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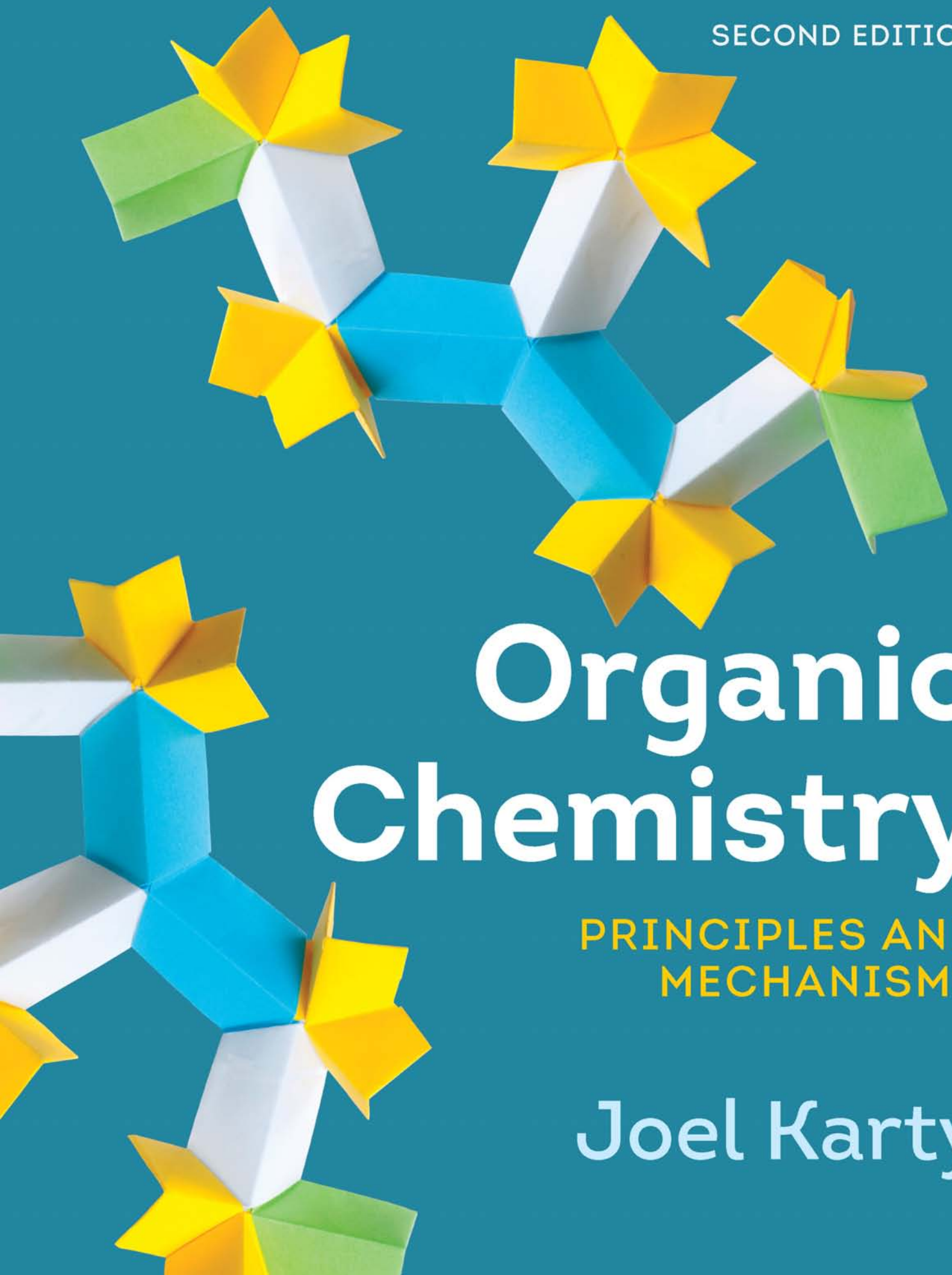


Organic Chemistry

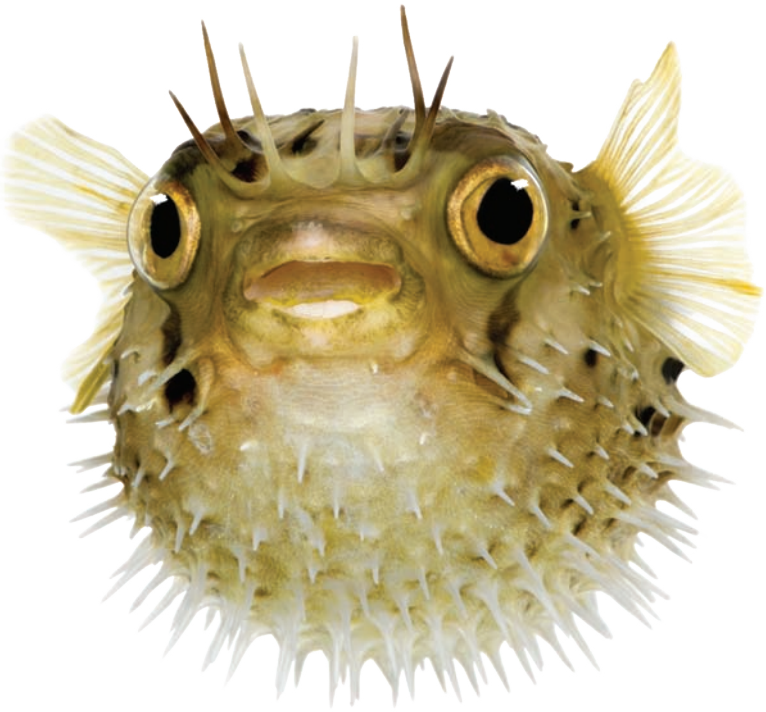
PRINCIPLES AND MECHANISMS

Joel Karty

Organic Chemistry
Principles and Mechanisms

SECOND EDITION

Joel M. Karty
Elon University



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About the Author

JOEL KARTY earned his B.S. in chemistry at the University of Puget Sound and his Ph.D. at Stanford University. He joined the faculty of Elon University in 2001, where he currently holds the rank of full professor. He teaches primarily the organic chemistry sequence and also teaches general chemistry. In the summer, Joel teaches at the Summer Biomedical Sciences Institute through the Duke University Medical Center. His research interests include investigating the roles of resonance and inductive effects in fundamental chemical systems and studying the mechanism of pattern formation in Liesegang reactions. He has written a very successful student supplement, *Get Ready for Organic Chemistry*, Second Edition (formerly called *The Nuts and Bolts of Organic Chemistry*).

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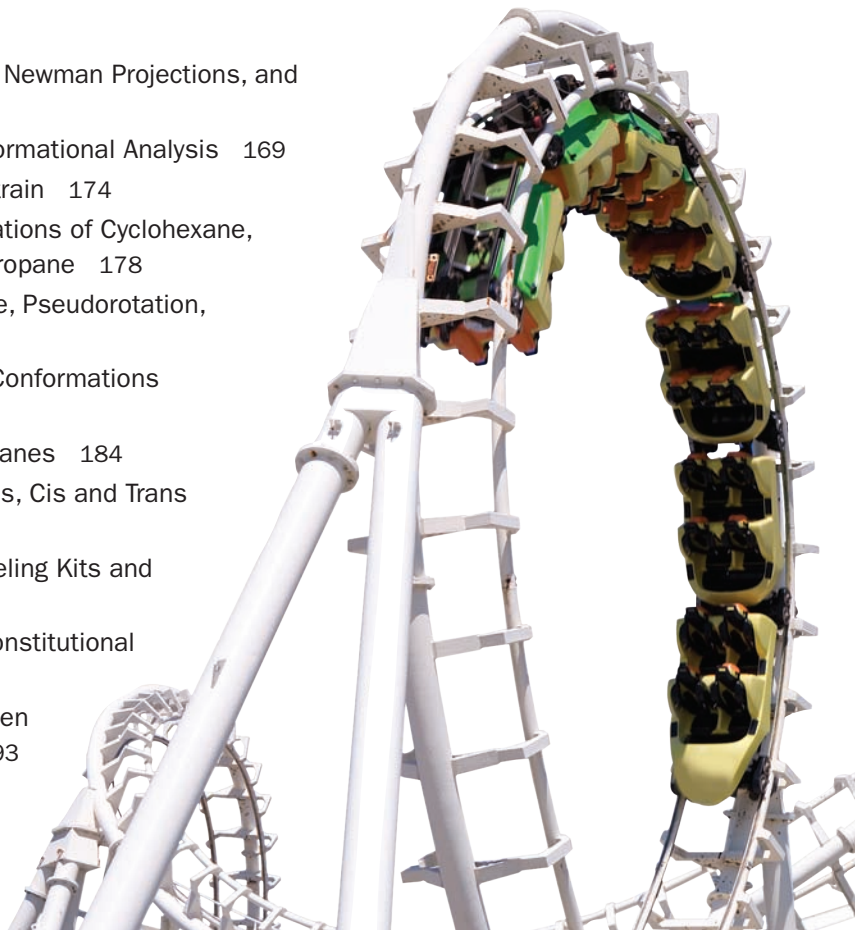

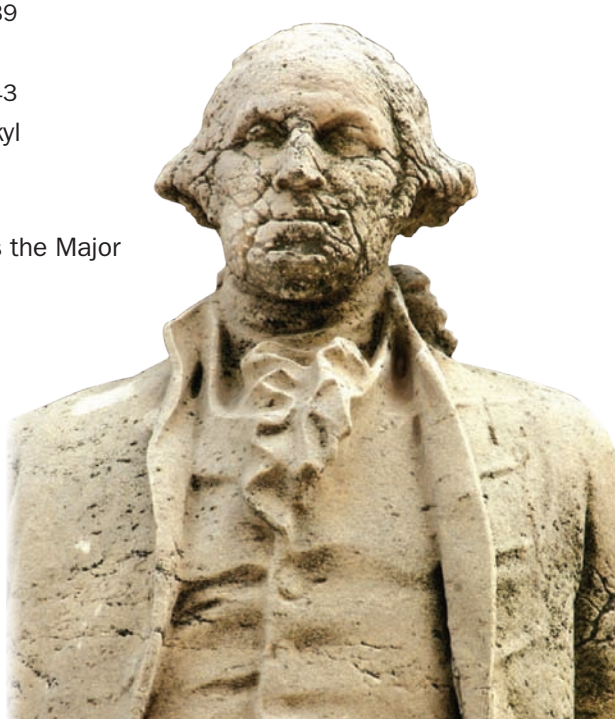

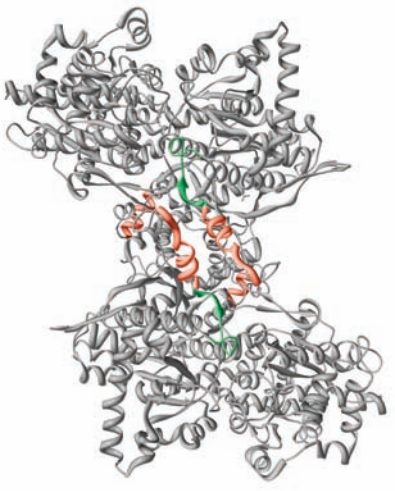

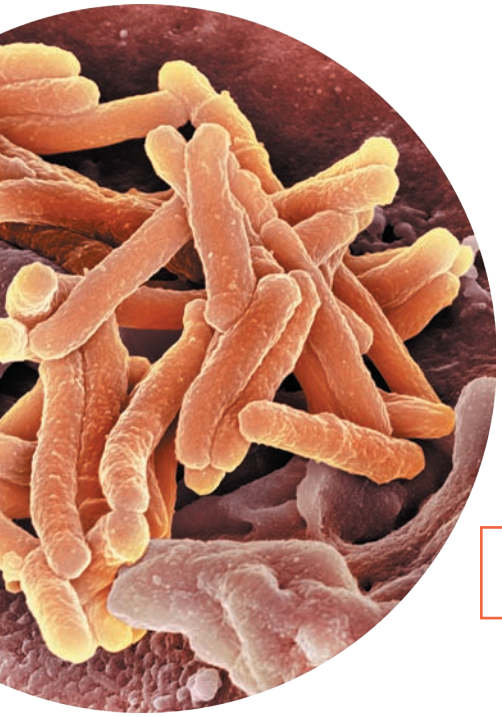

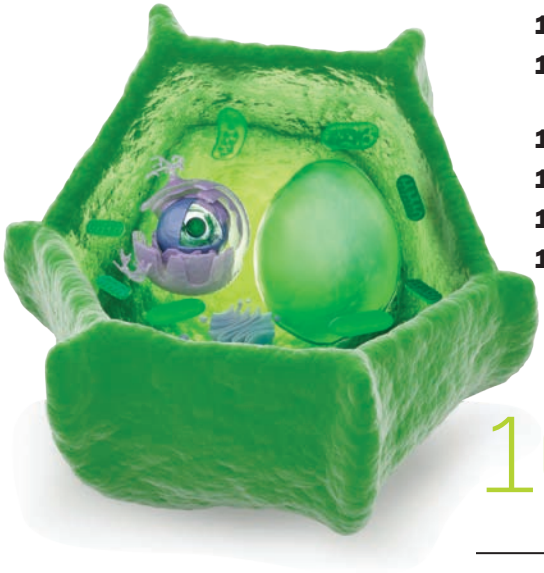

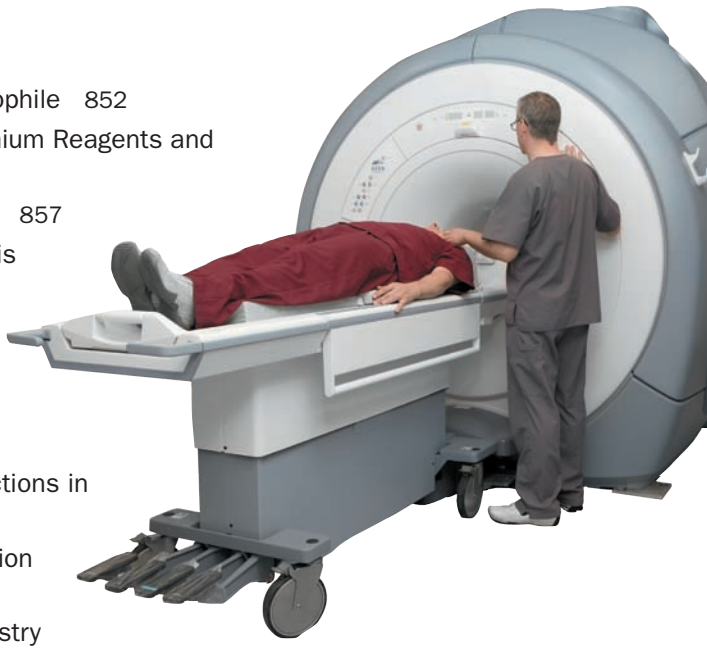

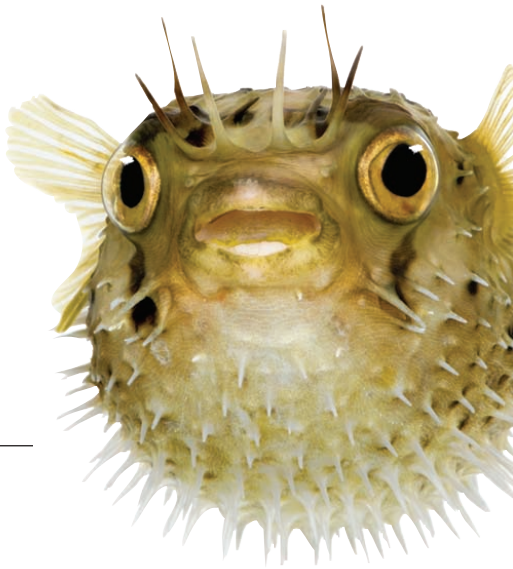

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Preface

Focused on the Student, Organized by Mechanism

When an organic reaction is presented to a novice, only the structural differences between the reactants and products are immediately apparent. Students tend to see only *what* happens, such as the transformation of one functional group into another, changes in connectivity, and aspects of stereochemistry. It should therefore not be surprising that students, when presented reactions, are tempted to commit the reactions to memory. But there are far too many reactions and accompanying details for memorization to work in organic chemistry.

This is where mechanisms come into play. Mechanisms allow us to understand the sequences of elementary steps—the step-by-step pathways—that convert the reactants to products, so we can see *how* and *why* reactions take place as they do. Moreover, the mechanisms that describe the large number of reactions in the course are constructed from just a handful of elementary steps, so mechanisms allow us to see *similarities* among reactions that are not otherwise apparent. In other words, mechanisms actually *simplify* organic chemistry. Thus, teaching students mechanisms—enabling students to understand and simplify organic chemistry—is an enormous key to success in the course.

At the outset of my teaching career, I fully appreciated the importance of mechanisms, so during my first couple years of teaching, I emphasized mechanisms *very* heavily. I did so under a functional group organization where reactions are pulled together according to the functional groups that react. That is the organization under which I learned organic chemistry, and it is also the way that most organic chemistry textbooks are organized. Despite my best efforts, the majority of my students struggled with even the basics of mechanisms and, consequently, turned to flash cards as their primary study tool. They tried to memorize their way through the course, which made matters worse.

I began to wonder what impact the *organization*—an organization according to functional group—had on deterring my students from mechanisms. I had good reason to be concerned because, as I alluded to earlier, functional groups tend to convey *what*, whereas mechanisms convey *how* and *why*. What kinds of mixed messages were my students receiving when I was heavily emphasizing mechanisms, while the organization of the material was giving priority to functional groups? To probe that question, I made a big change to my teaching.

The third year I taught organic chemistry, I rearranged the material to pull together reactions that had the same or similar mechanisms—that is, I taught under a *mechanistic organization*. I made no other changes that year; the course content, course structure, and my teaching style all remained the same. I even taught out of the same textbook. But that year I saw dramatic improvements in my students' mastery of mechanisms.[1] Students had *control* over the material, which proved to be a tremendous motivator. They were better able to solve different kinds of problems with confidence. Ultimately, I saw significant

[1]Bowman, B. G.; Karty, J. M.; Gooch, G. Teaching a Modified Hendrickson, Cram and Hammond Curriculum in Organic Chemistry. *J. Chem. Educ.* **2007**, *84*, 1209.

improvements in student performance, morale, and retention. I was convinced that students benefit remarkably from learning under a mechanistic organization.

My goal in writing this book is to support instructors who are seeking what I was seeking: getting students to use mechanisms to learn organic chemistry in order to achieve better performances and to have better experiences in their organic courses. Using a functional group organization to achieve these outcomes can be an uphill battle because of the high priority that it inherently places on functional groups. This textbook, on the other hand, allows students to receive the same message from both their instructor and their textbook—a clear and consistent message that mechanisms are vital to success in the course.

A Closer Look: Why Is a Mechanistic Organization Better?

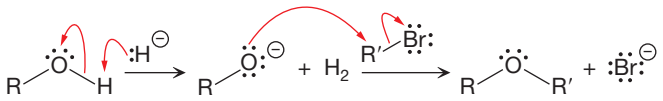
Consider what the novice sees when they begin a new *functional group chapter*. In an alcohols chapter, for example, students first learn how to recognize and name alcohols, then they study the physical properties of alcohols. Next, students might spend time on special spectroscopic characteristics of alcohols, after which they learn various routes that can be used to synthesize alcohols from other species. Finally, students move into the heart of the chapter: new reactions that alcohols undergo and the mechanisms that describe them. Within a particular functional group chapter, students find themselves bouncing among *several themes*.

Even within the discussion of new reactions and mechanisms that a particular functional group can undergo, students are typically faced with widely varying reaction types and mechanisms. Take again the example of alcohols. Students learn that alcohols can act as an acid or as a base; alcohols can act as nucleophiles to attack a saturated carbon in a substitution reaction, or to attack the carbon atom of a polar π bond in a nucleophilic addition reaction; protonated alcohols can act as electrophiles in an elimination reaction; and alcohols can undergo oxidation, too.

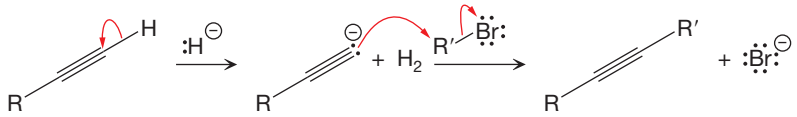
With the substantial jumping around that takes place within a particular functional group chapter, it is easy to see how students can become overwhelmed. Under a functional group organization, students don't receive intrinsic and clear guidance as to what they should focus on, not only within a particular functional group chapter, but also from one chapter to the next. Without clear guidance, and without substantial time for focus, students often see no choice but to memorize. And they will memorize what they perceive to be most important—predicting products of reactions, typically ignoring, or giving short shrift to, fundamental concepts and mechanisms.

Under the mechanistic organization in this book, students experience a *coherent story* of chemical reactivity. The story begins with molecular structure and energetics, and then guides students into reaction mechanisms through a few transitional chapters. Thereafter, students study how and why reactions take place as they do, focusing on one type of mechanism at a time. Ultimately, students learn how to intuitively use reactions in synthesis. In this manner, students have clear and consistent guidance as to what their focus should be on, both within a single chapter and throughout the entire book.

The *patterns* we, as experts, see become clear to students when they learn under this mechanistic organization. Consider the following four mechanisms:



(P-1)



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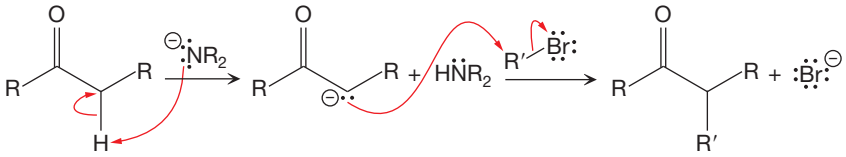
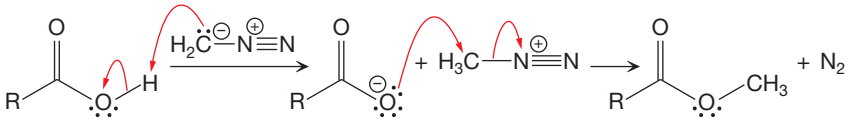


(P-3)



(P-4)

The mechanism in Equation P-1 is for a Williamson synthesis of an ether; the one in Equation P-2 is for an alkylation of a terminal alkyne; the one in Equation P-3 is for an alkylation of a ketone; and the one in Equation P-4 is for the conversion of a carboxylic acid to a methyl ester. In these four reactions, the reactants are an alcohol, an alkyne, a ketone, and a carboxylic acid. In a functional group organization, these reactions will be taught in *four separate chapters*. Because all four reaction mechanisms are identical—a deprotonation followed by an S_N2 step—all four reactions are taught in the *same* chapter in this book: Chapter 10.

Seeing these patterns early, students more naturally embrace mechanisms and use them when solving problems. Moreover, as students begin to see such patterns unfold in one chapter, they develop a better toolbox of mechanisms to draw on in subsequent chapters. Ultimately, students gain *confidence* in using mechanisms to predict what will happen and why. I believe this is vital to their success throughout the course and later on admission exams such as the MCAT.

Details about the Organization

Continuing with the success of the first edition, the book remains divided into three major parts:

Part I: Atomic and molecular structure

- Chapter 1: Atomic structure, Lewis structures and the covalent bond, and resonance theory, culminating in an introduction to functional groups
- Chapter 2: Aspects of three-dimensional geometry and its impacts on intermolecular forces
- Chapter 3: Structure in terms of hybridization and molecular orbital (MO) theory
- Chapters 4 and 5: Isomerism in its entirety, including constitutional isomerism, conformational isomerism, and stereoisomerism

Much of the material in Chapters 1–5 will be new to students, such as organic functional groups, protic and aprotic solvents, effective electronegativity, conformers and cyclohexane chair structures, and stereoisomers. Chapters 1–5 also contain a significant amount of material that students will recognize from general chemistry, such as electronic configurations, Lewis structures and resonance, intermolecular forces, VSEPR theory and hybridization, and constitutional isomers. Because most students do not retain everything they should from general chemistry, I have made the general chemistry topics in this textbook more extensive than in other textbooks. Knowing that this extended coverage is in the book, instructors should feel comfortable covering as much or as little of it as they see fit for their students.

Part II: Developing a toolbox for working with mechanisms

- Chapters 6 and 7: Ten common elementary steps of mechanisms
- Chapter 8: Beginnings of multistep mechanisms using S_N1 and E1 reactions as examples

Mechanisms are vital to succeeding in organic chemistry, but before tackling mechanisms, students must have the proper tools. Chapters 6–8 give students those tools, dealing with aspects of elementary steps in Chapters 6 and 7 before dealing with aspects of multistep mechanisms in Chapter 8. Therefore, the chapters in Part II act a transition from Part I to Part III, which deals more intently with reactions.

Chapter 7 is a particularly important part of this transition. Students learn how to work with elementary steps in Chapter 7 in a low-risk environment, where there are no demands to predict products. Thus, there is no pressure to memorize overall reactions. Furthermore, the fact that Chapter 7 brings together the 10 most common elementary steps—making up the mechanisms of the many hundreds of reactions students will encounter through Chapter 23—sends a strong message to students that mechanisms *simplify* organic chemistry. In turn, students take to heart from the outset that mechanisms are worthwhile to learn.

Part III: Major reaction types

- Chapters 9 and 10: Nucleophilic substitution and elimination
- Chapters 11 and 12: Electrophilic addition
- Chapters 17 and 18: Nucleophilic addition
- Chapters 20 and 21: Nucleophilic addition–elimination
- Chapters 22 and 23: Aromatic substitution
- Chapter 24: Diels–Alder reactions and other pericyclic reactions
- Chapter 25: Radical reactions
- Chapter 26: Polymerization

Several of these chapters come in pairs, where the first chapter is used to introduce key ideas about the reaction or mechanism and the second chapter explores the reaction or mechanism to greater depth and breadth.

Pairing the chapters this way provides flexibility. An instructor could teach all of the chapters in order. Alternatively, following the guidelines set by the American Chemical Society, an instructor could teach the first of each paired chapter in the first semester as part of "foundational" coursework. Then, the remaining chapters would represent "in-depth" coursework for the second semester. Teaching the chapters in this order would also allow an instructor to teach carbonyl chemistry in the first semester.

Interspersed in Part III are chapters dealing with multistep synthesis (Chapters 13 and 19), conjugation and aromaticity (Chapter 14), and spectroscopy (Chapters 15 and 16). The spectroscopy chapters are self-contained and can be taught earlier, at the instructor's discretion. They can even be taught separately in the laboratory. The spectroscopy chapters are movable like this because, with the mechanistic organization of the book, important aspects of spectroscopy are not integrated in reaction chapters like they typically are in a functional group text.

The two chapters devoted to multistep synthesis (Chapters 13 and 19), on the other hand, are strategically located. Chapter 13 appears after students have spent several chapters working with reactions. Having quite a few reactions under their belts, students can appreciate retrosynthetic analysis, as well as cataloging reactions as functional group transformations or reactions that alter the carbon skeleton. Moreover, Chapter 13 appears early enough so students can practice their skills devising multistep syntheses throughout the entire second half of the book; each subsequent chapter has multiple synthesis problems. Additionally, Chapter 13 is an excellent review of reactions students learned to that point in the book, so it could be taught at the end of the first semester as a capstone, or it could be taught at the beginning of the second semester to help jog students' memories in preparation for second semester.

Chapter 19 is delayed a few more chapters because it deals with content related to reactions from Chapter 18, including protecting groups and choosing carbon–carbon bond-forming reactions that result in the desired relative positioning of functional groups. The multistep synthesis topics in Chapter 19 are somewhat more challenging than the ones in Chapter 13, so whereas Chapter 13 should be covered in most mainstream courses, instructors can choose to cover only certain sections of Chapter 19.

I have found that treating multisynthesis in dedicated chapters makes it more meaningful to students. When I taught synthesis under a functional group organization, it became a distraction to the reactions that students were simultaneously learning. I also found that students often associated a synthetic strategy only with the functional group for which it was introduced. For example, when the idea of protecting groups is introduced in the ketones/aldehydes chapter of a textbook organized by functional group, students tended to associate protecting groups with ketones and aldehydes *only*. My dedicated synthesis chapters help students focus on synthesis without compromising their focus on reactions. Furthermore, synthesis strategies are discussed more holistically, so students can appreciate them in a much broader context rather than being applicable to just a single functional group.

Another major organizational feature of the book pertains to nomenclature. Nomenclature is separated out from the main chapters, in five relatively short interchapters—Interchapters A, B, C, E, and F. Separating nomenclature from the main chapters in this way removes distractions. It also allows students to focus on specific rules of nomenclature instead of specific compound classes. With each new nomenclature interchapter, the complexity of the material increases by applying the new rules to the ones introduced earlier.

The instructor has flexibility as to how to work with these nomenclature interchapters. They can be covered in lecture or easily assigned for self-study. They can be split over two semesters or could all be covered in the first semester. The locations of the interchapters in the book (i.e., immediately after Chapters 1, 3, 5, 7, and 9), however, should be taken as indicators as to the earliest that each interchapter should be assigned or taught. Covering a nomenclature interchapter substantially earlier than it appears in the book would expose students to compound classes well before those types of compounds are dealt with in the main chapters.

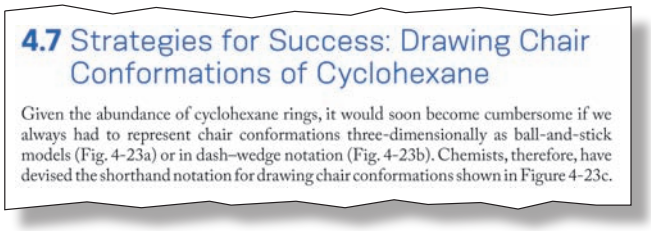
Finally, the application of MOs toward chemical reactions is separated from the main reaction chapters, and is presented, instead, as an optional, self-contained unit—Interchapter D. This interchapter appears just after Chapter 7, the overview of the 10 most common elementary steps. Each elementary step from Chapter 7 is revisited from the perspective of frontier MO theory. Because this interchapter is optional, chapters later in the book do not rely on coverage of this material.

Presenting this frontier MO theory material together in an optional unit, as I have done in Interchapter D in this book, offers two main advantages to students. First, it removes a potential distraction from the main reaction chapters and, being optional, instructors have the choice of not covering it at all. Another advantage comes from the fact that the MO pictures of all 10 common elementary steps appear together in the interchapter. Therefore, instructors who wish to cover this interchapter can expect their students to come away with a better understanding of the bigger picture of MO theory as it pertains to chemical reactions.

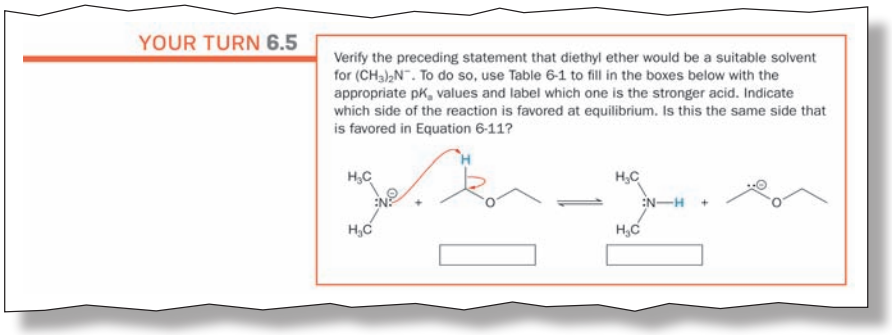
Focused on the Student

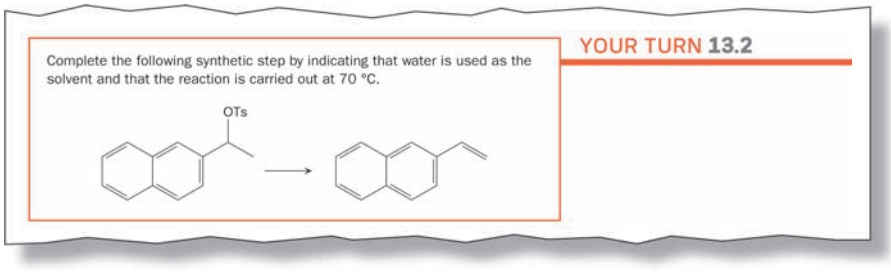
While the organization provides a coherent story, I've included pedagogy that promotes active learning and makes this book a better tool for students.

Strategies for Success. I wrote these sections to help students build specialized skills they need in this course. For example, Chapter 1 provides strategies for drawing all resonance structures of a given species, and sections in Chapters 2 and 3 are devoted to the importance of molecular modeling kits in working with the three-dimensional aspects of molecules and also with the different rotational characteristics of single and double bonds. In Chapter 4, students are shown step by step how to draw chair conformations of cyclohexane and how to draw all constitutional isomers of a given formula. Chapter 5 provides help with drawing mirror images of molecules. One Strategies for Success section in Chapter 6 helps students estimate pK_a values and another helps students rank acid and base strengths based only on their Lewis structures. In Chapter 14, I include a section that shows students how to use the Lewis structure to assess conjugation and aromaticity, and Chapter 16 has a section that teaches students the chemical distinction test for nuclear magnetic resonance.



Your Turn exercises. Getting students to read *actively* can be challenging, so I wrote the Your Turns in each chapter to motivate this type of behavior. Your Turns are basic exercises that ask students to either answer a question, look something up in a table, construct a molecule using a model kit, or interact with art in a figure or data in a plot. These exercises are also intended to be "reality checks" for students as they read. If a student cannot solve or answer a Your Turn exercise easily, then that student should interpret this as a signal to either reread the previous section(s) or seek help. Short answers to all Your Turns are provided in the back of the book and complete solutions to these exercises are provided in the *Study Guide and Solutions Manual*.





Consistent and effective problem-solving approach. Helping students become expert problem solvers, in this course and beyond, is one of my major goals. I have developed the Solved Problems in the book to train students how to approach a problem. Each Solved Problem is broken down into two parts: *Think* and *Solve*. In the Think part, students are provided a handful of guiding *questions* that I want them to be asking as they approach the problem. In the Solve part, those questions are answered and the problem is solved. This

mirrors the strategy I use to help students during office hours, and we have used these same steps for *every* problem in the *Study Guide and Solutions Manual* that accompanies the book.

Biochemistry and the MCAT. Most students taking organic chemistry are biology majors or are seeking a career in a health profession. They appreciate seeing how organic chemistry relates to their interests and look for ways in which this course will prepare them for the admissions exams (such as the MCAT) that may have a large impact on their future.

SOLVED PROBLEM 11.3

Predict the major product when indene is treated with HCl.

Think Which C═C double bond will undergo electrophilic addition? What are the *possible* products and the corresponding carbocation intermediates from which they are produced? Which carbocation intermediate is more stable?

Solve The rightmost C═C double bond is the one that will undergo electrophilic addition. The others make up a benzene ring and are much too stable to react under these conditions. The two possible products of HCl addition differ by which C atom gains the H^+ and which gains the Cl^-:

Rather than relegating biochemistry to the end of the book, I have placed self-contained Organic Chemistry of Biomolecules sections at the ends of several chapters, beginning with Chapter 1. The topics chosen for these sections cover many of the topics dealt with on the MCAT, which means that the Organic Chemistry of Biomolecules sections are not *in addition to* what students are expected to know for the MCAT; they are topics that students *should know* for the test. In even the earliest of chapters, students have the tools to start learning aspects of this traditional biochemistry coverage. More importantly, these sections provide reinforcement of topics. In each biomolecules section, the material is linked directly back to concepts encountered earlier in the chapter.

THE ORGANIC CHEMISTRY OF BIOMOLECULES

1.14 An Introduction to Proteins, Carbohydrates, and Nucleic Acids: Fundamental Building Blocks and Functional Groups

These Organic Chemistry of Biomolecules sections are both optional and flexible. Instructors can decide to cover only a few of these topics or none at all, and can do so either as they appear in the book or as special topics at the end of the second semester.

A range of interesting applications. In addition to the Organic Chemistry of Biomolecules sections, most chapters have two special interest boxes. These boxes apply a concept in the chapter to some depth toward a discovery or process that can have significant appeal to students, perhaps delving into a biochemical process or examining new and novel materials. In addition to reinforcing concepts from the chapter, these boxes are intended to provide *meaning* to what students are learning, and to motivate students to dig deeper.

In addition to these special interest boxes, several Connections boxes in each chapter provide glimpses into the everyday utility of molecules that students have just seen.

CONNECTIONS

4-Methylphenol, also called *para*-cresol, is one of the compounds responsible for the odor of pigs and is also found in human sweat. One of the main uses of 4-methylphenol is in the production of antioxidants.

New to the Second Edition

Organization of end-of-chapter problems. At the end of each chapter, problems are grouped by concept or section so students can easily identify the types of problems they need to work on. A set of Integrated Problems follows those sets of focused problems. These Integrated Problems require students to bring together major concepts from multiple sections within the chapter, or from multiple chapters, as they would on an exam. These problems also help students stay familiar with material from earlier in the book, thus reducing the time that students would need to spend separately for review. In addition to organizing problems this way, problems that relate to aspects of synthesis are labeled (SYN), so students and instructors can find those types of problem quickly.

More than 300 new problems. Based on user and reviewer feedback, several new problems have been added to each chapter to provide students even more opportunities to hone their problem-solving skills and to assess their mastery of the material. Some of these new problems are specifically geared toward material from the Organic Chemistry of Biomolecules sections from within the chapter, and are grouped together among the end-of-chapter problems to make them easily identifiable.

More Solved Problems. The first edition provided students with about seven Solved Problems per chapter on average. Several new Solved Problems have been added, bringing the average to about eight per chapter. This gives students more opportunities to receive guidance on the strategies they should use when solving a problem. In addition, Solved Problems have been added to each nomenclature interchapter. Nomenclature builds in complexity as new rules are introduced, and each Solved Problem is designed to help students navigate those new rules.

Nomenclature presented in five interchapters rather than four. In the first edition, nomenclature was presented in four interchapters. The fourth nomenclature interchapter dealt with all compound classes that call for the addition of a suffix, including amines, alcohols, ketones, aldehydes, and carboxylic acids and their derivatives. Users found this to be too much material for one chapter, so in the second edition, that interchapter has been split into two: Interchapters E and F. Interchapter E deals with alcohols, amines, ketones, and aldehydes; Interchapter F deals with carboxylic acids and their derivatives.

Addition of green chemistry. Based on user feedback, I have added a new section on green chemistry to Chapter 13, the first devoted chapter on multistep synthesis. Section 13.8b provides an overview of green chemistry and its importance, and then delves into three of the 12 main principles of green chemistry outlined by the American Chemical Society: less toxic reagents and solvents; safer synthesis routes; and minimizing by-products and other waste. In subsequent reaction chapters, students will find Green Chemistry boxes in the margin notes, which highlight green aspects of some reactions and provide green alternatives to others. For students planning on a career in chemistry, the goal is to instill in them the importance of considering green chemistry when designing and carrying out a synthesis. All students should know what green chemistry is, and should come to appreciate the fact that chemists in the 21st century are increasingly prioritizing the well-being of our planet.

New strategies to help students analyze IR, NMR, and mass spectra. Even with a strong foundation in the principles that underlie IR and NMR spectroscopy and mass spectrometry, it can still be quite a challenge for students to analyze a spectrum in a way that brings the individual pieces of information together. To help students along these lines in the first edition, I presented spectra of unknowns and then brought students through the analysis methodically, although somewhat passively. New to the second edition, I now present separate strategies up front to analyze IR, NMR, and mass spectra, with sequential steps that students can follow. Then I show students how to apply these strategies toward the analysis of spectra of unknowns. Students are encouraged to develop other strategies that might work better for them, but until then, students have an effective strategy that they can use and rely on.

Oxidation states moved to Chapter 17. In the first edition, calculating oxidation states of atoms was presented in Chapter 1 alongside the calculation of formal charges. Although grouping those two topics together makes sense because of the similarities between the two methods, users reported that students weren't sufficiently applying the ideas of oxidation states toward redox reactions until Chapter 17. Therefore, in the second edition, I moved the calculation of oxidation states to Section 17.3b, where hydride reductions are discussed.

Nobel Prize–winning coupling and metathesis reactions. Because of their importance to organic chemistry, transition metal coupling reactions and alkene metathesis reactions have been added to the second edition. These include: coupling reactions involving dialkylcurprates; the Suzuki reaction; the Heck reaction; and the Grubbs reaction. The utility of these reactions is primarily in organic synthesis, specifically in the formation of new carbon–carbon bonds, so these reactions have been added to Chapter 19, the second chapter devoted to organic synthesis.

Azo coupling and azo dyes. The presentation of azo coupling and a short discussion on azo dyes have been added to Chapter 23, the second chapter on aromatic substitution reactions. The benefits of this section are twofold. First, it is an application of diazotization (Chapter 22) and substituent effects in aromatic substitution (Chapter 23), so it provides reinforcement of newly learned concepts. Second, students can easily relate to dyes, so it is an excellent example of the daily impacts organic chemistry has on students' lives.

Connections boxes. Students often ask, "How does organic chemistry apply to me?" or, "Why should I care about organic chemistry?" For the chemistry major or the student going on to medical school or another health profession, the long-term answer might be apparent. Connections boxes, which are new to the second edition, are designed to help answer that question as it relates to the immediate. In the margins of each chapter, students will find several Connections boxes that highlight the importance or application of

a molecule that was just encountered. Students might see that the molecule is integral in the synthesis of a pharmaceutical drug, or that the molecule is important in the manufacture of a material that students use daily. More than just helping provide an answer to the above questions, these Connections boxes also help keep students *interested* in the material, and an interested student is a more successful student.

Acknowledgments

Special thanks to my wife Valerie and my boys Joshua and Jacob for being my biggest fans. Their love and immense support throughout my work on the second edition not only helped push me to the finish line, but they continue to make my achievements worthwhile.

Many thanks to my colleagues in the chemistry department at Elon for your understanding, especially Dan Wright and Karl Sienerth, who served as my department chairs during this endeavor. And a tremendous thank-you to Kathy Matera for the real-time feedback you have given me over the years, and for all the times I barged into your office to pick your brain when I was in the midst of working through a quandary with the book.

I remain indebted to my students. Thank you for bringing such great energy to learning organic chemistry year in and year out, and thank you for allowing me to learn from you.

I continue to be amazed with the members of the Norton team. Erik Fahlgren, thank you for your continued belief in me and in the potential this book has to help teachers teach and to help students learn. John Murdzek, your insights in the developmental process have truly enabled me to reach students more effectively and meaningfully. Arielle Holstein and Sara Bonacum, thank you for being the glue that has held this entire project together. And a further congratulations to Arielle for your new position as Associate Media Editor; thank you for the great work you have done on the book's ancillaries. To Carla Talmadge and Connie Parks, many thanks for holding me to a high standard in the copyediting and page proofing stages. Travis Carr and Elyse Rieder, I admire your patience and persistence when I need just the right photo. Christopher Rapp and Christine Pruis, thank you for your work on the online resources for the book, which not only add value to the book but also make the book more effective. Lisa Buckley, what a fantastic job on the interior design, giving the book a warm and inviting feel. And Stacy Loyal, you continue to amaze me with your vision and the creativity you bring to marketing the book.

A special thanks, once again, to Marie Melzer. With the energy and the insight that you have continued to bring, I could not imagine a better coauthor on the *Study Guide and Solutions Manual*. And to Steve Pruett, I truly value your work on the polymers chapter in the first edition.

Finally, I am indebted to the many reviewers, whose feedback has been instrumental in making several significant improvements over the first edition. I am especially grateful to Joachim Schantl, who accuracy-checked nearly the *entire* book! I am in awe of your breadth and depth of knowledge, as well as your attention to detail. Many, many thanks.

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Additional Resources

For Students

Study Guide and Solutions Manual

by Joel Karty, Elon University, and Marie Melzer

Written by two dedicated teachers, this guide provides students with fully worked solutions to all unworked problems in the text. Every solution follows the Think and Solve format used in the textbook, so the approach to problem solving is modeled consistently.

Smartwork5 (digital.wwnorton.com/karty2)

Smartwork5 is the most intuitive online tutorial and homework system available for organic chemistry. A powerful engine supports and grades a wide variety of problems written for the text, including numerous arrow-pushing problems. *Every* problem in Smartwork5 has hints and answer-specific feedback to coach students and provide the help they need, when they need it. Problems in Smartwork5 link directly to the appropriate page in the ebook so students have an instant reference and are prompted to read.

Assigning, editing, and administering homework within Smartwork5 is easy. Instructors can select from Norton's bank of more than 3200 high-quality, class-tested problems. Using the sort and search features, instructors can identify problems by chapter section, learning objective, question type, and more. Instructors can use premade assignments provided by Norton authors, modify those assignments, or create their own. Instructors

also have access to intuitive question authoring tools—the same ones Norton authors use. These tools make it easy to customize the question content to fit the course needs. Smartwork5 integrates seamlessly with most campus learning management systems and can be used on computers and tablets.

The Smartwork5 course features:

- **An expert author team.** The Smartwork5 course was authored by instructors who teach at a diverse group of schools: Arizona State University, Florida State University, Brigham Young University, Butler University, and Mesa Community College. The authors have translated their experience in teaching a diverse student population by creating a library of problems that will appeal to instructors at all schools.
- **An upgraded drawing tool.** Smartwork5 contains an upgraded 2-D drawing tool that mimics drawing on paper, reduces frustration, and helps students focus on the problem at hand. This intuitive drawing tool supports multistep mechanism and multistep synthesis problems and provides students with answer-specific feedback for every problem.
- **Ease of use for students.** The 2-D drawing tool has a variety of features that make drawing easy and efficient. Students are provided with templates including a variety of common rings and a carbon chain drawing tool. In addition, Smartwork5 presents students with commonly used elements, a simple click to add lone pairs option, and ease-of-use features such as undo, redo, simple-click erase, and zoom-in/zoom-out.
- **Question variety.** The Smartwork5 course offers a diverse set of problems including:
  - Nomenclature problems
  - Multistep Mechanism problems
  - Multistep Synthesis problems
  - Reaction problems
  - Spectroscopy problems
- Conceptual question types include:
  - Multiple-choice/multiple select
  - Ranking
  - Sorting
  - Labeling
  - Numeric entry
  - Short answer
- **Pooled problems.** Smartwork5 features sets of pooled problems for multistep mechanisms and nomenclature to promote independent work. Groups of similar problems are "pooled" into one problem so different students receive different problems from the pool. Instructors can choose our preset pools or create their own.

Ebook (digital.wwnorton.com/karty2)

An affordable and convenient alternative to the print text, the Norton Ebook lets students access the entire book and much more: They can search, highlight, and take notes with ease. The Norton Ebook allows instructors to share their notes with students. The ebook can be viewed on computers and tablets and will stay synced between devices. The online ebook is available at no extra cost with the purchase of a new print text or it may be purchased stand-alone with Smartwork5.

Molecular Model Kits

Norton partners with two model kits and can package either with the textbook for an additional cost.

Darling Molecular Model Kit. Atoms with their valences already attached are constructed by snapping together V-shaped pieces in a jigsaw style, emphasizing bond angles and symmetry elements of the atoms. Double bonds are independent, rectangular units to emphasize the planarity of sp^2-hybridized atoms. Large substituents can be represented by various colored marker balls.

This kit includes 120 pieces:

- 57 sp^3 pieces (black, red, blue, silver black, turquoise, gray)
- 16 sp^2 pieces (gray)
- 18 marker balls (white, red, green, blue)
- 7 double bonds (gray)
- 6 half double bonds (gray, red)
- 2 trigonal atoms (gray)
- 2 linear bonds (gray)
- 2 linear triple bonds (gray)
- 4 bond extenders
- 4 octahedral pieces (pink)
- 2 Atom Visions™ balls

HGS Molecular Structure Model Kit. The HGS kit reflects the traditional ball-and-stick model for constructing molecules. Conjugation can be illustrated using trigonal planar atoms that have five holes to accommodate three bonds and the two lobes of a *p* orbital. Double bonds can be constructed using curved sticks to occupy two valences of a tetrahedral atom.

This kit includes 210 pieces:

- 30 tetrahedral carbon atoms (black)
- 14 trigonal planar carbon atoms (black)
- 30 hydrogen atoms (light blue)
- 4 oxygen atoms (red)
- 6 nitrogen atoms (blue)
- 4 chlorine atoms (green)
- 2 metal atoms (grey)
- 12 orbital plates (green, blue)
- 108 bond pieces, 5 types (light blue, orange, green, yellow, white)

Please contact your Norton representative about ordering and pricing options for packaging model kits.

For Instructors

Instructor's Guide

by Michelle Boucher, Utica College, and Cliff Coss, Northern Arizona University

Written by users of the first edition, the *Instructor's Guide* is an invaluable resource for instructors organizing their course by mechanism for the first time. Based on their experience, Michelle and Cliff provide a brief overview of every chapter followed by a section-by-section summary that illustrates how easy and rewarding it is to teach a mechanistically organized course. In addition to providing an easy transition, the authors offer other resources, such as class-tested clicker questions that instructors may choose to incorporate into their course. While this guide is an excellent resource for adopters, it may also answer questions for instructors who are interested in a mechanistic organization but are concerned about the transition. The *Instructor's Guide* includes a chapter for each of the 26 chapters in the textbook, plus a chapter for the molecular orbital theory interchapter and a chapter for each of the nomenclature interchapters.

Clickers in Action: Active Learning in Organic Chemistry

by Suzanne M. Ruder, Virginia Commonwealth University

This instructor-oriented resource provides information on implementing clickers in organic chemistry courses. Part I gives instructors information on how to choose and manage a classroom response system, develop effective questions, and integrate the questions into their courses. Part II contains 140 class-tested, lecture-ready questions. Most

questions include histograms that show actual student response, generated in large classes with 200–300 students over multiple semesters. Each question also includes insights and suggestions for implementation. The 140 questions from the book are sorted to correspond to the chapters in the textbook.

Test Bank

by James Wollack, St. Catherine University, Jennifer Griffith, Western Washington University, and Chris Markworth, Western Washington University

After teaching with the first edition, our authors have written problems that will make assessing your students easy. Whether your exams are multiple choice, short answer and require drawing, or both, the variety and quality of the problems in the test bank will exceed your needs. The test bank contains approximately 1600 multiple-choice and short-answer questions classified by section and difficulty level. It is available with ExamView Test Generator software, allowing instructors to effortlessly create, administer, and manage assessments. The convenient and intuitive test-making wizard makes it easy to create customized exams with no software learning curve. Other key features include the ability to create paper exams with algorithmically generated variables and export files directly to Blackboard, Canvas, Desire2Learn, and Moodle.

Instructor's Resources: Flash Drive

This helpful classroom presentation tool features:

- Select photographs and every piece of line art in JPEG format
- Select photographs and every piece of line art in PowerPoint
- Lecture PowerPoint slides with integrated figures from the book
- *Instructor's Guide* in PDF format
- Test bank in PDF, Word, and ExamView formats
- Approximately 500 lecture-ready questions, in PowerPoint, from *Clickers in Action* as well as Joel Karty's course

Downloadable Instructor's Resources (wwnorton.com/instructors)

This instructor-only, password-protected site features instructional content for use in lecture and distance education, including test-item files, PowerPoint lecture slides, images, figures, and more. The instructor's website includes:

- Select photographs and every piece of line art in JPEG format
- Select photographs and every piece of line art in PowerPoint
- Lecture PowerPoint slides with integrated figures from the book
- *Instructor's Guide* in PDF format
- Test bank in PDF, Word, and ExamView formats
- Approximately 500 lecture-ready questions, in PowerPoint, from *Clickers in Action* as well as Joel Karty's course

Author Blog: www.teachthemechanism.com

In July 2012, Joel Karty started a blog about his approach and his experience teaching a course organized by mechanism. Now there are more than 120 guest blog posts written by professors who use Joel's book, garnering nearly 60,000 views and 20+ active conversations. What once was an informational blog has now grown into a platform for a community of instructors to share their experiences and insights, have open-forum discussions, view sample materials, and watch videos of Joel as he discusses a number of topics, including how he believes a mechanistic organization allows users of his book to have increased expectations about student understanding. You are encouraged to visit the blog and join the community.

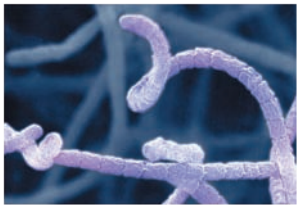
Preface for the Student

Organic Chemistry and You

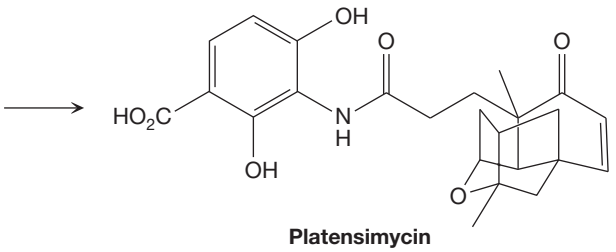
You are taking organic chemistry for a reason—you might be pursuing a career in which an understanding of organic chemistry is crucial, or the course might be required for your particular field of study, or both. You might even be taking the course simply out of interest. Regardless of the reason, organic chemistry impacts your life in significant ways.

Consider, for example, the growing concern about the increasing resistance of bacteria to antibiotics over the past several decades. Perhaps no germ has caused more alarm than methicillin-resistant *Staphylococcus aureus* (MRSA), a type of bacteria responsible for staph infections. Methicillin is a member of the penicillin family of antibiotics, and resistance to methicillin in these bacteria was first observed in 1961. Today MRSA, which has been called a *superbug*, is resistant to most antibiotics, including *all* penicillin-derived antibiotics.

A breakthrough in the fight against MRSA occurred in 2006 with the discovery of a compound called platensimycin, isolated from *Streptomyces* spores. The way that platensimycin targets bacteria is different from that of any other antibiotic in use and, therefore, it is not currently susceptible to bacterial resistance.



***Streptomyces* spores**



Platensimycin

Platensimycin is found in a type of South African mushroom, *Streptomyces platensis*, and was discovered by screening 250,000 natural product extracts for antibacterial activity. Sheo B. Singh (Merck Research Laboratories) and coworkers determined the structure of platensimycin using a technique called nuclear magnetic resonance (NMR) spectroscopy, which we discuss in Chapter 16. Not long after, K. C. Nicolaou and coworkers from the Scripps Research Institute (La Jolla, California) and the University of California, San Diego, were the first to devise a synthesis of platensimycin from other readily available chemicals.

The story of platensimycin, from discovery to synthesis, involves several of the subdisciplines that make up the field of organic chemistry.

- **Biological chemistry (biochemistry):** The study of the behavior of biomolecules and the nature of chemical reactions that occur in living systems.
- **Structure determination:** The use of established experimental techniques to determine the structure of newly discovered compounds.
- **Organic synthesis:** The design of pathways for making new compounds from existing, readily available compounds by means of known organic reactions.

Because each of these areas typically focuses on solving existing and practical problems, they are considered to be *applied* areas of organic chemistry. However, other areas of organic chemistry, considered to be *theoretical* in nature, provide the foundations on which such applications rest. They focus on answering questions about the *how* and *why* of chemical processes. For example, an understanding of the basic principles of NMR spectroscopy (an analytical technique discussed in Chapter 16) underlies our ability to determine molecular structure. Understanding the principles that govern organic reactions (such as those involved in the synthesis of platensimycin) may allow us to enhance yields, not only by altering reaction conditions, but also perhaps by devising

(a)

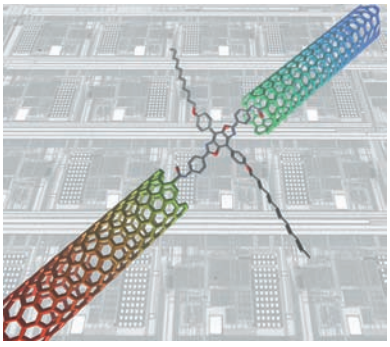
(b)

(c)

(d)

FIGURE P.1 Some uses of plastics Plastics, which are designed and created in the laboratories of organic chemists, are found in a wide range of products, such as (a) food packaging, (b) an artificial heart, (c) body armor made from Kevlar, and (d) a Boeing 787, a commercial jet whose body consists largely of composite materials made from plastics and carbon fibers.

(a)



(b)

FIGURE P.2 Organic chemistry in the electronics industry (a) A smartphone whose display is made from organic light-emitting diodes. (b) A molecular switch in which an organic molecule joins together two carbon nanotubes—sheets of carbon in the form of cylinders with a diameter on the order of 10^{-9} meter.

entirely new synthesis schemes. And understanding platensimycin's specific mode of attack on bacteria will likely guide us in modifying its chemical structure to make it even more effective.

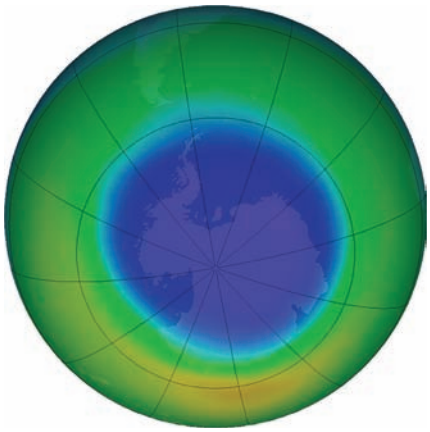
The story of platensimycin showcases the importance of organic chemistry in the pharmaceutical industry, but organic chemistry is at the center of other high-profile areas as well, including the fabrication of new materials such as plastics (the topic of Chapter 26). The durability and chemical stability of plastics have made them excellent choices for use in food packaging (Fig. P.1a) and the fabrication of the artificial heart (Fig. P.1b). Plastics are the source of synthetic fibers such as nylon and polyester, which are often used in the clothing industry, as well as Kevlar, which is used to make body armor (Fig. P.1c). Composite materials made from plastic and carbon fibers are so strong that some commercial jets are now constructed with a body made largely from plastics (Fig. P.1d).

Organic chemistry has also been at the forefront of generating new materials for electronic devices. Organic light-emitting diodes (OLEDs) are the main components of electronic displays for many high-end smartphones (Fig. P.2a), and single organic molecules can be used to make electronic switches tens of thousands of times smaller than those used in today's integrated circuits (Fig. P.2b).

Perhaps even more important to our lives is the impact that organic chemistry can have on our ability to understand, and solve, environmental problems, such as overflowing landfills (Fig. P.3a), the destruction of the stratospheric ozone layer (Fig. P.3b), and global warming (Fig. P.3c). Organic chemistry, for example, is helping provide new ways to recycle waste materials. Additionally, organic chemistry has been used to engineer new coolants that are safer for the environment than the chlorofluorocarbons (CFCs) used in the late 20th century in refrigerators and air conditioners. Finally, organic chemistry may lead us to economically feasible processes by which we can synthesize hydrogen gas, a fuel whose combustion product is only water. This could be a welcome alternative to coal and oil, whose combustion products not only cause air and water pollution, but also generate carbon dioxide, one of several greenhouse gases responsible for global warming.

Because organic chemistry is important in so many ways, you will find two special interest boxes in the main part of each chapter, which show how the material in the chapter directly connects to issues that you might find more relevant or more interesting. Take the time to read those boxes, and consider researching them even further. In addition to those special interest boxes, you will find several Connections boxes in the margins of each chapter, each of which provides a glimpse into how a molecule you just encountered relates to an aspect of everyday life.

(a)



(b) September 2016

(c)

FIGURE P.3 Organic chemistry and the environment Organic chemistry continues to play a significant role in solving environmental problems, such as (a) overflowing landfills, (b) ozone depletion (the area in blue represents the ozone hole over Antarctica), and (c) global warming (the ice sheets in Montana's Glacier National Park have been melting at a dramatically accelerating rate over the past 90 years).

Some Suggestions for Studying

Perhaps you have heard that organic chemistry is difficult. Perhaps you have heard that it requires an enormous amount of memorization. Are these statements true? It depends on how you approach the course. What is true is that this book contains a lot of information—*much more than you can memorize*. There is a better way.

Organic chemistry can be *understood* through models and theories that are built on *fundamental concepts*. Consider, for example, that when two compounds react under a given set of conditions, the outcome of that reaction is precisely the same each and every time. Is this because the reactant molecules have memorized what products they are supposed to make? No—they are obeying certain chemical laws, and those laws can be learned.

You will spend considerable effort throughout this course developing those models and theories. *Reaction mechanisms*—detailed steps that show how reactions take place—are among the most important ideas to develop. If you devote your time and energy to understanding them and learning how they are applied toward solving problems, you will find that much of organic chemistry can be conquered without rote memorization, and you will find the course to be quite rewarding and enjoyable. Moreover, the skills you develop in organic chemistry will apply to complex situations you will face beyond this course.

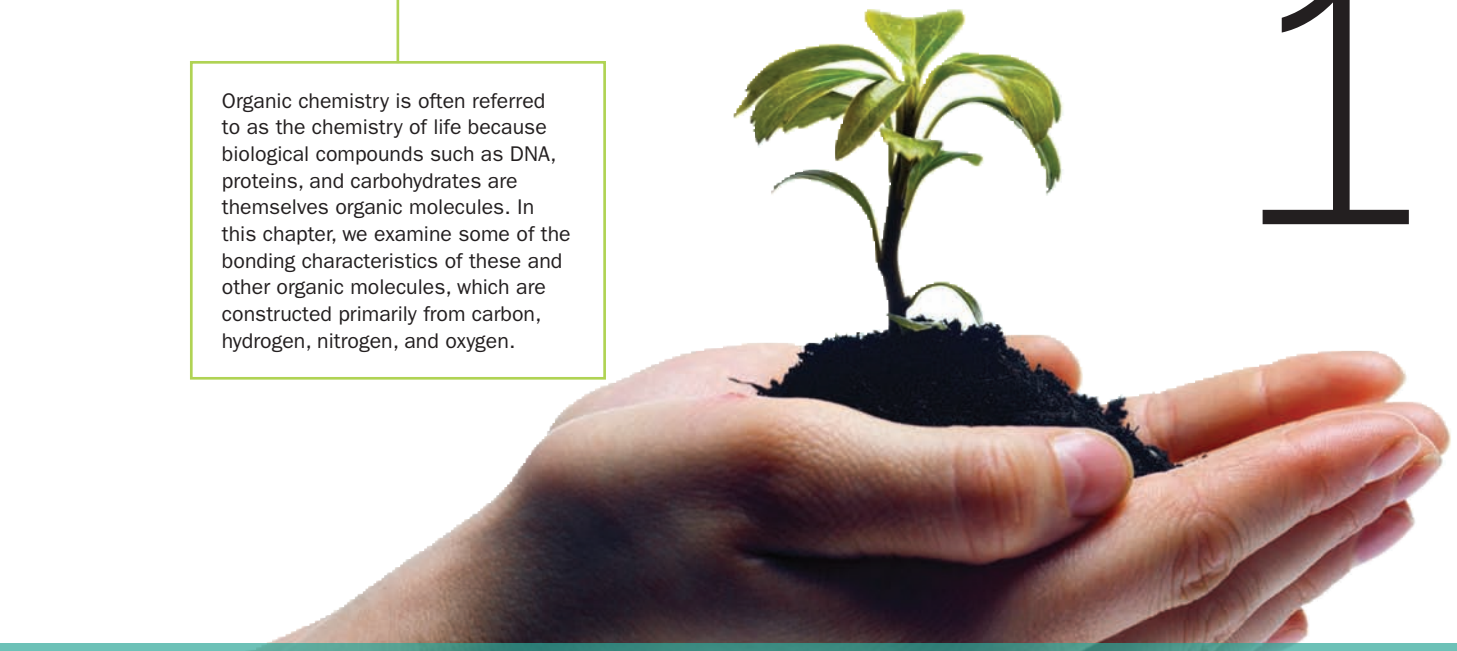
If you are planning on a career in a health profession, it is particularly important for you to focus on understanding and applying concepts as opposed to memorizing. On standardized exams like the MCAT, you will often need to choose between answers that look equally good to students who have memorized the material. To a student who is well versed in applying concepts and mechanisms toward solving problems, on the other hand, those choices are more easily discernible.

In light of how important it is to understand concepts and mechanisms, your success in this course will demand a lot of time and devotion. Therefore, you should consider the following suggestions for using that time, and this book, most efficiently:

- **Read actively and diligently.** You should try to read the assigned sections before class if possible. Reading prior to class means that you will see the material for the second time in class. This will allow you to better process information and give you ample opportunity to ask pertinent questions. When you read, you should have a pen or pencil in hand so you can underline or highlight what you feel is important, and take notes about what you find enlightening or confusing. When the text refers to a figure or reaction mechanism, take that as a cue to study that figure now. Be sure that what the text is describing makes sense to you before you move on. If you are referred to a previous chapter, flip to the appropriate page to refresh your memory.
- **Your Turns.** The Your Turn exercises are relatively short activities that ask you to complete a task based on what you have just read. These exercises were developed to help you remain *actively engaged* while you read. They should also help you quickly evaluate whether you understand the topic at hand. I encourage you to *work through all Your Turn exercises in each chapter* and quickly check the answers in the back of the book. Feedback from students who have used this book supports this advice.
- **Problems.** As with anything new you attempt, mastery requires practice. Most of your practice should come from solving problems. I have included more than 2000 problems throughout this book. Many are integrated into the chapters, but most are gathered at the end of each chapter. Take the time to work through as many problems as possible, and use them to assess areas of strength and weakness.

That said, it's time to get started. Keep your focus on concepts and mechanisms, work hard, and ask questions!

Organic chemistry is often referred to as the chemistry of life because biological compounds such as DNA, proteins, and carbohydrates are themselves organic molecules. In this chapter, we examine some of the bonding characteristics of these and other organic molecules, which are constructed primarily from carbon, hydrogen, nitrogen, and oxygen.



1 Atomic and Molecular Structure

Organic chemistry is often called "the chemistry of life" because certain types of compounds, and the reactions they undergo, are suitable to sustain life, while others are not. What are the characteristics of such compounds and what advantages do those compounds afford living organisms? Here in Chapter 1 we begin to answer these questions.

We review several aspects of atomic and molecular structure typically covered in a general chemistry course, including ionic and covalent bonding, the basics of Lewis dot structures, and resonance theory. We then begin to tighten our focus on organic molecules, presenting various types of shorthand notation that organic chemists often use and introducing you to functional groups commonly encountered in organic chemistry.

Toward the end of this chapter, we shift our focus to examining specific classes of biomolecules: amino acids, monosaccharides, and nucleotides. Not only does such a discussion provide insight into the relevance of organic chemistry to biological systems, but it also reinforces specific topics covered in the chapter, such as functional groups.

1.1 What Is Organic Chemistry?

Organic chemistry is the branch of chemistry involving *organic compounds*. What, then, is an organic compound?

In the late 1700s, scientists defined an **organic compound** as one that could be obtained from a *living* organism, whereas **inorganic compounds** encompassed

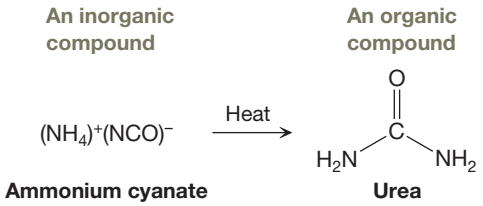
Chapter Objectives

On completing Chapter 1 you should be able to:

1. Distinguish organic compounds from inorganic ones.
2. Explain the advantages that come from carbon being the basis of organic molecules.
3. Describe the basic structure of an atom and understand that the vast majority of its volume is taken up by electrons.
4. Determine the ground state electron configuration of any atom in the first three rows of the periodic table and distinguish valence electrons from core electrons.
5. Define bond length and bond energy and understand how these two quantities depend on the number of bonds between a given pair of atoms.
6. Draw the Lewis structure of a species, given only its connectivity and total charge.
7. Differentiate between a nonpolar covalent bond, a polar covalent bond, and an ionic bond, and distinguish a covalent compound from an ionic compound.
8. Assign the formal charge to any atom in a molecular species, given only its Lewis structure.
9. Describe what a resonance structure is and explain the effect that resonance has on a species' stability.
10. Draw all resonance structures of a given species, as well as its resonance hybrid, and determine the relative stabilities of resonance structures.
11. Draw and interpret Lewis structures, condensed formulas, and line structures.
12. Explain why functional groups are important and identify functional groups that are common in organic chemistry.

everything else. It was believed that organic compounds could *not* be made in the laboratory; instead, only living systems could summon up a mysterious "vital force" needed to synthesize them. This belief was called **vitalism**. By this definition, many familiar compounds, such as glucose (a sugar), testosterone (a hormone), and deoxyribonucleic acid (DNA), are *organic* (Fig. 1-1).

This definition of organic compounds broke down in 1828, when Friedrich Wöhler (1800–1882), a German physician and chemist, synthesized urea (an organic compound known to be a major component of mammalian urine) by heating a solution of ammonium cyanate (an inorganic compound; Equation 1-1).

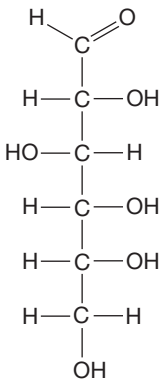


(1-1)

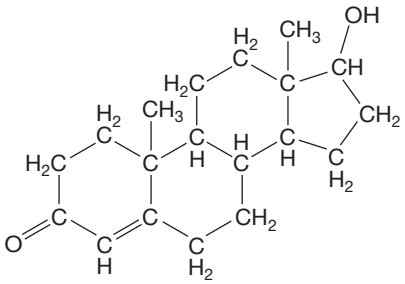
If vitalism couldn't account for the distinction between organic and inorganic compounds, what could? Gradually, chemists arrived at our modern definition:

> An **organic compound** contains a substantial amount of carbon and hydrogen.

This definition, however, is still imperfect, because it leaves considerable room for interpretation. For example, many chemists would classify carbon dioxide (CO_2) as *inorganic* because it does not contain any hydrogen atoms, whereas others would argue that it is *organic* because it contains carbon and is critical in living systems. In plants, it is a starting material in photosynthesis, and in animals, it is a by-product of respiration. Similarly, tetrachloromethane (carbon tetrachloride, CCl_4) contains no hydrogen, but many would classify it as an organic compound. Butyllithium (C_4H_9Li), on the other hand, is considered by many to be inorganic, despite the fact that 13 of its 14 atoms are carbon or hydrogen. Although this definition of an organic compound has its inadequacies, it does allow chemists to classify most molecules.



Glucose



Testosterone

DNA

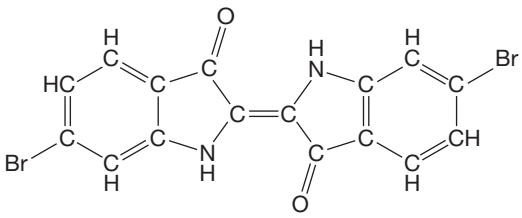
FIGURE 1-1 Some familiar organic compounds Glucose, testosterone, and DNA are organic compounds produced by living organisms.

The birth of organic chemistry as a distinct field occurred around the time that vitalism was dismissed, making the discipline less than 200 years old. However, humans have taken advantage of organic reactions and the properties of organic compounds for thousands of years! Since about 6000 BC, for example, civilizations have fermented grapes to make wine. Some evidence suggests that Babylonians, as early as 2800 BC, could convert oils into soaps.

Many clothing dyes are organic compounds. Among the most notable of these dyes is **royal purple**, also called **Tyrian purple**, which was obtained by ancient Phoenicians from a type of aquatic snail called *Bolinus brandaris* (Fig. 1-2). These organisms produced the compound in such small amounts, however, that an estimated 10,000 of them had to be processed to obtain a single gram of dye. Therefore, the dye was available almost exclusively to those who had substantial wealth and resources—royalty.

Organic chemistry has matured tremendously since its inception. Today, we can not only use organic reactions to reproduce complex molecules found in nature, but also engineer new molecules never before seen.

Bolinus brandaris



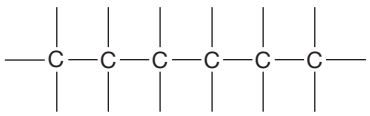
Royal purple

FIGURE 1-2 Royal purple Ancient Phoenicians processed about 10,000 aquatic snails, *Bolinus brandaris* (*top*), to yield 1 g of royal purple dye. The structure of the molecule responsible for the dye's color is shown (*bottom*).

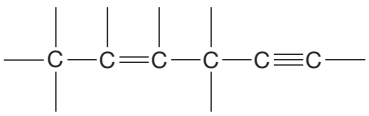
1.2 Why Carbon?

Why does the carbon atom play such a central role in the chemistry of life and what is so special about it? First of all, the compounds possible when carbon is their chief structural component are incredibly *diverse*. As we see in Section 1.6, the carbon atom can form four covalent bonds to other atoms—especially other carbon atoms.

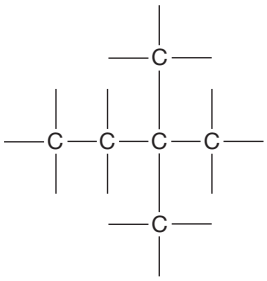
A chain of carbon atoms with single bonds only



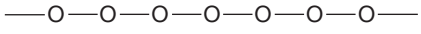
A chain of carbon atoms with a double and triple bond



A *branched* chain of carbon atoms



With a chain of oxygen atoms, no double bonds, triple bonds, or *branching* is possible.



Consequently, carbon atoms can link together in chains of almost any length and rings of various sizes, allowing for an enormous range in molecular size and shape. Moreover, the ability to form four bonds means there is potential for *branching* at each carbon in the chain. And each carbon atom is capable of forming not only single bonds, but double and triple bonds as well. These characteristics make possible a tremendous number of compounds, even with a relatively small number of carbon atoms. Indeed, to date, tens of millions of organic compounds are known, and the list is growing rapidly as we continue to discover or synthesize new compounds.

Far less diversity would be possible in compounds based on another element, such as oxygen. Oxygen atoms tend to form two covalent bonds, which would allow for a linear chain only (as shown in the hypothetical example on p. 3). No branching could occur, nor could other groups or atoms be attached to the chain except at the ends. Furthermore, the atoms along the chain could not participate in either double or triple bonds.

If carbon works so well, then why *not* silicon, which appears just below carbon in the periodic table? Elements in the same group (column) of the periodic table tend to exhibit similar chemical properties, so silicon, too, can form four covalent bonds, giving it the same potential for diversity as carbon.

The answer is *stability*. As we see in Section 1.4, the carbon atom forms rather strong bonds with a variety of atoms, including other carbon atoms. For example, it takes 339 kJ/mol (81 kcal/mol) to break an average C—C single bond, and 418 kJ/mol (100 kcal/mol) to break an average C—H bond. By contrast, it takes only 223 kJ/mol (53 kcal/mol) to break a typical Si—Si bond. The strength of typical bonds involving carbon atoms goes a long way toward keeping biomolecules intact—an essential characteristic for molecules whose job is to store information or provide cellular structure.

Even though organic molecules are based on the carbon atom, what would life be like, hypothetically, if silicon atoms were to replace carbon atoms in biomolecules such as glucose ($C_6H_{12}O_6$)? Glucose is broken down by our bodies through respiration to extract energy, according to the overall reaction in Equation 1-2. One of the by-products is carbon dioxide, a gas, which is exhaled from the lungs. In a world in which life is based on silicon, glucose would be $Si_6H_{12}O_6$, and its by-product would be silicon dioxide (SiO_2), as shown in Equation 1-3. Silicon dioxide, a solid, is the main component of sand; in its crystalline form, it is known as quartz (Fig. 1-3).

FIGURE 1-3 Quartz crystal Quartz (silicon dioxide) is the silicon analog of carbon dioxide. Whereas carbon dioxide is gaseous, silicon dioxide is a solid.

$$C_6H_{12}O_6(s) + 6\ O_2(g) \rightarrow 6\ CO_2(g) + 6\ H_2O(\ell) \quad (1\text{-}2)$$

$$Si_6H_{12}O_6(s) + 6\ O_2(g) \rightarrow 6\ SiO_2(s) + 6\ H_2O(\ell) \quad (1\text{-}3)$$

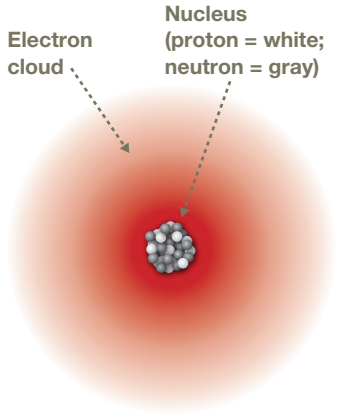


FIGURE 1-4 Basic structure of the atom Atoms are composed of a nucleus surrounded by a cloud of electrons. Protons (white) and neutrons (gray) make up the nucleus. (This figure is not to scale. If it were, the size of the electron cloud, which is much larger than the size of the nucleus, would have a radius on the order of 500 meters!)

1.3 Atomic Structure and Ground State Electron Configurations

In Section 1.2, we saw that carbon's bonding characteristics are what give rise to the large variety of organic molecules. Those bonding characteristics, and the bonding characteristics of all atoms, are governed by the electrons that the atom has.

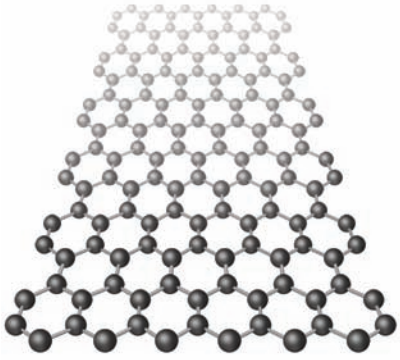
This section, then, is devoted to the nature of electrons in atoms. We first review the basic structure of an atom, followed by a discussion of orbitals and shells. Finally, we review electron configurations, distinguishing between *valence electrons*—electrons that can be used for bonding—and *core electrons*.

1.3a The Structure of the Atom

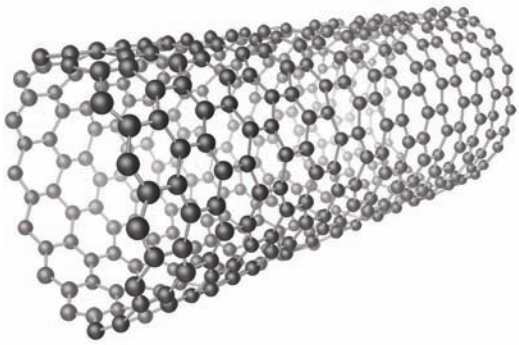
At the center of an atom (Fig. 1-4) is a positively charged nucleus, composed of *protons* and *neutrons*. Surrounding the nucleus is a cloud of negatively charged *electrons*, attracted to the nucleus by simple **electrostatic forces** (the forces by which opposite

Chemistry with Chicken Wire

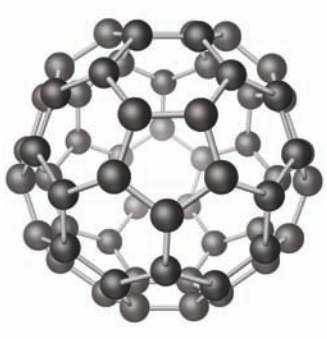
Even though carbon takes center stage in organic chemistry, organic molecules invariably include other atoms as well, such as hydrogen, nitrogen, oxygen, and halogen atoms. Some of the most exciting chemistry today, however, involves extended frameworks of *only* carbon. A single flat sheet of such a framework is called *graphene*, and resembles molecular chicken wire. Wrapped around to form a cylinder, a graphene sheet forms what is called a *carbon nanotube*. Pure carbon can even take the form of a soccer ball—the so-called *buckminsterfullerene*.



A sheet of graphene



A carbon nanotube



Buckminsterfullerene

These structures themselves have quite interesting electronic properties, giving them a bright future in nanoelectronics. Carbon nanotubes and buckminsterfullerenes have high tensile strength, moreover, giving them potential use for structural reinforcement in concrete, sports equipment, and body armor. Chemical modification gives these structures an even wider variety of potential uses. Graphene oxide, for example, has promising antimicrobial activity, and attaching certain molecular groups to the surface of a carbon nanotube or buckminsterfullerene has potential for use as drug carriers for cancer therapeutics.

charges attract one another and like charges repel one another). Individual electrons are incredibly small, even much smaller than the nucleus, but the space that electrons occupy (i.e., the *electron cloud*) is much larger than the nucleus. In other words:

- The size of an atom is essentially defined by the size of its electron cloud.
- The vast majority of an electron cloud (and thus the vast majority of an atom) is empty space.

Table 1-1 lists the mass and charge of each of these elementary particles. Notice that the masses of the proton and neutron are significantly greater than that of the electron, so the mass of an atom is essentially the mass of just the nucleus.

An atom, by definition, has no net charge. Consequently, the number of electrons in an atom must equal the number of protons. The number of protons in the nucleus, called the **atomic number (*Z*)**, defines the element. For example, a nucleus that has six protons has an atomic number of 6, and can only be a carbon nucleus.

If the number of protons and the number of electrons are unequal, then the entire **species** (that particular combination of protons, neutrons, and electrons) bears a net charge, and is called an **ion**. A negatively charged ion, an **anion** (pronounced AN-eye-on), results from an excess of electrons. A positively charged ion, a **cation** (pronounced CAT-eye-on), results from a deficiency of electrons.

TABLE 1-1 Charges and Masses of Subatomic Particles

Particle	Charge (e)[a]	Mass (u)[b]
Proton	+1	~1
Neutron	0	~1
Electron	−1	~0.0005

[a]e = Elementary charge.
[b]u = Unified atomic mass unit.

SOLVED PROBLEM 1.1

How many protons and electrons does a cation of the carbon atom have if its net charge is +1?

Think How many protons are there in the nucleus of a carbon atom? Does a cation have more protons than electrons, or vice versa? How many more, given the net charge of the species?

Solve A carbon atom's nucleus has six protons. A cation with a +1 charge should have one more proton than it has electrons, so this species must have five electrons.

PROBLEM 1.2 **(a)** How many protons and electrons does an anion of the carbon atom have if its net charge is −1? **(b)** How many protons and electrons does a cation of the oxygen atom have if its net charge is +1? **(c)** How many protons and electrons does an anion of the oxygen atom have if its net charge is −1?

1.3b Atomic Orbitals and Shells

Electrons in an isolated atom reside in **atomic orbitals**. As we shall see, the exact location of an electron can never be pinpointed. An orbital, however, specifies the region of space where the *probability* of finding a given electron is high. More simplistically, we can view orbitals as "rooms" that house electrons. Atomic orbitals are examined in greater detail in Chapter 3; for now, it will suffice to review some of their more basic concepts.

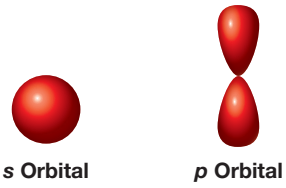


FIGURE 1-5 Orbitals Orbitals represent regions in space where an electron is likely to be. An s orbital is spherical, and a *p* orbital is a dumbbell.

- Atomic orbitals have different shapes. An *s* orbital, for example, is a sphere, whereas a *p* orbital has a dumbbell shape with two lobes (Fig. 1-5). Each orbital is centered on the nucleus of its atom or ion.
- Atomic orbitals are organized in *shells* (also known as *energy levels*). A **shell** is defined by the **principal quantum number**, ***n***. There are an infinite number of shells in an atom, given that n can assume any integer value from 1 to infinity.
  - The first shell ($n = 1$) contains only an *s* orbital, called 1*s*.
  - The second shell ($n = 2$) contains one *s* orbital and three *p* orbitals, called 2*s*, $2p_x$, $2p_y$, and $2p_z$.
  - The third shell ($n = 3$) contains one *s* orbital, three *p* orbitals, and five *d* orbitals.
- Up to two electrons are allowed in any orbital.
  - Therefore, the first shell can contain up to two electrons (a **duet**).
  - The second shell can contain up to eight electrons (an **octet**).
  - The third shell can contain up to 18 electrons.
- With increasing shell number, the *size* and *energy* of the atomic orbital increase. For example, comparing *s* orbitals in the first three shells, the size and energy increase in the order $1s < 2s < 3s$, as shown in Figure 1-6. Similarly, a 2*p* orbital is smaller in size and lower in energy than a 3*p* orbital.
- Within a given shell, an atomic orbital's energy increases in the following order: $s < p < d$, etc. In the second shell, for example, the 2*s* orbital is lower in energy than the 2*p*.

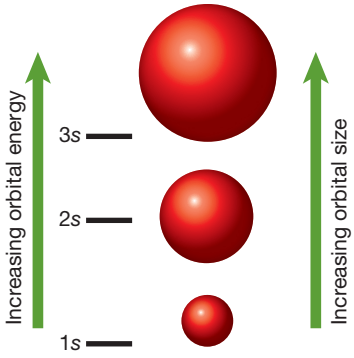


FIGURE 1-6 Relationship between principal quantum number, orbital size, and orbital energy As the shell number of an orbital increases, its size and energy increase, too. The horizontal black lines indicate each orbital's energy.

1.3c Ground State Electron Configurations: Valence Electrons and Core Electrons

The way in which electrons are arranged in atomic orbitals is called the atom's **electron configuration**. The *most stable* (i.e., the lowest energy) electron configuration is called the **ground state** configuration. Knowing an atom's ground state configuration provides insight into the atom's chemical behavior, as we will see.

With the relative energies of atomic orbitals established, an atom's ground state electron configuration can be obtained by applying the following three rules:

1. **Pauli's exclusion principle:** No more than two electrons (i.e., zero, one, or two electrons) can occupy a single orbital; two electrons in the same orbital must have opposite spins.
2. **Aufbau principle:** Each successive electron must fill the lowest energy orbital available.
3. **Hund's rule:** Before a second electron can be paired in the same orbital, all other orbitals *at the same energy* must contain a single electron.

According to these three rules, the first 18 electrons fill orbitals as indicated in Figure 1-7. Each arrow represents an electron, and the direction of the arrow—up or down—represents the electron's spin.

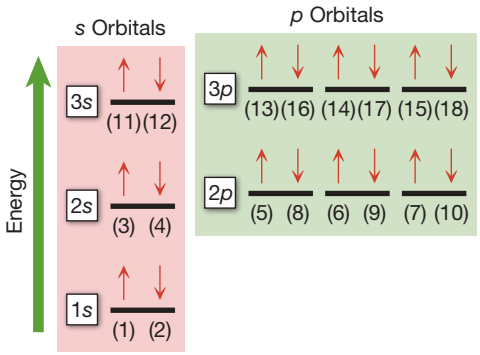


FIGURE 1-7 Energy diagram of atomic orbitals for the first 18 electrons The order of electron filling is indicated in parentheses. Each horizontal black line represents a single orbital. Each successive electron fills the lowest energy orbital available. Notice in the 2*p* and 3*p* sets of orbitals that no electrons are paired up until the addition of the fourth electron.

YOUR TURN 1.1

In Figure 1-7, place a box around all of the orbitals in the second shell and label them.

Answers to Your Turns are in the back of the book.

In the ground state, the six electrons found in a carbon atom would fill the orbitals as shown in Figure 1-8, with two electrons in the 1*s* orbital, two electrons in the 2*s* orbital, and one electron in each of two different 2*p* orbitals (it doesn't matter which two). The shorthand notation for this electron configuration is $1s^2 2s^2 2p^2$.

Knowing the ground state electron configuration of an atom, we can distinguish *valence* electrons from *core* electrons.

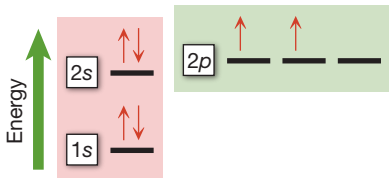


FIGURE 1-8 Energy diagram for the ground state electron configuration of the carbon atom This configuration is abbreviated $1s^2 2s^2 2p^2$.

- **Valence electrons** are those occupying the highest energy (i.e., valence) shell. For the carbon atom, the valence shell is the $n = 2$ shell.
- **Core electrons** occupy the remaining lower energy shells of the atom. For the carbon atom, the core electrons occupy the $n = 1$ shell.

Valence electrons are important because, as we discuss in Section 1.5, they participate in covalent bonds. As we can see in Figure 1-8, for example, carbon has four valence electrons and two core electrons, so bonding involving carbon is governed by those four valence electrons.

YOUR TURN 1.2

In Figure 1-8, place a circle around the valence electrons and label them. Place a box around all of the core electrons and label them.

We can use the periodic table to quickly determine how many valence electrons an atom has (a copy of the periodic table appears inside the book's front cover).

The number of valence electrons in an atom is the same as the atom's *group number*.

Carbon is located in group 4A, consistent with its four valence electrons, whereas chlorine (group 7A) has seven. According to its ground state electron configuration ($1s^2 2s^2 2p^6 3s^2 3p^5$), chlorine's valence electrons occupy the third shell.

Atoms are especially stable when they have completely filled valence shells. This is exemplified by the **noble gases** (group 8A), such as helium and neon, because they have completely filled valence shells and they do *not* form bonds to make compounds. Although the specific origin of this "extra" stability is beyond the scope of this book, the consequences are the basis for the octet and duet rules we routinely use when drawing Lewis structures (Section 1.5).

SOLVED PROBLEM 1.3

Write the ground state electron configuration of the nitrogen atom. How many valence electrons does it have? How many core electrons does it have?

Think How many total electrons are there in a nitrogen atom? What is the order in which the atomic orbitals should be filled (see Fig. 1-7)? What is the valence shell and where do the core electrons reside?

Solve There are seven total electrons ($Z = 7$ for N). The first two are placed in the 1s orbital and the next two in the 2s orbital, leaving one electron for each of the three 2*p* orbitals. The electron configuration is $1s^2 2s^2 2p^3$. The valence shell is the second shell, so there are five valence electrons and two core electrons.

PROBLEM 1.4 Write the ground state electron configuration of the oxygen atom. How many valence electrons and how many core electrons are there?

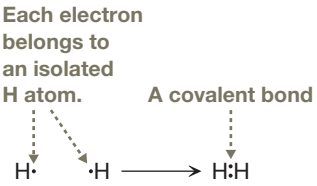


FIGURE 1-9 A covalent bond A covalent bond is the sharing of two electrons between nuclei.

1.4 The Covalent Bond: Bond Energy and Bond Length

In a compound, nuclei are held together by chemical bonds. Two types of fundamental bonds in chemistry are the *covalent bond* and the *ionic bond* (see Section 1.8). A **covalent bond** is characterized by the *sharing of valence electrons* between two or more atoms, as shown for two H atoms in a molecule of H_2 (hydrogen gas) in Figure 1-9.

In Section 1.5, we will explore how various molecules can be constructed from atoms through the formation of covalent bonds, but first let's examine the nature of covalent bonds more closely. Why do they form at all?

We can begin to answer this question by examining Figure 1-10a, which illustrates how the energy of two H atoms changes as a function of the distance between their nuclei. In particular, when two H atoms separated by a large distance are brought together, their total energy begins to decrease.

> Lower energy corresponds to greater stability.

At one particular internuclear distance, the energy of the molecule is at a minimum, while at shorter distances the energy rises dramatically.

The internuclear distance at which energy is the lowest is called the **bond length** of the H—H bond. The energy that is required to remove the H atoms from that internuclear distance to infinity (toward the right in the figure) is the **bond strength**, or **bond energy**, of the H—H bond.

CONNECTIONS Molecular hydrogen (Fig. 1-9) is a very light gas and was used for buoyancy in the *Hindenburg*, a commercial passenger airship in the 1930s. Unfortunately, hydrogen gas is also very highly flammable, and the airship caught fire and was destroyed over New Jersey on May 6, 1937, killing 36 people.

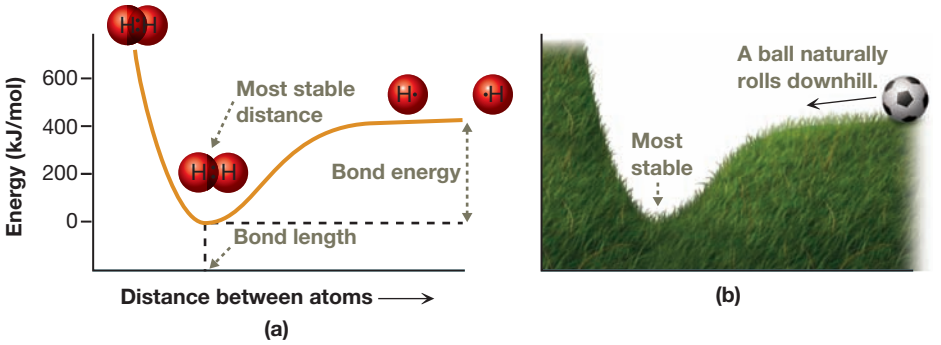


FIGURE 1-10 Formation of a chemical bond (a) Plot of energy as a function of the internuclear distance for two H atoms. The H atoms are most stable at the distance at which energy is a minimum. (b) A ball at the top of a hill becomes more stable at the bottom of the hill, and therefore tends to roll downhill.

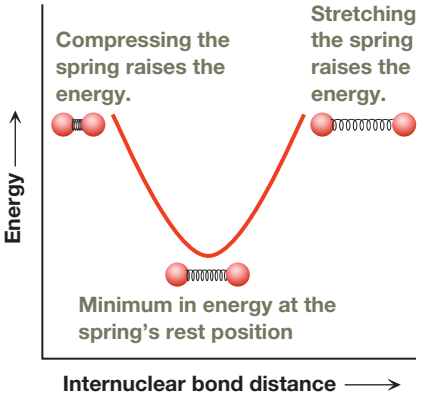


FIGURE 1-11 The spring model of a covalent bond The energy curve of a spring connecting two masses resembles that of the covalent bond shown in Figure 1-10a. Both stretching and compressing the spring from its rest position increase the energy in the spring.

This idea is analogous to a ball rolling down a hill (Fig. 1-10b). A ball at the top of a hill has more potential energy than a ball at the bottom, so the ball at the top tends to roll downhill, coming to rest at the bottom. By the same token, it takes energy to roll the ball from the bottom of the hill back to the top.

YOUR TURN 1.3

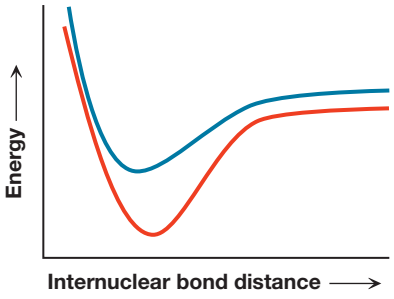
Estimate the bond energy of the bond represented by Figure 1-10a.

It is often convenient to *think of a covalent bond as a spring that connects two atoms.* Just as it takes energy to lengthen or shorten a covalent bond from its bond length, it takes energy to stretch or compress a spring from its rest position, as shown in Figure 1-11.

CONNECTIONS The behavior of covalent bonds as springs (Fig. 1-11) is what enables greenhouse gases like carbon dioxide (CO_2) and methane (CH_4) to absorb infrared radiation and warm the atmosphere.

SOLVED PROBLEM 1.5

In the diagram shown here, which curve represents a stronger covalent bond?



Think How can bond breaking be represented for each curve? Which of those processes requires more energy?

Solve Bond breaking is represented by climbing from the bottom of the curve toward the right (i.e., the internuclear bond distance increases toward the right). For this process, more energy is required for the red curve, so the red curve represents a stronger bond.

PROBLEM 1.6 Which of the two curves in Solved Problem 1.5 represents a longer bond?

Why are two hydrogen atoms connected by a covalent bond lower in energy than two isolated hydrogen atoms? Largely it is because of the additional electrostatic attraction experienced by electrons when they are *shared* between nuclei. In