



John McMurry

ORGANIC CHEMISTRY

7e

Periodic Table of the Elements

Key

79	Au	196.9665
Gold		

An element

Atomic number
Symbol
Name
Atomic mass

Metals
Semimetals
Nonmetals

Group number,
U.S. system
IUPAC system

1A
(1)

1	H Hydrogen 1.0079	1A (1)	8A (18)
2	Li Lithium 6.941	2A (2)	2 He Helium 4.0026
3	Na Sodium 22.9898	3B (3)	10 Ne Neon 20.1797
4	K Potassium 39.0983	4B (4)	16 Ar Argon 39.948
5	Rb Rubidium 85.4678	5B (5)	17 Cl Chlorine 35.4527
6	Cs Cesium 132.9054	6B (6)	18 S Sulfur 32.066
7	Fr Francium (223)	7B (7)	33 As Arsenic 74.9216
8	Ca Calcium 40.078	8B (8)	34 Se Selenium 78.96
9	Sc Scandium 44.9559	9B (9)	35 Br Bromine 79.904
10	Ti Titanium 47.88	10B (10)	52 Te Tellurium 127.60
11	V Vanadium 50.9415	11B (11)	53 I Iodine 126.9045
12	Mg Magnesium 24.3050	12B (12)	84 Po Polonium (209)
13	Al Aluminum 26.9815	13B (13)	85 At Astatine (210)
14	Si Silicon 28.0855	14B (14)	86 Rn Radon (222)
15	P Phosphorus 30.9738	15B (15)	
16	S Sulfur 32.066	16B (16)	
17	Cl Chlorine 35.4527	17A (17)	
18	Ar Argon 39.948	18A (18)	
19	K Potassium 39.0983	19A (19)	
20	Ca Calcium 40.078	20A (20)	
21	Sc Scandium 44.9559	21A (21)	
22	Ti Titanium 47.88	22A (22)	
23	V Vanadium 50.9415	23A (23)	
24	Cr Chromium 51.9961	24A (24)	
25	Mn Manganese 54.9380	25A (25)	
26	Fe Iron 55.847	26A (26)	
27	Co Cobalt 58.9332	27A (27)	
28	Ni Nickel 58.693	28A (28)	
29	Cu Copper 63.546	29A (29)	
30	Zn Zinc 65.39	30A (30)	
31	Ga Gallium 69.723	31A (31)	
32	Ge Germanium 72.61	32A (32)	
33	As Arsenic 74.9216	33A (33)	
34	Se Selenium 78.96	34A (34)	
35	Br Bromine 79.904	35A (35)	
36	Kr Krypton 83.80	36A (36)	
37	Rb Rubidium 85.4678	37A (37)	
38	Sr Strontium 87.62	38A (38)	
39	Y Yttrium 88.9059	39A (39)	
40	Zr Zirconium 91.224	40A (40)	
41	Nb Niobium 92.9064	41A (41)	
42	Mo Molybdenum 95.94	42A (42)	
43	Tc Technetium (98)	43A (43)	
44	Ru Ruthenium 101.07	44A (44)	
45	Rh Rhodium 102.9055	45A (45)	
46	Pd Palladium 106.42	46A (46)	
47	Ag Silver 107.8682	47A (47)	
48	Cd Cadmium 112.411	48A (48)	
49	In Indium 114.82	49A (49)	
50	Sn Tin 118.710	50A (50)	
51	Sb Antimony 121.757	51A (51)	
52	Te Tellurium 127.60	52A (52)	
53	I Iodine 126.9045	53A (53)	
54	Xe Xenon 131.29	54A (54)	
55	Cs Cesium 132.9054	55A (55)	
56	Ba Barium 137.327	56A (56)	
57	La Lanthanum 138.9055	57A (57)	
58	Ce Cerium 140.12	58A (58)	
59	Pr Praseodymium 140.9076	59A (59)	
60	Nd Neodymium 144.24	60A (60)	
61	Pm Promethium (145)	61A (61)	
62	Sm Samarium 150.36	62A (62)	
63	Eu Europium 151.965	63A (63)	
64	Gd Gadolinium 157.25	64A (64)	
65	Tb Terbium 158.9253	65A (65)	
66	Dy Dysprosium 162.50	66A (66)	
67	Ho Holmium 164.9303	67A (67)	
68	Er Erbium 167.26	68A (68)	
69	Tm Thulium 168.9342	69A (69)	
70	Yb Ytterbium 173.04	70A (70)	
71	Lu Lutetium 174.967	71A (71)	
72	Hf Hafnium 178.49	72A (72)	
73	Ta Tantalum 180.9479	73A (73)	
74	W Tungsten 183.85	74A (74)	
75	Re Rhenium 186.207	75A (75)	
76	Os Osmium 190.2	76A (76)	
77	Ir Iridium 192.22	77A (77)	
78	Pt Platinum 195.08	78A (78)	
79	Au Gold 196.9665	79A (79)	
80	Hg Mercury 200.59	80A (80)	
81	Tl Thallium 204.3833	81A (81)	
82	Pb Lead 207.2	82A (82)	
83	Bi Bismuth 208.9804	83A (83)	
84	Po Polonium (209)	84A (84)	
85	At Astatine (210)	85A (85)	
86	Rn Radon (222)	86A (86)	
87	Fr Francium (223)	87A (87)	
88	Ra Radium 226.0254	88A (88)	
89	Ac Actinium (227)	89A (89)	
90	Th Thorium 232.0381	90A (90)	
91	Pa Protactinium 231.0369	91A (91)	
92	U Uranium 238.0289	92A (92)	
93	Np Neptunium (237)	93A (93)	
94	Pu Plutonium (244)	94A (94)	
95	Am Americium (243)	95A (95)	
96	Cm Curium (247)	96A (96)	
97	Bk Berkelium (247)	97A (97)	
98	Cf Californium (251)	98A (98)	
99	Es Einsteinium (252)	99A (99)	
100	Fm Fermium (257)	100A (100)	
101	Md Mendelevium (258)	101A (101)	
102	No Nobelium (259)	102A (102)	
103	Lr Lawrencium (260)	103A (103)	
104		104A (104)	
105		105A (105)	
106		106A (106)	
107		107A (107)	
108		108A (108)	
109		109A (109)	
110	Ds Darmstadtium (289)	110A (110)	
111	Rg Roentgenium (272)	111A (111)	

6	Ce Cerium 140.115	6	71 Lu Lutetium 174.967
61	Pm Promethium (145)	6	70 Yb Ytterbium 173.04
62	Sm Samarium 150.36	68	69 Tm Thulium 168.9342
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70	Nd Neodymium 144.24	60	61 Pm Promethium (145)
71	Pa Protactinium 231.0369	59	60 Nd Neodymium 144.24
72	Th Thorium 232.0381	58	59 Pr Praseodymium 140.9076
73		57	58 Ce Cerium 140.115

Lanthanides

Actinides

Numbers in parentheses are mass numbers of radioactive isotopes.

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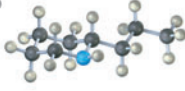
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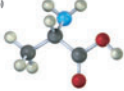
(Problems 1.1–1.17 appear within the chapter.)

1.18 ■ Convert each of the following molecular models into a skeletal structure, and give the formula of each. Only the connections between atoms are shown; multiple bonds are not indicated (gray = C, red = O, blue = N, ivory = H).



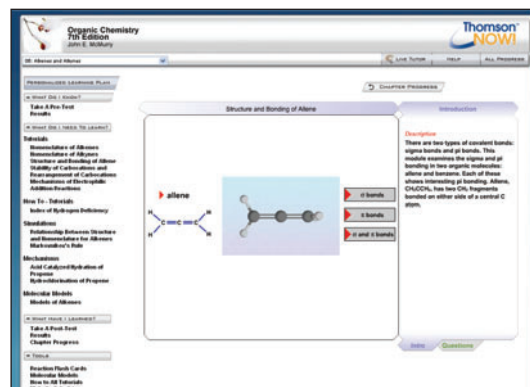
(a)

Coniline (the toxic substance in poison hemlock)



(b)

Alanine (an amino acid)



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Cornell University

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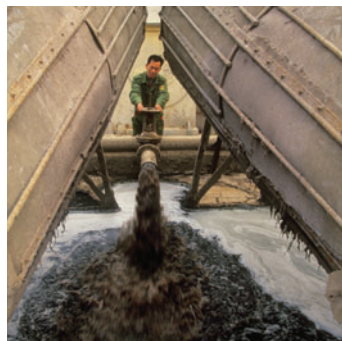
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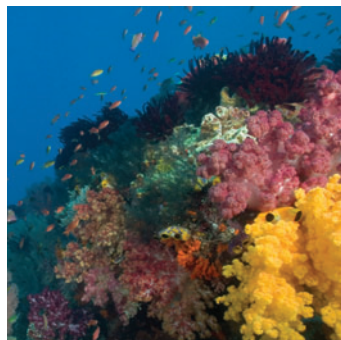
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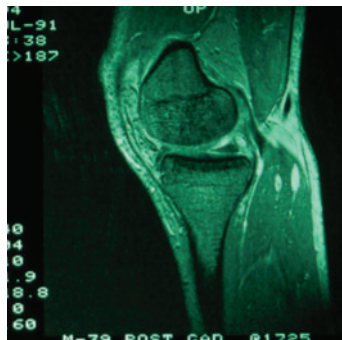


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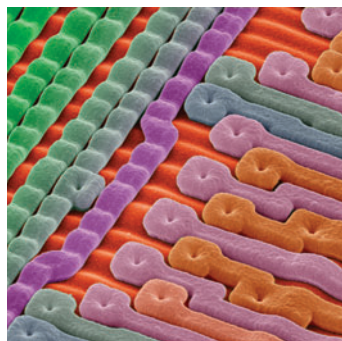
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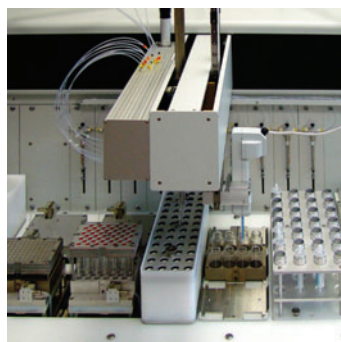
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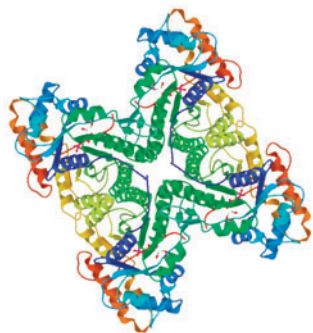
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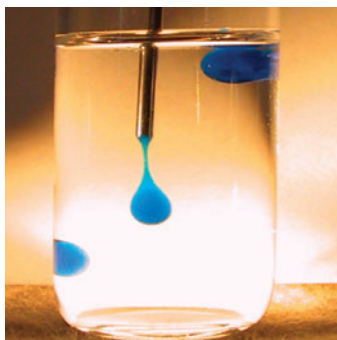
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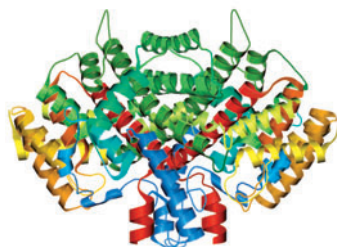
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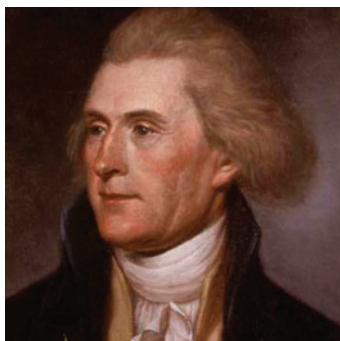
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Preface

I love to write. I get real pleasure from taking a complicated subject, turning it around until I see it clearly, and then explaining it in simple words. I write to explain chemistry to students today the way I wish it had been explained to me years ago.

The enthusiastic response to the six previous editions has been very gratifying and suggests that this book has served students well. I hope you will find that this seventh edition of *Organic Chemistry* builds on the strengths of the first six and serves students even better. I have made every effort to make this new edition as effective, clear, and readable as possible; to show the beauty and logic of organic chemistry; and to make organic chemistry enjoyable to learn.

Organization and Teaching Strategies This seventh edition, like its predecessors, blends the traditional functional-group approach with a mechanistic approach. The primary organization is by functional group, beginning with the simple (alkenes) and progressing to the more complex. Most faculty will agree that students new to the subject and not yet versed in the subtleties of mechanism do better this way. In other words, the *what* of chemistry is generally easier to grasp than the *why*. Within this primary organization, however, I place heavy emphasis on explaining the fundamental mechanistic similarities of reactions. This emphasis is particularly evident in the chapters on carbonyl-group chemistry (Chapters 19–23), where mechanistically related reactions like the aldol and Claisen condensations are covered together. By the time students reach this material, they have seen all the common mechanisms and the value of mechanisms as an organizing principle has become more evident.

The Lead-Off Reaction: Addition of HBr to Alkenes Students usually attach great importance to a text's lead-off reaction because it is the first reaction they see and is discussed in such detail. I use the addition of HBr to an alkene as the lead-off to illustrate general principles of organic chemistry for several reasons: the reaction is relatively straightforward; it involves a common but important functional group; no prior knowledge of stereochemistry or kinetics is needed to understand it; and, most important, it is a *polar* reaction. As such, I believe that electrophilic addition reactions represent a much more useful and realistic introduction to functional-group chemistry than a lead-off such as radical alkane chlorination.

Reaction Mechanisms In the first edition of this book, I introduced an innovative format for explaining reaction mechanisms in which the reaction steps are printed vertically, with the changes taking place in each step described next to the reaction arrow. This format allows a reader to see easily what is occurring at each step without having to flip back and forth between structures and text. Each successive edition has seen an increase in the number and quality of these vertical mechanisms, which are still as fresh and useful as ever.

Organic Synthesis Organic synthesis is treated in this text as a teaching device to help students organize and deal with a large body of factual information—the same skill so critical in medicine. Two sections, the first in Chapter 8 (Alkynes) and the second in Chapter 16 (Chemistry of Benzene), explain the thought processes involved in working synthesis problems and emphasize the value of starting from what is known and logically working backward. In addition, *Focus On* boxes, including The Art of Organic Synthesis, Combinatorial Chemistry, and Enantioselective Synthesis, further underscore the importance and timeliness of synthesis.

Modular Presentation Topics are arranged in a roughly modular way. Thus, certain chapters are grouped together: simple hydrocarbons (Chapters 3–8), spectroscopy (Chapters 12–14), carbonyl-group chemistry (Chapters 19–23), and biomolecules (Chapters 25–29). I believe that this organization brings to these subjects a cohesiveness not found in other texts and allows the instructor the flexibility to teach in an order different from that presented in the book.

Basic Learning Aids In writing and revising this text, I consistently aim for lucid explanations and smooth transitions between paragraphs and between topics. New concepts are introduced only when they are needed, not before, and they are immediately illustrated with concrete examples. Frequent cross-references to earlier material are given, and numerous summaries are provided to draw information together, both within and at the ends of chapters. In addition, the back of this book contains a wealth of material helpful for learning organic chemistry, including a large glossary, an explanation of how to name polyfunctional organic compounds, and answers to all in-text problems. For still further aid, an accompanying *Study Guide and Solutions Manual* gives summaries of name reactions, methods for preparing functional groups, functional-group reactions, and the uses of important reagents.

Changes and Additions for the Seventh Edition

The primary reason for preparing a new edition is to keep the book up to date, both in its scientific coverage and in its pedagogy. My overall aim is always to refine the features that made earlier editions so successful, while adding new ones.

- **The writing** has again been revised at the sentence level, streamlining the presentation, improving explanations, and updating a thousand small details. Several little-used reactions have been deleted (the alkali fusion of arenesulfonic acids to give phenols, for instance), and a few new ones have been added (the Sharpless enantioselective epoxidation of alkenes, for instance).
- Other notable **content changes** are:
 - Chapter 2, Polar Covalent Bonds; Acids and Bases**—A new Section 2.13 on non-covalent interactions has been added.
 - Chapter 3, Organic Compounds: Alkanes and Their Stereochemistry**—The chapter has been revised to focus exclusively on open-chain alkanes.
 - Chapter 4, Organic Compounds: Cycloalkanes and Their Stereochemistry**—The chapter has been revised to focus exclusively on cycloalkanes.
 - Chapter 5, An Overview of Organic Reactions**—A new Section 5.11 comparing biological reactions and laboratory reactions has been added.

Chapter 7, Alkenes: Reactions and Synthesis—Alkene epoxidation has been moved to Section 7.8, and Section 7.11 on the biological addition of radicals to alkenes has been substantially expanded.

Chapter 9, Stereochemistry—A discussion of chirality at phosphorus and sulfur has been added to Section 9.12, and a discussion of chiral environments has been added to Section 9.14.

Chapter 11, Reactions of Alkyl Halides: Nucleophilic Substitutions and Eliminations—A discussion of the E1cB reaction has been added to Section 11.10, and a new Section 11.11 discusses biological elimination reactions.

Chapter 12, Structure Determination: Mass Spectrometry and Infrared Spectroscopy—A new Section 12.4 discusses mass spectrometry of biological molecules, focusing on time-of-flight instruments and soft ionization methods such as MALDI.

Chapter 20, Carboxylic Acids and Nitriles—A new Section 20.3 discusses biological carboxylic acids and the Henderson–Hasselbalch equation.

Chapter 24, Amines and Heterocycles—This chapter now includes a discussion of heterocycles, and a new Section 24.5 on biological amines and the Henderson–Hasselbalch equation has been added.

Chapter 25, Biomolecules: Carbohydrates—A new Section 25.7 on the eight essential carbohydrates has been added, and numerous content revisions have been made.

Chapter 26, Biomolecules: Amino Acids, Peptides, and Proteins—The chapter has been updated, particularly in its coverage of solid-phase peptide synthesis.

Chapter 27, Biomolecules: Lipids—The chapter has been extensively revised, with increased detail on prostaglandins (Section 27.4), terpenoid biosynthesis (Section 27.5), and steroid biosynthesis, (Section 27.7).

Chapter 28, Biomolecules: Nucleic Acids—Coverage of heterocyclic chemistry has been moved to Chapter 24.

Chapter 29, The Organic Chemistry of Metabolic Pathways—The chapter has been reorganized and extensively revised, with substantially increased detail on important metabolic pathways.

Chapter 30, Orbitals and Organic Chemistry: Pericyclic Reactions—All the art in this chapter has been redone.

- **The order of topics** remains basically the same but has been changed to devote Chapter 3 entirely to alkanes and Chapter 4 to cycloalkanes. In addition, epoxides are now introduced in Chapter 7 on alkenes, and coverage of heterocyclic chemistry has been moved to Chapter 24.
- **The problems** within and at the end of each chapter have been reviewed, and approximately 100 new problems have been added, many of which focus on biological chemistry.
- **Focus On boxes** at the end of each chapter present interesting applications of organic chemistry relevant to the main chapter subject. Including topics from biology, industry, and day-to-day life, these applications enliven and reinforce the material presented within the chapter. The boxes have been updated, and new ones added, including Where Do Drugs Come From? (Chapter 5),

Green Chemistry (Chapter 11), X-Ray Crystallography (Chapter 22), and Green Chemistry II: Ionic Liquids (Chapter 24).

- **Biologically important molecules and mechanisms** have received particular attention in this edition. Many reactions now show biological counterparts to laboratory examples, many new problems illustrate reactions and mechanisms that occur in living organisms, and enhanced detail is given for major metabolic pathways.

More Features

- NEW!** ■ Why do we have to learn this? I've been asked this question so many times by students that I thought that it would be appropriate to begin each chapter with the answer. The *Why This Chapter?* section is a short paragraph that appears at the end of the introduction to every chapter and tells students why the material about to be covered is important.

- NEW!** ■ Thirteen Key Ideas are highlighted in the book. These include topics pivotal to students' development in organic chemistry, such as Curved Arrows in Reaction Mechanisms (Chapter 5) and Markovnikov's Rule (Chapter 6). These Key Ideas are further reinforced in end-of-chapter problems marked with a ▲ icon. A selection of these problems are also assignable in OWL, denoted by a ■.

- Worked Examples are now titled to give students a frame of reference. Each Worked Example includes a Strategy and a worked-out Solution, and then is followed by problems for students to try on their own. This book has more than 1800 in-text and end-of-chapter problems.

- An overview chapter, *A Preview of Carbonyl Chemistry*, follows Chapter 18 and highlights the author's belief that studying organic chemistry requires both summarizing and looking ahead.

Organic **KNOWLEDGE TOOLS**

- NEW!** ■ Thorough media integration with Organic Knowledge Tools: ThomsonNOW for Organic Chemistry and Organic OWL are provided to help students practice and test their knowledge of the concepts. ThomsonNOW is an online assessment program for self-study with interactive tutorials. Organic OWL is an online homework learning system. Icons throughout the book direct students to ThomsonNOW at www.thomsonedu.com. A fee-based access code is required for Organic OWL.

- NEW!** ■ About 15 to 20 end-of-chapter problems per chapter, denoted with a ■ icon, are assignable in the OWL online homework system. These questions are algorithmically generated, allowing students more practice.



- OWL (Online Web-based Learning) for Organic Chemistry, developed at the University of Massachusetts, Amherst; class-tested by thousands of students; and used by more than 50,000 students, provides fully class-tested questions and tutors in an easy-to-use format. OWL is also customizable and cross-platform. The OWL Online Web-based Learning system provides students with instant grading and feedback on homework problems, modeling questions, and animations to accompany this text. With parameterization, OWL for Organic Chemistry offers nearly 6000 different questions as well as MarvinSketch for viewing and drawing chemical structures.

- A number of the figures are animated in ThomsonNOW. These are designated as **Active Figures** in the figure legends.
- The Visualizing Chemistry Problems that begin the exercises at the end of each chapter offer students an opportunity to see chemistry in a different way by visualizing molecules rather than by simply interpreting structural formulas.
- Summaries and Key Word lists help students by outlining the key concepts of the chapter.
- Summaries of Reactions, at the ends of appropriate chapters, bring together the key reactions from the chapter in one complete list.

Companions to This Text

Supporting instructor materials are available to qualified adopters. Please consult your local Thomson Brooks/Cole representative for details.

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- Find your local representative
- Download electronic files of text art and ancillaries
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Ancillaries for Students

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1

Structure and Bonding

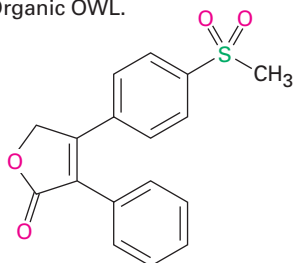
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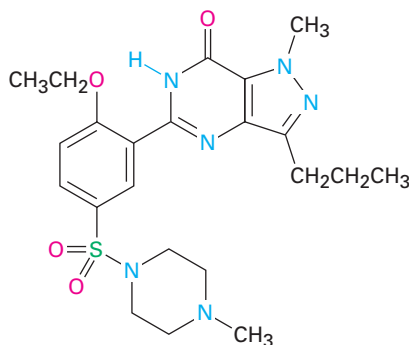


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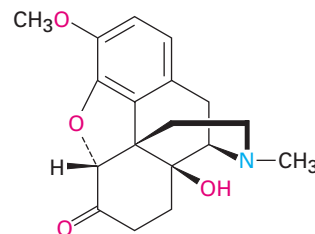
What is organic chemistry, and why should you study it? The answers to these questions are all around you. Every living organism is made of organic chemicals. The proteins that make up your hair, skin, and muscles; the DNA that controls your genetic heritage; the foods that nourish you; and the medicines that heal you are all organic chemicals. Anyone with a curiosity about life and living things, and anyone who wants to be a part of the many exciting developments now happening in medicine and the biological sciences, must first understand organic chemistry. Look at the following drawings for instance, which show the chemical structures of some molecules whose names might be familiar to you.



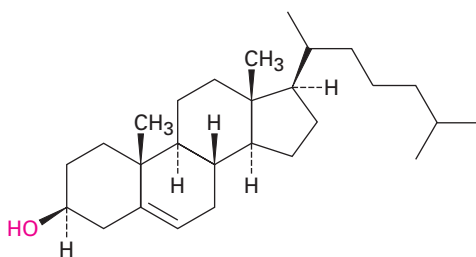
Rofecoxib
(Vioxx)



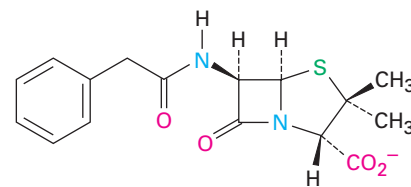
Sildenafil
(Viagra)



Oxycodone
(OxyContin)



Cholesterol



Benzylpenicillin

Although the drawings may appear unintelligible at this point, don't worry. Before long they'll make perfectly good sense and you'll be drawing similar structures for any substance you're interested in.

The foundations of organic chemistry date from the mid-1700s, when chemistry was evolving from an alchemist's art into a modern science. At that time, unexplainable differences were noted between substances obtained from living sources and those obtained from minerals. Compounds obtained from plants and animals were often difficult to isolate and purify. Even when pure, they were often difficult to work with, and they tended to decompose more easily than compounds obtained from minerals. The Swedish chemist Torbern Bergman in 1770 was the first to express this difference between "organic" and "inorganic" substances, and the term *organic chemistry* soon came to mean the chemistry of compounds found in living organisms.

To many chemists of the time, the only explanation for the differences in behavior between organic and inorganic compounds was that organic compounds must contain a peculiar "vital force" as a result of their origin in living sources. One consequence of this vital force, chemists believed, was that organic compounds could not be prepared and manipulated in the laboratory as could inorganic compounds. As early as 1816, however, this vitalistic theory received a heavy blow when Michel Chevreul found that soap, prepared by the reaction of alkali with animal fat, could be separated into several pure organic compounds, which he termed *fatty acids*. For the first time, one organic substance (fat) was converted into others (fatty acids plus glycerin) without the intervention of an outside vital force.

Michel-Eugène Chevreul

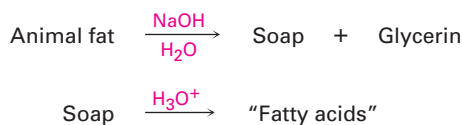
Michel-Eugène Chevreul (1786–1889) was born in Angers, France. After studies at the Collège de France in Paris, he became professor of physics at the Lycée Charlemagne in 1813 and professor of chemistry in 1830. Chevreul's studies of soaps and waxes led him to patent a method for manufacturing candles. He also published work on the psychology of color perception and of aging. All France celebrated his 100th birthday in 1886.

Friedrich Wöhler

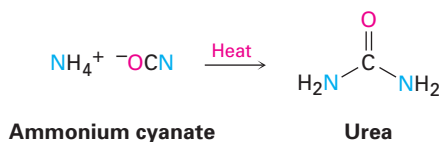
Friedrich Wöhler (1800–1882) was born in Eschersheim, Germany, and studied at Heidelberg under Leopold Gmelin. From 1836 to 1882, he was professor of chemistry at Göttingen. Wöhler developed the first industrial method for preparing aluminum metal, and he discovered several new elements. In addition, he wrote textbooks about both inorganic and organic chemistry.

William Thomas Brande

William Thomas Brande (1788–1866) was born in London, England. Trained as an apothecary, he became a lecturer in chemistry at the University of London in 1808 and was a professor at the Royal Institution from 1813 to 1852. His scientific achievements were modest, although he was the first person to discover naphthalene, now used in mothballs.



Little more than a decade later, the vitalistic theory suffered still further when Friedrich Wöhler discovered in 1828 that it was possible to convert the "inorganic" salt ammonium cyanate into the "organic" substance urea, which had previously been found in human urine.



By the mid-1800s, the weight of evidence was clearly against the vitalistic theory. As William Brande wrote in 1848, "No definite line can be drawn between organic and inorganic chemistry. . . . Any distinctions . . . must for the present be merely considered as matters of practical convenience calculated to further the progress of students." Chemistry today is unified, and the same principles explain the behaviors of all substances, regardless of origin or complexity. The only distinguishing characteristic of organic chemicals is that *all contain the element carbon*.

Organic chemistry, then, is the study of carbon compounds. But why is carbon special? Why, of the more than 30 million presently known chemical compounds, do more than 99% of them contain carbon? The answers to these questions come from carbon's electronic structure and its consequent position in the periodic table (Figure 1.1). As a group 4A element, carbon can share four valence electrons and form four strong covalent bonds. Furthermore, carbon atoms can bond to one another, forming long chains and rings. Carbon, alone of all elements, is able to form an immense diversity of compounds, from the simple to the staggeringly complex—from methane, with one carbon atom, to DNA, which can have more than *100 hundred million* carbons.

Figure 1.1 The position of carbon in the periodic table. Other elements commonly found in organic compounds are shown in the colors typically used to represent them.

		Group 1A																				8A
H	2A											3A	4A	5A	6A	7A	He					
Li	Be											B	C	N	O	F	Ne					
Na	Mg											Al	Si	P	S	Cl	Ar					
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr					
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe					
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn					
Fr	Ra	Ac																				

Not all carbon compounds are derived from living organisms, of course, and chemists over the years have developed a remarkably sophisticated ability to design and synthesize new organic compounds. Medicines, dyes, polymers, food additives, pesticides, and a host of other substances are now prepared in the laboratory. Organic chemistry touches the lives of everyone. Its study is a fascinating undertaking.

WHY THIS CHAPTER?

We'll ease into the study of organic chemistry by first reviewing some ideas about atoms, bonds, and molecular geometry that you may recall from your general chemistry course. Much of the material in this chapter and the next is likely to be familiar to you, but it's nevertheless a good idea to make sure you understand it before going on.

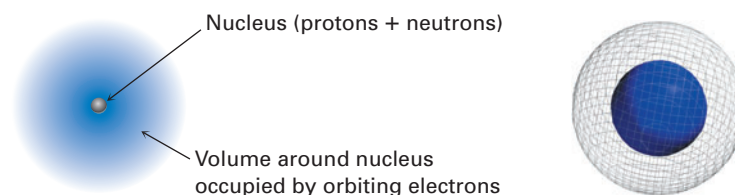
1.1 Atomic Structure: The Nucleus

As you probably know, an atom consists of a dense, positively charged *nucleus* surrounded at a relatively large distance by negatively charged *electrons* (Figure 1.2). The nucleus consists of subatomic particles called *neutrons*, which are electrically neutral, and *protons*, which are positively charged. Because an atom is neutral

overall, the number of positive protons in the nucleus and the number of negative electrons surrounding the nucleus are the same.

Although extremely small—about 10^{-14} to 10^{-15} meter (m) in diameter—the nucleus nevertheless contains essentially all the mass of the atom. Electrons have negligible mass and circulate around the nucleus at a distance of approximately 10^{-10} m. Thus, the diameter of a typical atom is about 2×10^{-10} m, or 200 *picometers* (pm), where $1 \text{ pm} = 10^{-12} \text{ m}$. To give you an idea of how small this is, a thin pencil line is about 3 million carbon atoms wide. Many organic chemists and biochemists, particularly in the United States, still use the unit *angstrom* (Å) to express atomic distances, where $1 \text{ Å} = 10^{-10} \text{ m} = 100 \text{ pm}$, but we'll stay with the SI unit picometer in this book.

Figure 1.2 A schematic view of an atom. The dense, positively charged nucleus contains most of the atom's mass and is surrounded by negatively charged electrons. The three-dimensional view on the right shows calculated electron-density surfaces. Electron density increases steadily toward the nucleus and is 40 times greater at the blue solid surface than at the gray mesh surface.



A specific atom is described by its *atomic number* (Z), which gives the number of protons in the atom's nucleus, and its *mass number* (A), which gives the total of protons plus neutrons in its nucleus. All the atoms of a given element have the same atomic number—1 for hydrogen, 6 for carbon, 15 for phosphorus, and so on—but they can have different mass numbers, depending on how many neutrons they contain. Atoms with the same atomic number but different mass numbers are called **isotopes**. The weighted average mass in atomic mass units (amu) of an element's naturally occurring isotopes is called the element's *atomic mass* (or *atomic weight*)—1.008 amu for hydrogen, 12.011 amu for carbon, 30.974 amu for phosphorus, and so on.

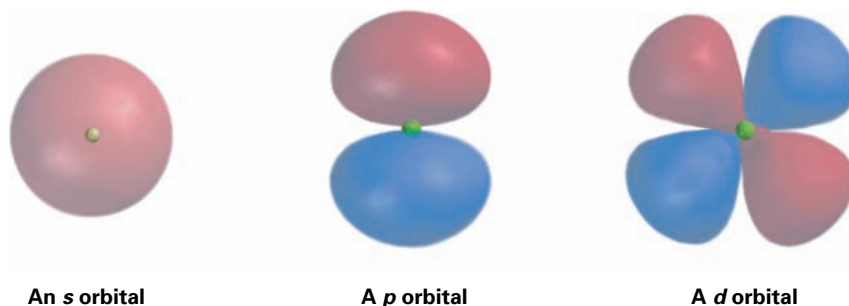
1.2 Atomic Structure: Orbitals

How are the electrons distributed in an atom? You might recall from your general chemistry course that, according to the quantum mechanical model, the behavior of a specific electron in an atom can be described by a mathematical expression called a *wave equation*—the same sort of expression used to describe the motion of waves in a fluid. The solution to a wave equation is called a *wave function*, or **orbital**, and is denoted by the Greek letter psi, ψ .

By plotting the square of the wave function, ψ^2 , in three-dimensional space, the orbital describes the volume of space around a nucleus that an electron is most likely to occupy. You might therefore think of an orbital as looking like a photograph of the electron taken at a slow shutter speed. The orbital would appear as a blurry cloud indicating the region of space around the nucleus where the electron has been. This electron cloud doesn't have a sharp boundary, but for practical purposes we can set the limits by saying that an orbital represents the space where an electron spends most (90%–95%) of its time.

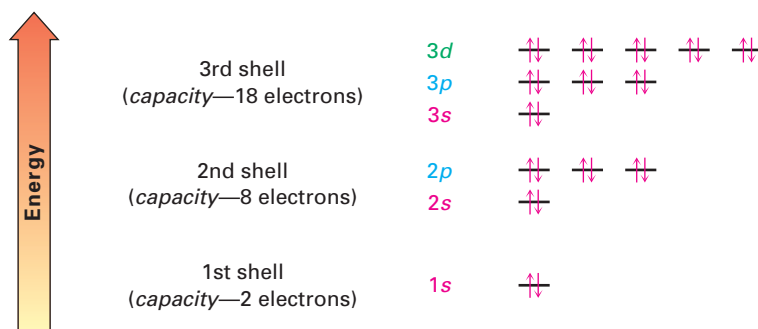
What do orbitals look like? There are four different kinds of orbitals, denoted s , p , d , and f , each with a different shape. Of the four, we'll be concerned primarily with s and p orbitals because these are the most common in organic and biological chemistry. The s orbitals are spherical, with the nucleus at their center; p orbitals are dumbbell-shaped; and four of the five d orbitals are cloverleaf-shaped, as shown in Figure 1.3. The fifth d orbital is shaped like an elongated dumbbell with a doughnut around its middle.

Figure 1.3 Representations of s , p , and d orbitals. The s orbitals are spherical, the p orbitals are dumbbell-shaped, and four of the five d orbitals are cloverleaf-shaped. Different lobes of p orbitals are often drawn for convenience as teardrops, but their true shape is more like that of a doorknob, as indicated.



The orbitals in an atom are organized into different layers, or **electron shells**, of successively larger size and energy. Different shells contain different numbers and kinds of orbitals, and each orbital within a shell can be occupied by two electrons. The first shell contains only a single s orbital, denoted $1s$, and thus holds only 2 electrons. The second shell contains one $2s$ orbital and three $2p$ orbitals and thus holds a total of 8 electrons. The third shell contains a $3s$ orbital, three $3p$ orbitals, and five $3d$ orbitals, for a total capacity of 18 electrons. These orbital groupings and their energy levels are shown in Figure 1.4.

Figure 1.4 The energy levels of electrons in an atom. The first shell holds a maximum of 2 electrons in one $1s$ orbital; the second shell holds a maximum of 8 electrons in one $2s$ and three $2p$ orbitals; the third shell holds a maximum of 18 electrons in one $3s$, three $3p$, and five $3d$ orbitals; and so on. The two electrons in each orbital are represented by up and down arrows, $\uparrow\downarrow$. Although not shown, the energy level of the $4s$ orbital falls between $3p$ and $3d$.



The three different p orbitals within a given shell are oriented in space along mutually perpendicular directions, denoted p_x , p_y , and p_z . As shown in Figure 1.5, the two lobes of each p orbital are separated by a region of zero electron density called a **node**. Furthermore, the two orbital regions separated by the node have different algebraic signs, $+$ and $-$, in the wave function. As we'll see in Section 1.11, the algebraic signs of the different orbital lobes have important consequences with respect to chemical bonding and chemical reactivity.