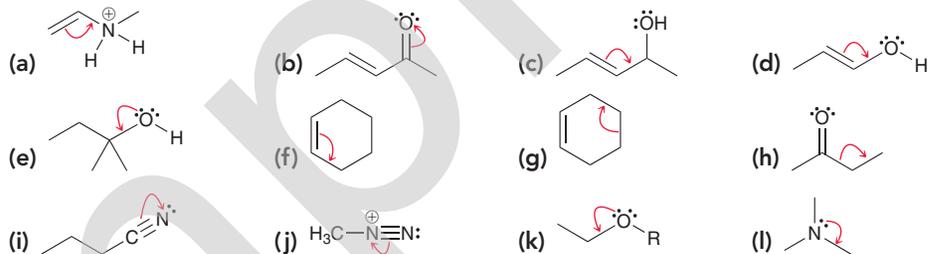
Therefore, the curved arrow will give the carbon atom a fourth bond, which does not violate the octet rule.

The curved arrow is valid, because the two rules were not violated. Both the tail and head of the arrow are acceptable.

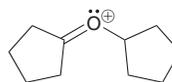


### PRACTICE the skill

**2.12** In each of the following cases, determine whether the curved arrow violates either of the two rules and describe the violation, if any. (Don't forget to count all hydrogen atoms and all lone pairs.)

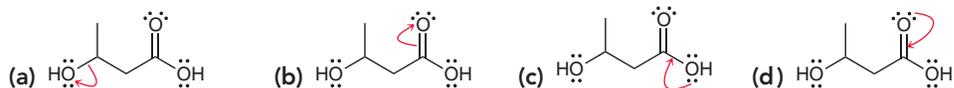
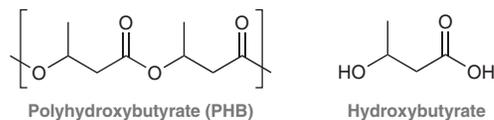


**2.13** Drawing the resonance structure of the following compound requires one curved arrow. The head of this curved arrow is placed on the oxygen atom, and the tail of the curved arrow can only be placed in one location without violating the rules for drawing curved arrows. Draw this curved arrow.

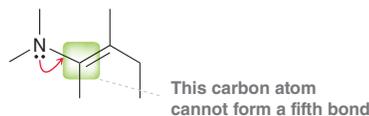


### APPLY the skill

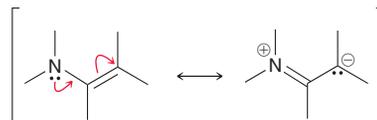
**2.14** Polyhydroxybutyric acid (PHB) is a component of biodegradable plastics that can be used in dissolving sutures or as a scaffold for skin regeneration.<sup>6</sup> PHB is synthesized by linking together hydroxybutyric acid molecules. Inspect the arrows drawn for possible hydroxybutyric acid resonance and determine whether each curved arrow violates either of the two rules for drawing curved arrows in resonance structures. Describe any violations that occur.



Whenever more than one curved arrow is used, all curved arrows must be taken into account in order to determine if any of the rules have been violated. For example, the following arrow violates the octet rule:



However, by adding another curved arrow, we remove the violation:

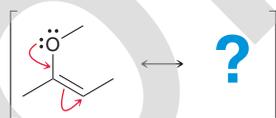


The second curved arrow removes the violation of the first curved arrow. In this example, both arrows are acceptable, because taken together, they do not violate our rules.

Arrow pushing is much like bike riding. The skill of bike riding cannot be learned by watching someone else ride. Learning to ride a bike requires practice. Falling occasionally is a necessary part of the learning process. The same is true with arrow pushing. The only way to learn is with practice. The remainder of this chapter is designed to provide ample opportunity for practicing and mastering resonance structures.

## 2.9 Formal Charges in Resonance Structures

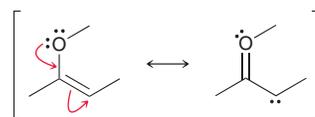
In Section 1.4, we learned how to calculate formal charges. Resonance structures very often contain formal charges, and it is absolutely critical to draw them properly. Consider the following example:



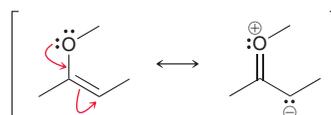
### WATCH OUT

The electrons are not really moving. We are just treating them as if they were.

In this example, there are two curved arrows. The first arrow pushes one of the lone pairs to form a bond, and the second arrow pushes the  $\pi$  bond to form a lone pair on a carbon atom. When both arrows are pushed at the same time, neither of the rules is violated. So, let's focus on how to draw the resonance structure by following the instructions provided by the curved arrows. We delete one lone pair from oxygen and place a  $\pi$  bond between carbon and oxygen. Then we must delete the C—C  $\pi$  bond and place a lone pair on carbon:



However, the structure is not complete without drawing formal charges. If we apply the rules of assigning formal charges, oxygen acquires a positive charge and carbon acquires a negative charge:



Another way to assign formal charges is to think about what the arrows are indicating. In this case, the curved arrows indicate that the oxygen atom is losing a lone pair and gaining a bond. In other words, it is losing two electrons and only gaining one back. The net result is the loss of one electron, indicating that oxygen must incur a positive charge in the resonance structure. A similar analysis for the carbon atom on the bottom right shows that it must incur a negative charge. Notice that the overall net charge is the same in each resonance structure. Let's practice assigning formal charges in resonance structures.

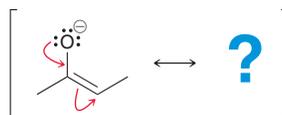
## SKILLBUILDER



### 2.7 ASSIGNING FORMAL CHARGES IN RESONANCE STRUCTURES

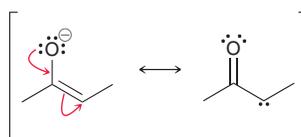
#### LEARN the skill

Draw the resonance structure below. Be sure to include formal charges.



#### SOLUTION

The arrows indicate that we must delete one lone pair on oxygen, place a double bond between carbon and oxygen, delete the carbon-carbon double bond, and place a lone pair on carbon:



#### STEP 1

Carefully read what the curved arrows indicate.

