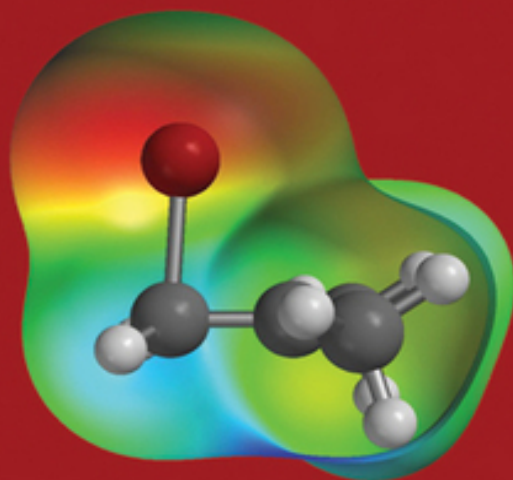


S E C O N D E D I T I O N

Perspectives on
**Structure and
Mechanism**
in Organic Chemistry



FELIX A. CARROLL

 WILEY

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PERSPECTIVES ON STRUCTURE AND MECHANISM IN ORGANIC CHEMISTRY

Second Edition

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Preface

This book is the result of my experience teaching physical organic chemistry at Davidson College. During this time I felt a need for a text that not only presents concepts that are central to the understanding and practice of physical organic chemistry but that also teaches students to think about organic chemistry in new ways, particularly in terms of complementary conceptual models. Because of this approach, the first edition of *Perspectives on Structure and Mechanism in Organic Chemistry* attracted attention beyond the chemistry community and was even quoted in a philosophy dissertation.¹

Soon after the first edition appeared, I received a telephone call from a student of the philosophy of science, who asked how I came to write a book with this emphasis. I did not have a ready answer, but as we talked I realized that this was primarily due to the influences of George Hammond and Jacob Bronowski. I was a graduate student with George Hammond. Although I cannot recall ever discussing conceptual models with him, his views were nonetheless imprinted on me—but in such a subtle way that I did not fully recognize it at the time. Jacob Bronowski's impact was more distinct because it resulted from a single event—the film *Knowledge or Certainty* in a series titled *The Ascent of Man*. That film offers a powerful commentary on both the limits of human knowledge and the nature of science as “a tribute to what we can know although we are fallible.”^{2a} Perhaps a hybridization of their influences led me to emphasize that familiar conceptual models are only beginning points for describing structures and reactions and that using complementary models can provide a deeper understanding of organic chemistry than can using any one model alone.

As with the first edition, the first five chapters of this book consider structure and bonding of stable molecules and reactive intermediates. There is a chapter on methods organic chemists use to study reaction mechanisms, and then acid-base reactions, substitution reactions, addition reactions, elimination reactions, pericyclic reactions, and photochemical reactions are considered in subsequent chapters. In each case I have updated the content to reflect developments since publication of the first edition.

It is essential for an advanced text to provide complete references. The literature citations in this edition range from 1851 to 2009. They direct interested readers to further information about all of the topics and also acknowledge the researchers whose efforts produced the information summarized here. A teaching text must also provide a set of problems of varying difficulty. The nearly 400 problems in this edition do more than just allow students to test their understanding of the facts and concepts presented in a chapter. They also encourage readers to actively engage the chemical literature and to develop and defend their own ideas. Some problems represent straightforward applications of the information in the text, but other problems can best be answered by consulting the literature for background information before attempting a solution. Still other problems are open-ended, with no one "correct" answer. I have prepared a solutions manual giving answers for problems in the first two categories as well as comments about the open-ended problems.

In *Knowledge or Certainty*, Bronowski shows many portraits of the same human face and observes that "we are aware that these pictures do not so much fix the face as explore it... and that each line that is added strengthens the picture but never makes it final."^{2b} So it is with this book. It is not a photograph but is, instead, a portrait of physical organic chemistry. As with the human face, it is not possible

to fix a continually changing science—we can only explore it. I hope that the lines added in this edition will better enable readers to develop a deeper and more complete understanding of physical organic chemistry.

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¹ Weisberg, M. *When Less is More: Tradeoffs and Idealization in Model Building*; Ph.D. Dissertation, Stanford University, 2003. See also Weisberg, M. *Philos. Sci.* **2004**, *71*, 1071.

² The quotations are from the book with the same title as the film series: Bronowski, J. *The Ascent of Man*; Little, Brown and Company, Boston, 1973; (a) p. 374; (b) p. 353.

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F. A. C

Introduction

Every organic chemist instantly recognizes the drawing in [Figure 1](#) as benzene, or at least one of the Kekulé structures of benzene. Yet, it is not benzene. It is a geometric figure consisting of a regular hexagon enclosing three extra lines, prepared by marking white paper with black ink. When we look at the drawing, however, we see benzene. That is, we visualize a colorless liquid, and we recall a pattern of physical properties and chemical reactivity associated with benzene and with the concept of aromaticity. The drawing in [Figure 1](#) is therefore only a macroscopic representation of a presumed submicroscopic entity. Even more, the drawing symbolizes the *concept* of benzene, particularly its structural features and patterns of reactivity.¹

[FIGURE 1.1](#) A familiar drawing.



That all organic chemists instantly recognize the drawing in [Figure 1](#) as benzene is confirmation that they have been initiated into the chemical fraternity. The tie that binds the members of this fraternity is more than a collective interest. It is also a common way of viewing problems and their solutions. The educational process that initiates members into this fraternity, like other initiations, can lead to considerable conformity of thinking and of behavior.² Such conformity facilitates communication among members of the group, but it can limit independent behavior and action.

This common way of looking at problems was explored by T. S. Kuhn in *The Structure of Scientific Revolutions*.³ Kuhn described processes fundamental to all of the sciences, and he discussed two related meanings of the term *paradigm*:

On the one hand, it stands for the entire constellation of beliefs, values, techniques, and so on shared by the members of a given community. On the other it denotes one sort of element in that constellation, the concrete puzzle solutions which, employed as models or examples, can replace explicit rules as a basis for the solution of the remaining puzzles of normal science. ^{3a,4}

The parallel with a fraternity is more closely drawn by Kuhn's observation

... one of the things a scientific community acquires with a paradigm is a criterion for choosing problems that, while the paradigm is taken for granted, can be assumed to have solutions. To a great extent these are the only problems that the community will admit as scientific or encourage its members to undertake. Other problems... are rejected as metaphysical, as the concern of another discipline, or sometimes as just too problematic to be worth the time. A paradigm can, for that matter, even insulate the community from those socially important problems that are not reducible to the puzzle form, because they cannot be stated in terms of the conceptual and instrumental tools the paradigm supplies. ^{3b,5,6}

The history of *phlogiston* illustrates how paradigms can dictate chemical thought. Phlogiston was said to be the "principle" of combustibility—a substance thought to be given off by burning matter.⁷ The phlogiston theory was widely accepted and was taught to students as established fact.⁸ As is the case with the ideas we accept, the phlogiston theory could rationalize observable phenomena (combustion) and could account for new observations (such as the death of animals confined in air-tight containers).⁹ As is also the case with contemporary theories, the phlogiston model could be modified to account for results that did not agree with its predictions. For example, experiments

showed that some substances actually gained weight when they burned, rather than losing weight as might have been expected if a real substance had been lost by burning. Rather than abandoning the phlogiston theory, however, some of its advocates rationalized the results by proposing that phlogiston had negative weight.

As this example teaches us, once we have become accustomed to thinking about a problem in a certain way, it becomes quite difficult to think about it differently. Paradigms in science are therefore like the operating system of a computer: they dictate the input and output of information and control the operation of logical processes. Chamberlin stated the same idea with a human metaphor:

The moment one has offered an original explanation for a phenomenon which seems satisfactory, that moment affection for his intellectual child springs into existence.... From an unduly favored child, it readily becomes master, and leads its author whithersoever it will.¹⁰

Recognizing that contemporary chemistry is based on widely (if perhaps not universally) accepted paradigms does not mean that we should resist using them. This point was made in 1929 in an address by Irving Langmuir, who was at that time president of the American Chemical Society.

Skepticism in regard to an absolute meaning of words, concepts, models or mathematical theories should not prevent us from using all these abstractions in describing natural phenomena. The progress of physical chemistry was probably set back many years by the failure of the chemists to take full advantage of the atomic theory in describing the phenomena that they observed. The rejection of the atomic theory for this purpose was, I believe, based primarily upon a mistaken attempt to describe nature in some absolute manner. That is, it was thought that such concepts as energy, entropy, temperature, chemical potential, etc., represented

something far more nearly absolute in character than the concept of atoms and molecules, so that nature should preferably be described in terms of the former rather than the latter. We must now recognize, however, that all of these concepts are human inventions and have no absolute independent existence in nature. Our choice, therefore, cannot lie between fact and hypothesis, but only between two concepts (or between two models) which enable us to give a better or worse description of natural phenomena.¹¹

Langmuir's conclusion is correct but, I think, incomplete. Saying that we often choose between two models does not mean that we must, from the time of that choice forward, use only the model that we accept. Instead, we must continually make selections, consciously or subconsciously, among many complementary models.¹² Our choice of models is usually shaped by the need to solve the problems at hand. For example, Lewis electron dot structures and resonance theory provide adequate descriptions of the structures and reactions of organic compounds for some purposes, but in other cases we need to use molecular orbital theory or valence bond theory. Frequently, therefore, we find ourselves alternating between these models. Furthermore, consciously using complementary models to think about organic chemistry reminds us that our models are only human constructs and are not windows into reality.

In each of the chapters of this text, we will explore the use of different models to explain and predict the structures and reactions of organic compounds. For example, we will consider alternative explanations for the hybridization of orbitals, the σ, π description of the carbon-carbon double bond, the effect of branching on the stability of alkanes, the electronic nature of substitution reactions, the acid-base properties of organic compounds, and the nature of concerted reactions. The complementary models presented

in these discussions will give new perspectives on the structures and reactions of organic compounds.

¹ For a discussion of “Representation in Chemistry,” including the nature of drawings of benzene rings, see Hoffmann, R.; Laszlo, P. *Angew. Chem. Int. Ed. Engl.* **1991**, *30*,1. For a discussion of the iconic nature of some chemical drawings, see Whitlock, H. W. J. *Org. Chem.* **1991**, *56*, 7297.

² Moreover, the interaction of these scientists with those who do not share their interests can be inhibited through what might be called a “sociological hydrophobic effect.”

³ Kuhn, T. S. *The Structure of Scientific Revolutions*, 2nd ed.; The University of Chicago Press: Chicago, 1970; (a) p. 175; (b) p. 37.

⁴ The paradigm that we may think of chemistry only through paradigms may be an appropriate description of Western science only. For an interesting discussion of “Sushi Science and Hamburger Science,” see Motokawa, T. *Perspect. Biol. Med.* **1989**, *32*, 489.

⁵ See also the discussion of Sternberg, R. J. *Science* **1985**, *230*, 1111.

⁶ The peer review process for grant proposals can be one way a scientific community limits the problems its members are allowed to undertake.

⁷ White, J. H. *The History of the Phlogiston Theory*; Edward Arnold & Co.: London, 1932.

⁸ Conant, J. B. *Science and Common Sense*; Yale University Press: New Haven, 1951; pp. 170–171.

⁹ Note the defense of phlogiston by Priestly cited by Pimentel, G. *Chem. Eng. News* **1989** (May 1), p. 53.

¹⁰ Chamberlin, T. C. *Science* **1965**, *148*, 754; reprinted from *Science* (old series) **1890**, *15*, 92. For further discussion of this view, see Bunnett, J. F. in Lewis, E. S., Ed. *Investigation of Rates and Mechanisms of Reactions*, 3rd ed., Part I; Wiley-Interscience: Hoboken, NJ, 1975; p. 478-479.

¹¹ Langmuir, I. *J. Am. Chem. Soc.* **1929**, *51*, 2847.

¹² For other discussions of the role of models in chemistry, see (a) Hammond, G. S.; Osteryoung, J.; Crawford, T. H.; Gray, H. B. *Models in Chemical Science: An Introduction to General Chemistry*; W. A. Benjamin, Inc.: New York, 1971; pp. 2-7; (b) Sunko, D. E. *Pure Appl. Chem.* **1983**, *55*, 375; (c) Bent, H. A. *J. Chem. Educ.* **1984**, *61*, 774; (d) Goodfriend, P. L. *J. Chem. Educ.* **1976**, *53*, 74; (e) Morwick, J. J. *J. Chem. Educ.* **1978**, *55*, 662; (f) Matsen, F. A. *J. Chem. Educ.* **1985**, *62*, 365; (g) Dewar, M. J. S. *J. Phys. Chem.* **1985**, *89*, 2145.

CHAPTER 1

Fundamental Concepts of Organic Chemistry

1.1 ATOMS AND MOLECULES

Fundamental Concepts

Organic chemists think of atoms and molecules as basic units of matter. We work with mental pictures of atoms and molecules, and we rotate, twist, disconnect, and reassemble physical models in our hands.^{1,2} Where do these mental images and physical models come from? It is useful to begin thinking about the fundamental concepts of organic chemistry by asking a simple question: What do we know about atoms and molecules, and how do we know it? As Kuhn pointed out,

Though many scientists talk easily and well about the particular individual hypotheses that underlie a concrete piece of current research, they are little better than laymen at characterizing the established bases of their field, its legitimate problems and methods.³

The majority of what we know in organic chemistry consists of what we have been taught. Underlying that teaching are observations that someone has made and someone has interpreted. The most fundamental observations are those that we can make directly with our senses. We note the physical state of a substance—solid, liquid, or gas. We see its color or lack of color. We observe

whether it dissolves in a given solvent or whether it evaporates if exposed to the atmosphere. We might get some sense of its density by seeing it float or sink when added to an immiscible liquid. These are qualitative observations, but they provide an important foundation for further experimentation.

It is only a modest extension of direct observation to the use of some simple experimental apparatus for quantitative measurements. We use a heat source and a thermometer to determine melting and boiling ranges. We use other equipment to measure indices of refraction, densities, surface tensions, viscosities, and heats of reaction. Through classical elemental analysis, we determine what elements are present in a sample and what their mass ratios seem to be. Then we might determine a formula weight through melting point depression. In all of these experiments, *we use some equipment but still make the actual experimental observations by eye.* These limited experimental techniques can provide essential information nonetheless. For example, if we find that 159.8 grams of bromine will always be decolorized by 82.15 grams of cyclohexene, then we can observe the law of definite proportions. Such data are consistent with a model of matter in which submicroscopic particles combine with each other in characteristic patterns, just as the macroscopic samples before our eyes do. It is then only a matter of definition to call the submicroscopic particles atoms or molecules and to further study their properties. It is essential, however, to remember that our laboratory experiments are conducted with *materials*. While we may talk about the addition of bromine to cyclohexene in terms of individual molecules, we really can only infer that such a process occurs on the basis of experimental data collected with macroscopic samples of the reactants.

Modern instrumentation has opened the door to a variety of investigations, most unimaginable to early chemists, that

expand the range of observations beyond those of the human senses. These instruments extend our eyes from seeing only a limited portion of the electromagnetic spectrum to practically the entire spectrum, from X-rays to radio waves, and they let us “see” light in other ways (e.g., in polarimetry). They allow us to use entirely new tools, such as electron or neutron beams, magnetic fields, and electrical potentials or current. They extend the range of conditions for studying matter from near atmospheric pressure to high vacuum and to high pressure. They effectively expand and compress the time scale of the observations, so we can study events that require eons or that occur in femtoseconds.^{4,5}

The unifying characteristic of modern instrumentation is that we no longer observe the chemical or physical change directly. Instead, we observe it only indirectly, such as through the change in illuminated pixels on a computer display. With such instruments, it is essential that we recognize the difficulty in freeing the observations from constraints imposed by our expectations. *To a layperson*, a UV-vis spectrum may not seem all that different from an upside-down infrared spectrum, and a capillary gas chromatogram of a complex mixture may appear to resemble a mass spectrum. But the chemist sees these traces not as lines on paper but as vibrating or rotating molecules, as electrons moving from one place to another, as substances separated from a mixture, or as fragments from molecular cleavage. Thus, implicit assumptions about the origins of experimental data both make the observations interpretable and influence the interpretation of the data.⁶

With that caveat, what do we know about molecules and how do we know it? We begin with the idea that organic compounds and all other substances are composed of atoms—indivisible particles which are the smallest units of that particular kind of matter that still retain all its

properties. It is an idea whose origin can be traced to ancient Greek philosophers.⁷ Moreover, it is convenient to correlate our observation that substances combine only in certain proportions with the notion that these submicroscopic entities called atoms combine with each other only in certain ways.

Much of our fundamental information about molecules has been obtained from spectroscopy.⁸ For example, a 4000 V electron beam has a wavelength of 0.06 Å, so it is diffracted by objects larger than that size.⁹ Interaction of the electron beam with gaseous molecules produces characteristic circular patterns that can be interpreted in terms of molecular dimensions.¹⁰ We can also determine internuclear distance through infrared spectroscopy of diatomic molecules, and we can use X-ray or neutron scattering to calculate distances of atoms in crystals.

“Pictures” of atoms and molecules maybe obtained through atomic force microscopy (AFM) and scanning tunneling microscopy (STM).^{11,12} For example, Custance and co-workers reported using atomic force microscopy to identify individual silicon, tin, and lead atoms on the surface of an alloy.¹³ Researchers using these techniques have reported the manipulation of individual molecules and atoms.¹⁴ There have been reports in which STM was used to dissociate an individual molecule and then examine the fragments,¹⁵ to observe the abstraction of a hydrogen atom from H₂S and from H₂O,¹⁶ and to reversibly break a single N-H bond.¹⁷ Such use of STM has been termed *angstrochemistry*.¹⁸ Moreover, it was proposed that scanning tunneling microscopy and atomic force microscopy could be used to image the lateral profiles of individual sp^3

hybrid orbitals.¹⁹ Some investigators have reported imaging single organic molecules in motion with a very different technique, transmission electron microscopy,²⁰ and others have reported studying electron transfer to single polymer molecules with single-molecule spectroelectrochemistry.²¹

Even though “seeing is believing,” we must keep in mind that in all such experiments we do not really see molecules; we see only computer graphics. Two examples illustrate this point: STM features that had been associated with DNA molecules were later assigned to the surface used to support the DNA,²² and an STM image of benzene molecules was reinterpreted as possibly showing groups of acetylene molecules instead.²³

Organic chemists also reach conclusions about molecular structure on the basis of logic. For example, the fact that one and only one substance has been found to have the molecular formula CH_3Cl is consistent with a structure in which three hydrogen atoms and one chlorine atom are attached to a carbon atom in a tetrahedral arrangement. If methane were a trigonal pyramid, then two different compounds with the formula CH_3Cl might be possible—one with chlorine at the apex of the pyramid and another with chlorine in the base of the pyramid. The existence of only one isomer of CH_3Cl does not require a tetrahedral arrangement, however, since we might also expect only one isomer if the four substituents to the carbon atom were arranged in a square pyramid with a carbon atom at the apex or in a square planar structure with a carbon atom at the center. Since we also find one and only one CH_2Cl_2 molecule, however, we can also rule out the latter two geometries. Therefore we infer that the parent compound, methane, is also tetrahedral. This view is reinforced by the

existence of two different structures (enantio-mers) with the formula CHClBrF . Similarly, we infer the flat, aromatic structure for benzene by noting that there are three and only three isomers of dibromobenzene.²⁴

Organic chemists do not think of molecules only in terms of atoms, however. We often envision molecules as collections of nuclei and electrons, and we consider the electrons to be constrained to certain regions of space (orbitals) around the nuclei. Thus, we interpret UV-vis absorption, emission, or scattering spectroscopy in terms of movement of electrons from one of these orbitals to another. These concepts resulted from the development of quantum mechanics. The Bohr model of the atom, the Heisenberg uncertainty principle, and the Schrödinger equation laid the foundation for our current ways of thinking about chemistry. There may be some truth in the statement that

The why? and how? as related to chemical bonding were in principle answered in 1927; the details have been worked out since that time.²⁵

We will see, however, that there are still uncharted frontiers of those details to explore in organic chemistry.

TABLE 1.1 Bond Lengths and Bond Angles for Methyl Halides

Source: Reference 29.

Molecule	$r_{\text{C-H}}$ (Å)	$r_{\text{C-X}}$ (Å)	$\angle_{\text{H-C-H}}$	$\angle_{\text{H-C-X}}$
CH_3F	1.105	1.385	$109^\circ 54'$	$109^\circ 2'$
CH_3Cl	1.096	1.781	$110^\circ 52'$	$108^\circ 0'$
CH_3Br	1.10	1.939	$111^\circ 38'$	$107^\circ 14'$
CH_3I	1.096	2.139	$111^\circ 50'$	$106^\circ 58'$

Molecular Dimensions

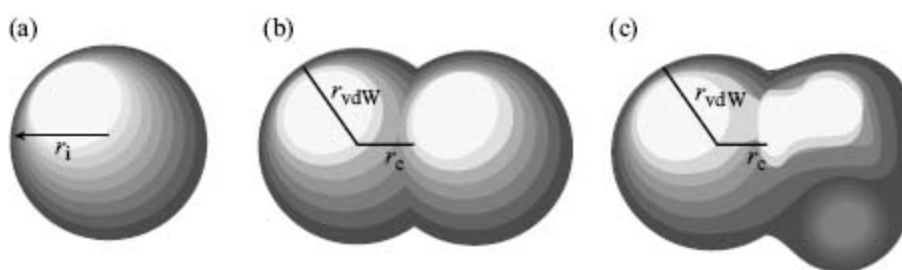
Data from spectroscopy or from X-ray, electron, or neutron diffraction measurements allow us to determine the distance between atomic centers as well as to measure the angles between sets of atoms in covalently bonded molecules.²⁶ The most detailed information comes from microwave spectroscopy, although that technique is more useful for lower molecular weight than higher molecular weight molecules because the sample must be in the vapor phase.²⁷ Diffraction methods locate a center of electron density instead of a nucleus. The center of electron density is close to the nucleus for atoms that have electrons below the valence shell. For hydrogen, however, the electron density is shifted toward the atom to which it is bonded, and bonds to hydrogen are determined by diffraction methods to be shorter than are bond lengths determined with spectroscopy.²⁸ With solid samples, the possible effect of crystal packing forces must also be considered. Therefore, the various techniques give slightly different measures of molecular dimensions.

[Table 1.1](#) shows data for the interatomic distances and angles of the methyl halides.²⁹ These distances and angles only provide geometric information about the location of nuclei (or local centers of electron density) as points in space. We infer that those points are connected by chemical bonds, so that the distance $r_{\text{C-H}}$ is the length of a C-H bond and the angle $\angle_{\text{H-C-H}}$ is the angle between two C-H bonds.

We may also define atomic dimensions, including the ionic radius (r_i), the covalent radius (r_c), and the van der Waals radius (r_{vdW}) of an atom.³⁰ The ionic radius is the apparent size of the electron cloud around an ion as deduced from the packing of ions into a crystal lattice.³¹ As might be expected, this value varies with the charge on the ion. The

ionic radius for a C^{4+} ion is 0.15 Å, while that for a C^{4-} ion is 2.60 Å.³⁰ The van der Waals radius is the effective size of the atomic cloud around a covalently bonded atom as perceived by another atom to which it is not bonded, and it also is determined from interatomic distances found in crystals. Note that the van der Waals radius is not the distance at which the repulsive interactions of the electrons on the two atoms outweigh the attractive forces between them, as is often assumed. Rather, it is a crystal packing measurement that gives a smaller value.^{32,33} The covalent radius of an atom indicates the size of an atom when it is part of a covalent bond, and this distance is much less than the van der Waals radius.³⁴ Figure 1.1 illustrates these radii for chlorine. The computer-drawn plots of electron density surfaces represent the following: (a) r_i for chloride ion; (b) r_c and r_{vdW} for chlorine in Cl_2 ; (c) r_c and r_{vdW} for chlorine in CH_3Cl .³⁵

FIGURE 1.1 Radii values for chlorine.



[Table 1.2](#) lists ionic and covalent radii values for several atoms. Note that the covalent radius for an atom depends on its bonding. A carbon atom with four single bonds has a covalent radius of 0.76 Å. The value is 0.73 Å for a carbon atom with one double bond, while the covalent radius for a triple-bonded carbon atom is 0.69 Å. The covalent radius of hydrogen varies considerably. The value of r_c for hydrogen

is calculated to be 0.30 Å in H₂O and 0.32 Å in CH₄.³⁰ We can also assign an r_{vdW} to a group of atoms. The value for a CH₃ or CH₂ group is 2.0 Å, while the van der Waals thickness of half the electron cloud in an aromatic ring is 1.85 Å.³⁰ Knowledge of van der Waals radii is important in calculations of molecular structure and reactivity, particularly with regard to proteins.³⁶

We may use the atomic radii to calculate the volume and the surface area of an atom. Then using the **principle of additivity** (meaning that the properties of a molecule can be predicted by summing the contributions of its component parts), we may calculate values for the volumes and surface areas of molecules. Such calculations were described by Bondi, and a selected set of atomic volume and surface areas is given in [Table 1.3](#). For example, we estimate the molecular volume of propane by counting $2 \times 13.67 \text{ cm}^3/\text{mol}$ for the two methyl groups plus $10.23 \text{ cm}^3/\text{mol}$ for the methylene group, giving a total volume of $37.57 \text{ cm}^3/\text{mol}$. Similarly, we calculate that the volume of the atoms in hexane is $2 \times 13.67 \text{ cm}^3/\text{mol}$ for the two methyl groups plus $4 \times 10.23 \text{ cm}^3/\text{mol}$ for the four methylene groups, making a total volume of $68.26 \text{ cm}^3/\text{mol}$. The volume of one mole of liquid hexane at 20° is 130.5 mL, which means that nearly half of the volume occupied by liquid hexane corresponds to space that is outside the boundaries of the carbon and hydrogen atoms as defined above.

[TABLE 1.2](#) Comparison of van der Waals, Ionic, and Covalent Radii for Selected Atoms (Å)

Source: Reference 30.

Atom	van der Waals Radius (r_{vdW}) ^a	Ionic Radius		Covalent Radii (r_c)		
		Ion	r_i	Single Bonded ^b	Double Bonded	Triple Bonded
H	1.11 Å	H ⁻	2.08 Å	0.31 Å		
C	1.68	C ⁴⁻	2.60	0.76	0.73 ^b	0.69 ^b
N	1.53	N ³⁻	1.71	0.71		
O	1.50	O ²⁻	1.40	0.66		
F	1.51	F ⁻	1.36	0.57		
Cl	1.84	Cl ⁻	1.81	1.02	0.89	
Br	1.96	Br ⁻	1.95	1.20	1.04	
I	2.13	I ⁻	2.16	1.39	1.23	
P	1.85	P ³⁻	2.12	1.07	1.00	0.93
S	1.82	S ²⁻	1.64	1.05	0.94	0.87
Si	2.04	Si ⁴⁻	2.71	1.11	1.07	1.00

^aReference 37.

^bReference 34.

TABLE 1.3 Group Contributions to van der Waals Atomic Volume (V_W) and Surface Area (A_W)

Source: Reference 32.

Group	V_W (cm ³ /mole)	A_W (cm ² /mole x 10 ⁹)
Alkane, C bonded to four other carbon atoms	3.33	0
Alkane, CH bonded to three other carbon atoms	6.78	0.57
Alkane, CH ₂ bonded to two other carbon atoms	10.23	1.35
Alkane, CH ₃ bonded to one other carbon atom	13.67	2.12
CH ₄	17.12	2.90
F, bonded to a 1° carbon atom	5.72	1.10
F, bonded to a 2° or 3° carbon atom	6.20	1.18
Cl, bonded to a 1° carbon atom	11.62	1.80
Cl, bonded to a 2° or 3° carbon atom	12.24	1.82
Br, bonded to a 1° carbon atom	14.40	2.08