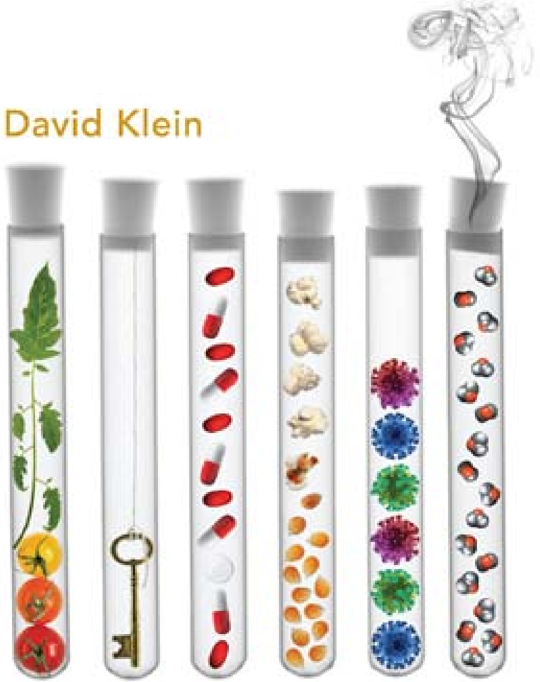
David Klein



Organic Chemistry

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Organic Chemistry

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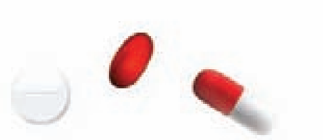

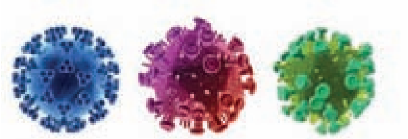

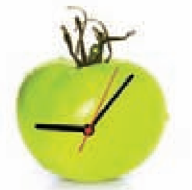

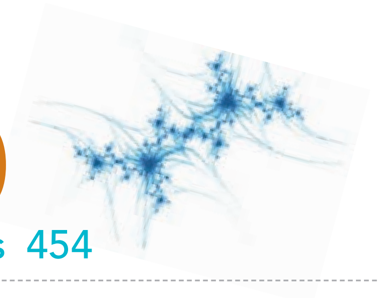

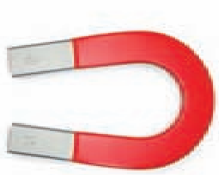

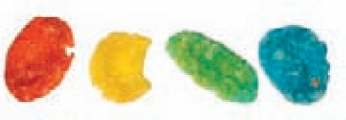

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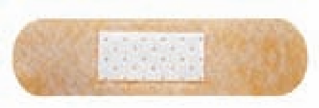

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Preface

Why Did I Write This Book?

Students often say, "I studied 40 hours for this exam and I still didn't do well. Where did I go wrong?" Most instructors hear this complaint every year. In many cases, it is true that the student invested countless hours, only to produce abysmal results. Often, inefficient study habits are to blame. The important question is: why do so many students have difficulty preparing themselves for organic chemistry exams? There are certainly several factors at play here, but perhaps the most dominant factor is a fundamental disconnect between what students learn and the tasks expected of them. To illustrate this disconnect, consider the following analogy.

Imagine that a prestigious university offers a one-week course entitled "Bike-Riding 101." On the first day of the course, a physics professor delivers a fascinating lecture on the physics of bicycle riding. On the second day, an engineering professor delivers a captivating lecture on how bicycles have been engineered to minimize air-resistance. The week continues with exciting lectures, and the students invest significant time reviewing all of the information delivered throughout the week. On the last day of class, the final exam is unveiled: each student must ride a bike for a distance of 100 feet. Perhaps one or two students in the class have innate talents and are able to accomplish the task without falling even once. A large number of students fall several times, but are able to get back on the bike and slowly make it to the finish line, bruised and hurt. Other students, however, simply cannot ride for even one second without falling, even though they invested countless hours studying the material. There is a disconnect between what the students learned and what they were expected to do for their exam. A similar disconnect exists in organic chemistry textbook instruction.

The Current State of Organic Chemistry Instruction

Current organic chemistry textbooks as well as lectures provide the students with extensive coverage of the principles, but exams focus on very specific problem-solving tasks. It is often expected that students will independently develop the necessary skills for solving problems. This expectation is not much different than the expectation that students will be able to ride a bike without falling after attending a week of fascinating lectures. Organic chemistry is much like bicycle riding. It requires constant practice of very specific skills. There are key skills necessary to predict products, propose mechanisms, propose syntheses, etc. Although a few students have innate talents and are able to develop the necessary skills independently, most students require guidance. This guidance is not consistently integrated within current textbooks.

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 Organic Chemistry Instruction

To address the disconnect in organic chemistry instruction, I have developed a textbook that utilizes 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 to support these concepts. This emphasis upon skills development will provide 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.

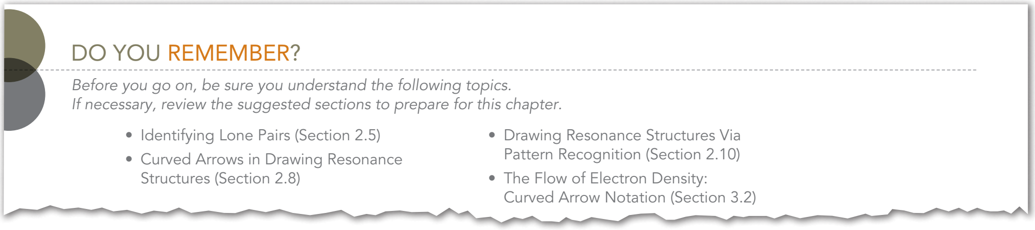
As an example, resonance structures are used repeatedly throughout the course, and students must become masters of resonance structures early in the course. Therefore, a significant portion of Chapter 2 is devoted to pattern-recognition for drawing resonance structures. Rather than just providing a list 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.

As another example of the skills-based approach, Chapter 7, Substitution Reactions, places special emphasis on the skills necessary for drawing all of the mechanistic steps for S_N2 and S_N1 processes. Students are often confused when they see an S_N1 process whose mechanism is comprised of four or five mechanistic steps (proton transfers, carbocation rearrangements, etc.). This chapter contains a novel approach that trains students to identify the number of mechanistic steps required in a substitution process. Students are provided with numerous examples and are given ample opportunity to practice drawing mechanisms.

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 skill development as one of the primary vehicles for instruction.

Pedagogical Tools that Support a Skills-Based Approach

The textbook utilizes several pedagogical tools designed to integrate the skills-based approach consistently throughout all chapters. Each chapter begins with a thought-provoking question followed by **Do You Remember?**, which is a list of relevant skills from previous chapters that should have been mastered before proceeding with the current chapter.



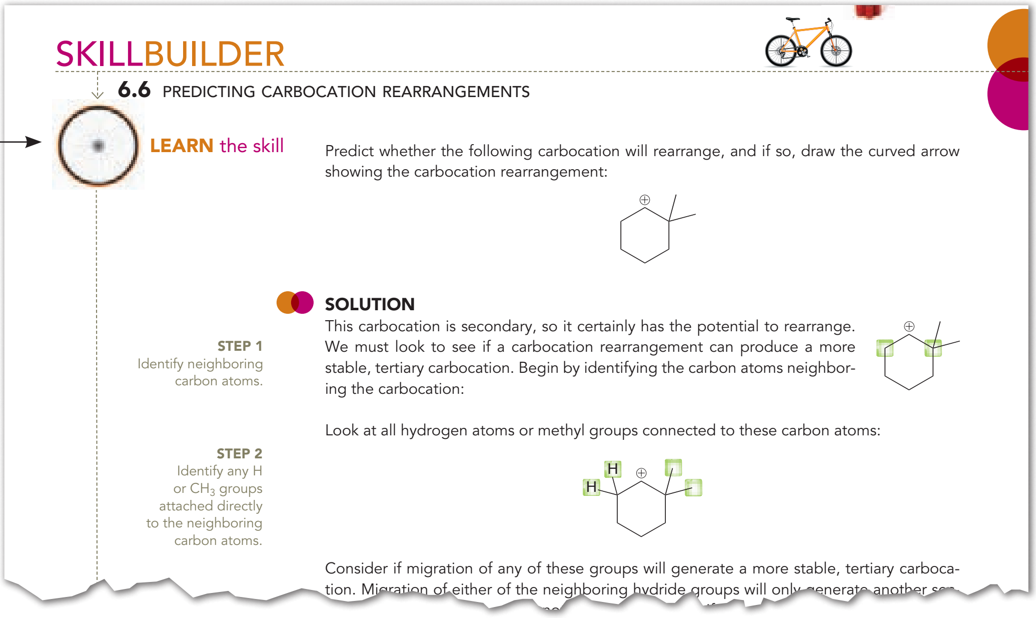
DO YOU REMEMBER?

Before you go on, be sure you understand the following topics.
If necessary, review the suggested sections to prepare for this chapter.

- Identifying Lone Pairs (Section 2.5)
- Curved Arrows in Drawing Resonance Structures (Section 2.8)
- Drawing Resonance Structures Via Pattern Recognition (Section 2.10)
- The Flow of Electron Density: Curved Arrow Notation (Section 3.2)

The main body of each chapter contains numerous **SkillBuilders**, each of which is designed to foster a specific skill. For example, SkillBuilder 6.6 focuses on drawing carbocation rearrangements. Each SkillBuilder contains three parts.

LEARN THE SKILL
A solved problem that demonstrates a particular skill.



SKILLBUILDER

6.6 PREDICTING CARBOCATION REARRANGEMENTS

LEARN the skill

Predict whether the following carbocation will rearrange, and if so, draw the curved arrow showing the carbocation rearrangement:

SOLUTION

STEP 1
Identify neighboring carbon atoms.

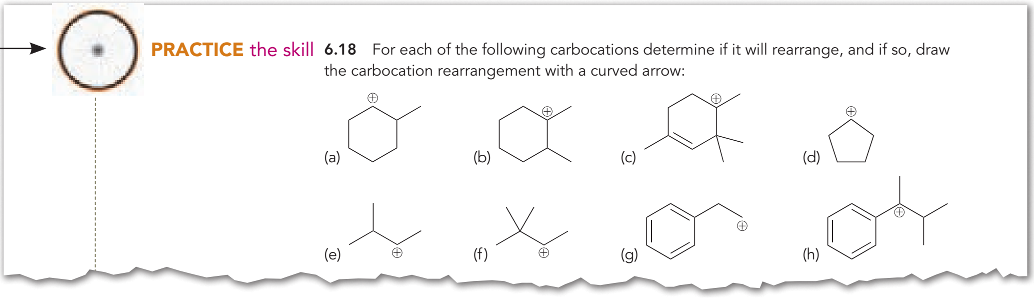
This carbocation is secondary, so it certainly has the potential to rearrange. We must look to see if a carbocation rearrangement can produce a more stable, tertiary carbocation. Begin by identifying the carbon atoms neighboring the carbocation:

STEP 2
Identify any H or CH_3 groups attached directly to the neighboring carbon atoms.

Look at all hydrogen atoms or methyl groups connected to these carbon atoms:

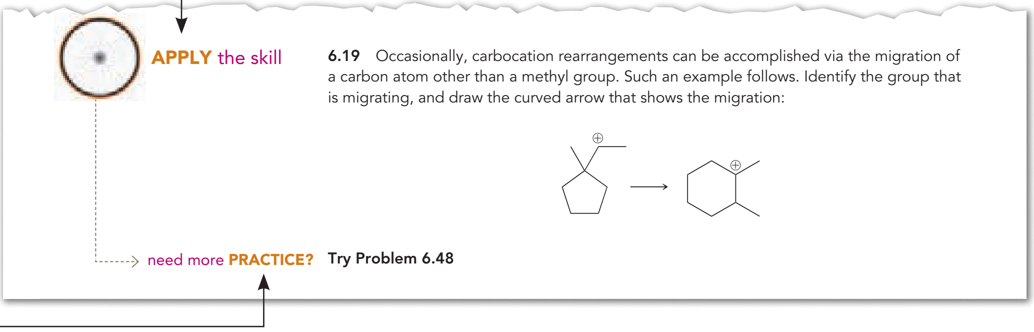
Consider if migration of any of these groups will generate a more stable, tertiary carbocation. Migration of either of the neighboring hydride groups will only generate another sec-

PRACTICE THE SKILL
Numerous problems (similar to the Solved Problem) that give students valuable opportunity to practice and master the skill.



PRACTICE the skill **6.18** For each of the following carbocations determine if it will rearrange, and if so, draw the carbocation rearrangement with a curved arrow:

APPLY THE SKILL
One or two more challenging problems in which the student must apply the skill in a slightly different environment. 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.

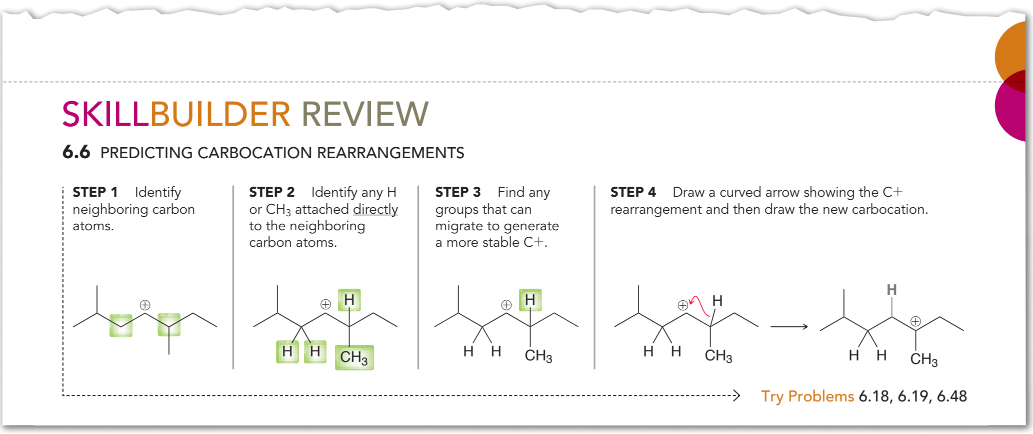


APPLY the skill **6.19** Occasionally, carbocation rearrangements can be accomplished via the migration of a carbon atom other than a methyl group. Such an example follows. Identify the group that is migrating, and draw the curved arrow that shows the migration:

need more **PRACTICE?** **Try Problem 6.48**

NEED MORE PRACTICE?
Suggests end of chapter exercise(s) that students can work to practice the skill.

All SkillBuilders are visually summarized at the end of each chapter within the **SkillBuilder Review.**



SKILLBUILDER REVIEW

6.6 PREDICTING CARBOCATION REARRANGEMENTS

STEP 1 Identify neighboring carbon atoms.

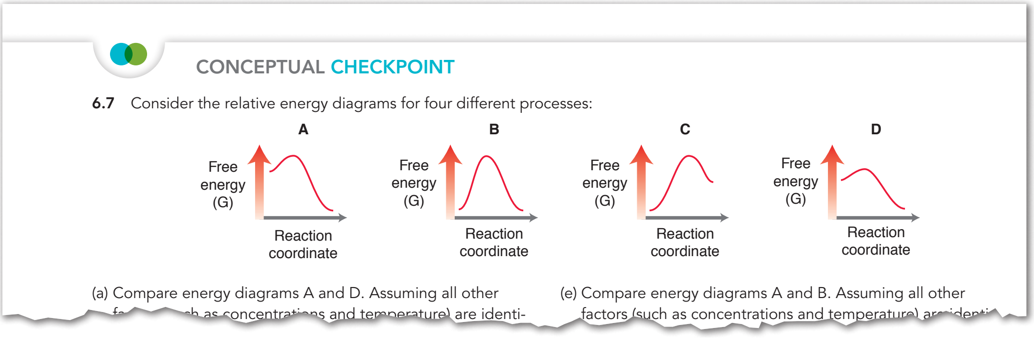
STEP 2 Identify any H or CH_3 attached directly to the neighboring carbon atoms.

STEP 3 Find any groups that can migrate to generate a more stable C+.

STEP 4 Draw a curved arrow showing the C+ rearrangement and then draw the new carbocation.

Try Problems 6.18, 6.19, 6.48

In addition to the Skillbuilders, additional practice is provided within the chapter by way of the **Conceptual Checkpoints**.



CONCEPTUAL CHECKPOINT

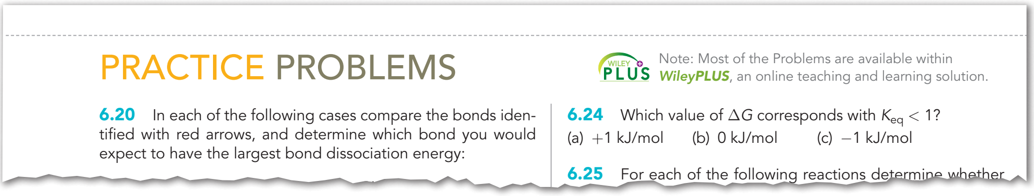
6.7 Consider the relative energy diagrams for four different processes:

(a) Compare energy diagrams A and D. Assuming all other
ch as concentrations and temperature) are identi-

(e) Compare energy diagrams A and B. Assuming all other
factors (such as concentrations and temperature) are identi

End-of-chapter **Practice Problems** provide valuable additional skill-based exercises for continuing skills development. The **Practice Problems** are followed by **Integrated Problems**, which give the students opportunities to combine skills from the current chapter with skills from previous chapters. The end-of-chapter problems conclude with a set of **Challenge Problems**, which are designed to provide students with opportunities to apply their skills in more challenging situations. These **Challenge Problems** require students to think outside of the box and demonstrate skills mastery.

The SkillBuilder approach within the textbook is reinforced by the meaningful practice available within ***WileyPLUS***, an innovative online environment for effective teaching and learning.



PRACTICE PROBLEMS

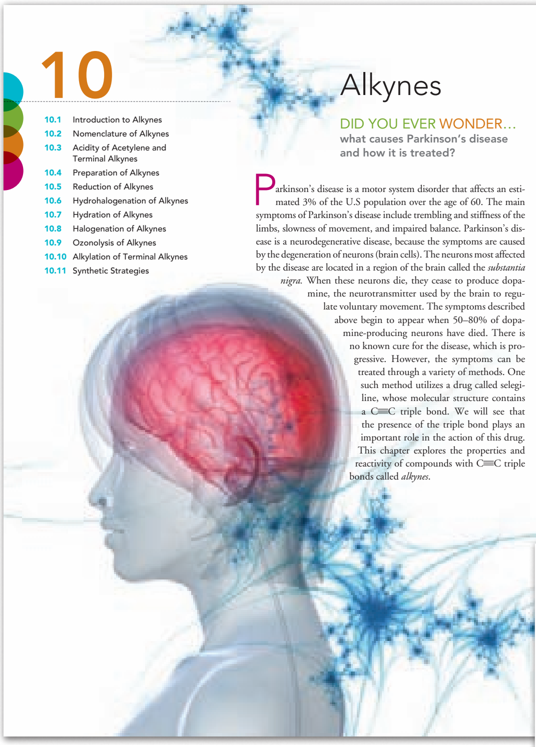
Note: Most of the Problems are available within *WileyPLUS*, an online teaching and learning solution.

6.20 In each of the following cases compare the bonds identified with red arrows, and determine which bond you would expect to have the largest bond dissociation energy:

6.24 Which value of ΔG corresponds with $K_{eq} < 1$?
(a) $+1$ kJ/mol (b) 0 kJ/mol (c) -1 kJ/mol

6.25 For each of the following reactions determine whether

There is breadth and depth of assessment within ***WileyPLUS***, consisting of **Practice the Skill** and **Learn the Skill** (from the SkillBuilders), many of the end-of-chapter problems, and a rich testbank. In addition, **Reaction Explorer** is a vast database of mechanism and synthesis questions. Professors can create online homework assignments or quizzes from these different assessment types and student responses are automatically graded. There are many forms of assistance available to students as they work questions within ***WileyPLUS***, including link(s) to the relevant section of the text and guided problem-solving tutorials.



10 Alkynes

10.1 Introduction to Alkynes
10.2 Nomenclature of Alkynes
10.3 Acidity of Acetylene and Terminal Alkynes
10.4 Preparation of Alkynes
10.5 Reduction of Alkynes
10.6 Hydrohalogenation of Alkynes
10.7 Hydration of Alkynes
10.8 Halogenation of Alkynes
10.9 Ozonolysis of Alkynes
10.10 Alkylation of Terminal Alkynes
10.11 Synthetic Strategies

DID YOU EVER WONDER…
what causes Parkinson's disease and how it is treated?

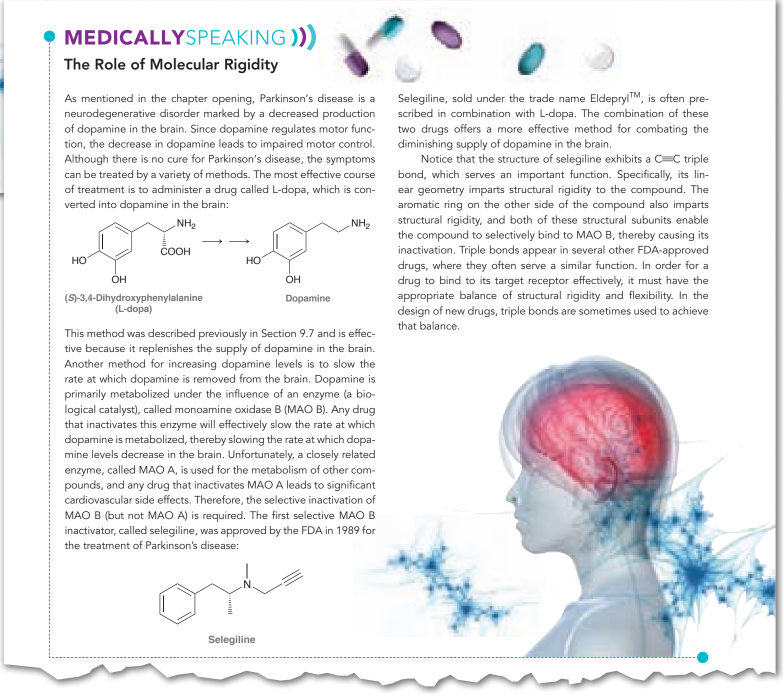
Parkinson's disease is a motor system disorder that affects an estimated 3% of the U.S population over the age of 60. The main symptoms of Parkinson's disease include trembling and stiffness of the limbs, slowness of movement, and impaired balance. Parkinson's disease is a neurodegenerative disease, because the symptoms are caused by the degeneration of neurons (brain cells). The neurons most affected by the disease are located in a region of the brain called the *substantia nigra.* When these neurons die, they cease to produce dopamine, the neurotransmitter used by the brain to regulate voluntary movement. The symptoms described above begin to appear when 50–80% of dopamine-producing neurons have died. There is no known cure for the disease, which is progressive. However, the symptoms can be treated through a variety of methods. One such method utilizes a drug called selegiline, whose molecular structure contains a C≡C triple bond. We will see that the presence of the triple bond plays an important role in the action of this drug. This chapter explores the properties and reactivity of compounds with C≡C triple bonds called *alkynes*.

Applications to Illustrate Relevancy

Alongside the numerous exercises built in to facilitate student understanding of the skills and concepts of organic chemistry, many real-world applications are featured throughout the chapters to demonstrate the relevance of organic chemistry in our everyday lives. These applications appear in a variety of ways, including ***Medically Speaking*** boxes which feature medicinal and pharmaceutical applications, as well as ***Practically Speaking*** boxes which feature commercial applications of organic chemistry. These real-world applications are highlighted in the detailed Table of Contents.

Each chapter begins by posing a question ("Did You Ever Wonder") which is then revisited within that chapter. For instance, in Chapter 10, a question is posed about Parkinson's disease.

The chapter opener question is always revisited and explored within that chapter, in this case within a "Medically Speaking" application box.



MEDICALLYSPEAKING

The Role of Molecular Rigidity

As mentioned in the chapter opening, Parkinson's disease is a neurodegenerative disorder marked by a decreased production of dopamine in the brain. Since dopamine regulates motor function, the decrease in dopamine leads to impaired motor control. Although there is no cure for Parkinson's disease, the symptoms can be treated by a variety of methods. The most effective course of treatment is to administer a drug called L-dopa, which is converted into dopamine in the brain:

(*S*)-3,4-Dihydroxyphenylalanine
(L-dopa)

Dopamine

This method was described previously in Section 9.7 and is effective because it replenishes the supply of dopamine in the brain. Another method for increasing dopamine levels is to slow the rate at which dopamine is removed from the brain. Dopamine is primarily metabolized under the influence of an enzyme (a biological catalyst), called monoamine oxidase B (MAO B). Any drug that inactivates this enzyme will effectively slow the rate at which dopamine is metabolized, thereby slowing the rate at which dopamine levels decrease in the brain. Unfortunately, a closely related enzyme, called MAO A, is used for the metabolism of other compounds, and any drug that inactivates MAO A leads to significant cardiovascular side effects. Therefore, the selective inactivation of MAO B (but not MAO A) is required. The first selective MAO B inactivator, called selegiline, was approved by the FDA in 1989 for the treatment of Parkinson's disease:

Selegiline

Selegiline, sold under the trade name Eldepryl™, is often prescribed in combination with L-dopa. The combination of these two drugs offers a more effective method for combating the diminishing supply of dopamine in the brain.

Notice that the structure of selegiline exhibits a C≡C triple bond, which serves an important function. Specifically, its linear geometry imparts structural rigidity to the compound. The aromatic ring on the other side of the compound also imparts structural rigidity, and both of these structural subunits enable the compound to selectively bind to MAO B, thereby causing its inactivation. Triple bonds appear in several other FDA-approved drugs, where they often serve a similar function. In order for a drug to bind to its target receptor effectively, it must have the appropriate balance of structural rigidity and flexibility. In the design of new drugs, triple bonds are sometimes used to achieve that balance.

Text Organization

The sequence of chapters and topics in *Organic Chemistry* do 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 (for example, ketal formation and enamine formation, which are mechanistically quite similar). No shortcuts were taken in any of the mechanisms, and all steps are clearly illustrated, including all proton transfer steps.

Two chapters (6 and 12) 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 12, 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 15 and 16) were written to be stand-alone and portable, so that instructors can cover these chapters in any order desired. In fact, two of the chapters (Chapters 13 and 14) that precede the spectroscopy chapters include end-of-chapter spectroscopy problems, for those students who covered spectroscopy earlier. Spectroscopy coverage appears in subsequent functional group chapters, specifically Chapter 18 (Aromatic Compounds), Chapter 20 (Aldehydes and Ketones), Chapter 21 (Carboxylic Acids and Their Derivatives), Chapter 23 (Amines), Chapter 24 (Carbohydrates), and Chapter 25 (Amino Acids, Peptides and Proteins).

ACKNOWLEDGEMENTS

Certainly, books are not written in a vacuum, and this textbook is no exception. Over the last four years, I have benefitted greatly from the many, many reviewers and accuracy checkers who engaged with the materials as they were being developed and polished. I also benefited enormously from the extensive class test program in which 75 professors and over 4,000 students participated and offered valuable user feedback. Each individual played a crucial role in allowing us to develop a very high quality product.

This book could not have been created without the incredible efforts of the following people at John Wiley and Sons, Inc. Illustration Editor Sandra Rigby helped create a compelling art program. Photo Editor Lisa Gee helped identify exciting photos. Freelance designers Carole Anson and Anne DeMarinis conceived of a visually refreshing and compelling interior design and cover. Production Editor Elizabeth Swain, kept this book on schedule and was vital to ensuring such a high-quality product. The development team, consisting of Leslie Kraham, Barbara Heaney and Joan Kalkut, were invaluable in the creation of this first edition. The tireless efforts of Joan and Leslie, together with their day-to-day guidance and insight, made this project possible. Freelance editor Deena Cloud provided thoughtful and constructive guidance about how best to frame and present my ideas. Media Editors Tom Kulesa, Marc Wezdecki and Geraldine Osnato conceived of and built a compelling ***WileyPLUS*** course. Marketing Manager Kristine Ruff enthusiastically created an exciting message for this book. Editorial assistants Cathy Donovan and Lauren Stauber helped to manage many facets of the review and supplements process. Associate Editor Jennifer Yee helped with the PowerPoint slides. Associate Publisher Petra Recter provided strong vision and guidance in bringing this book to market.

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.

David R. Klein, Ph.D.
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The Development Story

REVIEWED AND TESTED BY OVER 315 PROFESSORS AND 4,000 STUDENTS!

The creation, development, and execution of this first edition is the result of incredibly extensive professor and student involvement, every step of the way. Our solution (the textbook and the accompanying ***WileyPLUS*** course) has been carefully designed to meet the dual needs of faculty and students. Over the past four years, we have exhaustively tested and reviewed the manuscript, the art program, the design, the problems, and the value of the SkillBuilder approach to ensure accuracy and effectiveness in the classroom.

Adopters of the Preliminary Edition To meet customer demand, we created a preliminary edition that seven schools adopted for Fall 2010.

Class Testers Seventy-five instructors and over 4,000 students class tested materials in 2009 and Fall 2010 prior to publication. Their feedback was overwhelmingly supportive and enthusiastic, with over 98% of all instructors stating that the Klein materials met their course goals. They offered valuable suggestions that can only come from use in the classroom, and their comments factored into each decision that was made to produce the final textbook.

Accuracy Checkers Ten professors participated in accuracy checking at each stage of the manuscript development and proof process to ensure that the end product is as error-free as possible.

Reviewers More than 240 professors across the United States and Canada reviewed the manuscript to ensure the content was clear and precise and facilitated student engagement and understanding.

5 Professor Focus Groups Thirty-two professors participated to provide invaluable feedback on the art program and interior design, our *WileyPLUS* solution, and the specific needs of different schools.

Multiple Student Focus Groups Over 50 students participated in a variety of focus groups to provide feedback on the design and insights into their preferred learning style. These students confirmed that our design and pedagogy were appropriate and added value.

Developmental Review Over the past four years, a team of development editors, including line editors and art editors, have worked with the author to hone his distinctive voice, test explanation of concepts in the classroom, and confirm that the pedagogy was consistent and added value to the learning process.

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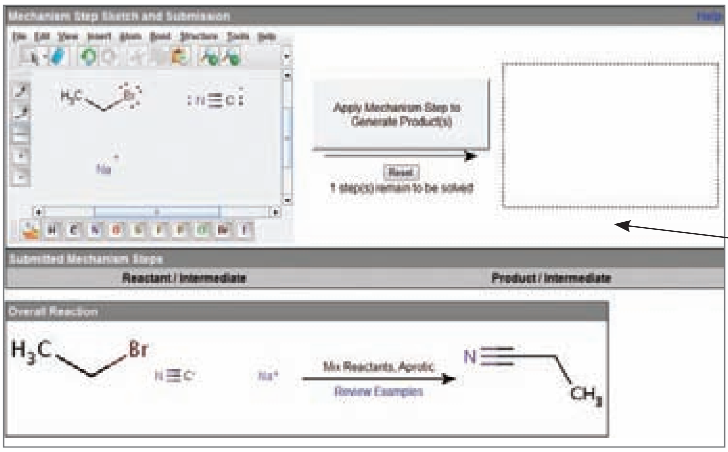

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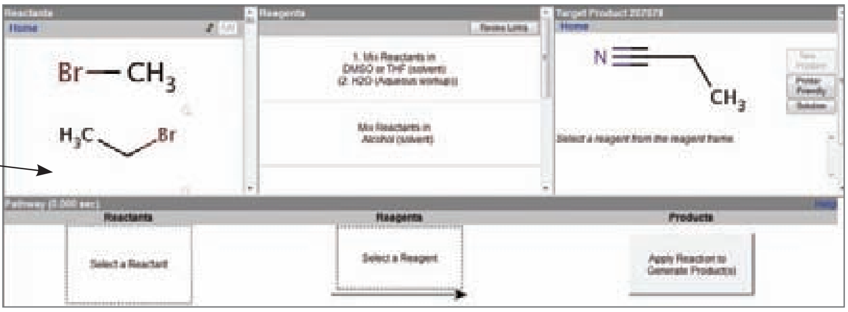

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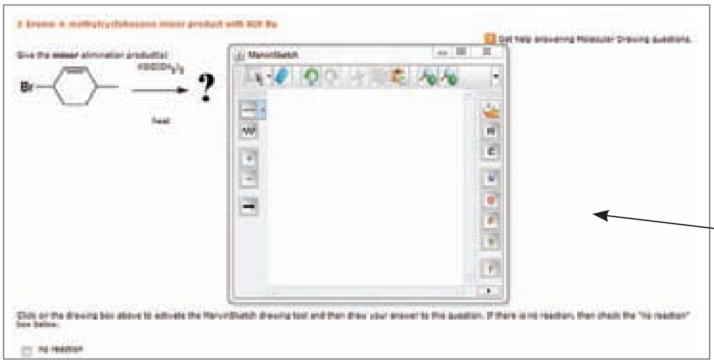

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About the Author

David Klein is a Senior Lecturer in the Department of Chemistry at The Johns Hopkins University where he has taught organic chemistry since 1999. Having worked with thousands of students, he has intense first-hand knowledge of how they learn and the difficulties they encounter. He received his bachelor's degree in chemistry from The Johns Hopkins University and his PhD from the University of California at Los Angeles under the supervision of Professor Orville Chapman. Motivated by his experiences teaching organic chemistry as a graduate student at UCLA, David wrote *Organic Chemistry as a Second Language* (John Wiley & Sons, 2004, updated 2nd edition published in 2008), which has become a highly valued student study resource. David has received numerous teaching awards at both UCLA and Johns Hopkins for his unique, skill-building approach to organic chemistry instruction. David is married, with five children, and enjoys skiing, scuba-diving, and Tae Kwon Do.

1

A Review of General Chemistry

ELECTRONS, BONDS, AND MOLECULAR PROPERTIES

DID YOU EVER WONDER…

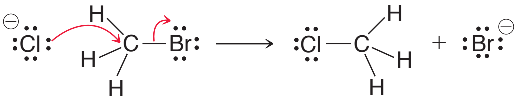
what causes lightning?

Believe 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

continued >

must recognize that *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:

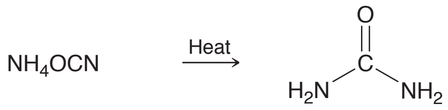


Throughout this course, we will learn how, when, and why electrons flow during reactions. We will learn about the barriers that prevent electrons from flowing, and we will learn how to overcome those barriers. In short, we will study the behavioral patterns of electrons, enabling us to predict, and even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



Ammonium cyanate
(Inorganic)

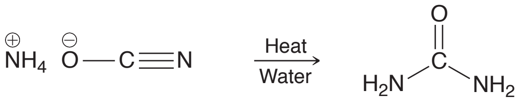
Urea
(Organic)

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.

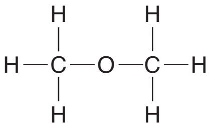
1.2 The Structural Theory of Matter

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 structures of ammonium cyanate and urea from Wöhler's experiment:

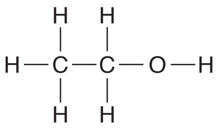


Ammonium cyanate **Urea**

These compounds have the same molecular formula (CH_4N_2O), 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. Consider the following two compounds:



Dimethyl ether
Boiling point = −23°C



Ethanol
Boiling point = 78.4°C

These compounds have the same molecular formula (C_2H_6O) but different constitution, so they are constitutional isomers. 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. The term **valence** describes the number of bonds usually formed by each element. 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).

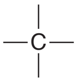
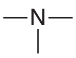
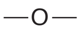
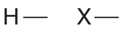
Tetravalent	*Trivalent*	*Divalent*	*Monovalent*
			 (where X = F, Cl, Br, or I)
Carbon generally forms ***four*** bonds.	Nitrogen generally forms ***three*** bonds.	Oxygen generally forms ***two*** bonds.	Hydrogen and halogens generally form ***one*** bond.

FIGURE 1.1
Valencies of some common elements encountered in organic chemistry.

SKILLBUILDER

1.1 DETERMINING THE CONSTITUTION OF SMALL MOLECULES

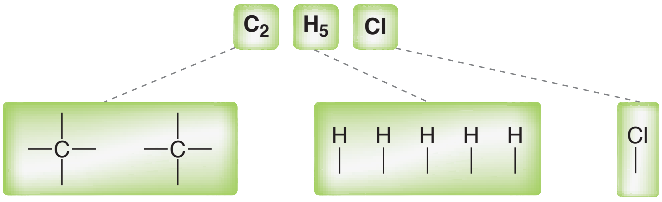
LEARN the skill

There is only one compound that has molecular formula C_2H_5Cl. Determine the constitution of this compound.

SOLUTION

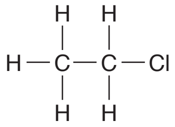
The molecular formula indicates which atoms are present in the compound. In this example, the compound contains two carbon atoms, five hydrogen atoms, and one chlorine atom. Begin by determining the valency of each atom that is present in the compound. Each carbon atom is expected to be tetravalent, while the chlorine and hydrogen atoms are all expected to be monovalent:

STEP 1
Determine the valency of each atom in the compound.



Now we must determine how these atoms are connected. The atoms with the most bonds (the carbon atoms) are likely to be in the center of the compound. In contrast, the chlorine atom and hydrogen atoms can each form only one bond, so those atoms must be placed at the periphery. In this example, it does not matter where the chlorine atom is placed. All six possible positions are equivalent.

STEP 2
Determine how the atoms are connected—atoms with the highest valency should be placed at the center and monovalent atoms should be placed at the periphery.



PRACTICE the skill

1.1 Determine the constitution of the compounds with the following molecular formulas:

(a) CH_4O (b) CH_3Cl (c) C_2H_6 (d) CH_5N

(e) C_2F_6 (f) C_2H_5Br (g) C_3H_8

APPLY the skill

1.2 Draw two constitutional isomers that have molecular formula C_3H_7Cl.

1.3 Draw three constitutional isomers that have molecular formula C_3H_8O.

1.4 Draw all constitutional isomers that have molecular formula $C_4H_{10}O$.

need more **PRACTICE?** **Try Problems 1.34, 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 ΔH. The energy diagram in Figure 1.2 plots the total 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 (Å). 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. The lowest point on the curve represents the lowest energy (most stable) state. This state determines both the bond length (0.74 Å) and the bond strength (436 kJ/mol).

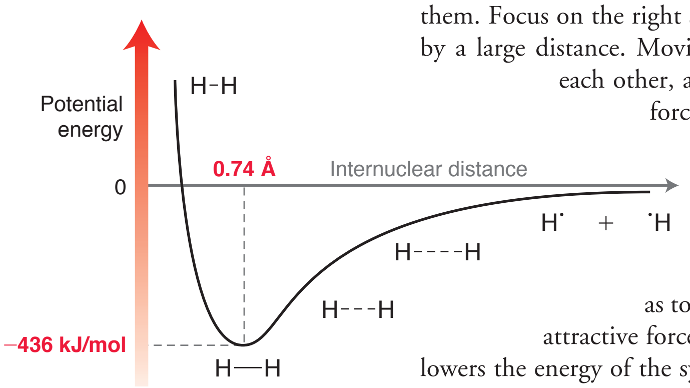


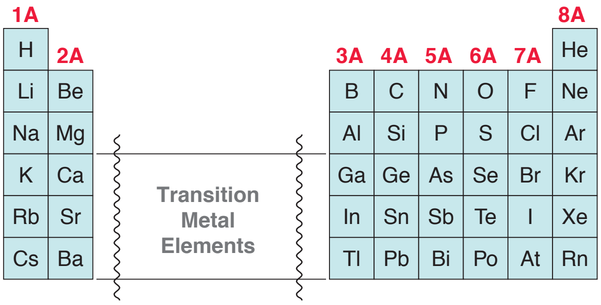
FIGURE 1.2
An energy diagram showing the total energy as a function of the internuclear distance between two hydrogen atoms.

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).

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.



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

FIGURE 1.3
A periodic table showing group numbers.

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.

SOLUTION

STEP 1
Determine the number of valence electrons.

(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) on a side of the B, like this:

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

(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 filled:

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

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

1.5 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

APPLY the skill

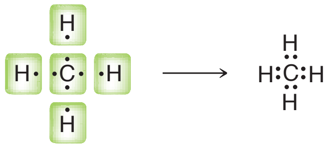
1.6 Compare the Lewis dot structure of nitrogen and phosphorus and explain why you might expect these two atoms to exhibit similar bonding properties.

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

1.8 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?

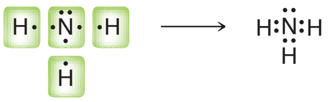
1.9 Draw a Lewis structure of a carbon atom that has one extra valence electron (and therefore bears a negative charge). Which second-row element does this carbon atom resemble in terms of the number of valence electrons?

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 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

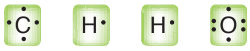
LEARN the skill

Draw the Lewis structure of CH_2O.

SOLUTION

STEP 1
Draw all individual atoms.

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

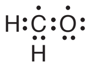


STEP 2
Connect atoms that form more than one bond.

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.

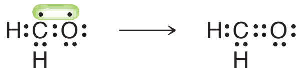
STEP 3
Connect the hydrogen atoms.

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

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

(a) C_2H_6 (b) C_2H_4 (c) C_2H_2

(d) C_3H_8 (e) C_3H_6 (f) CH_3OH

APPLY the skill

1.11 Borane (BH_3) is very unstable and quite reactive. Draw a Lewis structure of borane and explain the source of the instability.

1.12 There are four constitutional isomers with molecular formula C_3H_9N. Draw a Lewis structure for each isomer and determine the number of lone pairs on the nitrogen atom in each case.

need more **PRACTICE?** **Try Problems 1.35, 1.38, 1.42**

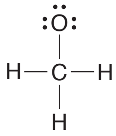
1.4 Identifying Formal Charges

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:

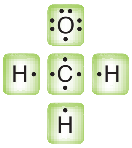
1. Determine the appropriate number of valence electrons for an atom.
2. Determine whether the atom exhibits the appropriate number of electrons.

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.

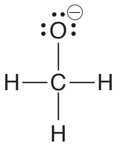
After identifying the appropriate number of electrons for each atom in a Lewis structure, the next task is to determine if any of the atoms in the Lewis structure exhibit an unexpected number of electrons. For example, consider this structure:



Remember that each bond represents two shared electrons. We split each bond apart equally, and then count the number of electrons on each atom:

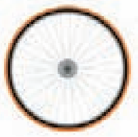


Each hydrogen atom exhibits one valence electron, as expected. The carbon atom also exhibits the appropriate number of valence electrons (four), but the oxygen atom does not. The oxygen atom in this structure exhibits seven valence electrons, but it should only have six. In this case, the oxygen atom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



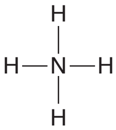
SKILLBUILDER

1.4 CALCULATING FORMAL CHARGE



LEARN the skill

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



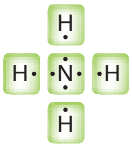
SOLUTION

STEP 1 Determine the appropriate number of valence electrons.

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.

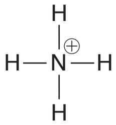
STEP 2 Determine the actual number of valence electrons in this case.

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

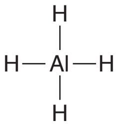


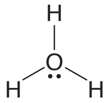
In this case, the nitrogen atom exhibits only four valence electrons. It is missing one electron, so it must bear a positive charge, which is shown like this:

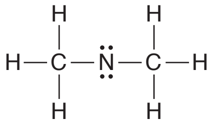
STEP 3 Assign a formal charge.

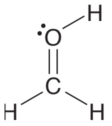


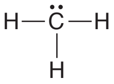
PRACTICE the skill **1.13** Identify any formal charges in the compounds below:

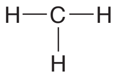
(a)


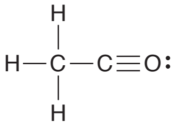
(b)


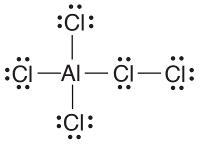
(c)


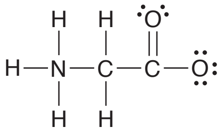
(d)


(e)


(f)


(g)


(h)


(i)


APPLY the skill **1.14** Draw a Lewis structure for each of the following ions; in each case, indicate which atom possesses the formal charge:

(a) BH_4^- (b) NH_2^- (c) $C_2H_5^+$

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

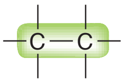
Increasing electronegativity →

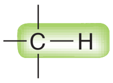
			H 2.1			
Li 1.0	**Be** 1.5	**B** 2.0	**C** 2.5	**N** 3.0	**O** 3.5	**F** 4.0
Na 0.9	**Mg** 1.2	**Al** 1.5	**Si** 1.8	**P** 2.1	**S** 2.5	**Cl** 3.0
K 0.8						**Br** 2.8

↑ Increasing electronegativity

When two atoms form a bond, there is one critical question that 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:

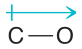




The C—C bond is clearly covalent, because there is no difference in electronegativity between the two atoms forming the bond. Even a C—H bond is considered to be covalent, because the difference in electronegativity between C and H is less than 0.5.

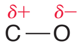
If the difference in electronegativity is between 0.5 and 1.7, the electrons are not shared equally between the atoms, resulting in a **polar covalent bond**. For example, consider a bond between carbon and oxygen (C—O). Oxygen is significantly more electronegative (3.5) than carbon (2.5), and therefore 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:



$\overset{+\!\!\longrightarrow}{C—O}$

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



$\overset{\delta+}{C}—\overset{\delta-}{O}$

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):

$\overset{\oplus}{Na} \quad :\overset{\ominus\,\cdot\cdot}{\underset{\cdot\cdot}{O}}H$

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 the 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).

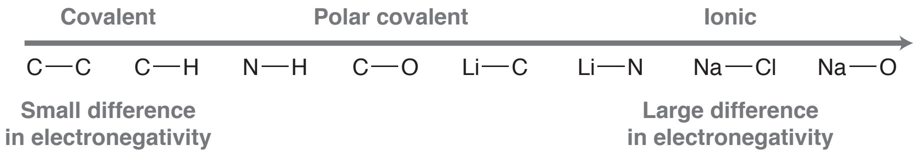
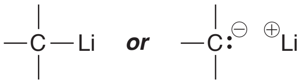


FIGURE 1.4 The nature of various bonds commonly encountered in organic chemistry.

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 Na—O 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.



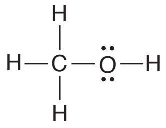
Another reason to avoid absolute cutoff numbers when comparing electronegativity values is that the electronegativity values shown above are obtained via a method developed by Linus Pauling. However, there are at least seven other methods for calculating electronegativity values, each of which provides 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.



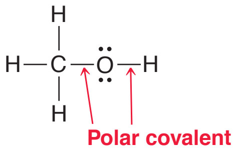
Methanol

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.

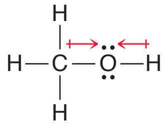
The C—O bond and the O—H bond are both polar covalent bonds:

STEP 1
Identify all polar covalent bonds.



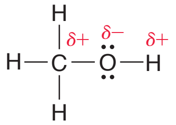
Now determine the direction of the inductive effects. Oxygen is more electronegative than C or H, so the inductive effects are shown like this:

STEP 2
Determine the direction of each dipole.



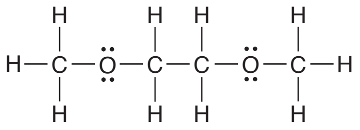
These inductive effects dictate the locations of the partial charges:

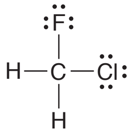
STEP 3
Indicate the location of partial charges.



PRACTICE the skill

1.15 For each of the following compounds, identify any polar covalent bonds by drawing δ+ and δ− symbols in the appropriate locations.


(a)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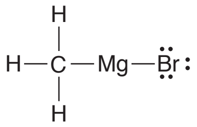
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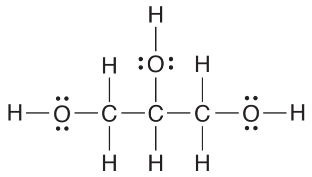
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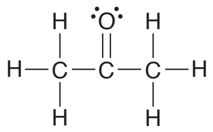
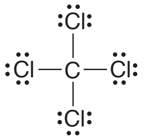
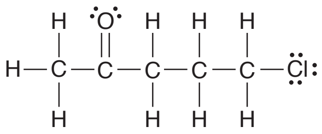

(e)


(f)

APPLY the skill

1.16 The regions of δ+ in a compound are the regions most likely to be attacked by an anion, such as hydroxide (HO^-). In the compound below, identify the two carbon atoms that are most likely to be attacked by a hydroxide ion:

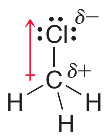


need more **PRACTICE?** **Try Problems 1.36, 1.37, 1.48, 1.57**

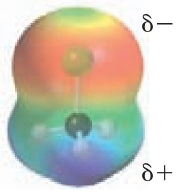
PRACTICALLYSPEAKING

Electrostatic Potential Maps

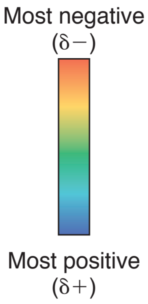
Partial charges can be visualized with three-dimensional, rainbow-like images called **electrostatic potential maps**. As an example, consider the electrostatic potential map of chloromethane.



Chloromethane



Electrostatic potential map of chloromethane



Color scale

In the image, a color scale is used to represent areas of δ− and δ+. As indicated, red represents a region that is δ−, while blue represents a region that is δ+. 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 δ−, while a small attraction indicates a position of δ+. 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 (ψ) is used to denote each wavefunction (ψ_1, ψ_2, ψ_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 (ψ_1, ψ_2, ψ_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 (ψ^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 ψ^2 will generate an image of an atomic orbital (Figure 1.5).

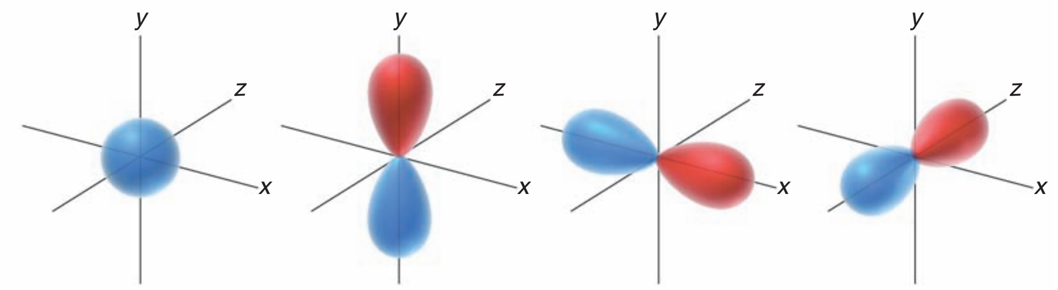


FIGURE 1.5
Illustrations of an *s* orbital and three *p* orbitals.

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: "ψ^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 only come in a small number of 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.

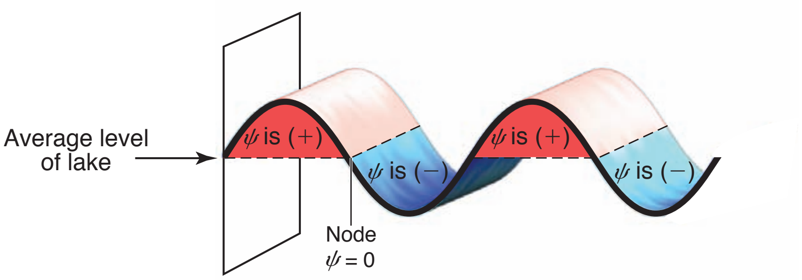


FIGURE 1.6
Phases of a wave moving across the surface of a lake.

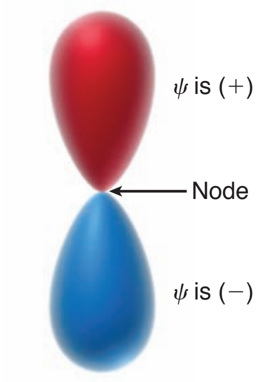


FIGURE 1.7
The phases of a *p* orbital.

Consider a wave that moves across the surface of a lake (Figure 1.6). The wavefunction (ψ) mathematically describes the wave, and the value of the wavefunction is dependent on location. Locations above the average level of the lake have a positive value for ψ (indicated in red), and locations below the average level of the lake have a negative value for ψ (indicated in blue). Locations where the value of ψ is zero are called **nodes**.

Similarly, orbitals can have regions where the value of ψ 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 ψ are positive, while the bottom lobe is a region where the values of ψ 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 ψ (+ or −) with electrical charge. A positive value for ψ does not imply a positive charge. The value of ψ (+ or −) is a mathematical convention that refers to the *phase* of the wave (just like in the lake). Although ψ can have positive or negative values, nevertheless ψ^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 (ψ^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 ψ 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 1*s* orbital, the 2*s* orbital, and the three 2*p* orbitals. Our discussions will therefore focus primarily on these orbitals (Figure 1.8). Electrons are lowest in energy when they occupy a 1*s* orbital, because the 1*s* orbital is closest to the nucleus and it has no nodes (the more nodes that an orbital has, the greater its energy). The 2*s* orbital has one node and is farther away form the nucleus; it is therefore higher in energy than the 1*s* orbital. After the 2*s* orbital, there are three 2*p* orbitals that are all equivalent in energy to one another. Orbitals with the same energy level are called **degenerate orbitals**.

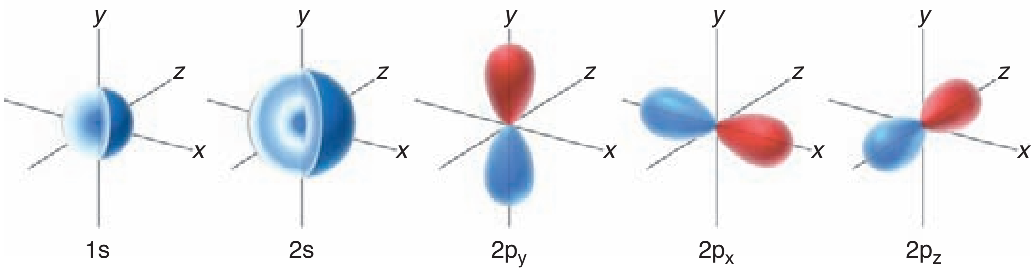


FIGURE 1.8
Illustrations of *s* orbitals and three *p* orbitals.

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

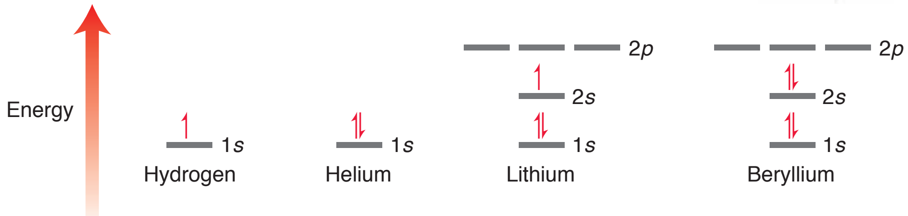


FIGURE 1.9
Energy diagrams showing the electron configurations for H, He, Li, and Be.

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 ⇂ or ↾). In order for the orbital to accommodate two electrons, the electrons must have opposite spin states.

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).

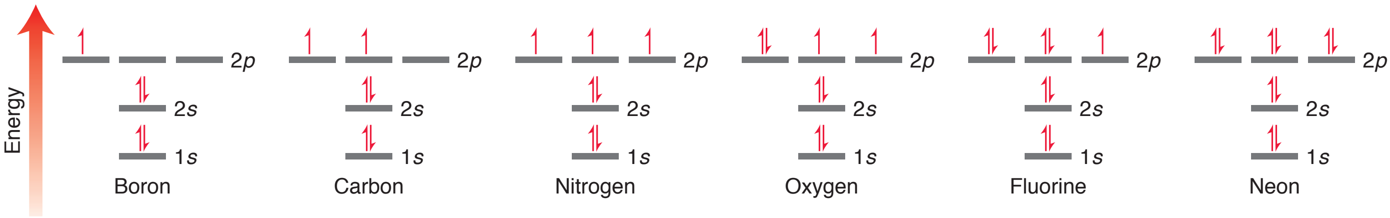


FIGURE 1.10
Energy diagrams showing the electron configurations for B, C, N, O, F, and Ne.

SKILLBUILDER

1.6 IDENTIFYING ELECTRON CONFIGURATIONS

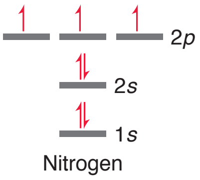
LEARN the skill

Identify the electron configuration of a nitrogen atom.

SOLUTION

STEP 1
Place the valence electrons in atomic orbitals using the Aufbau principle, the Pauli exclusion principle, and Hund's rule.

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 two electrons being placed in each orbital:



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

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

$$1s^22s^22p^3$$

PRACTICE the skill

1.17 Determine the electron configuration for each of the following atoms:

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

APPLY the skill

1.18 Determine the electron configuration for each of the following ions:

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

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).

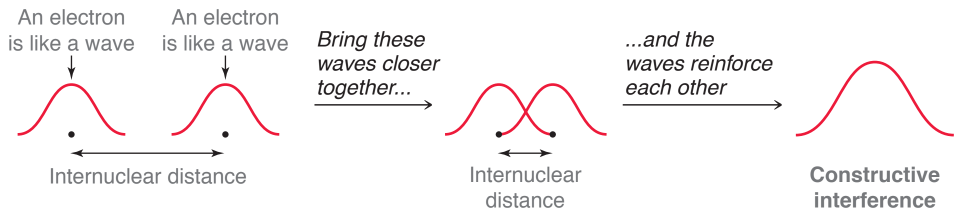


FIGURE 1.11 Constructive interference resulting from the interaction of two electrons.

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).

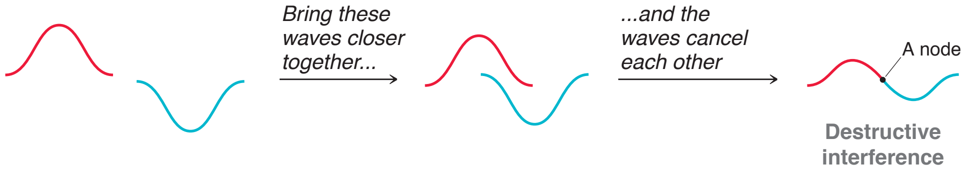


FIGURE 1.12 Destructive interference resulting from the interaction of two electrons.

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 (H_2). This bond is formed from the overlap of the 1*s* 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 (σ) 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 σ bonds and will be true of all purely single bonds. Therefore, *all single bonds are σ bonds*.

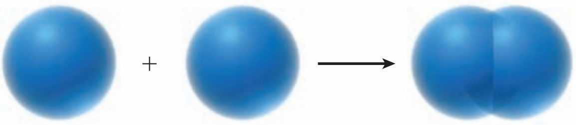


FIGURE 1.13 The overlap of the 1*s* atomic orbitals of two hydrogen atoms, forming molecular hydrogen (H_2).

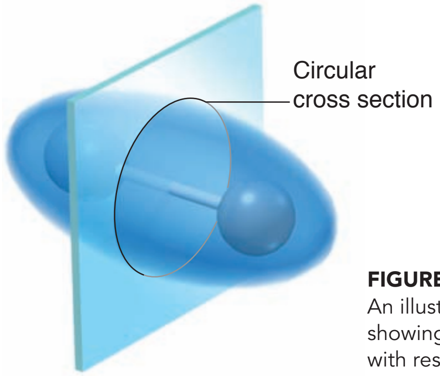


FIGURE 1.14 An illustration of a sigma bond, showing the circular symmetry with respect to the bond axis.

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.

Much like valence bond theory, **molecular orbital (MO) theory** also describes a bond in terms of the constructive interference between two overlapping atomic orbitals. However, MO theory goes one step further and 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).

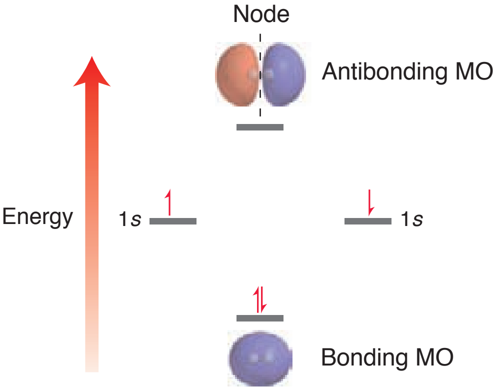


FIGURE 1.15
An energy diagram showing the relative energy levels of bonding and antibonding molecular orbitals.

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 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 two of the many molecular orbitals of CH_3Br. Each of the two images in Figure 1.16 represents a molecular orbital capable of accommodating up to two electrons. In each molecular orbital, red and blue regions indicate the different phases, as described in Section 1.6. As we saw with molecular hydrogen,

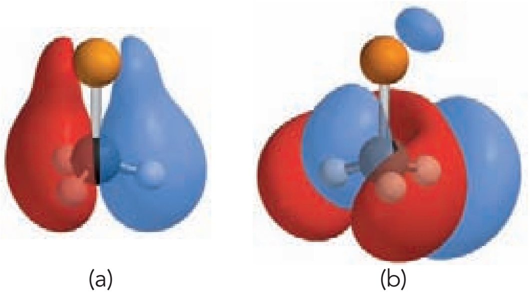

(a) (b)

FIGURE 1.16
(a) A low-energy molecular orbital of CH_3Br.
(b) A high-energy molecular orbital of CH_3Br.

not all molecular orbitals will be occupied. The bonding electrons will occupy the lower energy molecular orbitals (such as the one shown in Figure 1.16a), while the higher energy molecular orbitals (as in Figure 1.16b) 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 CH_3Br is attacked by a hydroxide ion (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 CH_3Br (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.

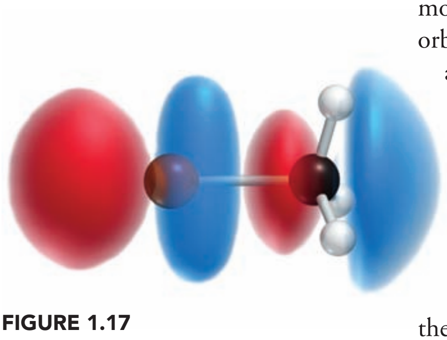


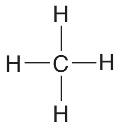
FIGURE 1.17
The LUMO of CH_3Br.

We will use MO theory several times in the chapters that follow. Most notably, in Chapter 17, 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:



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

Methane

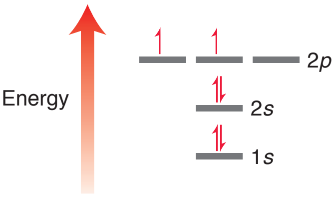


FIGURE 1.18
An energy diagram showing the electron configuration of carbon.

Recall the electron configuration of carbon (Figure 1.18). This electron configuration cannot satisfactorily describe the bonding structure of methane (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 2*s* electron has been promoted to a higher energy 2*p* orbital. Now the carbon atom has four atomic orbitals capable of forming bonds, but there is yet another problem here. The geometry of the 2*s* and three 2*p* orbitals does not satisfactorily explain the observed three-dimensional geometry of methane (Figure 1.20). All bond angles are 109.5°, 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° (as seen in Figure 1.5) rather than 109.5°.

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 2*s* orbital and the three 2*p* 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. Rather, it is a mathematical procedure that is used to arrive

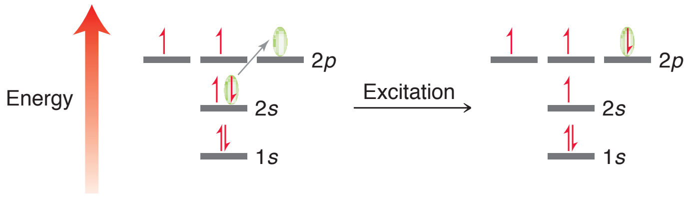


FIGURE 1.19
An energy diagram showing the electronic excitation of an electron in a carbon atom.

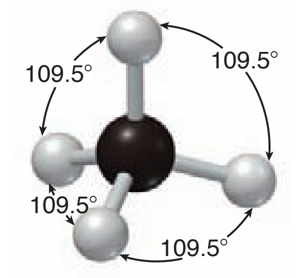


FIGURE 1.20
The tetrahedral geometry of methane. All bond angles are 109.5°.

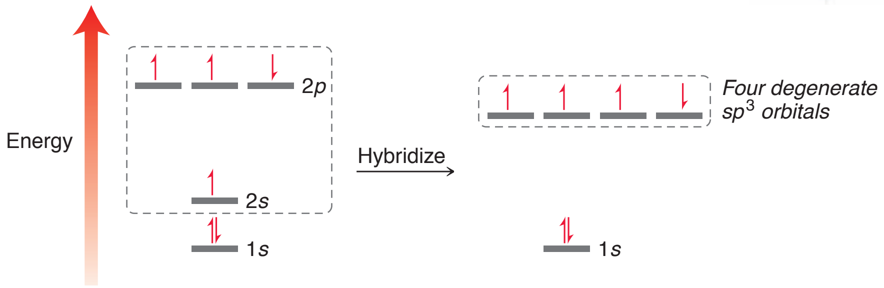


FIGURE 1.21
An energy diagram showing four degenerate hybridized atomic orbitals.

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.

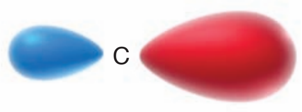


FIGURE 1.22
An illustration of an *sp*^{3}-hybridized atomic orbital.

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.

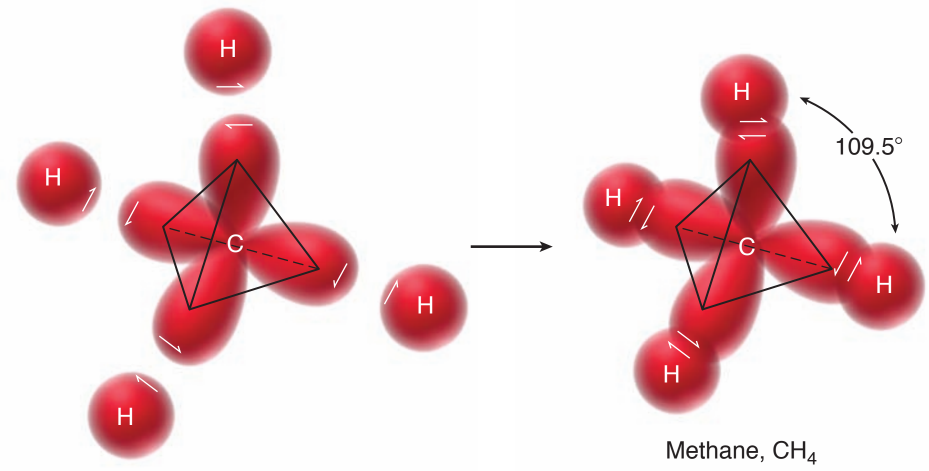
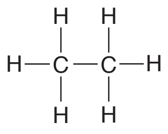


FIGURE 1.23
A tetrahedral carbon atom using each of its four *sp*^{3}-hybridized orbitals to form a bond.

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



$$H_3C{-}CH_3$$

Ethane

All bonds in this compound are single bonds, and therefore they are all σ 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).

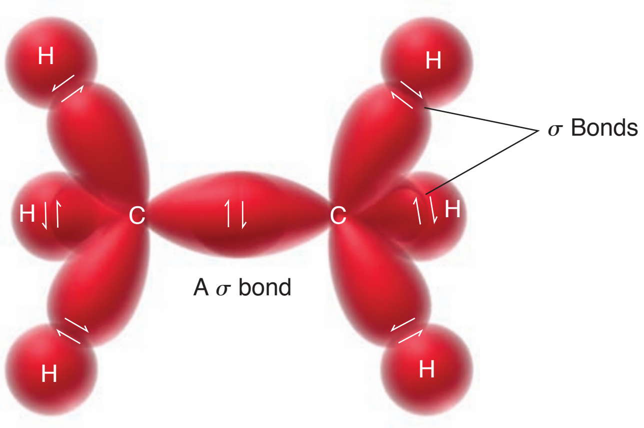
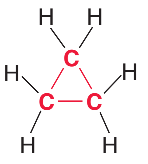


FIGURE 1.24
A valence bond picture of the bonding in ethane.

CONCEPTUAL CHECKPOINT

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

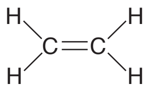


Cyclopropane

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:



Ethylene

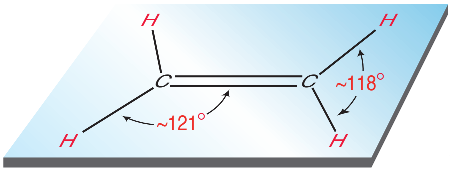


FIGURE 1.25
All six atoms of ethylene are in one plane.

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 before 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.

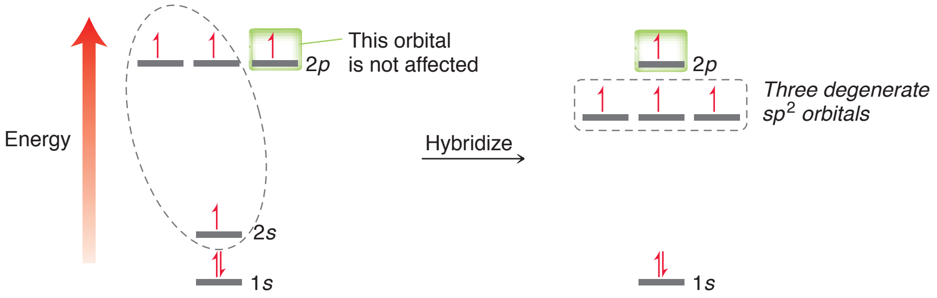


FIGURE 1.26
An energy diagram showing three degenerate sp^2-hybridized atomic orbitals.

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.

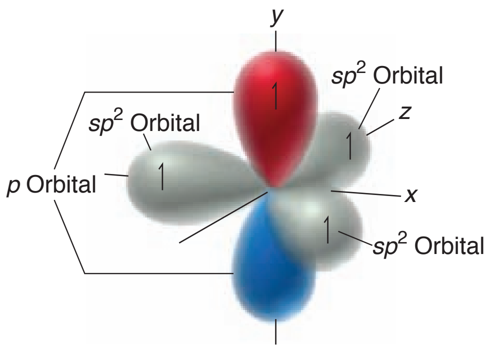


FIGURE 1.27
An illustration of an *sp*^{2}-hybridized carbon atom.

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

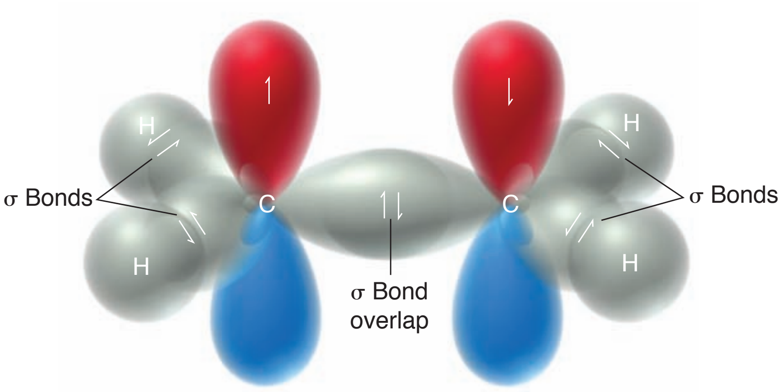


FIGURE 1.28
An illustration of the σ bonds in ethylene.

In addition, each carbon atom has one *p* orbital (shown in Figure 1.28 with blue and red lobes). These *p* orbitals actually overlap with each other as well, which is a separate bonding interaction called a **pi (π) bond** (Figure 1.29). Do not be confused by the nature of this type of bond. It is true that the π 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 π bond.

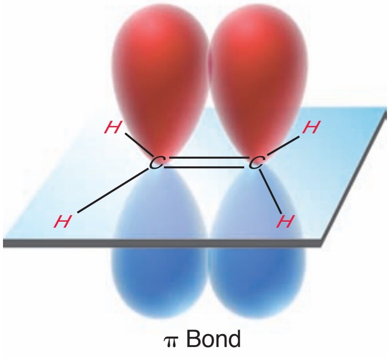


FIGURE 1.29
An illustration of the π bond in ethylene.

The picture of the π 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 π bond. Compare Figure 1.29 with the bonding MO in Figure 1.30.

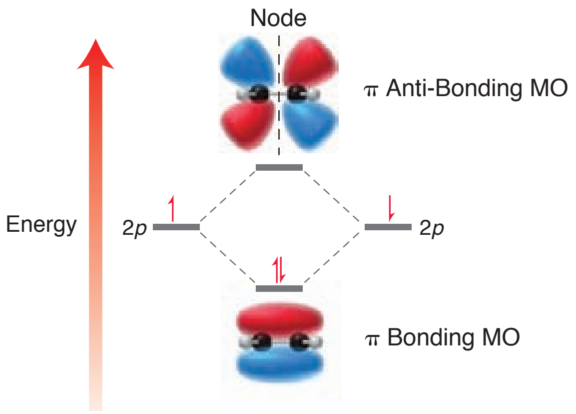
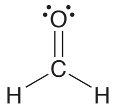


FIGURE 1.30 An energy diagram showing images of bonding and antibonding MOs in ethylene.

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

CONCEPTUAL CHECKPOINT

1.20 Consider the structure of formaldehyde:



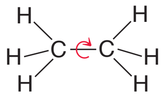
Formaldehyde

(a) Identify the type of bonds that form the C═O double bond.

(b) Identify the atomic orbitals that form each C—H bond.

(c) What type of atomic orbitals do the lone pairs occupy?

1.21 Sigma bonds experience free rotation at room temperature:



In contrast, π bonds do not experience free rotation. Explain. (*Hint*: Compare Figures 1.24 and 1.29, focusing on the orbitals used in forming a σ bond and the orbitals used in forming a π 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:

H—C≡C—H

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* orbit-

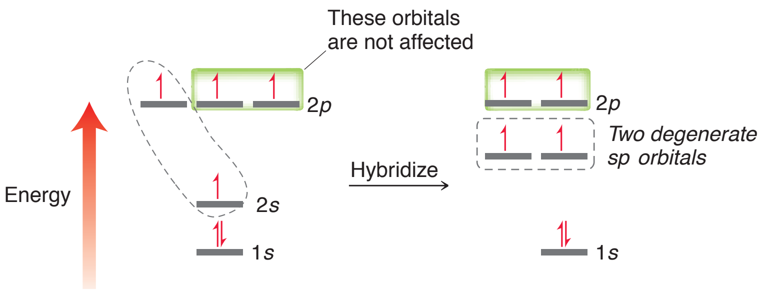


FIGURE 1.31 An energy diagram showing two degenerate *sp*-hybridized atomic orbitals.

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

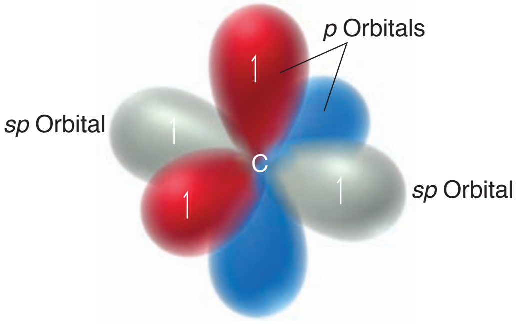


FIGURE 1.32
An illustration of an *sp*-hybridized carbon atom. The *sp*-hybridized orbitals are shown in gray.

The two *sp*-hybridized orbitals are available to form σ bonds (one on either side), and the two *p* orbitals are available to form π 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 σ bond and two π bonds. The σ bond results from the overlap of *sp* orbitals, while each of the two π bonds result from overlapping *p* orbitals. As shown in Figure 1.33, the geometry of the triple bond is linear.

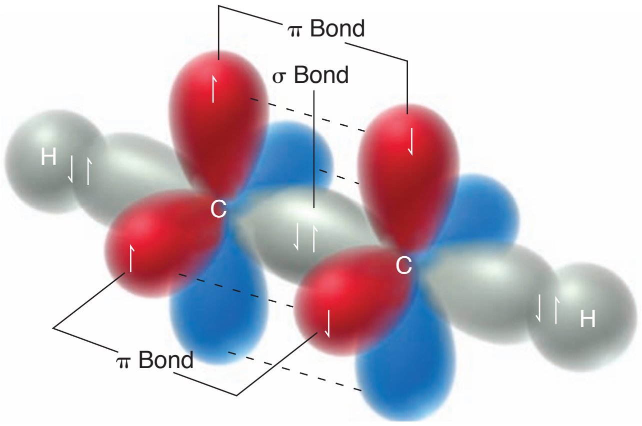


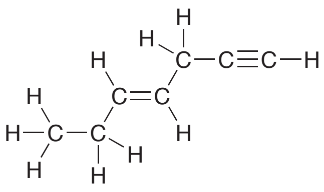
FIGURE 1.33
An illustration of the σ bonds and π bonds in acetylene.

SKILLBUILDER

1.7 IDENTIFYING HYBRIDIZATION STATES

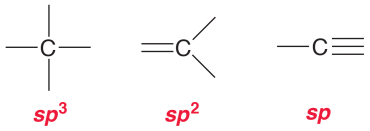
LEARN the skill

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



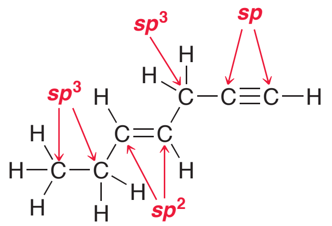
SOLUTION

To determine the hybridization state of an uncharged carbon atom, simply count the number of σ bonds and π bonds:

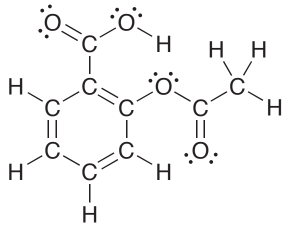


A carbon atom with four single bonds (four σ bonds) will be sp^3 hybridized. A carbon atom with three σ bonds and one π bond will be sp^2 hybridized. A carbon atom with two σ bonds and two π bonds will be *sp* hybridized. Carbon atoms bearing a positive or negative charge will be discussed in more detail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

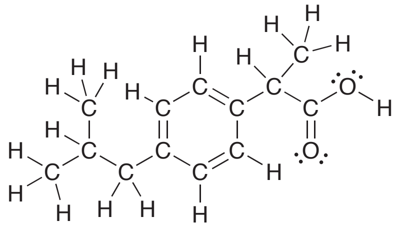
Using the simple scheme above, the hybridization state of most carbon atoms can be determined instantly:



PRACTICE the skill **1.22** Below are the structures of two common over-the-counter pain relievers. Determine the hybridization state of each carbon atom in these compounds:

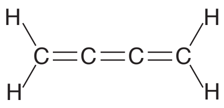


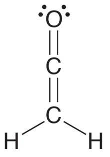
(a) **Acetylsalicyclic acid**
(aspirin)



(b) **Ibuprofen**
(Advil or Motrin)

APPLY the skill **1.23** Determine the hybridization state of each carbon atom in the following compounds:

(a) 

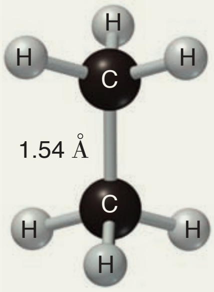
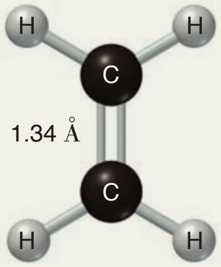
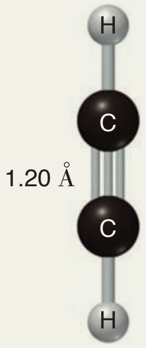
(b) 

need more **PRACTICE?** **Try Problems 1.55, 1.56, 1.58**

Bond Strength and Bond Length

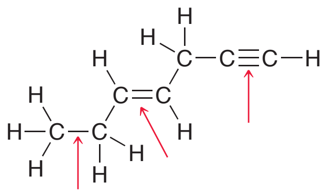
The information we have seen in this section allows us to compare single bonds, double bonds, and triple bonds. A single bond has only one bonding interaction (a σ bond), a double bond has two bonding interactions (one σ bond and one π bond), and a triple bond has three bonding interactions (one σ bond and two π 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

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



1.10 VSEPR Theory: Predicting Geometry

In order to predict the geometry of a small compound, we focus on the central atom and count the number of σ bonds and lone pairs. The total (σ bonds plus lone pairs) is called the **steric number**. Figure 1.34 gives several examples in which the steric number is 4 in each case.

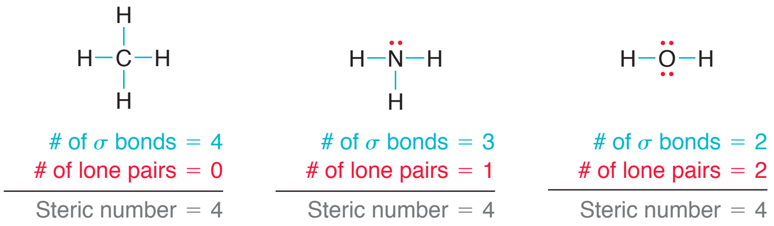


FIGURE 1.34 Calculation of the steric number for methane, ammonia, and water.

The steric number indicates the number of electron pairs (bonding and nonbonding) that are repelling each other. The repulsion causes the electron pairs to arrange themselves in three-dimensional space so as to achieve maximal distance from each other. As a result, the geometry of the central atom will be determined by the steric number. This principle is called the ***v***alence ***s***hell ***e***lectron ***p***air ***r***epulsion (**VSEPR**) theory. Let's take a closer look at the geometry of each of the compounds above.

Geometries Resulting from sp^3 Hybridization

In all of the previous examples, there are four pairs of electrons (steric number 4). In order for an atom to accommodate four electron pairs, it must use four orbitals and is therefore sp^3 hybridized. Recall that the geometry of methane is **tetrahedral** (Figure 1.35). In fact, any sp^3-hybridized atom will have four sp^3-hybridized orbitals arranged in a shape approximating a tetrahedron. This is true for the nitrogen atom in ammonia as well (Figure 1.36). The nitrogen atom is using four orbitals and is therefore sp^3 hybridized. As a result, its orbitals are arranged in a tetrahedron (shown on the left in Figure 1.36). However, there is one important difference between ammonia and methane. In the case of ammonia, one of the four orbitals is housing a nonbonding pair of electrons (a lone pair). This lone pair repels the other bonds more strongly, causing bond angles to be smaller than 109.5°. Bond angles for ammonia have been determined to be 107°.

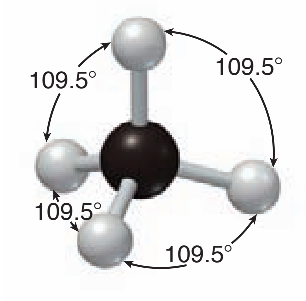


FIGURE 1.35
The tetrahedral geometry of methane.

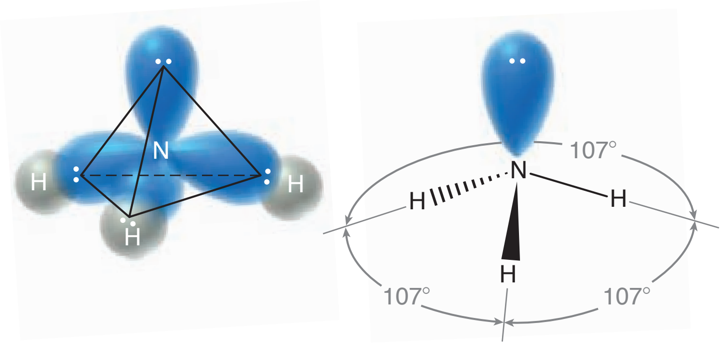


FIGURE 1.36
The orbitals of ammonia are arranged in a tetrahedral geometry.

The term "geometry" does not refer to the arrangement of electron pairs. Rather, it refers to the arrangement of atoms. When we show only the positions of the atoms (ignoring the lone pairs), ammonia appears as in Figure 1.37. This geometry is called **trigonal pyramidal** (Figure 1.37). "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.

FIGURE 1.37
The geometry of ammonia is trigonal pyramidal.

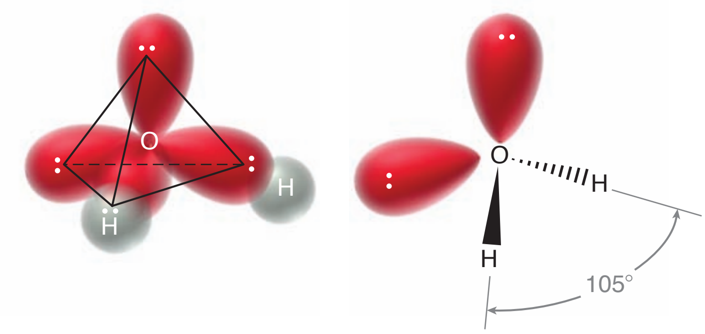


FIGURE 1.38
The orbitals of H_2O are arranged in a tetrahedral geometry.

Another example of sp^3 hybridization is water (H_2O). The oxygen atom has a steric number of 4, and it therefore requires the use of four orbitals. As a result, it must be sp^3 hybridized, with its four orbitals in a tetrahedral arrangement (Figure 1.38). Once again, lone pairs repel each other more strongly than bonds, causing the bond angle between the two O—H bonds to be even smaller than the bond angles in ammonia. The bond angle of water has been determined to be 105°. In order to describe the geometry, we ignore the lone pairs and focus only on the arrangement of atoms, which gives a **bent** geometry in this case (Figure 1.39). In summary, there are only three different types of geometry arising from sp^3 hybridization: tetrahedral, trigonal pyramidal, and bent. In all cases, the electrons were arranged in a tetrahedron, but the lone pairs were ignored when describing geometry. Table 1.3 summarizes this information.

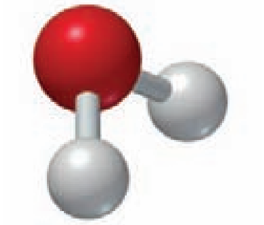


FIGURE 1.39
The geometry of water is bent.

TABLE 1.3 GEOMETRIES RESULTING FROM sp^3 HYBRIDIZATION

EXAMPLE	STERIC NUMBER	HYBRIDIZATION	ARRANGEMENT OF ELECTRON PAIRS	ARRANGEMENT OF ATOMS (GEOMETRY)
CH_4	4	sp^3	Tetrahedral	Tetrahedral
NH_3	4	sp^3	Tetrahedral	Trigonal pyramidal
H_2O	4	sp^3	Tetrahedral	Bent

Geometries Resulting from sp^2 Hybridization

When the central atom of a small compound has a steric number of 3, it will be sp^2 hybridized. As an example, consider the structure of BF_3. Boron has three valence electrons, each of which is used to form a bond. The result is three bonds and no lone pairs, giving a steric number of 3. The central boron atom therefore requires three orbitals, rather than four, and must be sp^2 hybridized. Recall that sp^2-hybridized orbitals achieve maximal separation in a **trigonal planar** arrangement (Figure 1.40): "trigonal" because the boron is connected to three other atoms and "planar" because all atoms are found in the same plane (as opposed to trigonal pyramidal).

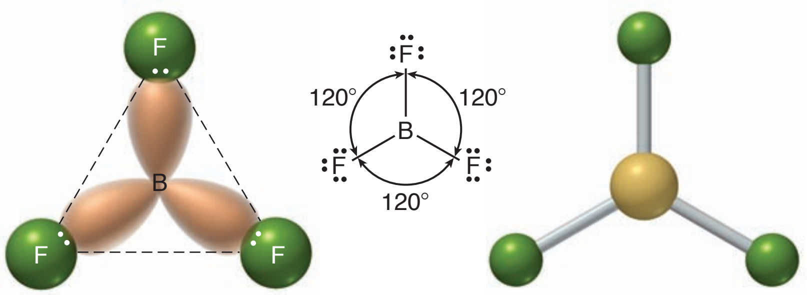
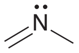


FIGURE 1.40
The geometry of BF_3 is trigonal planar.

As another example, consider the nitrogen atom of an imine:



An imine

LOOKING AHEAD
We will explore imines in more detail in Chapter 20.

To determine the geometry of the nitrogen atom, we first consider the steric number, which is not affected by the presence of the π bond. Why not? Recall that a π bond results from the overlap of *p* orbitals. The steric number of an atom is meant to indicate how many hybridized orbitals are necessary (*p* orbitals are not included in this count). The steric number in this case is 3 (Figure 1.41). As a result, the nitrogen atom must be sp^2 hybridized. The sp^2 hybridization state is always characterized by a trigonal planar arrangement of electron pairs, but when describing geometry, we focus only on the atoms (ignoring any lone pairs). The geometry of this nitrogen atom is therefore bent.

FIGURE 1.41
The steric number of the nitrogen atom of an imine.

Geometry Resulting from *sp* Hybridization

When the central atom of a small compound has a steric number of 2, the central atom will be *sp* hybridized. As an example, consider the structure of BeH_2. Beryllium has two valence electrons, each of which is used to form a bond. The result is two bonds and no lone pairs, giving a steric number of 2. The central beryllium atom therefore requires only two orbitals and must be *sp* hybridized. Recall that *sp*-hybridized orbitals achieve maximal separation when they are **linear** (Figure 1.42).

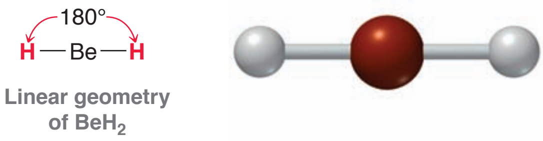
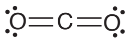


FIGURE 1.42 The geometry of BeH_2 is linear.

As another example of *sp* hybridization, consider the structure of CO_2:


$$O=C=O$$

Once again, the π bonds do *not* impact the calculation of the steric number, so the steric number is 2. The carbon atom must be *sp* hybridized and is therefore linear.

As summarized in Figure 1.43, the three hybridization states give rise to five common geometries.

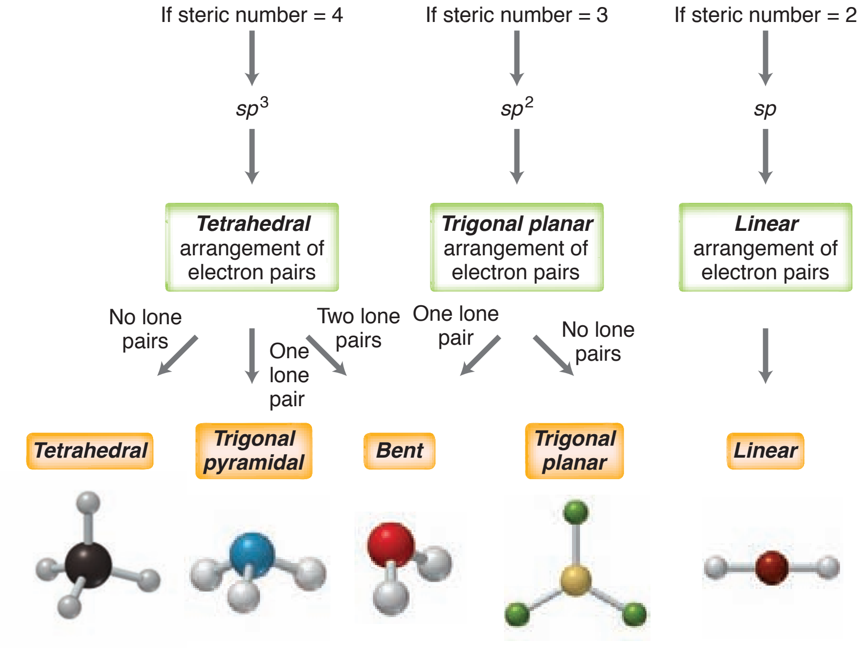


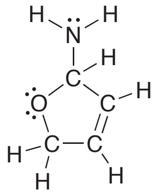
FIGURE 1.43 A decision tree for determining geometry.

SKILLBUILDER

1.8 PREDICTING GEOMETRY

LEARN the skill

Predict the geometry for all atoms (except hydrogens) in the compound below:



SOLUTION

For each atom, the following three steps are followed:

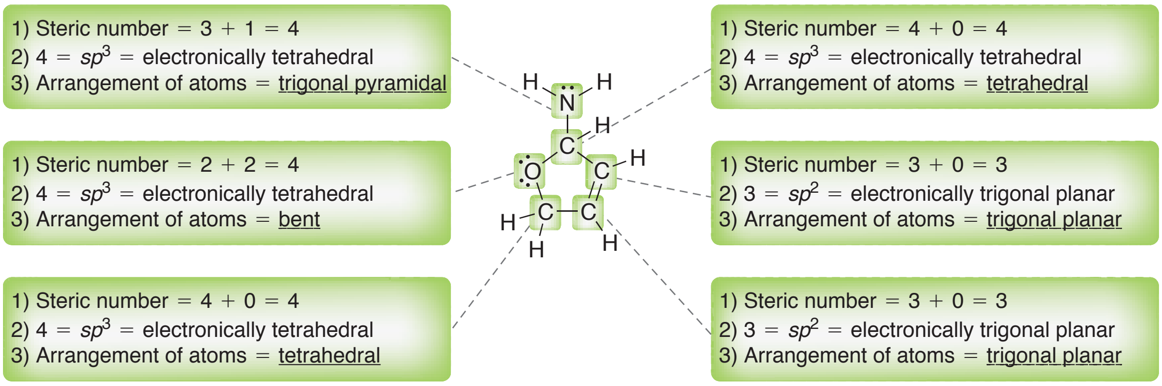
STEP 1
Determine the steric number.

STEP 2
Determine the hybridization state and electronic arrangement.

1. Determine the steric number by counting the number of lone pairs and σ bonds.
2. Use the steric number to determine the hybridization state and electronic arrangement:
    - If the steric number is 4, then the atom will be sp^3 hybridized, and the electronic arrangement will be tetrahedral.
    - If the steric number is 3, then the atom will be sp^2 hybridized, and the electronic arrangement will be trigonal planar.
    - If the steric number is 2, then the atom will be sp hybridized, and the electronic arrangement will be linear.

STEP 3
Ignore lone pairs and describe the resulting geometry.

3. Ignore any lone pairs and describe the geometry only in terms of the arrangement of atoms:


1) Steric number = 3 + 1 = 4
2) 4 = sp^3 = electronically tetrahedral
3) Arrangement of atoms = trigonal pyramidal

1) Steric number = 4 + 0 = 4
2) 4 = sp^3 = electronically tetrahedral
3) Arrangement of atoms = tetrahedral

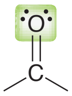
1) Steric number = 2 + 2 = 4
2) 4 = sp^3 = electronically tetrahedral
3) Arrangement of atoms = bent

1) Steric number = 3 + 0 = 3
2) 3 = sp^2 = electronically trigonal planar
3) Arrangement of atoms = trigonal planar

1) Steric number = 4 + 0 = 4
2) 4 = sp^3 = electronically tetrahedral
3) Arrangement of atoms = tetrahedral

1) Steric number = 3 + 0 = 3
2) 3 = sp^2 = electronically trigonal planar
3) Arrangement of atoms = trigonal planar

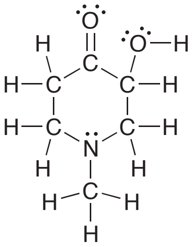
It is not necessary to describe the geometry of hydrogen atoms. Each hydrogen atom is monovalent, so the geometry is irrelevant. Geometry is only relevant when an atom is connected to at least two other atoms. For our purposes, we can also disregard the geometry of the oxygen atom in a C═O double bond because it is connected to only one atom:

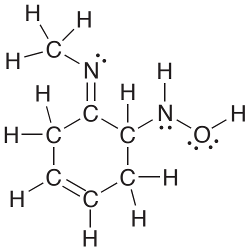


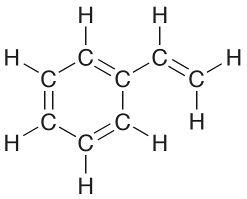
can disregard the geometry of this oxygen

PRACTICE the skill **1.25** Predict the geometry for the central atom in each of the compounds below:
(a) NH_3 (b) H_3O^+ (c) BH_4^- (d) BCl_3 (e) BCl_4^- (f) CCl_4 (g) $CHCl_3$ (h) CH_2Cl_2

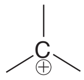
1.26 Predict the geometry for all atoms except hydrogen in the compounds below:

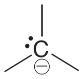

(a)


(b)


(c)

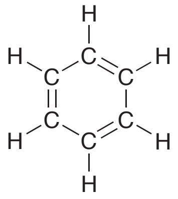
APPLY the skill **1.27** Compare the structures of a carbocation and a carbanion:


Carbocation


Carbanion

In one of these ions, the central carbon atom is trigonal planar; in the other it is trigonal pyramidal. Assign the correct geometry to each ion.

1.28 Identify the hybridization state and geometry of each carbon atom in benzene. Use that information to determine the geometry of the entire molecule:



Benzene

need more **PRACTICE?** **Try Problems 1.39–1.41, 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 1.44a the arrow shows the inductive effect of the chlorine atom. Figure 1.44b 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** (μ) is used as an indicator of polarity, where μ is defined as the amount of partial charge (δ) 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 (μ) will generally have an order of magnitude of around 10^{-18} esu · cm. The dipole moment of chloromethane, for example, is 1.87×10^{-18} esu • 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.

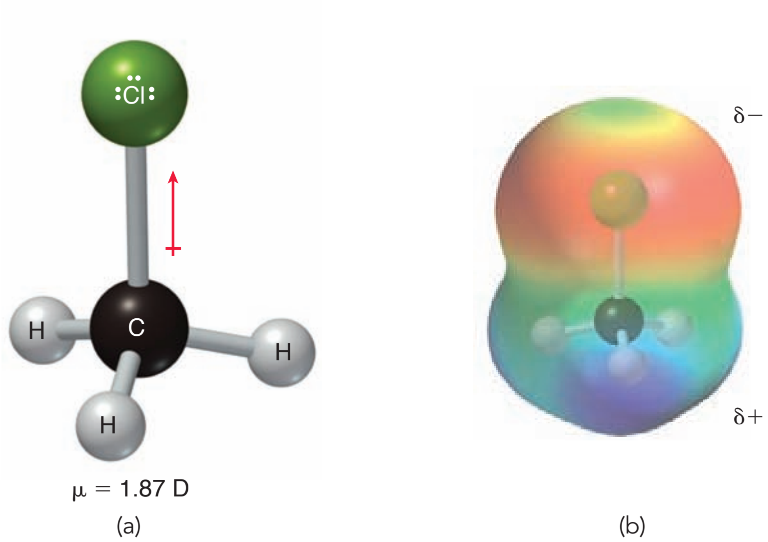


FIGURE 1.44
(a) Ball-and-stick model of chloromethane showing the dipole moment.
(b) An electrostatic potential map of chloromethane.

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 1.772×10^{-8} cm, and an electron has a charge of 4.80×10^{-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:

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

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 20-22 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 μ (D)	PERCENT IONIC CHARACTER
C—O	1.41	0.7 D	$\frac{(0.7 \times 10^{-18}\ \text{esu} \cdot \text{cm})}{(4.80 \times 10^{-10}\ \text{esu})\ (1.41 \times 10^{-8}\ \text{cm})} \times 100\% = \boxed{10\%}$
O—H	0.96	1.5 D	$\frac{(1.5 \times 10^{-18}\ \text{esu} \cdot \text{cm})}{(4.80 \times 10^{-10}\ \text{esu})\ (0.96 \times 10^{-8}\ \text{cm})} \times 100\% = \boxed{33\%}$
C═O	1.227	2.4 D	$\frac{(2.4 \times 10^{-18}\ \text{esu} \cdot \text{cm})}{(4.80 \times 10^{-10}\ \text{esu})\ (1.23 \times 10^{-8}\ \text{cm})} \times 100\% = \boxed{41\%}$

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 1.45). 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.

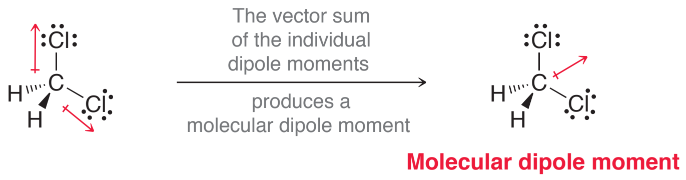


FIGURE 1.45
The molecular dipole moment of dichloromethane is the net sum of all dipole moments in the compound.

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. Common examples are ammonia and water (Figure 1.46).

FIGURE 1.46
The net dipole moments of ammonia and water.

In this way, the lone pairs contribute significantly to the magnitude of the molecular dipole moment, although they do not contribute to its direction. That is, the direction of the molecular dipole moment would be the same with or without the contribution of the lone pairs.

Table 1.5 shows experimentally observed molecular dipole moments (at 20°C) for several common solvents. Notice that carbon tetrachloride (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 1.47) demonstrates that we must take geometry into account when assessing molecular dipole moments.

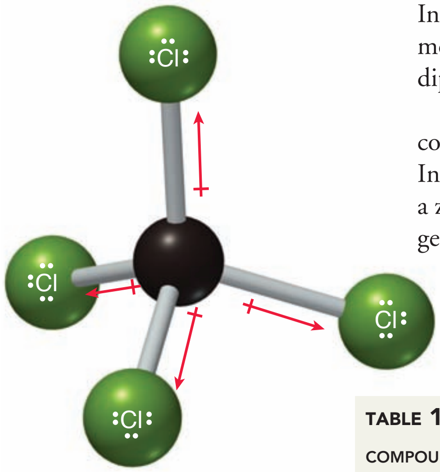
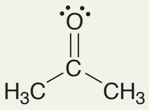
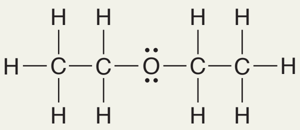
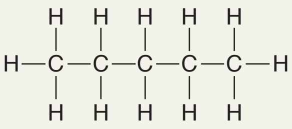
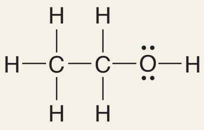


FIGURE 1.47
A ball-and-stick model of carbon tetrachloride. The individual dipole moments cancel to give a zero net dipole moment.

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

COMPOUND	STRUCTURE	DIPOLE MOMENT	COMPOUND	STRUCTURE	DIPOLE MOMENT
Methanol	CH_3OH	2.87 D	Ammonia	$:NH_3$	1.47 D
Acetone		2.69 D	Diethyl ether		1.15 D
Chloromethane	CH_3Cl	1.87 D	Methylene chloride	CH_2Cl_2	1.14 D
Water	H_2O	1.85 D	Pentane		0 D
Ethanol		1.66 D	Carbon tetrachloride	CCl_4	0 D

SKILLBUILDER

1.9 IDENTIFYING THE PRESENCE OF MOLECULAR DIPOLE MOMENTS

LEARN the skill

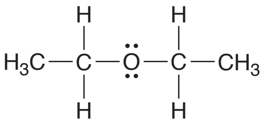
Identify whether each of the following compounds exhibits a molecular dipole moment. If so, indicate the direction of the net molecular dipole moment:

(a) $CH_3CH_2OCH_2CH_3$ (b) CO_2

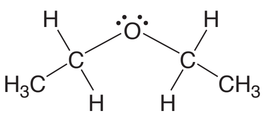
SOLUTION

(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:

STEP 1 Predict the molecular geometry.



Linear



Bent

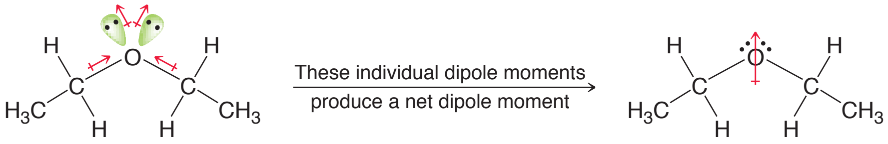
To make this determination, we use the three-step method from the previous section:

1. The steric number is 4.
2. Therefore, the hybridization state must be sp^3, and the arrangement of electron pairs must be tetrahedral.
3. Ignore the lone pairs, and the oxygen has a 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:

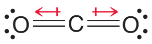
STEP 2
Identify the direction of all dipole moments.

STEP 3
Draw the net dipole moment.



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

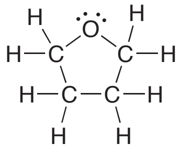
(b) Carbon dioxide (CO_2) has two C═O bonds, each of which exhibits a dipole moment. In order to determine whether the individual dipole moments cancel each other completely, we must first predict the molecular geometry. We apply our three-step method: the steric number is 2, the hybridization state is *sp*, and the compound has a linear geometry. As a result, we expect the dipole moments to fully cancel each other:

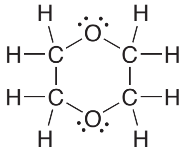


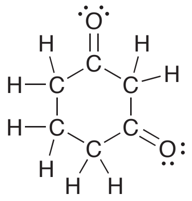
In a similar way, the dipole moments associated with the lone pairs also cancel each other, and therefore CO_2 does not have a net molecular dipole moment.

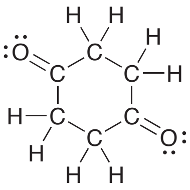
PRACTICE the skill **1.29** Identify whether each of the following compounds exhibits a molecular dipole moment. For compounds that do, indicate the direction of the net molecular dipole moment:

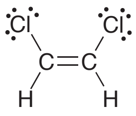
(a) $CHCl_3$ (b) CH_3OCH_3 (c) NH_3 (d) CCl_2Br_2

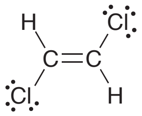
(e) 

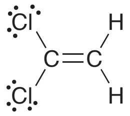
(f) 

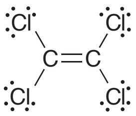
(g) 

(h) 

(i) 

(j) 

(k) 

(l) 

APPLY the skill **1.30** Which of the following compounds has the larger dipole moment? Explain your choice:

$CHCl_3$ or $CBrCl_3$

1.31 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.

need more **PRACTICE?** **Try Problems 1.37, 1.40, 1.43, 1.61, 1.62**

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 1.48).

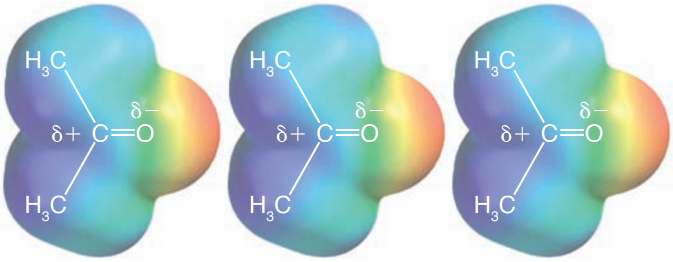
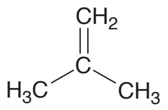
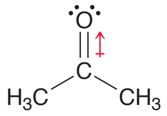


FIGURE 1.48 In solids, molecules align themselves so that their dipole moments experience attractive forces.

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 then 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
Melting point = −140.3°C
Boiling point = −6.9°C



Acetone
Melting point = −94.9°C
Boiling point = 56.3°C

Isobutylene lacks a significant dipole moment, but acetone does have a 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, the hydrogen atom will bear a partial positive charge (δ+) as a result of induction. This δ+ can then interact with a lone pair from an electronegative atom of another molecule. This can be illustrated with water or ammonia (Figure 1.49). This attractive interac-

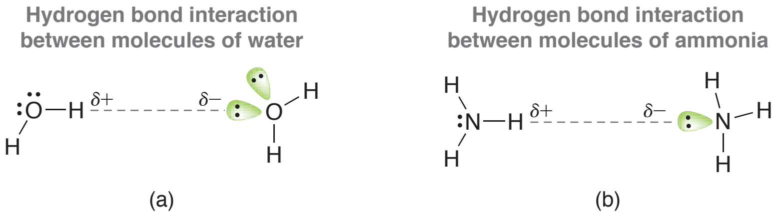


FIGURE 1.49 (a) Hydrogen bonding between molecules of water. (b) Hydrogen bonding between molecules of ammonia.

tion can occur with any **protic** compound, that is, any compound that has a proton connected to an electronegative atom. Ethanol, for example, exhibits the same kind of attractive interaction (Figure 1.50).

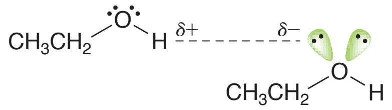
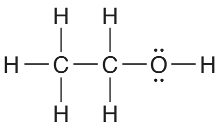
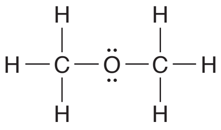


FIGURE 1.50
Hydrogen bonding between molecules of ethanol.

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:

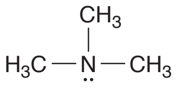

$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\ddot{\underset{..}{O}}-H$

Ethanol
Boiling point = 78.4°C

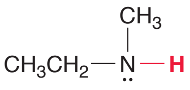

$H-\underset{H}{\overset{H}{C}}-\ddot{\underset{..}{O}}-\underset{H}{\overset{H}{C}}-H$

Methoxymethane
Boiling point = −23°C

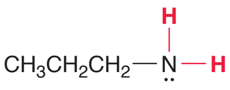
These compounds have the same molecular formula, but they have very different boiling points. Ethanol experiences intermolecular hydrogen bonding, giving rise to a very high boiling point. Methoxymethane does not experience intermolecular hydrogen bonding, giving rise to a relatively lower boiling point.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


$H_3C-\underset{..}{\overset{CH_3}{N}}-CH_3$

Trimethylamine
Boiling point = 3.5°C


$CH_3CH_2-\underset{..}{\overset{CH_3}{N}}-H$

Ethylmethylamine
Boiling point = 37°C

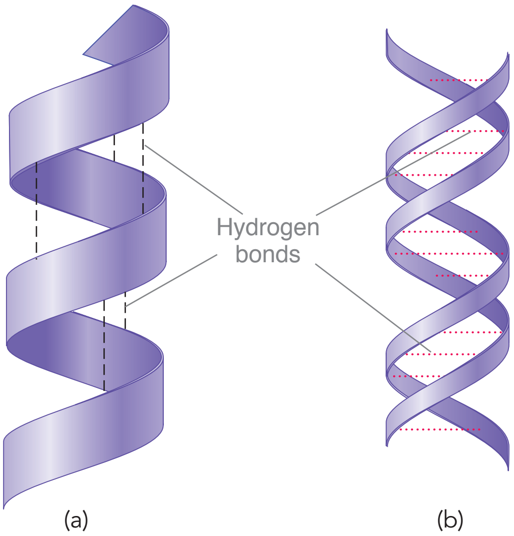

$CH_3CH_2CH_2-\underset{..}{\overset{H}{N}}-H$

Propylamine
Boiling point = 49°C

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 1.51a). 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 1.51b). 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



(a)

(b)

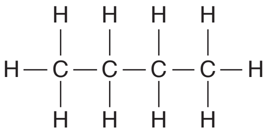
FIGURE 1.51
(a) An alpha helix of a protein.
(b) The double helix in DNA.

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

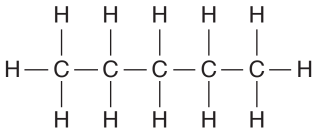
helix, in which the hydrogen-bonding interactions appear *as if* they were actually bonds. Nevertheless, it is relatively easy to "unzip" the double helix and retrieve the individual strands.

Fleeting Dipole-Dipole Interactions

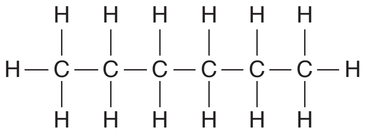
Some compounds have no permanent dipole moments, and yet analysis of boiling points indicates that they must have fairly strong intermolecular attractions. To illustrate this point, consider the following compounds:



Butane
(C_4H_{10})
Boiling point = 0°C



Pentane
(C_5H_{12})
Boiling point = 36°C



Hexane
(C_6H_{14})
Boiling point = 69°C

LOOKING AHEAD
Hydrocarbons will be discussed in more detail in Chapters 4, 17, and 18.

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 mol-

PRACTICALLY SPEAKING

Biomimicry and Gecko Feet

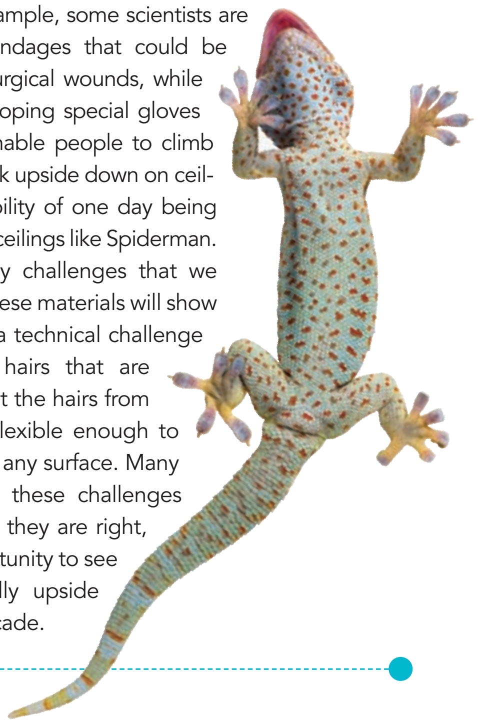
The term biomimicry describes the notion that scientists often draw creative inspiration from studying nature. By investigating some of nature's processes, it is possible to mimic those processes and to develop new technology. One such example is based on the way that geckos can scurry up walls and along 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.



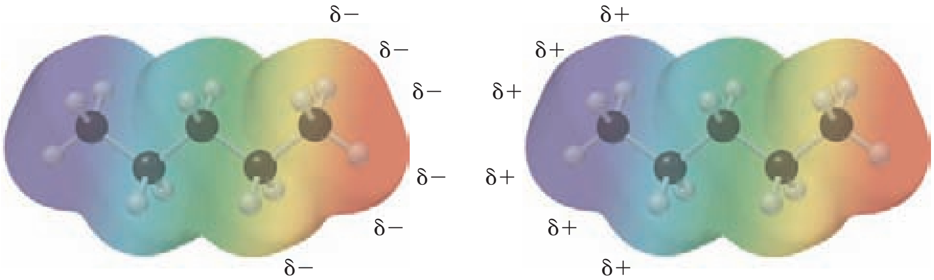
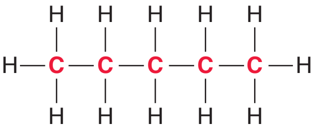


FIGURE 1.52
The fleeting attractive forces between two molecules of pentane.

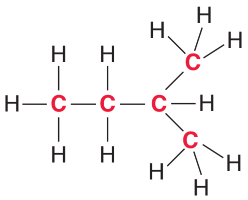
ecules (Figure 1.52). These attractive forces are called **London dispersion forces,** named after German-American physicist Fritz London. Large hydrocarbons have more surface area than smaller hydrocarbons and therefore experience these attractive forces to a larger extent.

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.

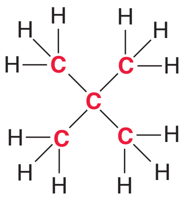
A branched hydrocarbon generally has a smaller surface area than its corresponding straight-chain isomer, and therefore, branching causes a decrease in boiling point. This trend can be seen by comparing the following constitutional isomers of C_5H_{12}:



Pentane
Boiling point = 36°C

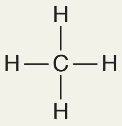
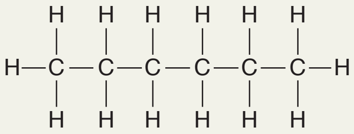
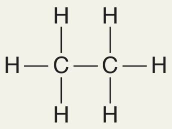
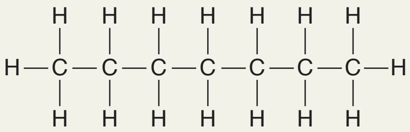
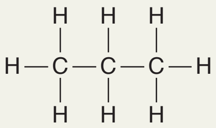
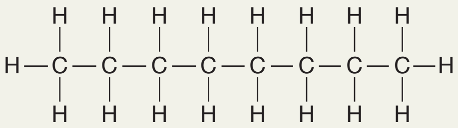
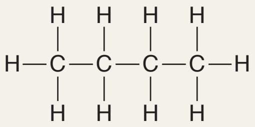
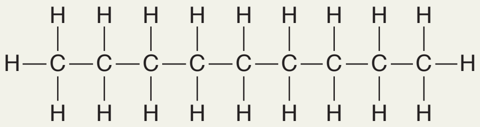
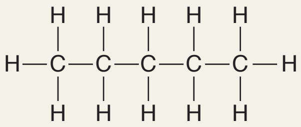
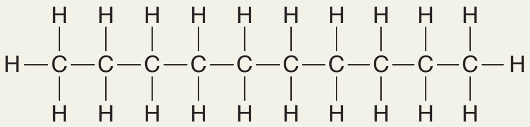


2-Methylbutane
Boiling point = 28°C



2,2-Dimethylpropane
Boiling point = 10°C

TABLE 1.6 BOILING POINTS FOR HYDROCARBONS OF INCREASING MOLECULAR WEIGHT

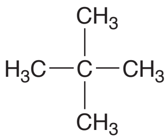
STRUCTURE	BOILING POINT (°C)	STRUCTURE	BOILING POINT (°C)
	−164		69
	−89		98
	−42		126
	0		151
	36		174

SKILLBUILDER

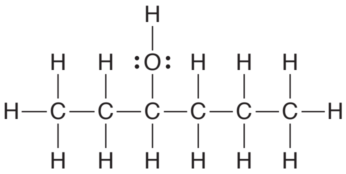
1.10 PREDICTING PHYSICAL PROPERTIES OF COMPOUNDS BASED ON THEIR MOLECULAR STRUCTURE

LEARN the skill

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



Neopentane



3-Hexanol

SOLUTION

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

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.

1. Are there any dipole-dipole interactions in either compound?

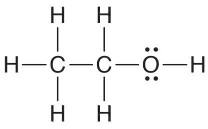
2. Will either compound form hydrogen bonds?

3a. How many carbon atoms are in each compound?

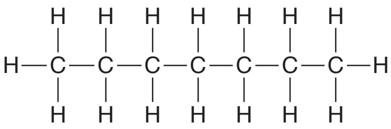
3b. How much branching is in each compound?

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.

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

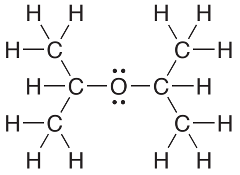


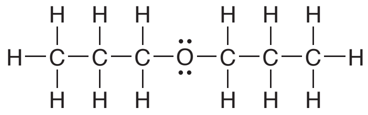
Heptane

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.

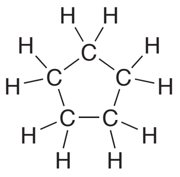
PRACTICE the skill **1.32** For each of the following pairs of compounds, identify the higher boiling compound and justify your choice:

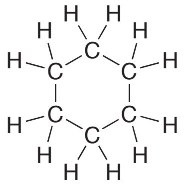
(a)



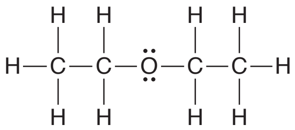


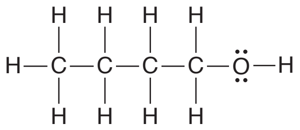
(b)



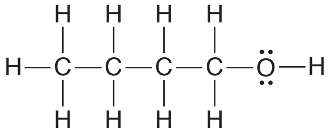


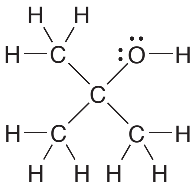
(c)



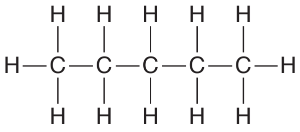


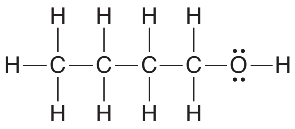
(d)

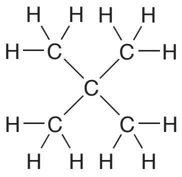


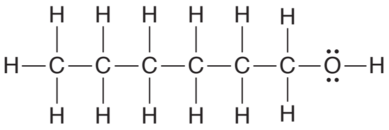


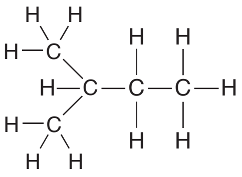
APPLY the skill **1.33** Arrange the following compounds in order of increasing boiling point:









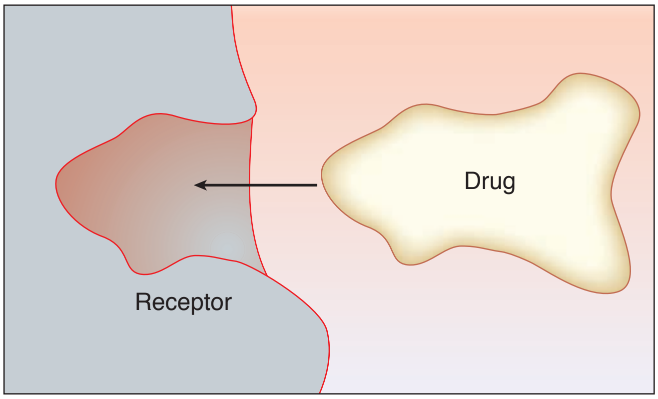


need more **PRACTICE?** **Try Problems 1.52, 1.53, 1.60**

MEDICALLYSPEAKING

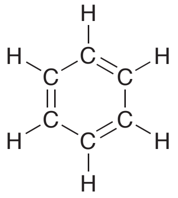
Drug-Receptor Interactions

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:



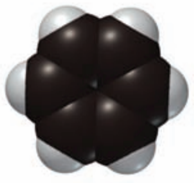
Initially, this mechanism was considered to work much like a lock and key. That is, a drug molecule would function as a key, either fitting or not fitting into a particular receptor. Extensive research on drug-receptor interactions has forced us to modify this simple lock-and-key model. It is now understood 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.

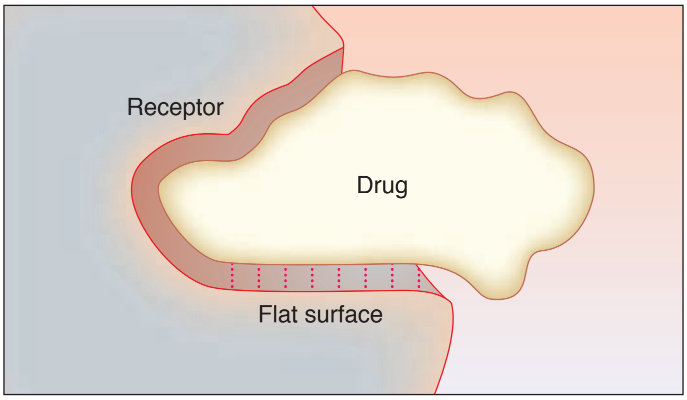


Benzene

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 1.53).

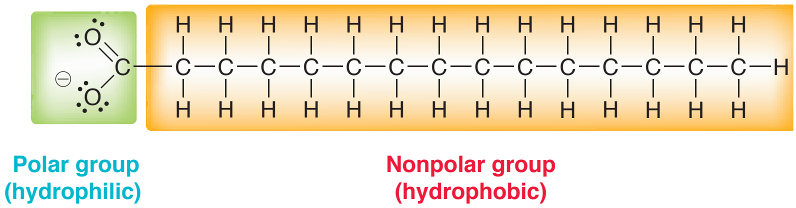


FIGURE 1.53
The hydrophilic and hydrophobic ends of a soap molecule.

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 1.54).

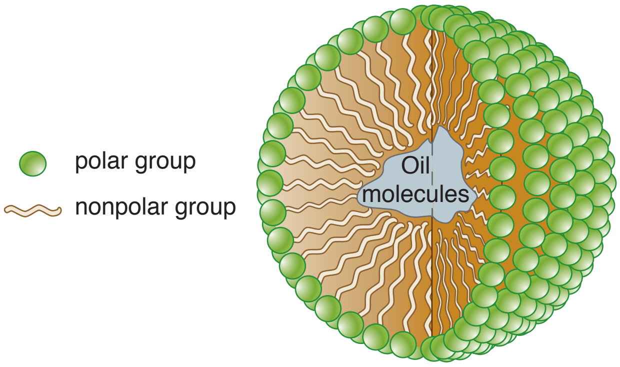
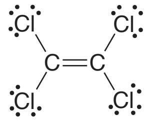


FIGURE 1.54
A micelle is formed when the hydrophobic tails of soap molecules surround the nonpolar oil molecules.

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.



Tetrachloroethylene

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.
- The predictable number of bonds usually formed by an atom of an element is its **valence**. 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** (δ-). **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** (ψ), where ψ^2 represents the probability of finding an electron in a particular location.
- **Atomic orbitals** are represented visually by generating three-dimensional plots of ψ^2; nodes indicate that the value of ψ 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** (σ) **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 orbita**l, 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 (π) bond. The carbon atoms of ethylene are connected via a σ bond, resulting from the overlap of sp^2 hybridized atomic orbitals, and via a π 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 σ bond, resulting from overlapping *sp* orbitals, and two π 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 σ 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 tetrahedral arrangement of orbitals indicates ***sp*^{3} hybridization** (steric number 4). A compound's geometry depends on the number of lone pairs and can be tetrahedral, trigonal pyramidal, or bent.
- A trigonal planar arrangement of orbitals indicates ***sp*^{2} hybridization** (steric number 3); however, the geometry may be bent, depending on the number of lone pairs.
- Linear geometry indicates ***sp* hybridization** (steric number 2).

SECTION 1.11

- **Dipole moments** (μ) 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.

KEY TERMINOLOGY

antibonding MO	17
atomic orbitals	13
Aufbau principle	14
bent	26
bonding MO	17
constitution	3
constitutional isomers	3
constructive interference	16
covalent bond	5
debye	30
degenerate orbitals	14
destructive interference	16
dipole-dipole interactions	34
dipole moment	30
divalent	3
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electrostatic potential maps	12
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HOMO	18
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sigma (σ) bond	16
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***sp*^{3}-hybridized orbitals**	19
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tetravalent	3
trigonal planar	27
trigonal pyramidal	26
trivalent	3
valence	3
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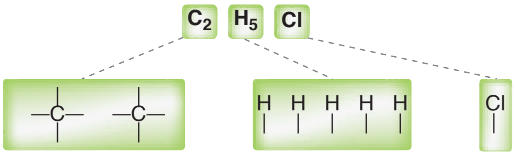
valence electrons	5
VSEPR theory	25
wave equation	12
wavefunction	12

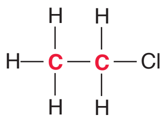
SKILLBUILDER REVIEW

1.1 DETERMINING THE CONSTITUTION OF SMALL MOLECULES

STEP 1 Determine the valency of each atom in the compound.



STEP 2 Determine how the atoms are connected. Atoms with highest valency should be placed at the center, and monovalent atoms should be placed at the periphery.



Try Problems 1.1–1.4, 1.34, 1.46, 1.47, 1.54.

1.2 DRAWING THE LEWIS DOT STRUCTURE OF AN ATOM

STEP 1 Determine the number of valence electrons.

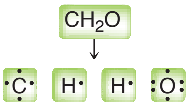
STEP 2 Place one electron by itself on each side of the atom.

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

Try Problems 1.5–1.9.

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.

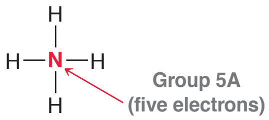
STEP 3 Connect hydrogen atoms.

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

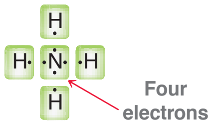
Try Problems 1.10–1.12, 1.35, 1.38, 1.42.

1.4 CALCULATING FORMAL CHARGE

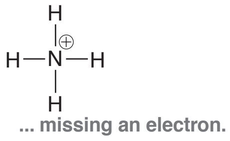
STEP 1 Determine appropriate number of valence electrons.



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



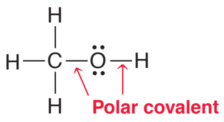
STEP 3 Assign a formal charge.



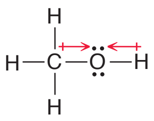
Try Problems 1.13, 1.14, 1.41.

1.5 LOCATING PARTIAL CHARGES

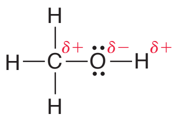
STEP 1 Identify all polar covalent bonds.



STEP 2 Determine the direction of each dipole.



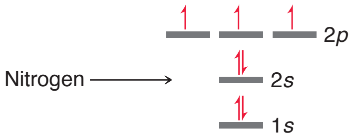
STEP 3 Indicate location of partial charges.



Try Problems 1.15, 1.16, 1.36, 1.37, 1.48, 1.57.

1.6 IDENTIFYING ELECTRON CONFIGURATIONS

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

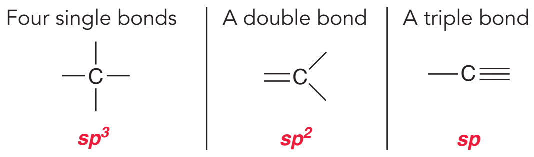


STEP 2 Summarize using the following notation:

$1s^22s^22p^3$

Try Problems 1.17, 1.18, 1.44.

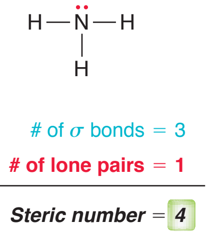
1.7 IDENTIFYING HYBRIDIZATION STATES



Try Problems 1.22, 1.23, 1.55, 1.56, 1.58.

1.8 PREDICTING GEOMETRY

STEP 1 Determine the steric number by adding the number of σ bonds and lone pairs.



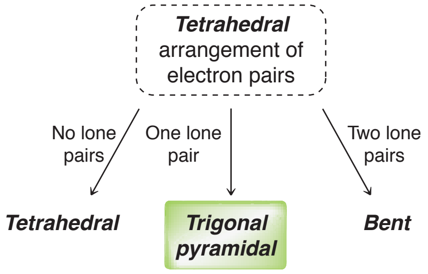
STEP 2 Use steric number to determine hybridization state and electronic geometry.

4 ⟶ sp^3 ⟶ Tetrahedral

3 ⟶ sp^2 ⟶ Trigonal planar

2 ⟶ sp ⟶ Linear

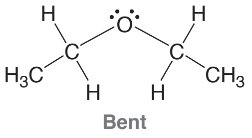
STEP 3 Ignore lone pairs and describe geometry.



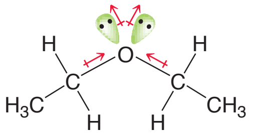
Try Problems 1.25–1.28, 1.39–1.41, 1.50, 1.55, 1.56, 1.58.

1.9 IDENTIFYING MOLECULAR DIPOLE MOMENTS

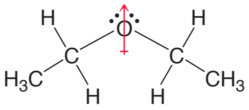
STEP 1 Predict geometry



STEP 2 Identify direction of all dipole moments.



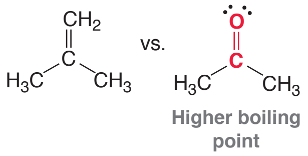
STEP 3 Draw net dipole moment.



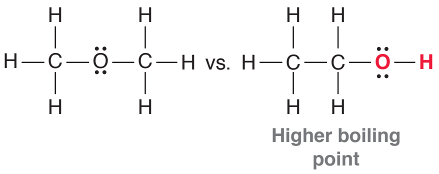
Try Problems 1.29–1.31, 1.37, 1.40, 1.43, 1.61, 1.62.

1.10 PREDICTING PHYSICAL PROPERTIES

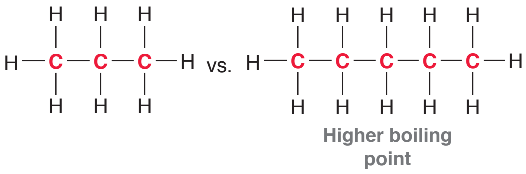
STEP 1 Identify dipole-dipole interactions.



STEP 2 Identify H-bonding interactions.



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



Try Problems 1.32, 1.33, 1.52, 1.53, 1.60.

PRACTICE PROBLEMS

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

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

(a) C_4H_{10} (b) C_5H_{12} (c) C_6H_{14}

(d) C_2H_5Cl (e) $C_2H_4Cl_2$ (f) $C_2H_3Cl_3$

1.35 Draw structures for all constitutional isomers with the molecular formula C_4H_8 that have:

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

1.36 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) H_2O (d) CH_4O

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

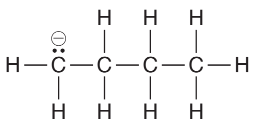
(a) NaBr or HBr (b) BrCl or FCl

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

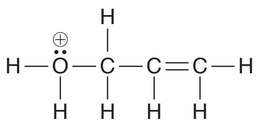
(a) CH_3CH_2OH (b) CH_3CN

1.39 Predict the geometry of each atom except hydrogen in the compounds below:

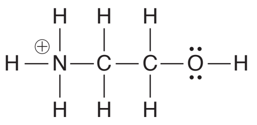
(a)



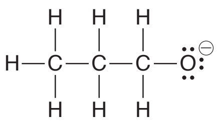
(b)



(c)



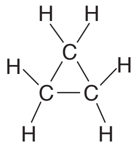
(d)



1.40 Draw a Lewis structure for a compound with molecular formula $C_4H_{11}N$ 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 $AlBr_4^-$ and determine its geometry.

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



Cyclopropane

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

(a) CH_4 (b) NH_3 (c) H_2O

(d) CO_2 (e) CCl_4 (f) CH_2Br_2

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

(a) $1s^22s^22p^4$ (b) $1s^22s^22p^5$ (c) $1s^22s^22p^2$

(d) $1s^22s^22p^3$ (e) $1s^22s^22p^63s^23p^5$

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

(a) NaBr (b) NaOH (c) $NaOCH_3$

(d) CH_3OH (e) CH_2O

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

(a) C_2H_6O (b) $C_2H_6O_2$ (b) $C_2H_4Br_2$

1.47 Draw structures for any five constitutional isomers with molecular formula $C_2H_6O_3$.

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

(a) C—O (b) C—Mg (c) C—N (d) C—Li

(e) C—Cl (f) C—H (g) O—H (h) N—H

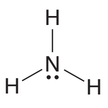
1.49 Predict the bond angles for all bonds in the following compounds:

(a) CH_3CH_2OH (b) CH_2O (c) C_2H_4 (d) C_2H_2

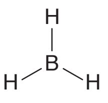
(e) CH_3OCH_3 (f) CH_3NH_2 (g) C_3H_8 (h) CH_3CN

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

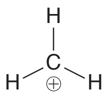
(a)



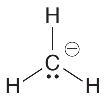
(b)



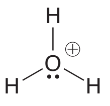
(c)



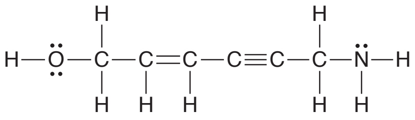
(d)



(e)



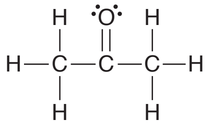
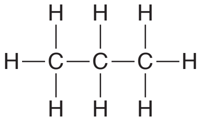
1.51 Count the total number of σ bonds and π bonds in the compound below:



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

(a) $CH_3CH_2CH_2OCH_3$ or $CH_3CH_2CH_2CH_2OH$

(b) $CH_3CH_2CH_2CH_3$ or $CH_3CH_2CH_2CH_2CH_3$

(c)  or 

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

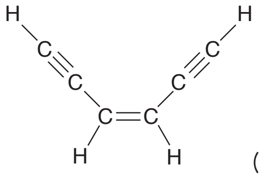
(a) CH_3CH_2OH (b) CH_2O (c) C_2H_4 (d) C_2H_2

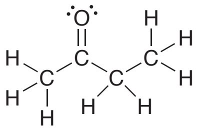
(e) CH_3OCH_3 (f) CH_3NH_2 (g) C_3H_8 (h) NH_3

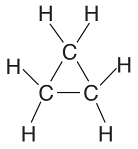
1.54 For each case below, identify the most likely value for x:

(a) BH_x (b) CH_x (c) NH_x (d) CH_2Cl_x

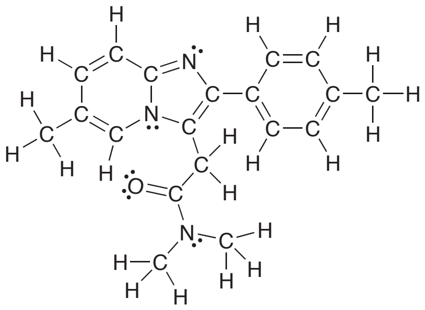
1.55 Identify the hybridization state and geometry of each carbon atom in the following compounds:

(a) 

(b) 

(c) 

1.56 Ambien^{TM} 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:

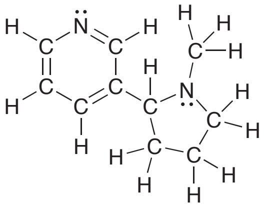


Zolpidem
(Ambien^{TM})

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

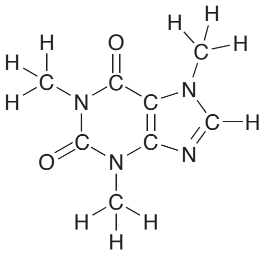
(a) $CH_3OCH_2CH_2NH_2$ (b) CH_2ClCH_2F (c) CH_3Li

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

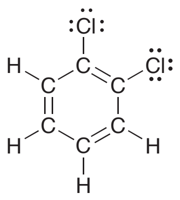
1.59 Below is the structure of caffeine, but its lone pairs are not shown. Identify the location of all lone pairs in this compound:

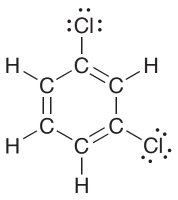


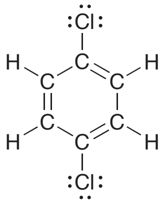
Caffeine

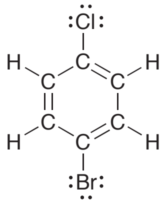
1.60 There are two different compounds with molecular formula C_2H_6O. One of these isomers has a much higher boiling point than the other. Explain why.

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

(a) 

(b) 

(c) 

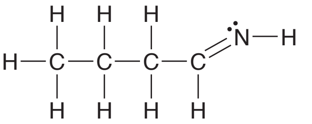
(d) 

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.

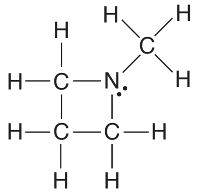
INTEGRATED PROBLEMS

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

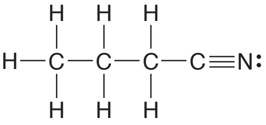
(a) Which two compounds are constitutional isomers?



Compound A



Compound B



Compound C

(b) Which compound contains a nitrogen atom with trigonal pyramidal geometry?

(c) Identify the compound with the greatest number of σ bonds.

(d) Identify the compound with the fewest number of σ bonds.

(e) Which compound contains more than one π bond?

(f) Which compound contains an sp^2-hybridized carbon atom?

(g) Which compound contains only sp^3-hybridized atoms (in addition to hydrogen atoms)?

(h) Which compound do you predict will have the highest boiling point? Explain.

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

(a) All six carbon atoms are sp^2 hybridized.

(b) 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).

(c) There is a ring, and all of the carbon atoms are sp^3 hybridized.

(d) 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).

CHALLENGE PROBLEMS

1.65 Draw all constitutional isomers with molecular formula C_5H_{10} that possess one π bond.

1.66 With current spectroscopic techniques (discussed in Chapters 15–17), 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 π 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.)

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