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.

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[1] For a detailed discussion of physical models in chemistry, see Walton, A. *Molecular and Crystal Structure Models*; Ellis Horwood: Chichester, England, 1978.

[2] For an interesting application of physical models to infer molecular properties, see Teets, D. E.; Andrews, D. H. *J. Chem. Phys.* **1935**, *3*, 175.

[3] Kuhn, T. S. *The Structure of Scientific Revolutions*, 2nd ed.; The University of Chicago Press: Chicago, 1970; p. 47.

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]

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[4] A femtosecond (fs) is 10^{-15} s. Rosker, M. J.; Dantus, M.; Zewail, A. H. *Science* **1988**, *241*, 1200 reported that the photodissociation of ICN to I and CN occurs in ca. 100 femtoseconds. See also Dantus, M.; Zewail, A. *Chem. Rev.* **2004**, *104*, 1717 and subsequent papers in this issue.

[5] Baker, S.; Robinson, J. S.; Haworth, C. A.; Teng, H.; Smith, R. A.; Chirlǎ, C. C.; Lein, M.; Tisch, J. W. G.; Marangos, J. P. *Science* **2006**, *312*, 424; Osborne, I.; Yeston, J. *Science* **2007**, *317*, 765 and subsequent papers.

[6] "Innocent, unbiased observation is a myth."—P. Medawar, quoted in *Science* **1985**, *227*, 1188.

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 may be 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 H_2S and from H_2O,[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

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[7] Asimov, I. *A Short History of Chemistry*; Anchor Books: Garden City, NY, 1965; pp. 8–14.

[8] For a review of structure determination methods, see Gillespie, R. J.; Hargittai, I. *The VSEPR Model of Molecular Geometry*; Allyn and Bacon: Boston, 1991; pp. 25–39.

[9] Moore, W. J. *Physical Chemistry*, 3rd ed.; Prentice-Hall: Englewood Cliffs, NJ, 1962; p. 575 ff.

[10] For discussions of structure determination with gas phase electron diffraction, see Karle, J. in Maksić, Z. B.; Eckert-Maksić, M., Eds. *Molecules in Natural Science and Medicine*; Ellis Horwood: Chichester, England, 1991; pp. 17–27; Hedberg, K. *ibid.*; pp. 29–42.

[11] Hou, J. G.; Wang, K. *Pure Appl. Chem.* **2006**, *78*, 905.

[12] See Ottensmeyer, F. P.; Schmidt, E. E.; Olbrecht, A. J. *Science* **1973**, *179*, 175 and references therein; Robinson, A. L. *Science* **1985**, *230*, 304; *Chem. Eng. News* **1986** (Sept. 1), 4; Hansma, P. K.; Elings, V. B.; Marti, O.; Bracker, C. E. *Science* **1988**, *242*, 209; Parkinson, B. A. *J. Am. Chem. Soc.* **1990**, *112*, 1030; Frommer, J. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1298.

[13] Sugimoto, Y.; Pou, P.; Abe, M.; Jelinek, P.; Perez, R.; Morita, S.; Custance, O. *Nature* (*London*) **2007**, *446*, 64.

[14] Weisenhorn, A. L.; Mac Dougall, J. E.; Gould, S. A. C.; Cox, S. D.; Wise, W. S.; Massie, J.; Maivald, P.; Elings, V. B.; Stucky, G. D.; Hansma, P. K. *Science* **1990**, *247*, 1330; Whitman, L. J.; Stroscio, J. A.; Dragoset, R. A.; Celotta, R. J. *Science* **1991**, *251*, 1206; Leung, O. M.; Goh, M. C. *Science* **1992**, *255*, 64.

[15] Dujardin, G.; Walkup, R. E.; Avouris, P. *Science* **1992**, *255*, 1232.

[16] Lauhon, L. J.; Ho, W. *J. Phys. Chem. B*, **2001**, *105*, 3987.

[17] Katano, S.; Kim, Y.; Hori, M.; Trenary, M.; Kawai, M. *Science* **2007**, *316*, 1883.

[18] For a review of the application of scanning tunneling microscopy to manipulation of bonds, see Ho, W. *Acc. Chem. Res.* **1998**, *31*, 567.

[19] Chen, J. C. *Nanotechnology* **2006**, *17*, S195.

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 (enantiomers) 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.

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[20] Koshino, M.; Tanaka, T.; Solin, N.; Suenaga, K.; Isobe, H.; Nakamura, E. *Science*, **2007**, *316*, 853.

[21] Palacios, R. E.; Fan, F.-R. F.; Bard, A. J.; Barbara, P. F. *J. Am. Chem. Soc.* **2006**, *128*, 9028.

[22] Clemmer, C. R.; Beebe, T. P., Jr. *Science* **1991**, *251*, 640.

[23] Moler, J. L.; McCoy, J. R. *Chem. Eng. News* **1988** (Oct 24), 2.

[24] These examples were discussed in an analysis of "topological thinking" in organic chemistry by Turro, N. J. *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 882.

[25] Ballhausen, C. J. *J. Chem. Educ.* **1979**, *56*, 357.

TABLE 1.1   Bond Lengths and Bond Angles for Methyl Halides

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

Source: Reference 29.

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 $r_{C–H}$ is the length of a C–H bond and the angle $\angle_{H–C–H}$ 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

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[26] A tabulation of common bond length values was provided by Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc. Perkin Trans. 2* **1987**, S1.

[27] Wilson, E. B. *Chem. Soc. Rev.* **1972**, *1*, 293 and references therein; see also Harmony, M. D. *Acc. Chem. Res.* **1992**, *25*, 321.

[28] Clark, T. *A Handbook of Computational Chemistry*; John Wiley & Sons: New York, 1985; chapter 2.

[29] (a) Tabulations of bond length and bond angle measurements for specific molecules are available in *Tables of Interatomic Distances and Configuration in Molecules and Ions*; compiled by Bowen, H. J. M.; Donohue, J.; Jenkin, D. G.; Kennard, O.; Wheatley P. J.; Whiffen, D. H.; Special Publication No. 11, Chemical Society (London): Burlington House, W1, London, 1958. (b) See also the 1965 Supplement.

[30] Pauling, L. *Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

[31] For an extensive discussion of ionic radii, see Marcus, Y. *Ion Properties*; Marcel Dekker: New York, 1997.
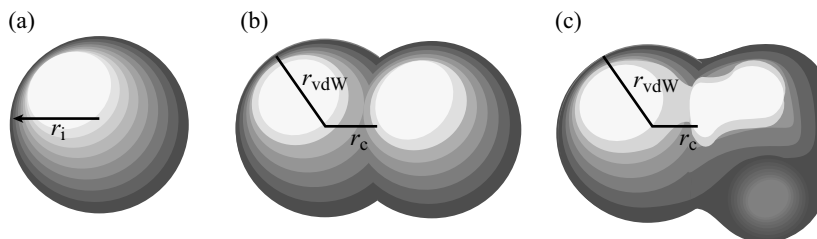
FIGURE 1.1

Radii values for chlorine.

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]

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 H_2O and 0.32 Å in CH_4.[30] We can also assign an r_{vdW} to a group of atoms. The value for a CH_3 or CH_2 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 $2 \times 13.67\ cm^3/mol$ for the two methyl groups plus $10.23\ cm^3/mol$ for the methylene group, giving a total volume of $37.57\ cm^3/mol$. Similarly, we calculate that the volume of the atoms in hexane is $2 \times 13.67\ cm^3/mol$ for the two methyl groups plus $4 \times 10.23\ cm^3/mol$ for the four methylene groups, making a total volume of $68.26\ cm^3/mol$. The volume of one mole of liquid hexane at 20° is 130.5 mL,

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[32] Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

[33] The difference is that distances between atoms in a crystal are determined by all of the forces acting on the molecules containing those atoms, not just the forces between those two atoms alone.

[34] Cordero, B.; Gómez, V.; Platero-Prats, A. E.; Revés, M.; Echeverría, J.; Cremades, E.; Barragán, F.; Alvarez, S. *Dalton Trans.* **2008**, 2832.

[35] The images were produced with a CAChe™ WorkSystem (CAChe Scientific).

[36] For example, see Proserpio, D. M.; Hoffmann, R.; Levine, R. D. *J. Am. Chem. Soc.* **1991**, *113*, 3217.

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

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	C⁴⁻	2.60	0.76	0.73^b	0.69^b
N	1.53	N³⁻	1.71	0.71		
O	1.50	O²⁻	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	P³⁻	2.12	1.07	1.00	0.93
S	1.82	S²⁻	1.64	1.05	0.94	0.87
Si	2.04	Si⁴⁻	2.71	1.11	1.07	1.00

Source: Reference 30.

[a]Reference 37.

[b]Reference 34.

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

| Group	V_W (cm³/mole)	A_W (cm²/mole × 10⁹)
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
Br, bonded to a 2° or 3° carbon atom	14.60	2.09
I, bonded to a 1° carbon atom	19.18	2.48
I, bonded to a 2° or 3° carbon atom	20.35	2.54

Source: Reference 32.

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.

Increasingly, values for atomic and molecular volume are available from theoretical calculations. The calculated values vary somewhat, depending on

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[37] Many sets of van der Waals radii are available in the literature. The data shown are values reported by Chauvin, R. *J. Phys. Chem.* **1992**, *96*, 9194. These values correlate well with—but are sometimes slightly different from—values given by Pauling (reference 30), Bondi (reference 32), and O'Keefe, M.; Brese, N. E. *J. Am. Chem. Soc.* **1991**, *113*, 3226. A set of van der Waals radii of atoms found in proteins was reported by Li, A.-J.; Nussinov, R. *Proteins* **1998**, *32*, 111.

FIGURE 1.2

Contour maps and van der Waals radii arcs for methane (left) and propane (right). (Reproduced from reference 38.)
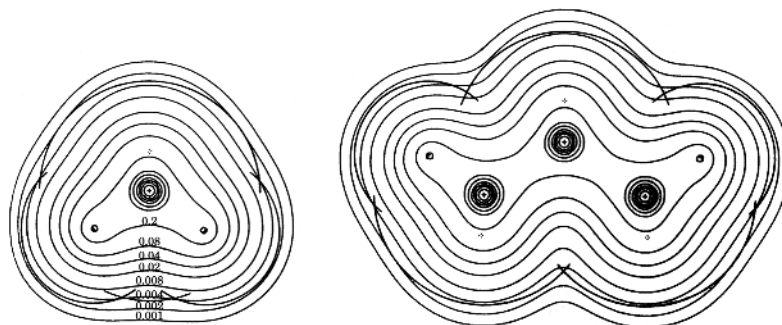
the definition of the surface of the atom or molecule. Usually the boundary of an atom is defined as a certain minimum value of electron density in units of au ($1.00\,\mathrm{au} = 6.748\,\mathrm{e}/\mathring{A}^3$). Bader and co-workers determined that the 0.001 au volumes of methane and ethane are 25.53 and 39.54 cm^3/mol, respectively, while the corresponding 0.002 au volumes are 19.58 and 31.10 cm^3/mol.[38] Thus, it appears that the 0.002 au values are closer to, but still somewhat larger than, those calculated empirically using the values in Table 1.3. The relationships between atomic volumes and van der Waals radii are illustrated for cross sections through methane and propane in Figure 1.2. The contour lines represent the electron density contours, and the intersecting arcs represent the van der Waals radii of the atoms.

1.2 HEATS OF FORMATION AND REACTION

Experimental Determination of Heats of Formation

Thermochemical measurements provide valuable insights into organic structures and reactions. The **heat of formation** ($\Delta H_\mathrm{f}^\circ$) of a compound is defined as the difference in enthalpy between the compound and the starting elements in their standard states.[39] For a hydrocarbon with molecular formula ($C_m H_n$), we define $\Delta H_\mathrm{f}^\circ$ as the heat of reaction ($\Delta H_\mathrm{r}^\circ$) for the reaction

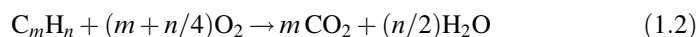$$m\,C_{(graphite)} + (n/2)H_{2(gas)} \rightarrow C_m H_n \tag{1.1}$$
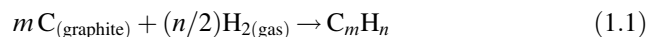
We usually determine the heat of formation of an organic compound indirectly by determining the heat of reaction of the compound to form other substances for which the heats of formation are known, and the heat of combustion ($\Delta H^\circ{}_{combustion}$) of a substance is often used for this purpose. Consider the combustion of a compound with the formula $C_m H_n$. The
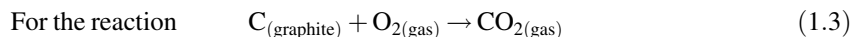
[38] Bader, R. F. W.; Carroll, M. T.; Cheeseman, J. R.; Chang, C. *J. Am. Chem. Soc.* **1987**, *109*, 7968. See the discussion of the theory of atoms in molecules in Chapter 4.

[39] Mortimer, C. T. *Reaction Heats and Bond Strengths*; Pergamon Press: New York, 1962; Clark, T.; McKervey, M. A. in Stoddart, J. F., Ed. *Comprehensive Organic Chemistry*, Vol. 1; Pergamon Press: Oxford, England, 1979; p. 66 ff. For a discussion of the experimental techniques involved in calorimetry experiments, see (a) Wiberg, K. in Liebman, J. F.; Greenberg, A., Eds. *Molecular Structure and Energetics*, Vol. 2; VCH Publishers: New York, 1987; p. 151; (b) Sturtevant, J. M. in Weissberger, A.; Rossiter, B. W., Eds. *Physical Methods of Chemistry*, Vol. I, Part V; Wiley-Interscience: New York, 1971; p. 347.
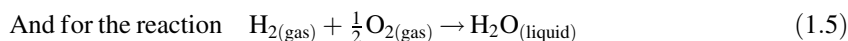
balanced chemical equation is

$$C_mH_n + (m + n/4)O_2 \rightarrow m\,CO_2 + (n/2)H_2O \qquad (1.2)$$

We know the heats of formation of CO_2 and H_2O:

For the reaction $\qquad C_{(graphite)} + O_{2(gas)} \rightarrow CO_{2(gas)} \qquad (1.3)$

$$\Delta H_r^\circ = \Delta H_f^\circ(CO_2) \qquad (1.4)$$

And for the reaction $\quad H_{2(gas)} + \frac{1}{2}O_{2(gas)} \rightarrow H_2O_{(liquid)} \qquad (1.5)$

$$\Delta H_r^\circ = \Delta H_f^\circ(H_2O) \qquad (1.6)$$

Combining the above equations, we obtain

$$\Delta H_f^\circ(C_mH_n) = m\,\Delta H_f^\circ(CO_2) + (n/2)\Delta H_f^\circ(H_2O) - \Delta H_{combustion}^\circ(C_mH_n) \qquad (1.7)$$

As an example, the heat of combustion of 1,3-cyclohexanedione was found to be -735.9 kcal/mol.[40,41] Taking -94.05 kcal/mol and -68.32 kcal/mol as the standard heats of formation of CO_2 and H_2O, respectively, gives a standard heat of formation for crystalline 1,3-cyclohexanedione of $6(-94.05) + 4$ $(-68.32) - (-735.9) = -101.68$ kcal/mol. It is sometimes necessary to correct heats of reaction for the heats associated with phase changes in the reactants or products. To convert from a condensed phase to the gas phase (e.g., for comparison with values calculated theoretically) the relevant terms are the heat of vaporization (ΔH_v°) of a liquid or heat of sublimation (ΔH_s°) of a solid.[42–44] Correcting for the standard heat of sublimation of 1,3-cyclohexanedione, $+21.46$ kcal/mol, gives its standard heat of formation in the gas phase of -80.22 kcal/mol.

If we are interested only in the difference between the heats of formation of two compounds, we may be able to measure their relative enthalpies more accurately by measuring the heat of a less exothermic reaction. That is, we measure very accurately the ΔH of a reaction in which the two different reactants combine with identical reagents to give the same product(s). Figure 1.3 illustrates how the difference in enthalpy of reactants A and B can be calculated in this manner. If the reaction of A and C to give D has a ΔH_r of $-X$ kcal/mol, and if the reaction of B and C to give D has a ΔH_r of $-Y$ kcal/ mol, then the difference in energy between A and B must be $(X - Y)$ kcal/mol. For example, Wiberg and Hao determined that ΔH_r values for the reaction of trifluoroacetic acid with 2-methyl-1-butene and with 2-methyl-2-butene were

[40] Pilcher, G.; Parchment, O. G.; Hillier, I. H.; Heatley, F.; Fletcher, D.; Ribeiro da Silva, M. A. V.; Ferrão, M. L. C. C. H.; Monte, M. J. S.; Jiye, F. *J. Phys. Chem.* **1993**, *97*, 243.

[41] The reported value (converted from kJ/mol) was -735.9 ± 0.2 kcal/mol. Experimental uncertainties will not be carried through this discussion because the emphasis is on the calculation procedure and not the precision of the experimental method.

[42] Determination of heats of sublimation was discussed by Chickos, J. S. in Liebman, J. F.; Greenberg, A., Eds. *Molecular Structure and Energetics*, Vol. 2; VCH Publishers: New York, 1987; p. 67.

[43] The enthalpy associated with transformation of a solid to a liquid is the **heat of fusion**. For a discussion, see Chickos, J. S.; Braton, C. M.; Hesse, D. G.; Liebman, J. F. *J. Org. Chem.* **1991**, *56*, 927.

[44] Data for heat capacity can be used to correct ΔH values measured at one temperature to another temperature. See Orchin, M.; Kaplan, F.; Macomber, R. S.; Wilson, R. M.; Zimmer, H. *The Vocabulary of Organic Chemistry*; Wiley-Interscience: New York, 1980; pp. 255–256.
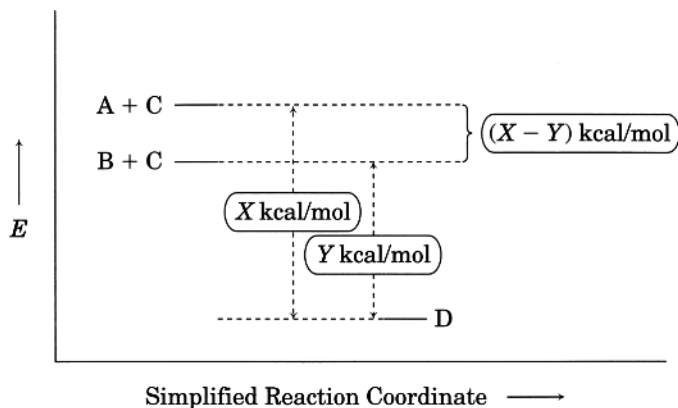
FIGURE 1.3

Calculation of the enthalpy difference of isomers.

−10.93 kcal/mol and −9.11 kcal/mol, respectively.[45] Therefore, the 2-alkene was judged to be 1.82 kcal/mol lower in energy than the 1-alkene. Heats of hydrogenation are also used to determine the difference in heats of formation of alkenes even though heats of combustion may be measured much more *precisely* than heats of hydrogenation. Because heats of hydrogenation are smaller in magnitude than are heats of combustion, small enthalpy differences between isomers may be determined more *accurately* by hydrogenation.[46]

Bond Increment Calculation of Heats of Formation

Table 1.4 shows experimental ΔH_f° values for some linear alkanes.[47] There is a general trend in the data: each homolog higher than ethane has a ΔH_f° value about 5 kcal/mol more negative than the previous alkane. This observation suggests that it should be possible to use the principle of additivity (page 6) to predict the heat of formation of an organic compound by summing the contribution each component makes to ΔH_f°.[48] Extensive work in this area was done by Benson, who published tables of **bond increment contributions** to heats of formation and other thermodynamic properties.[48–53] A portion of one such table is reproduced as Table 1.5.

The heats of formation of some linear alkanes calculated by the bond increment method are shown in Table 1.4. As an example of such calculations, let us determine the ΔH_f° values for methane and ethane. For methane, there

[45] Wiberg, K. B.; Hao, S. *J. Org. Chem.* **1991**, *56*, 5108.

[46] Davis, H. E.; Allinger, N. L.; Rogers, D. W. *J. Org. Chem.* **1985**, *50*, 3601.

[47] Experimental data for ΔH_f° at 298 K are from tabulations in Stull, D. R.; Westrum, E. F., Jr.; Sinke, G. C. *The Thermodynamics of Organic Compounds*; John Wiley & Sons: New York, 1969; pp. 243–245.

[48] Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley-Interscience: New York, 1976; p. 24.

[49] Benson, S. W.; Buss, J. H. *J. Chem. Phys.* **1959**, *29*, 546.

[50] Benson, S. W.; Cruickshank, F. R.; Golden, D. M.; Haugen, G. R.; O'Neal, H. E.; Rodgers, A. S.; Shaw, R.; Walsh, R. *Chem. Rev.* **1969**, *69*, 279.

[51] For a discussion of the development of bond increment and group increment calculations, see Schleyer, P. v. R.; Williams, J. E.; Blanchard, K. R. *J. Am. Chem. Soc.* **1970**, *92*, 2377.

[52] Calculation of group increments to heats of formation of linear hydrocarbons was reported by Pitzer, K. S. *J. Chem. Phys.* **1940**, *8*, 711 and to nonlinear hydrocarbons by Franklin, J. L. *Ind. Eng. Chem.* **1949**, *41*, 1070.

[53] Cohen, N.; Benson, S. W. *Chem. Rev.* **1993**, *93*, 2419.

TABLE 1.4 Experimental and Calculated Heats of Formation of Linear Alkanes at 298 K

Compound	ΔH_f° (kcal/mol) obs.	ΔH_f° (kcal/mol) calc.[a]
Methane	−17.89	−15.32
Ethane	−20.24	−20.25
Propane	−24.82	−25.18
Butane	−30.15	−30.11

[a]Calculations are based on bond increment values in Table 1.5.

are four C–H bonds, each contributing −3.83 kcal/mol, so the ΔH_f° value is −15.32 kcal/mol. For ethane, the ΔH_f° value is $6 \times (-3.83) + 1 \times (2.73)$ for the six C–H and one C–C bonds, respectively, and the total is −20.25 kcal/mol. As the chain is extended, each additional CH_2 group contributes $2 \times (-3.83) + 1 \times (2.73) = -4.93$ kcal/mol to the ΔH_f° value.

There is a problem with the ΔH_f° values obtained from the simple bond increment data in Table 1.5. The five isomers of hexane listed in Table 1.6 all have five C–C bonds and fourteen C–H bonds. Using the bond increment values in Table 1.5, we would predict each to have the same heat of formation (−39.97 kcal/mol). As shown in Table 1.6, however, the experimental heats of formation become more negative as the branching increases. Specifically, the structure with a quaternary carbon atom is more stable than an isomeric structure with two tertiary carbon atoms, and the structure with two tertiary

TABLE 1.5 Bond Increment Contributions to ΔH_f°

Bond	ΔH_f° (kcal/mol)	Bond	ΔH_f° (kcal/mol)
C–H	−3.83	N–H	−2.6
C–D	−4.73	S–H	−0.8
C–C	2.73	S–S	−6.0
C–F	−52.5	C–S	6.7
C–Cl	−7.4	C_d–C	6.7
C–Br	2.2	C_d–H	3.2
C–I	14.1	C_d–F	−39.0
C–O	−12.0	C_d–Cl	−5.0
O–H	−27.0	C_d–Br	9.7
O–D	−27.9	C_d–I	21.7
O–O	21.5	C_d–C_d	7.5

Source: Reference 48.

TABLE 1.6 Heats of Formation (kcal/mol) of Isomeric C_6H_{14} Structures

Compound	ΔH_f°, obs.[a]	ΔH_f°, calc.[b]	ΔH_f°, corr.[c]
Hexane	−39.96	−39.96	−39.96
2-Methylpentane	−41.66	−42.04	−41.24
3-Methylpentane	−41.02	−42.04	−41.24
2,2-Dimethylbutane	−44.35	−44.77	−43.16
2,3-Dimethylbutane	−42.49	−44.12	−42.52

[a]Experimental data for ΔH_f° at 298 K are from reference 47, pp. 247–249.
[b]Calculated from group increments in Table 1.7 without correcting for gauche interactions.
[c]Data from the previous column corrected for gauche interactions. See Table 1.7 and Figure 1.4.

carbon atoms is more stable than structures with only one tertiary carbon atom, even though all isomers have the same number of C–C and C–H bonds. Thus, we must conclude that the heat of formation of a compound depends not only on the number of carbon–carbon bonds, but also on the nature of the carbon–carbon bonds.

One way to describe the extent to which heats of formation depend on bonding patterns is to consider an **isodesmic reaction**—a reaction in which both the reactants and the products have the same number of bonds of a given type, even though there may be changes in the relationship of one bond to another.[54,55] For example, consider the hypothetical conversion of *n*-hexane to 2,2-dimethylbutane. Both the reactant and the product have five C–C and fourteen C–H bonds. The simple bond increment approach would calculate that the heat of the reaction should be 0, but the data in Table 1.6 indicate that the heat of the reaction should be −4.4 kcal/mol. Therefore, the heat of an isodesmic reaction is an indication of deviation from the additivity of bond energies.[54,56]

Group Increment Calculation of Heats of Formation

An alternative to the bond increment method is the **group increment** approach, which allows calculation of enthalpy differences that result from different arrangements of bonds within molecules. We consider not the bonds holding atoms together but the groups that result from these bonds. Table 1.7 lists the group increment values for a series of organic functional groups.[50] Using these data, we can closely approximate the heats of formation of the isomeric hexanes. Consider 2-methylpentane. Three methyl groups [C–(H)$_3$(C) in the table] contribute −10.08 kcal/mol each to the heat of formation, two methylene units [C–C(H)$_2$(C)$_2$] contribute −4.95 kcal/mol each, and one methine unit [C–(H)(C)$_3$] contributes −1.90 kcal/mol. Thus, estimated heat of formation is

$$\Delta H_f^\circ = 3 \times (-10.08) + 2 \times (-4.95) + 1 \times (-1.90) = -42.04 \text{ kcal/mol} \quad (1.8)$$

The experimental value is (−41.66 kcal/mol).[47]

Note that the estimated heats of formation calculated in this way assign the same contribution to each group without regard to its position in the molecule and without regard to strain. In branched acyclic alkanes, the major form of strain to consider is van der Waals repulsion due to *unavoidable* butane gauche interactions, which may be assigned 0.8 kcal/mol each.[57] Figure 1.4 shows a Newman projection and gives the number of

[54] Hehre, W. J.; Ditchfield, R.; Radom, L.; Pople, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 4796. See also Ponomarev, D. A.; Takhistov, V. V. *J. Chem. Educ.* **1997**, *74*, 201.

[55] A **homodesmotic reaction** is a reaction in which not only are the number of bonds of each type conserved, but the number of carbon atoms with zero, one, two, or three hydrogen atoms is also conserved. For details, see George, P.; Trachtman, M.; Bock, C. W.; Brett, A. M. *Tetrahedron* **1976**, *32*, 317. Isomers interconverted by homodesmotic reactions are termed **isologous** (cf. Engler, E. M.; Andose, J. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 8005).

[56] Isodesmic reactions are widely used in theoretical studies because errors in the energies of reactants and products are more likely to cancel, thereby allowing simple computational approaches to give accurate estimates of heats of reactions. For a discussion, see Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab initio Molecular Orbital Theory*; Wiley-Interscience: New York, 1986.

[57] Molecular conformation and van der Waals strain will be discussed in Chapter 3.

TABLE 1.7 Group Increment Contributions to Heats of Formation

Group	$\Delta H^\circ_{f,298}$ (kcal/mol)	Group	$\Delta H^\circ_{f,298}$ (kcal/mol)
C–(H)$_3$(C)	−10.08	C$_d$–(C$_B$)(C)	8.64
C–(H)$_2$(C)$_2$	−4.95	C–(C$_B$)(C)(H)$_2$	−4.86
C–(H)(C)$_3$	−1.90	C–(C$_B$)(C)$_2$(H)	−0.98
C–(C)$_4$	0.50	C$_t$–(H)	26.93
C$_d$–(H)$_2$	6.26	C$_t$–(C)	27.55
C$_d$–(H)(C)	8.59	C$_t$–(C$_d$)	29.20
C$_d$–(C)$_2$	10.34	C$_B$–(H)	3.30
C$_d$–(C$_d$)(H)	6.78	C$_B$–(C)	5.51
C$_d$–(C$_d$)(C)	8.88	C$_B$–(C$_d$)	5.68
[C$_d$–(C$_B$)(H)]	6.78		

Source: Reference 50.

gauche interactions for each of the isomers of hexane. Correcting the initial ΔH°_f of 2-methylpentane for one such interaction gives −41.24 kcal/mol, which is closer to the experimental value. Angle strain corrections must be applied for ring compounds. For example, cyclopropane, cyclobutane, and cyclopentane rings add 27.6, 26.2, and 6.3 kcal/mol, respectively, to a heat of formation calculated from the data in Table 1.7.[50,58]

The origin of the increased stability of branched alkanes relative to nonbranched isomers has been the subject of some debate. Benson and Luria proposed that alkanes have polarized $C^{\delta-}$–$H^{\delta+}$ bonds and that the sum of the electrostatic interactions of a branched compound is lower in energy than the sum of electrostatic interactions in a linear structure.[59] Laidig calculated that branched hydrocarbons have overall smaller distances between atoms than do linear isomers and that the resulting increase in nucleus–electron attraction in a branched compound outweighs the increase in nuclear–nuclear and electron–electron repulsion.[60] More recently, the stabilization of branched alkanes has been attributed to attractive interactions involving alkyl groups bonded to the same carbon atom.[61]
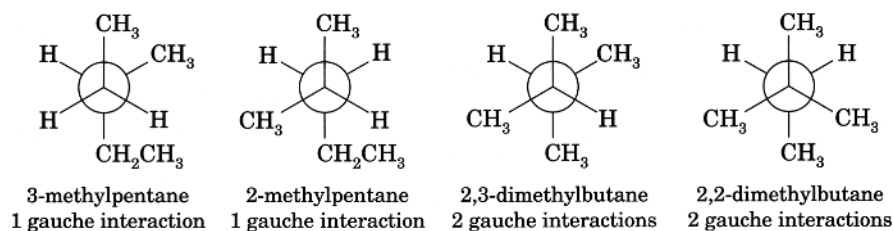
FIGURE 1.4

Gauche interactions in hexane isomers.

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[58] These examples only hint at the analysis of heats of formation of organic compounds that is possible. Benson and co-workers summarized the methods and data for calculations for the major functional groups in organic chemistry.[48,50] In addition, the data allow calculation of heat capacities and entropies of these compounds in the same manner in which heats of formation are determined. Heats of formation are valuable reference points in discussing the stabilities of various isomers or products of reactions, whether they are calculated by bond increments or group increments or are derived as part of a theoretical calculation.

[59] Benson, S. W.; Luria, M. *J. Am. Chem. Soc.* **1975**, *97*, 704.

[60] Laidig, K. E. *J. Phys. Chem.* **1991**, *95*, 7709.

[61] Schreiner, P. R. *Angew. Chem. Int. Ed.* **2007**, *46*, 4217.

TABLE 1.8   Calculation of Gas Phase ΔH_f° Values^a of Alkanes Assuming Geminal Interactions Are Repulsive

Compound	n_{C-C}	n_{C-H}	n_{H-C-H}	n_{H-C-C}	n_{C-C-C}	n_C	n_H	ΔH_f (calculated)	ΔH_f (literature)
Methane	0	4	6	0	0	1	4	−17.2	−17.9
Ethane	1	6	6	6	0	2	6	−20.4	−20.0
Propane	2	8	7	10	1	3	8	−25.3	−25.0
Butane	3	10	8	14	2	4	10	−30.2	−30.4
2-Methylpropane	3	10	9	12	3	4	10	−31.9	−32.1
n-Pentane	4	12	9	18	3	5	12	−35.1	−35.1
2-Methylbutane	4	12	10	16	4	5	12	−36.8	−36.7
2,2-Dimethylpropane	4	12	12	12	6	5	12	−40.3	−40.1
Hexane	5	14	10	22	4	6	14	−40.0	−40.0
Cyclohexane	6	12	6	24	6	6	12	−29.4	−29.4
	E_{C-C}	E_{C-H}	E_{H-C-H}	E_{H-C-C}	E_{C-C-C}	E_C	E_H		
	−146.00	−124.20	6.64	9.29	10.20	60.70	52.10		

Source: Reference 62.

^{a} Energies are in kcal/mol.

Gronert proposed a very different explanation.[62] He noted that van der Waals interactions between nonbonded groups that are closer than the sum of their van der Waals radii, such as C1 and C4 in the gauche conformation of butane, are known to be repulsive. Since C1 and C3 in neopentane are even closer to each other than are C1 and C4 in gauche butane, he argued that their interaction should be repulsive as well. Moreover, the interactions between two hydrogen atoms bonded to the same carbon as well as those between hydrogen and carbon atoms bonded to the same carbon were also said to be repulsive. The effect of branching (e.g., conversion of butane to isobutane) is to reduce the number of H–C–C interactions while increasing the number of H–C–H and C–C–C interactions. Gronert proposed that the steric energy of an H–C–C interaction is less than the average of those for the H–C–H and C–C–C interactions, so the effect of the branching is to decrease overall intramolecular repulsion and produce a more stable isomer. Using equations 1.9 and 1.10, along with the interaction values (E) for C–H and C–C bonding and specific values for repulsive 1,3 interactions shown in Table 1.8, Gronert was able to reproduce the observed gas phase ΔH_f° values of a series of alkanes. For example, the ΔH_f° of *n*-pentane in kcal/mol is calculated as shown in equation 1.11.

$$\Delta H_f = n_{C-C}E_{C-C} + n_{C-H}E_{C-H} + n_{C-C-C}E_{C-C-C} + n_{C-C-H}E_{C-C-H}$$

$$+ n_{H-C-H}E_{H-C-H} + f(C,H) \tag{1.9}$$

where

$$f(C,H) = (170.6 + E_C)n_C + 52.1\,n_H \tag{1.10}$$

$$\Delta H_f = 4\,(-146) + 12\,(-124.2) + 9\,(6.64) + 18\,(9.29) + 3\,(10.2)$$

$$+ 5\,(231.3) + 12\,(52.1) = -35.1\,\text{kcal/mol} \tag{1.11}$$

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[62] Gronert, S. *J. Org. Chem.* **2006**, *71*, 1209; 9560. The literature values in Table 1.8 are from this source. The values of the *E* parameters at the bottom of the table are shown to two decimal places, while those in the sources cited here were reported to one decimal place.

TABLE 1.9 Calculation of Gas Phase ΔH_f° Values[a] of Alkanes Assuming Geminal Methyl Interactions Are Stabilizing

Alkane	n_{CH_2}	$n_{primary\ branches}$	$n_{tertiary\ branches}$	$n_{quartenary\ branches}$	ΔH_f° (calculated)	ΔH_f° (literature)
Methane	0	0	0	0	−17.89	−17.89
Ethane	1	0	0	0	−20.04	−20.04
Propane	2	1	0	0	−25.02	−25.02
Butane	3	2	0	0	−30.00	−32.07
Isobutane	3	0	1	0	−32.08	−2.07
Pentane	4	3	0	0	−34.98	−35.08
Isopentane	4	1	1	0	−37.06	−36.73
Neopentane	4	0	0	1	−39.98	−40.14
Hexane	5	4	0	0	−39.96	−39.96

Source: Reference 64.

[a] Energies are in kcal/mol.

Gronert's explanation for the stability of branched alkanes was supported by some investigators, but disputed by others.[63] In particular, Wodrich and Schleyer pointed out that comparable results could be obtained by assuming that the interactions of geminal methyl groups are stabilizing (equation 1.12).[64,65] Here n_{CH_2} is the number of methylene units conceptually added to methane to form the alkane, $n_{primary\ branches}$ is the number of C–CH₂–C units, $n_{tertiary\ branches}$ is the number of 3° carbon units, and $n_{quaternary\ branches}$ is the number of 4° carbons in the structure. Some results obtained with this approach are shown in Table 1.9, and a calculation of ΔH_f° for *n*-pentane is shown in equation 1.13.

$$\Delta H_f = -17.89 - 2.15\, n_{CH_2} - 2.83\, n_{primary\ branches} - 7.74\, n_{tertiary\ branches}$$

$$- 13.49\, n_{quartenary\ branches} \tag{1.12}$$

$$\Delta H_f = -17.89 + 4\,(-2.15) + 3\,(-2.83) + 0\,(-7.74)$$

$$+ 0\,(-13.49) = -35\ \text{kcal/mol} \tag{1.13}$$

We will explore the nature of geminal interactions more fully in the context of radical stabilities (Chapter 5). The points to be made here are (i) two very different models can be used to predict the heats of formation of alkanes, and (ii) a good correlation does not necessarily establish a cause and effect relationship. As Wodrich and Schleyer noted, the fact that the number of births in some European countries correlates with the number of storks in those countries does not demonstrate that babies are delivered by storks. It

[63] Mitoraj, M.; Zhu, H.; Michalak, A.; Ziegler, T. *J. Org. Chem.* **2006**, *71*, 9208.

[64] Wodrich, M. D.; Schleyer, P. v. R. *Org. Lett.* **2006**, *8*, 2135.

[65] Wodrich, M. D.; Wannere, C. S.; Mo, Y.; Jarowski, P. D.; Houk, K. N.; Schleyer, P. v. R. *Chem. Eur. J.* **2007**, *13*, 7731 proposed the concept of *protobranching* to explain the energy-lowering effect of geminal interactions.

TABLE 1.10 $DH°$ **Values (kcal/mol) for Bonds to Hydrogen**

Compound	$DH°$ (kcal/mol)	Compound	$DH°$ (kcal/mol)
H–H	104.2	H–F	136.3
H–CN	126.3	H–Cl	103.2
H–NH$_2$	107.6	H–Br	87.5
HO–H	118.8	H–I	71.3
H–CH$_2$OH	96.1	HS–H	91.2
CH$_3$O–H	104.6	H–ONO$_2$	101.7
CH$_3$S–H	87.4	CH$_3$CH$_2$O–H	104.7
H–CH$_2$SH	94	(CH$_3$)$_2$CHO–H	105.7
HOO–H	87.8	(CH$_3$)$_3$CO–H	106.3
CH$_3$OO–H	88	C$_6$H$_5$O–H	90
H–CHO	88.1	CH$_3$CH$_2$OO–H	85
CH$_3$C(O)–H	89.4	(CH$_3$)$_3$COO–H	84
HCOO–H	112	CH$_3$COO–H	112
H–COOH	>96	C$_6$H$_5$COO–H	111

Source: Reference 69.

will be useful to remember this comment as we consider explanations for other chemical phenomena in later chapters.[66]

Homolytic and Heterolytic Bond Dissociation Energies

Heats of reaction are important values for processes that involve reactive intermediates. For example, the **standard homolytic bond dissociation enthalpy** of compound A–B, denoted $DH°(A–B)$ or $DH_{298}(A–B)$, is the heat of reaction ($\Delta H_r°$) at 298 K for the gas phase dissociation reaction in equation 1.14.

$$A - B_{(g)} \rightarrow A\bullet_{(g)} + B\bullet_{(g)} \tag{1.14}$$

$DH°(A–B)$ values can be calculated from the relationship[67,68]

$$DH°(A - B) = \Delta H_{r(equation1.14)}° = \Delta H_f°(A\bullet) + \Delta H_f°(B\bullet) - \Delta H_f°(A - B) \tag{1.15}$$

Here $\Delta H_f°$ (A•) is the heat of formation of radical A•, $\Delta H_f°$ (B•) is the heat of formation of radical B•, and $\Delta H_f°$ (A–B) is the heat of formation of A–B. $DH°$ (A–B) is also called the **bond dissociation energy** of A–B. Table 1.10 gives a list of standard bond dissociation enthalpies for bonds involving hydrogen atoms, and Table 1.11 gives a list of $DH°$ values for bonds between carbon atoms in various alkyl groups and a number of common organic substituents.[69]

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[66] See also Stanger, A. *Eur. J. Org. Chem.* **2007**, 5717.

[67] Benson, S. W. *J. Chem. Educ.* **1965**, *42*, 502.

[68] A standard bond dissociation energy is different from an **average** bond dissociation energy. The latter is just the value obtained by calculating the heat of atomization of a compound (the enthalpy change on converting the molecule to individual atoms) divided by the number of bonds from one atom to another in the molecule. For more details on this distinction, see reference 67.
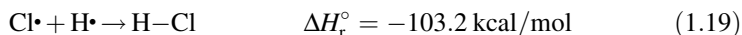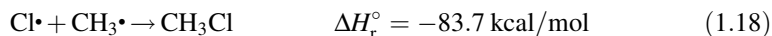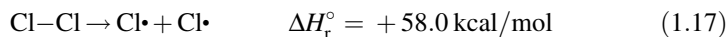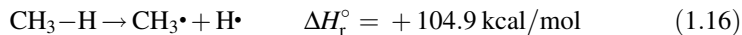
[69] Blanksby, S. J.; Ellison, G. B. *Acc. Chem. Res.*, **2003**, *36*, 255. This reference provides the uncertainties for the values in Tables 1.10 and 1.11.

TABLE 1.11 $DH°$ **Values (kcal/mol) for Selected Bonds to Alkyl Groups**

Substituent\R	CH_3	CH_3CH_2	$(CH_3)_2CH$	$(CH_3)_3C$	$CH_2{=}CH$	$CH_2{=}CHCH_2$	C_6H_5	$C_6H_5CH_2$	CH_3O	$HC(O)$	$CH_3CH(O)$
H	104.9	101.1	98.6	96.5	110.7	88.8	112.9	89.7	104.6	88.1	89.4
F	115	—	110.6	—	123.3	—	127.2	98.7	—	—	122.2
Cl	83.7	84.8	85.2	84.9	91.2	—	97.1	74	—	—	84.7
Br	72.1	72.4	73.9	72.6	80.8	59	84	63	—	—	71.7
I	57.6	56.9	57	55.6	—	45.6	67	51	—	—	53.8
HO	92.1	94.0	95.5	95.8	—	80.1	112.4	82.6	—	109.5	109.9
CH_3O	83.2	85	85.8	84	—	—	101	—	38	99.6	100
NH_2	85.2	84.8	86.0	85.7	—	—	104.2	71.7	—	—	99.1
CN	122.4	121.6	120.9	117.8	133	108.7	134	—	—	—	—
NO_2	61.0	61.6	62.9	62.8	—	—	72.5	50.5	42	—	—
CH_3	90.1	89.0	88.6	87.5	101.4	76.5	103.5	77.6	*	84.8	84.5
CH_3CH_2	*	87.9	87.1	85.6	100.0	75.4	102.2	76.7	*	83.3	83.5
$(CH_3)_2CH$	*	*	85.6	82.7	99.2	75.2	101.0	76.4	*	83.1	81.9
$(CH_3)_3C$	*	*	*	78.6	97.8	73.2	98.3	—	*	—	79.4
$CH_2{=}CH$	*	*	*	*	116	87.3	116	—	—	—	41
$CH_2{=}CHCH_2$	*	*	*	*	*	62.7	—	—	—	—	—
$HC{\equiv}C$	126.5	125.1	124.5	122.3	—	—	—	—	—	—	—
$HC{\equiv}CCH_2$	78	77	—	—	—	—	—	—	—	—	—
C_6H_5	*	*	*	*	118	—	118	*	*	99.3	98.8
$C_6H_5CH_2$	*	*	*	—	97	—	97	65.2	—	—	71.4

Note: * Means a redundant entry. — Means not available.
Source: Reference 69.

Values of ΔH_r° for dissociation reactions can be combined to allow prediction of heats of reaction. A familiar example is the calculation of ΔH_r° for the reaction of chlorine with methane to produce HCl plus methyl chloride. Using Table 1.11 and the bond dissociation enthalpies of Cl_2 and HCl,[70] we can write the following reactions:

$$CH_3{-}H \rightarrow CH_3\textbf{·} + H\textbf{·} \qquad \Delta H_r^\circ = +104.9 \, \text{kcal/mol} \qquad (1.16)$$

$$Cl{-}Cl \rightarrow Cl\textbf{·} + Cl\textbf{·} \qquad \Delta H_r^\circ = +58.0 \, \text{kcal/mol} \qquad (1.17)$$

$$Cl\textbf{·} + CH_3\textbf{·} \rightarrow CH_3Cl \qquad \Delta H_r^\circ = -83.7 \, \text{kcal/mol} \qquad (1.18)$$

$$Cl\textbf{·} + H\textbf{·} \rightarrow H{-}Cl \qquad \Delta H_r^\circ = -103.2 \, \text{kcal/mol} \qquad (1.19)$$

Summing these four equations and canceling the radicals that appear on both sides gives

$$CH_3{-}H + Cl{-}Cl \rightarrow CH_3Cl + HCl \quad \Delta H_r^\circ = -24.0 \, \text{kcal/mol} \qquad (1.20)$$

Note that the calculation of ΔH_r° does not presume that the reaction takes place by a radical pathway. Rather, according to Hess' law, the difference in enthalpy between reactants and products is independent of the path of the reaction.[46]

If a bond dissociation occurs so that one of the species becomes a cation and the other becomes an anion, then the energy of the reaction is termed a **standard heterolytic bond dissociation energy**:

$$A{-}B_{(g)} \rightarrow A^+_{(g)} + B{:}^-_{(g)} \qquad (1.21)$$

Therefore,

$$DH(A^+, B{:}^-) = \Delta H_{het}^\circ = \Delta H_f^\circ(A^+) + \Delta H_f^\circ(B{:}^-) - \Delta H_f^\circ(A{-}B) \qquad (1.22)$$

As will be discussed in Chapter 7, it is possible to relate homolytic and heterolytic reaction enthalpies by using data for ionization potential (the energy required to remove an electron from a species) and electron affinity (the energy gained by adding an electron to a species).[71]

In the gas phase, heterolytic bond dissociation enthalpies are much higher than homolytic bond dissociation enthalpies because energy input is needed to separate the two ions as well as to break the bond. For example, the heterolytic bond dissociation energy of HCl in the gas phase is 333.4 kcal/mol, which is more than three times the 103.2 kcal/mol homolytic bond dissociation energy.[72] Solvation of the ions can reduce the value of ΔH_{het}° dramatically, however, and HCl readily ionizes in aqueous solution. Similarly, the calculated homolytic dissociation energy of a C–Cl bond in 2,2′-dichloro-diethyl sulfide (**1**) decreases only slightly from the gas phase to a solvent with $\varepsilon = 5.9$, while the heterolytic dissociation energy of that bond decreases from

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[70] Lide, D. R., Jr. *CRC Handbook of Chemistry and Physics,* 84th ed.; CRC Press: Boca Raton, FL, 2003, Section 9.

[71] Arnett, E. M.; Flowers, R. A. II *Chem. Soc. Rev.* **1993**, *22*, 9.

[72] Berkowitz, J.; Ellison, G. B.; Gutman, D. *J. Phys. Chem.* **1994**, *98*, 2744.

154.8 kcal/mol in the gas phase to 138.5 kcal/mol in the same solvent.[73–75] Even carbon–carbon σ bonds can dissociate heterolytically. One hydrocarbon was reported to exist as a covalently bonded compound in benzene, as a mixture of molecules and ions in acetonitrile, and as an ionic species in dimethyl sulfoxide.[76]

Cl⌒⌒S⌒⌒Cl

1
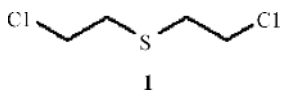
1.3 BONDING MODELS

The preceding discussion implicitly assumed the simple view of chemical bonding developed by G. N. Lewis.[77] Atoms are represented by element symbols with dots around them to indicate the number of electrons in the valence shell of the atom. Covalent bonds are formed by the sharing of one or more pairs of electrons between atoms so that both atoms achieve an electron configuration corresponding to a filled outer shell.[78] For example, combination of two chlorine atoms can produce a chlorine molecule, as shown in Figure 1.5.

    This elementary description of bonding assumes some knowledge of electron shells of the atoms, but it does not presume a detailed knowledge of the results of quantum mechanics. The representation of Cl_2 does not specify what orbitals are populated, the geometric shapes of these orbitals, or the distribution of electrons in the final molecule of chlorine. This approach to describing chemical bonding might be adequate for some purposes, but it leaves many questions unanswered. In particular, this bonding description is purely qualitative. It would be desirable to have a mathematical description of bonding so that quantitative predictions about bonding can be compared with experimental observations.

    It is helpful to distinguish here two types of information that we wish to acquire about organic molecules. The first type is physically *observable* data

$$:\ddot{C}l\cdot + :\ddot{C}l\cdot \longrightarrow :\ddot{C}l-\ddot{C}l:$$
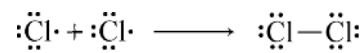
FIGURE 1.5

A representation of bonding in Cl_2.

[73] Politzer, P.; Habibollahzadeh, D. *J. Phys. Chem.* **1994**, *98*, 1576.

[74] The effects of solvent are thought to be negligible when carbon-centered radicals are formed, but solvent effects can be significant in the case of oxygen-centered radicals. Borges dos Santos, R. M.; Cabral, B. J. C.; Martinho Simões, J. A. *Pure Appl. Chem.* **2007**, *79*, 1369.

[75] In one case merely adding ether to a pentane solution of a compound was seen to produce heterolytic dissociation: Arnett, E. M.; Amarnath, K.; Harvey, N. G.; Cheng, J.-P. *Science* **1990**, *247*, 423.

[76] Kitagawa, T.; Takeuchi, K. *J. Phys. Org. Chem.* **1998**, *11*, 157.

[77] The Lewis concept has been called "the most widely used model in contemporary chemistry." Frenking, G.; Shaik, S. *J. Comput. Chem.* **2007**, *28*, 1.

[78] Lewis, G. N. *J. Am. Chem. Soc.* **1916**, *38*, 762. It is interesting to note that Lewis proposed a model for bonding in which electrons were positioned at the corners of a cube, so an octet meant an electron at every corner. Single bonds were constructed by allowing two cubes to share one edge (and thus one pair of electrons). In the case of a double bond, the two cubes shared a face (and therefore two pairs of electrons). The cubical model offered no simple representation for triple bonds, but a model based on tetrahedral arrangement of carbon valences was able to do so. For a discussion of the role of G. N. Lewis in the development of structural theory in organic chemistry, see Calvin, M. *J. Chem. Educ.* **1984**, *61*, 14; Zandler, M. E.; Talaty, E. R. *J. Chem. Educ.* **1984**, *61*, 124; Saltzman, M. D. *J. Chem. Educ.* **1984**, *61*, 119; Stranges, A. N. *J. Chem. Educ.* **1984**, *61*, 185; Pauling, L. *J. Chem. Educ.* **1984**, *61*, 201; Shaik, S. *J. Comput. Chem.* **2007**, *28*, 51.

that are characteristic of entire molecules or samples of molecules. A molecular dipole moment belongs to this category. The second kind of information includes those *nonobservable* constituent properties of a structure that, taken together, give rise to the overall molecular properties. Partial atomic charges and bond dipole moments belong to this category.

A dipole moment is a vector quantity that measures the separation of electrical charge. Dipole moments have units of electrical charge (a full plus or minus charge corresponding to 4.80×10^{-10} esu) times distance, and they are usually expressed in units of debye (D), with $1\,D = 10^{-18}$ esu cm.[79,80] Thus, a system consisting of two atoms, one with a partial charge of $+0.1$ and the other a partial charge of -0.1, located 1.5 Å apart would have a dipole moment of

$$0.1 \times (4.8 \times 10^{-10}\text{esu}) \times (1.5 \times 10^{-8}\text{cm}) = 0.72 \times 10^{-18}\text{esu}\cdot\text{cm} = 0.72\,\text{D} \quad (1.23)$$

Molecular dipole moments can be measured by several techniques, including the determination of the dielectric constant of a substance as a gas or in a nonpolar solution and the study of the effect of electrical fields on molecular spectra (Stark effect).

Molecular dipole moments are useful to us primarily as a source of information about molecular structure and bonding. While the center of charge need not coincide with the center of an atom, that is a convenient first approximation. For example, the dipole moment of CH_3F is 1.81 D.[81,82] We associate the charge separation with the bonding between C and F. Since those atoms are 1.385 Å apart (Table 1.1), the partial charge can be calculated to be $+0.27$ on one of the atoms and -0.27 on the other.

If there is more than one bond dipole moment in a molecule, then the molecular dipole moment is the vector sum of the individual moments. This idea can be useful in determining the structures and bonding of molecules. For example, Smyth determined that the three isomers of dichlorobenzene have dipole moments of 2.30, 1.55, and 0 D.[83] The dipole moment of chlorobenzene was known to be 1.61 D. Smyth reasoned that two C–Cl bond dipole moments add to each other in one isomer of dichlorobenzene, that they cancel each other partially in a second isomer, and that they cancel each other completely in the third isomer. Using the relationship

$$\mu = 2 \times 1.61 \times 10^{-18} \times \cos(0.5A) \quad (1.24)$$

where A is the angle between the two bond dipole moments, Smyth calculated that the three isomers of dichlorobenzene had A values of 89°, 122°, and 180° and that these values corresponded to the ortho, meta, and para isomers of dichlorobenzene, respectively. The expected angle for

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[79] For background on the theory and measurement of dipole moments, see Minkin, V. I.; Osipov, O. A.; Zhdanov, Y. A. in Hazzard, B. J., trans. *Dipole Moments in Organic Chemistry*; Vaughan, W. E.; Plenum Press: New York, 1970.

[80] Smyth, C. P. in Weissberger, A.; Rossiter, B. W., Eds. *Physical Methods of Chemistry*, Vol. 1, Part IV; Wiley-Interscience: New York, 1972; pp. 397–429.

[81] McClellan, A. L. *Tables of Experimental Dipole Moments*, Vol. 2; Rahara Enterprises: El Cerrito, CA, 1974; p. 167.

[82] A value of 1.857 D is given in reference 29b. That is a more recent value and may be more accurate than the number used here. The values for the other methyl fluorides there are very similar to those given in reference 81.

[83] Smyth, C. P.; Morgan, S. O. *J. Am. Chem. Soc.* **1927**, *49*, 1030.

o-dichlorobenzene is 60°, but Smyth argued that the apparent angle is larger because repulsion of the two adjacent chlorines enlarges the angle between the dipoles but does not appreciably alter the geometry of the benzene ring.[84]

To account for the dipole moment associated with a covalent bond, we say that the electrons in the bond are not shared equally between the two atoms. One atom must have a greater ability to attract the pair of shared electrons than the other. As a result, a bond can be described as having a mixture of both ionic and covalent bonding. It is useful to define a weighting parameter, λ, to indicate how much ionic character is mixed into the covalent bond. Thus, we may write

$$\text{Polar Bond} = [\text{Covalent Bond}] + \lambda[\text{Ionic Bond}] \qquad (1.25)$$

The percentage ionic character[85] in the bond is related to λ by equation 1.26:

$$\% \text{ Ionic Character} = \frac{\lambda^2}{(1 + \lambda^2)} \times 100\,\% \qquad (1.26)$$

In an HCl molecule with partial charges of $+0.17$ on the hydrogen atom and -0.17 on the chlorine atom, the value of λ is 0.45.

Electronegativity and Bond Polarity

The polarity of covalent bonds is attributed to **electronegativity**, which Pauling defined as "the power of an atom in a molecule to attract electrons to itself."[86] It is generally the case that the bond dissociation energy of a polar diatomic molecule A–B is greater than one-half of the sum of the bond dissociation energies of A–A and B–B.[87] For example, the average of the bond strengths of H_2 and Cl_2 is 81.1 kcal/mol, but the homolytic dissociation energy of H–Cl is 103.2 kcal/mol.[88,89] We ascribe the increased bond dissociation energy to the ionic character of the polar bond because the bond dissociation must overcome Coulombic effects in addition to the covalent bonding interaction. Pauling obtained a set of electronegativity values (χ_P) by correlating standard bond dissociation energies between different atoms (A–B) with the average of the standard bond dissociation energies of identical atoms (A–A and B–B) as shown in equation 1.27, where $\Delta\chi$ is the difference in χ values of A and B.[86] The electronegativity of fluorine was

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[84] Not only did this study identify which isomer of dichlorobenzene was which, but it also reinforced the view that benzene is a planar molecule. Alternative structures, such as Baeyer, Körner, or Ladenburg benzene, would have given different molecular dipole moments.

[85] Coulson, C. A. *Valence*; Clarendon Press: Oxford, England, 1952; p. 128.

[86] Pauling, L. *J. Am. Chem. Soc.* **1932**, *54*, 3570.

[87] This idea was called the "postulate of the additivity of normal covalent bonds" by Pauling (reference 30).

[88] The premise that covalent bonds between atoms with different electronegativity values are stronger than the corresponding bonds between identical atoms is not always found to be true. Benson (reference 67) pointed out that the reaction of Hg_2 with Cl_2 to produce 2 HgCl, is endothermic by at least 10 kcal/mol.

[89] Reddy, R. R.; Rao, T. V. R.; Viswanath, R. *J. Am. Chem. Soc.* **1989**, *111*, 2914.

TABLE 1.12   Comparison of Electronegativity Values^a

Atom	χ_P	χ_M	χ_{spec}	χ_α	V_x
H	2.20	3.059	2.300	2.27	2.70
Li	0.91	1.282	0.912	0.94	0.75
Be	1.57	1.987	1.576	1.55	2.08
B	2.04	1.828	2.051	2.02	3.66
C	2.55	2.671	2.544	2.56	5.19
N	3.04	3.083	3.066	3.12	6.67
O	3.44	3.215	3.610	3.62	8.11
F	3.98	4.438	4.193	4.23	9.915
Na	0.93	1.212	0.869	0.95	0.65
Mg	1.31	1.630	1.293	1.32	1.54
Al	1.61	1.373	1.613	1.55	2.40
Si	1.90	2.033	1.916	1.87	3.41
P	2.19	2.394	2.253	2.22	4.55
S	2.58	2.651	2.589	2.49	5.77
Cl	3.16	3.535	2.869	2.82	7.04
K	0.82	1.032	0.734	0.84	0.51
Ca	1.00	1.303	1.034	1.11	1.15
Br	2.96	3.236	2.685	2.56	6.13
I	2.66	2.880	2.359	2.27	5.25

^{a} Values for χ_P, χ_M, and χ_{spec} are taken from the compilation of Allen (reference 95). Values for χ_α are taken from reference 94. Values of V_x are from reference 100.

arbitrarily set to 4.0, and the electronegativities of other atoms were then determined (Table 1.12).

$$D_{A-B} = \sqrt{D_{A-A}D_{B-B}} + 30\,(\Delta\chi)^2 \qquad (1.27)$$

On the one hand, the concept of electronegativity has been called "perhaps the most popular intuitive concept in chemistry."[90] On the other hand, it is difficult to determine precise values for electronegativity because a set of electronegativity values amounts to "a chemical pattern recognition scheme which is not amenable to direct physical measurement."[91] Therefore, a great variety of other approaches have been taken in describing and quantifying electronegativity.

The Pauling electronegativity scale is inherently dependent on measurements made on molecules, but there have been many attempts to define electronegativity as an atomic property. Sanderson's definition of electronegativity as "the effectiveness of the nuclear charge as sensed within an outer orbital vacancy" of an atom suggests that some atomic properties should be related to electronegativity.[92] Mulliken introduced an electronegativity scale (χ_M) based on the average of the ionization potential (I) and electron affinity (A) of atoms; that is, $\chi = (I + A)/2$.[93] (A greater electron affinity means a greater attraction of an atom for an electron from outside the atom; a greater

[90] Sen, K. D. in the Editor's Note to reference 97.

[91] Allen, L. C.; Egolf, D. A.; Knight, E. T.; Liang, C. *J. Phys. Chem.* **1990**, *94*, 5602 (quotation from p. 5605).

[92] Sanderson, R. T. *J. Chem. Educ.* **1988**, *65*, 112, 227. See also Pauling, L. *J. Chem. Educ.* **1988**, *65*, 375.

[93] Mulliken, R. S. *J. Chem. Phys.* **1934**, *2*, 782; **1935**, *3*, 573.

ionization potential means a greater affinity of an atom for a nonbonded electron localized on the atom.) Nagle introduced an electronegativity value based on atomic polarizability.[94] Allen proposed electronegativity values based on the average ionization potential of all of the p and s electrons on an atom.[95–97] Domenicano and co-workers developed a set of group electronegativities based on the effect of a substituent on a benzene ring.[98] Building on a suggestion of Yuan,[99] Benson proposed another measure of electronegativity, V_x, which is calculated by dividing the number of valence electrons about an atom by its covalent radius.[100] Thus, seven electrons in the valence shell of a fluorine atom, divided by 0.706 Å, gives a V_x value of 9.915 for fluorine. Values of V_x correlate well with a number of physical properties.[100]

Table 1.12 compares the electronegativity values reported by Pauling (χ_P), Mulliken (χ_M), Allen (χ_{spec}), Nagle (χ_α), and Benson (V_x).[101] The Pauling, Allen, and Nagle values are usually quite similar, suggesting that the properties of atoms in molecules may indeed be related to the properties of isolated atoms. However, while the Mulliken values are similar to the other values, there are some differences, particularly for hydrogen. The Benson values are likewise larger in magnitude, but (except for hydrogen) they generally correlate well with the Pauling values.

Theoretical studies have offered additional perspectives on electronegativity. Parr and co-workers[102] defined a quantity, μ, as the "electronic chemical potential," which measures "the escaping tendency" of the electrons in the system.[103] The value of μ is approximately the same as $(I + A)/2$, the Mulliken electronegativity, so the value χ_M has been termed *absolute* electronegativity.[103] Closely related to the concept of electronegativity is the concept of **chemical potential**, which is also given the symbol μ and which is defined as $\partial E/\partial N$, where E is the energy of the system and N is the number of

[94] Nagle, J. K. *J. Am. Chem. Soc.* **1990**, *112*, 4741.

[95] Allen, L. C. *J. Am. Chem. Soc.* **1989**, *111*, 9003. Allen called this definition of electronegativity "the third dimension of the periodic table." For a summary, see Borman, S. A. *Chem. Eng. News* **1990** (Jan 1), 18. Also see Politzer, P.; Murray, J. S.; Grice, M. E. *Collect. Czech. Chem. Commun.* **2005**, *70*, 550; Murphy, L. R.; Meek, T. L.; Allred, A. L.; Allen, L. C. *J. Phys. Chem. A* **2000**, *104*, 5867.

[96] For other treatments of electronegativity, see Boyd, R. J.; Edgecombe, K. E. *J. Am. Chem. Soc.* **1988**, *110*, 4182; Bratsch, S. G. *J. Chem. Educ.* **1988**, *65*, 223; Li, K.; Wang, X.; Xue, D. *J. Phys. Chem. A* **2008**, *112*, 7894.

[97] For a summary of these electronegativity scales, see Mullay, J. in Sen, K. D.; Jorgensen, C. K., Eds. *Electronegativity*; Springer-Verlag: Berlin, 1987.

[98] Campanelli, A. R.; Domenicano, A.; Ramondo, F.; Hargittai, I. *J. Phys. Chem. A.* **2004**, *108*, 4940.

[99] Yuan, H. C. *Acta Chim. Sin.* **1964**, *30*, 341; cf. reference 100; *Chem. Abstr.* **1965**, *62*, 2253h.

[100] Luo, Y.-R.; Benson, S. W. *J. Phys. Chem.* **1988**, *92*, 5255; *J. Am. Chem. Soc.* **1989**, *111*, 2480; *J. Phys. Chem.* **1989**, *93*, 3304. See also Luo, Y.-R.; Pacey, P. D. *J. Am. Chem. Soc.* **1991**, *113*, 1465 and references therein; Luo, Y.-R.; Benson, S. W. *Acc. Chem. Res.* **1992**, *25*, 375.

[101] Table 1.12 lists χ values for atoms only, but it is also possible to calculate "group electronegativities" to take into account the net effect of a group of atoms. For a tabulation of group electronegativities calculated by a variety of methods, see Bratsch, S. G. *J. Chem. Educ.* **1985**, *62*, 101. As an example, the group electronegativity of the CH_3 group is about 2.3, while that for CF_3 is about 3.5.

[102] Parr, R. G.; Donnelly, R. A.; Levy, M.; Palke, W. E. *J. Chem. Phys.* **1978**, *68*, 3801.

[103] Pearson, R. G. *Acc. Chem. Res.* **1990**, *23*, 1.

electrons.[104–106] Parr and co-workers defined

$$\chi = -\mu = -\delta E/\delta \rho \qquad (1.28)$$

where the energy is related to a theoretical treatment of electron density.[107]

As a result of the many theoretical treatments, chemists now find themselves using one term to mean different things, since "the electronic chemical potential, $\mu, \ldots$ is an entirely different chemical quantity" from the concept of electronegativity as the origin of bond polarity.[106] As Pearson noted:

> The fact that there are two different measures both called (electronegativity) scales creates considerable opportunity for confusion and misunderstanding. Since the applications are so different, it is not a meaningful question to ask which scale is more correct. Each scale is more correct in its own area of use.[103]

Usually we will use the term *electronegativity* in the sense originally proposed by Pauling, but we must recognize the alternative meanings in the literature. Moreover, we see that a simple idea that is intuitively useful in understanding some problems of structure and bonding (e.g., dipole moments) may become more difficult to use as we attempt to make it more precise. The next section will further illustrate this theme.

Complementary Theoretical Models of Bonding

The Lewis model for forming a chemical bond by sharing an electron pair leads to a theoretical description of bonding known as **valence bond theory** (**VB theory**).[108] The key to VB theory is that we consider a structure to be formed by bringing together complete atoms and then allowing them to interact to form bonds. In **molecular orbital theory** (**MO theory**), on the other hand, we consider molecules to be constructed by bringing together nuclei (or nuclei and filled inner shells) and then placing electrons in orbitals calculated for the entire array of nuclei.[85] Therefore, MO theory does not generate discrete chemical bonds. Rather, it generates a set of orbitals that allow electrons to roam over many nuclei, perhaps an entire molecule, so it does not restrict them to any particular pair of nuclei.

Both VB and MO theories utilize mathematical expressions that can rapidly become complex, even for simple organic molecules. Moreover, VB theory and MO theory are usually described with different symbols, so it can be difficult to distinguish the similarities among and differences between them. Therefore, it may be useful to consider first a very simple bonding problem, the formation of a hydrogen molecule from two hydrogen atoms. The principles will be the same as for larger molecules, but the comparison of the two approaches will be more apparent in the case of H_2.

The discussion that follows has been adapted from several introductory texts on bonding, which may be consulted for more

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[104] Pritchard, H. O.; Sumner, F. H. *Proc. R. Soc. (London)* **1956**, *A235*, 136.

[105] Iczkowski, R. P.; Margrave, J. L. *J. Am. Chem. Soc.* **1961**, *83*, 3547.

[106] Allen, L. C. *Acc. Chem. Res.* **1990**, *23*, 175.

[107] Here ρ is actually a functional, and the approach is known as density functional theory. For an introduction, see (a) Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989; (b) March, N. H. *Electron Density Theory of Atoms and Molecules*; Academic Press: New York, 1991.

[108] A summary of the development of VB theory and a discussion of the merits of VB and MO theories was given by Klein, D. J.; Trinajstić, N. *J. Chem. Educ.* **1990**, *67*, 633.

details.[109] We begin with two isolated hydrogen atoms, as shown in Figure 1.6. Each atom has one electron in a $1s$ orbital. We can write a wave equation for the $1s$ orbital, since the hydrogen atom can be solved exactly in quantum mechanics. Electron 1 is initially associated with hydrogen nucleus a, and electron 2 is associated with hydrogen nucleus b. Bringing the two atoms together allows bonding to occur, as shown in Figure 1.6.

Now we want to write a wave equation that will mathematically describe the electron distribution in the hydrogen molecule. The valence bond method initially used by Heitler and London described one possible wave function as[110]

$$\Psi_1 = ca(1)b(2) \tag{1.29}$$

in which c is a constant, $a(1)$ is the wave function for electron 1 in a $1s$ orbital on hydrogen nucleus a, and $b(2)$ is the wave function for electron 2 in a $1s$ orbital on hydrogen nucleus b. Since the electrons are indistinguishable, it should be equally acceptable to write

$$\Psi_2 = ca(2)\, b(1) \tag{1.30}$$

Both descriptions are possible, so both need to be included in the wave function for the molecule. Therefore, Heitler and London wrote that

$$\Psi_{\text{VB}} = ca(1)b(2) + ca(2)b(1) \tag{1.31}$$

In this case the constants are chosen so that the overall wave function is properly normalized and made antisymmetric with respect to spin.

The molecular orbital approach to describing hydrogen also starts with two hydrogen nuclei (a and b) and two electrons (1 and 2), but we make no initial assumption about the location of the two electrons.[109] We solve (at least in principle) the Schrödinger equation for the molecular orbitals around the pair of nuclei, and we then write a wave equation for one electron in a resulting MO:

$$\Psi_1 = c_1 a(1) + c_2 b(1) \tag{1.32}$$

Note that electron 1 is associated with both nuclei. Similarly,

$$\Psi_2 = c_1 a(2) + c_2 b(2) \tag{1.33}$$

The combined MO wave function, then, is the product of the two one-electron wave functions:

$$\Psi_{\text{MO}} = \Psi_1\,\Psi_2 = c_1^2 a(1)a(2) + c_2^2 b(1)b(2) + c_1 c_2[a(1)b(2) + a(2)b(1)] \tag{1.34}$$

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[109] For examples, see reference 9, p. 517 ff; Eyring, H.; Walter, J.; Kimball, G. E. *Quantum Chemistry*; John Wiley & Sons: New York, 1944; p. 212 ff. The mathematics is described in some detail in Slater, J. C. *Quantum Theory of Molecules and Solids, Vol. I. Electronic Structure of Molecules*; McGraw-Hill: New York, 1963.

[110] Heitler, W.; London, F. *Z. Physik* **1927**, *44*, 455.

We see that Ψ_{MO} is more complex than Ψ_{VB}, and that, in fact, Ψ_{VB} is incorporated into Ψ_{MO}. Specifically, the third term of Ψ_{MO} is the same as Ψ_{VB} if the constants are made the same. What is the physical significance of the differences in Ψ_{VB} and Ψ_{MO}? Ψ_{MO} includes two terms that Ψ_{VB} does not: $a(1)$ $a(2)$ and $b(1)b(2)$. Each of these terms represents a **configuration** (arrangement of electrons in orbitals) in which *both* electrons are formally localized in what had been a $1s$ orbital on *one* of the hydrogen atoms. Therefore, these terms describe ionic structures. In other words, $a(1)a(2)$ represents $a:^-b^+$, and $b(1)b(2)$ represents $a^+b:^-$. We now see that the MO treatment appears to give large weight to terms that represent electronic configurations in which both electrons are on one nucleus, while the VB treatment ignores these terms.

Which approach is correct? Usually our measure of the "correctness" of any calculation is how accurately it reproduces a known physical property. In the case of H_2, a relevant property is the homolytic bond dissociation energy. The simple VB calculation described here gives a value of 3.14 eV (72.4 kcal/mol) for H_2 dissociation.[109] The simple MO calculation gives a value of 2.70 eV (62.3 kcal/mol). The experimental value is 4.75 eV (109.5 kcal/mol).[109] Obviously, neither calculation is correct unless one takes order of magnitude agreement as satisfactory; in that case, both calculations are correct.

It may seem reasonable that the MO method gives a result that underestimates the bond dissociation energy because the wave equation includes patterns of electron density that resemble ionic species such as $a^+b:^-$. But why is the VB result also in error? The answer seems to be that, while the MO approach places too much emphasis on these ionic electron distributions, the VB approach underutilizes them. A strong bond apparently requires that both electrons spend a lot of time in the region of space between the two protons. Doing so must make it more likely that the two electrons will, at some instant, be on the same atom.[111] Thus, we might improve the accuracy of the VB calculation if we add some terms that keep the electrons closer together between the nuclei.

Similarly, we could improve the MO calculation by adding some terms that would decrease the ionic character of the bonding orbital. If we include a description of the hydrogen atoms in which the electron in each case has some probability of being in an orbital higher than the $1s$ orbital, then excessively repulsive interactions will become less significant in the final molecular orbital.[112] There are other changes we can make as well. Table 1.13 shows how the calculated stability of H_2 varies according to the complexity of the MO calculation.[113,114] Including 13 terms makes a major improvement. From that point on almost any change decreases the stability of the calculated structure almost as much as it increases it, but small gains can be won. An MO

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[111] Colloquial terminology is used here to be consistent with the level of presentation of the theory.

[112] This procedure is called *configuration interaction*; cf. Coffey, P.; Jug, K. *J. Chem. Educ.* **1974**, *51*, 252. See also Coulson, C. A.; Fischer, I. *Philos. Mag.* **1949**, *40*, 386.

[113] (a) Data from McWeeny, R. *Coulson's Valence,* 3rd ed.; Oxford University Press: Oxford, England, 1979; p. 120 and references therein. (b) See also Davis, J. C., Jr. *Advanced Physical Chemistry*; Ronald Press: New York, 1965; p. 426.

[114] For additional references, see King, G. W. *Spectroscopy and Molecular Structure*; Holt, Rinehart and Winston: New York, 1964; p. 149.

TABLE 1.13 Calculated Values for H$_2$ Stability

Calculation Method	DE (calc.)
Simple valence bond theory	3.14 eV
Simple molecular orbital theory	2.70 eV
James–Cooledge (13 parameters)	4.72 eV
Kolos–Wolniewicz (100 terms)	4.7467 eV
Experimental value	4.7467 eV

Source: Reference 113.

equation with 50 terms does quite well. Similarly, a VB calculation with a large number of terms can also produce an answer that is within experimental error of the measured value. If enough terms are included, therefore, the two methods can produce equivalent results.[85,115]

There are several conclusions to be drawn from this analysis:

1. Neither *simple* VB theory nor *simple* MO theory produces a value for the dissociation energy (DE) that is very close to the experimental value.
2. Both VB and MO theories can be modified to produce more accurate results. Even for a simple molecule such as H$_2$, however, many terms may be required to produce an acceptable value for the property of interest.

More important for our purposes here are the following conclusions:

3. As both simple VB theory and simple MO theory are modified to give a more accurate result, they must necessarily produce more nearly equivalent results. In that sense they must become more like each other, and the modifications may make their theoretical bases more nearly equivalent as well.
4. Both simple VB theory and simple MO theory should be regarded only as *approaches* for the calculation of molecular properties, not as final answers. They should be viewed as complementary initial models for computational chemistry, not as depictions of reality.

This last point was emphasized by Shaik and Hiberty:

A modern chemist should know that there are two ways of describing electronic structure... [that are] not two contrasting theories, but rather two representations or two guises of the same reality. Their capabilities and insights into chemical problems are complementary....[116]

Why then don't we just talk about high level theoretical calculations and ignore the simple theories? The elementary theories are useful to us because they provide good conceptual models for the computational process. We can visualize the interactions represented by equation 1.34, as well as the physical situation suggested by equation 1.31. It is much more difficult for us to envision the interactions involved in a 50- or 100-term wave function, however. As the accuracy of the model is increased, its simplicity is decreased.

[115] Kolos, W.; Wolniewicz, L. *J. Chem. Phys.* **1968**, *49*, 404.

[116] Shaik, S.; Hiberty, P. C. *Helv. Chim. Acta* **2003**, *86*, 1063.
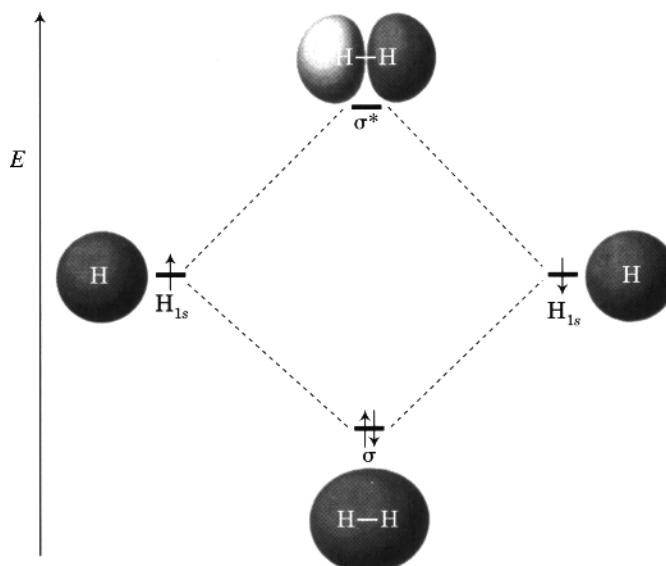
FIGURE 1.7

Combination of atomic hydrogen orbitals to produce molecular hydrogen.

We must choose the model that is sufficiently accurate for our computational purposes, yet still simple enough that we have some understanding of what the model describes. Otherwise the model is a black box, and we have no understanding of what it does. Perhaps we do not even know whether the answers it produces are physically reasonable.

Pictorial Representations of Bonding Concepts

The MO and VB methods described above illustrate the use of mathematical models in chemistry. Chemists often use other, nonmathematical models to depict the results of calculations in schematic or pictorial form. Continuing the example of H_2, we represent the combination of two atomic hydrogen 1s orbitals to make two new molecular orbitals, the familiar σ and σ^* orbitals (Figure 1.7). The vertical arrow on the left in Figure 1.7 indicates that the σ and σ^* orbitals differ in energy, the σ MO being lower in energy than the original hydrogen 1s orbitals, and the σ^* orbital being higher in energy.[117] The σ orbital is a bonding orbital, and population of the σ MO with two electrons produces a stable H_2 molecule. On the other hand, σ^* is an anti-bonding orbital, and population of this orbital with an electron destabilizes the molecule.

Let us apply this pictorial representation of bonding to one of the fundamental concepts in organic chemistry—the bonding of methane. We usually begin with the atomic orbitals of the carbon atom and then consider

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[117] This figure is somewhat stylized, since it shows the σ and σ^* orbitals symmetrically displaced above and below the energy of the initial hydrogen 1s orbitals. In fact, the σ^* should be more antibonding than the σ orbital is bonding. For details, see Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; Wiley-Interscience: New York, 1985; p. 12 ff. In addition, Willis, C. J. *J. Chem. Educ.* **1988**, *65*, 418 calculated that the H–H bond energy is only about 19% of the energy gained by moving two electrons from hydrogen 1s orbitals to the H_2 σ bonding orbital. The other 81% of that energy is consumed in offsetting electrical repulsion within the molecule.

the four hydrogen atoms. We represent the energies of the orbitals of atomic carbon as shown in Figure 1.8. Each horizontal line represents the energy associated with a particular atomic wave function calculated from quantum mechanics. The small arrows represent electrons, and the direction of each arrow indicates the spin quantum number of the electron it represents. We know that we may put no more than two arrows on each horizontal line (i.e., two electrons in the same atomic orbital), and then only if the arrows point in opposite directions (meaning that the two electrons have paired spins).

If we combine the energy level diagram for carbon with the bonding model shown schematically in Figure 1.7, we can construct a representation of a one-carbon hydrocarbon in which each unpaired electron in a 2p orbital on carbon is paired with an electron from a hydrogen atom to form a C–H bond (Figure 1.9). While this result is the logical extension of the bonding model illustrated in Figure 1.8, it clearly is not correct. There is abundant experimental data indicating that methane has the molecular formula CH_4, not CH_2.

FIGURE 1.8
Energy levels of atomic carbon orbitals.

The *sp*^{3} Hybridization Model for Methane

Once a model is fixed in our minds, we find it almost impossible to discard or ignore it unless another model is available to take its place. Instead, models are almost always modified to fit new data—and that is what we do here. We use the concept of **hybridization** to change our mental picture of the atomic orbitals of carbon to a more useful one. The procedure was described by Pauling and has been discussed by a number of authors.[118–121]

Beginning with the unhybridized carbon orbitals in Figure 1.10(a), we promote an electron from a 2s orbital to a 2p orbital, as shown in Figure 1.10(b). Then we combine the s and p orbitals to produce four sp^3 hybrid orbitals that are equal in energy, as shown in Figure 1.10(c).[122–124] Promotion of the electron requires about 96 kcal/mol, but this is more than offset by the additional stabilization (about 200 kcal/mol) gained by forming two additional C–H bonds.[125] The wave functions of the hybrid orbitals (where C_{2s} represents the wave function for a 2s orbital on carbon, etc.) are shown in equations 1.35–1.38.[126]

FIGURE 1.9
A bonding model of "methane" as CH_2.

[118] (a) Pauling, L. *J. Am. Chem. Soc.* **1931**, *53*, 1367; reference 30, p. 118; (b) See also Slater, J. C. *Phys. Rev.* **1931**, *37*, 481.

[119] Compare Hsu, C.-Y.; Orchin, M. *J. Chem. Educ*. **1973**, *50*, 114.

[120] Root, D. M.; Landis, C. R.; Cleveland, T. *J. Am. Chem. Soc.* **1993**, *115*, 4201.

[121] For a reconsideration of the concept of hybridization, see Magnusson, E. *J. Am. Chem. Soc.* **1984**, *106*, 1177.

[122] Matteson, D. S. *Organometallic Reaction Mechanisms of the Nontransition Elements*; Academic Press: New York, 1974; p. 5.

[123] Ogilvie, J. F. *J. Chem. Educ*. **1990**, *67*, 280.

[124] Strictly speaking, there are hybridized *orbitals* but not hybridized *atoms*. However, organic chemists frequently use the term "sp^3-hybridized carbon" to refer to a carbon atom with sp^3 hybrid orbitals.

[125] See the discussion in Hameka, H. F. *Quantum Theory of the Chemical Bond*; Hafner Press: New York, 1975; p. 216 ff.

[126] Bernett, W. A. *J. Chem. Educ*. **1969**, *46*, 746.

(a)   (b)   (c)

FIGURE 1.10

Hybridization of carbon orbitals to produce sp^3 hybridized orbitals.
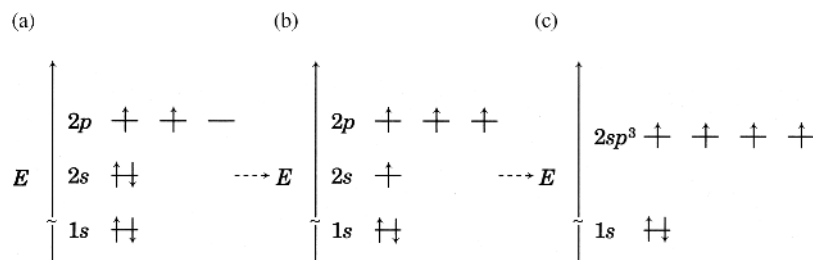
$$\phi_{sp^3_{(1)}} = \tfrac{1}{2}(C_{2s} + C_{2p_x} + C_{2p_y} + C_{2p_z}) \tag{1.35}$$

$$\phi_{sp^3_{(2)}} = \tfrac{1}{2}(C_{2s} + C_{2p_x} - C_{2p_y} - C_{2p_z}) \tag{1.36}$$

$$\phi_{sp^3_{(3)}} = \tfrac{1}{2}(C_{2s} - C_{2p_x} + C_{2p_y} - C_{2p_z}) \tag{1.37}$$

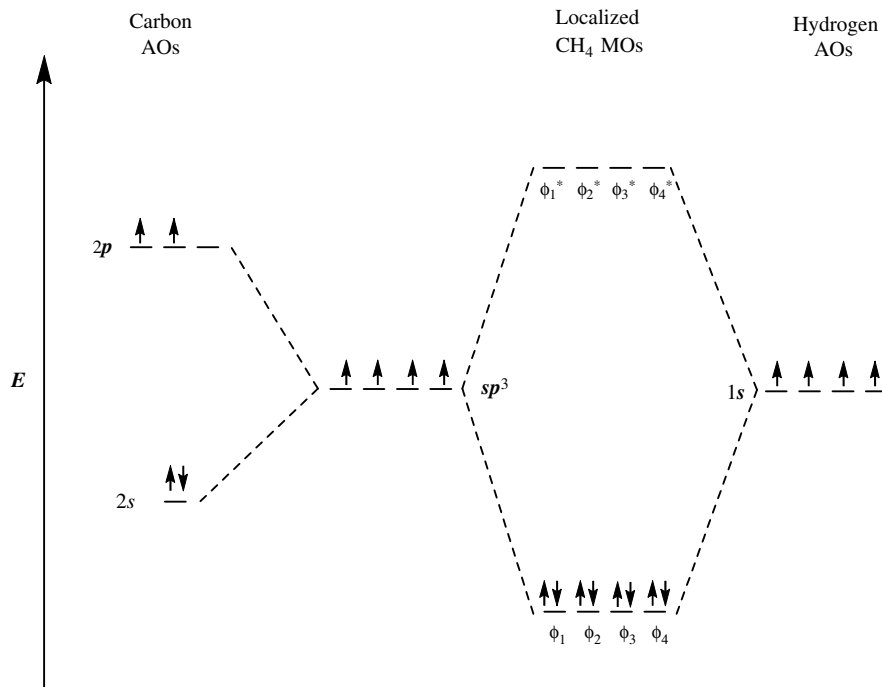$$\phi_{sp^3_{(4)}} = \tfrac{1}{2}(C_{2s} - C_{2p_x} - C_{2p_y} + C_{2p_z}) \tag{1.38}$$

Figure 1.11 shows the contours of one of the sp^3 orbitals as well as those of carbon 2s, 2p, sp, and sp^2 hybrids.[127] Each of the sp^3 orbitals in equations 1.35–1.38 has a large lobe and a small lobe. The two lobes have a different mathematical sign, and the four large lobes point toward the corners of a regular tetrahedron.[128] Now we can describe methane as CH_4 by combining each of the four carbon sp^3 hybrid orbitals with a 1s orbital on hydrogen. A qualitative energy diagram for the process is shown in Figure 1.12. The four
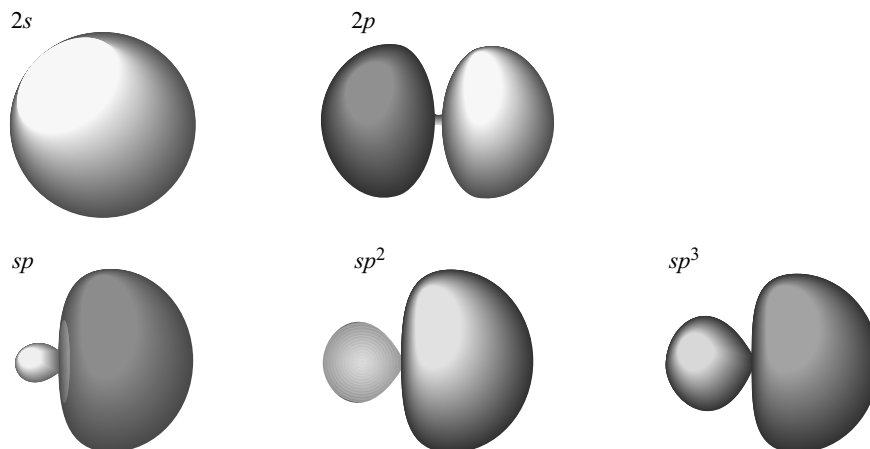
FIGURE 1.11

Sizes and shapes of carbon atomic and hybrid orbitals.

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[127] The orbital contours were generated with CACheᵀᴹ visualization software.

[128] The shapes of these orbitals are quite different from the representations shown in many chemistry textbooks. Compare Allendoerfer, R. D. *J. Chem. Educ.* **1990**, *67*, 37.

Carbon
AOs

Localized
CH_4 MOs

Hydrogen
AOs

sp^3 hybrid orbitals point to the corners of a tetrahedron, which is consistent with CH_4 having tetrahedral geometry (Figure 1.13).[29,129]

It is important to note in this discussion that we hybridize the atomic orbitals to produce a different model. As Ogilvie noted,

> According to *Coulson's Valence*, "hybridization is not a physical effect but merely a feature of [a] theoretical description". . ... Despite the fact that many authors of textbooks of general chemistry have written that CH_4 has a tetrahedral structure because of sp^3 hybridization, there neither exists now, nor has ever existed, any quantitative experimental or theoretical justification of such a statement.[123,130]

In addition, Matteson noted that

> Hybridization is not something that atoms do or have done to them. It is purely a mental process gone through by the chemist, who wants to group atomic orbitals according to their symmetry properties so he can talk about one localized bond and ignore the rest. Hybridization does not change the shape of the electron distribution in any atom.[122]

Are There *sp*³ Hybrid Orbitals in Methane?

The hybridization concept is so ingrained in organic chemistry that we often use the concepts of sp^3 hybridization and tetrahedral geometry interchangeably.[120] We will now discuss one important experimental technique that will cause us to rethink what we have said about methane. The technique

FIGURE 1.12

Mixing of hydrogen 1*s* and carbon *sp*³ orbitals to make localized MOs of methane. (Adapted from reference 138.)
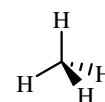
$l_{C\text{-}H} = 1.091\,\text{Å}$

FIGURE 1.13

Experimental geometry of methane.

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[129] We usually write the bond angle as 109.5°. Mathematically, it is 109° 28′, which corresponds to 109.47°. A method for the calculation of *sp*, *sp*², and *sp*³ interorbital angles was given by Duffey, G. H. *J. Chem. Educ.* **1992**, *69*, 171.

[130] For a rebuttal of this view, see Pauling, L. *J. Chem. Educ.* **1992**, *69*, 519.
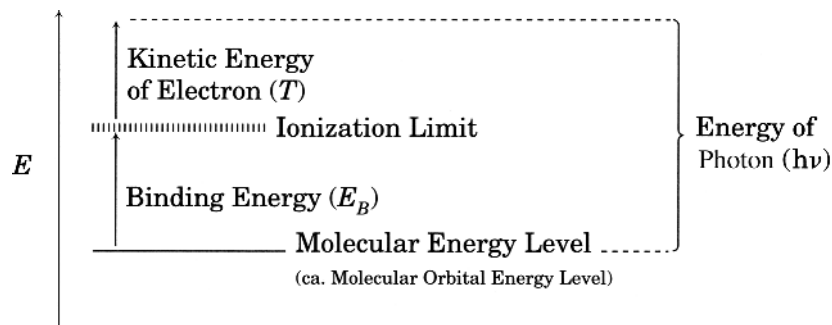
FIGURE 1.14

Energy relationships in photoelectron spectroscopy.

is **photoelectron spectroscopy** (PES), which is used to probe the energy levels that electrons occupy within molecules.[131,132] The essence of PES is the measurement of the energies of electrons that have been ejected from molecules or atoms by high energy photons (light). As shown in Figure 1.14, the difference between the energies of the electrons (energy out) and the energy of the photons causing the displacement (energy in) is taken to be a measure of the binding energy holding the electrons in the molecule or atom. The higher the energy level from which an electron is removed, the less is its binding energy, and the greater will be its kinetic energy. This relationship is shown in equation 1.39, where $h\nu$ is the energy of the photon, T is the kinetic energy of the electron ejected from the molecule, and E_B is the binding energy of the electron in the molecule. Based on Koopmans' theorem, we associate the number and position of binding energy levels in a structure with the energies of its atomic or molecular orbitals.[133]

$$h\nu = T + E_B \tag{1.39}$$

Figure 1.15 shows a PES spectrum of methane.[134] One peak at very high binding energy ($>290\,\text{eV}$) is characteristic of molecules with electrons in carbon $1s$ orbitals. However, there are two peaks at lower energy: one at $23.0\,\text{eV}$ and one at $12.7\,\text{eV}$. Therefore, we are led to the conclusion that the electrons in methane are in three different energy levels, one energy level corresponding to the carbon $1s$ electrons, and two different energy levels corresponding to the other electrons in the molecule. It is somewhat difficult to reconcile this experimental result with an intuitive bonding model in which methane is constructed of four equivalent $\text{C}(sp^3)$–$\text{H}(1s)$ bonds produced by overlap of four equivalent sp^3 hybrid orbitals on a carbon atom with four hydrogen $1s$ orbitals (Figure 1.12).

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[131] A related procedure is called electron spectroscopy for chemical **a**nalysis (**ESCA**). For a discussion of PES, ESCA, and similar techniques, see Baker, A. D.; Brundle, C. R.; Thompson, M. *Chem. Soc. Rev.* **1972**, *1*, 355; Baker, A. D. *Acc. Chem. Res.* **1970**, *3*, 17. Another technique, Auger spectroscopy, is discussed in reference 133.

[132] Bock, H.; Mollère, P. D. *J. Chem. Educ.* **1974**, *51*, 506; Baker, A. D. *Acc. Chem. Res.* **1970**, *3*, 17; Ballard, R. E. *Photoelectron Spectroscopy and Molecular Orbital Theory*; John Wiley & Sons: New York, 1978.

[133] For a discussion of the application of Koopmans' theorem in PES, see Albridge, R. G. in Weissberger, A.; Rossiter, B. W., Eds. *Physical Methods of Chemistry*, Vol. I, Part IIID; Wiley-Interscience: New York, 1972; p. 307.

[134] Hamrin, K.; Johansson, G.; Gelius, U.; Fahlman, A.; Nordling, C.; Siegbahn, K. *Chem. Phys. Lett.* **1968**, *1*, 613.
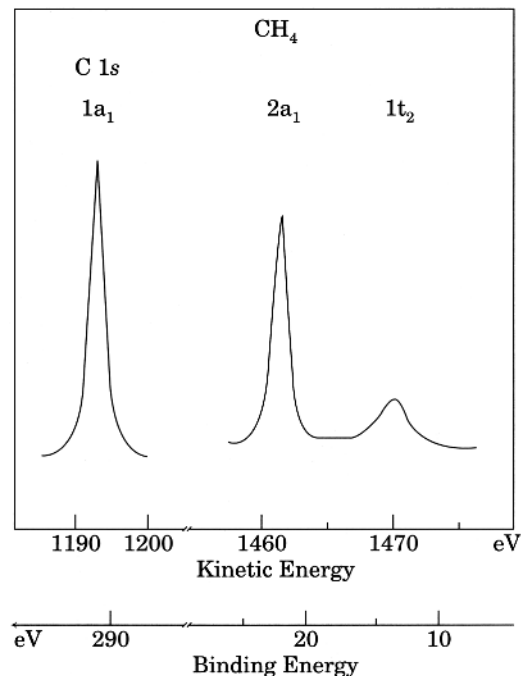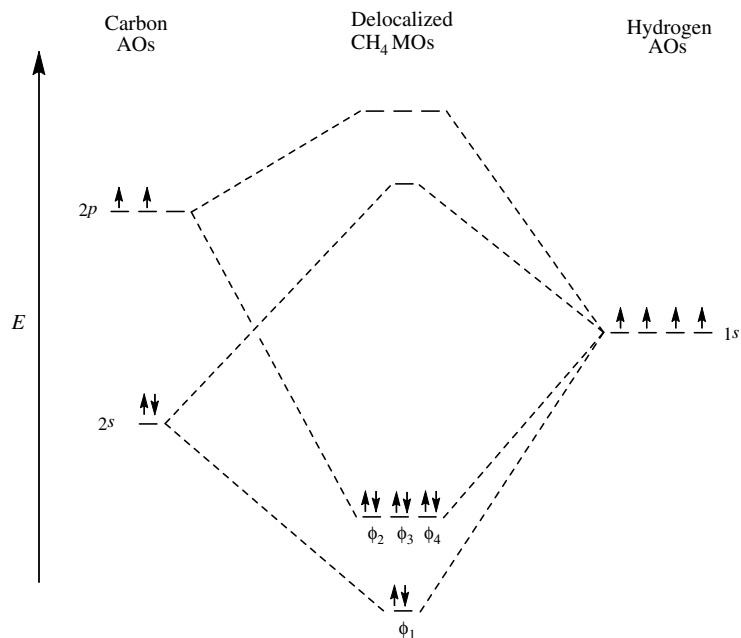
FIGURE 1.15
PES spectrum of methane.
(Adapted from reference 134.)

One important aspect of MO theory—the concept of **symmetry-correct molecular orbitals**—not only makes it possible to explain this experimental result but, in fact, requires it. A fundamental property of molecular orbitals is that they have the full symmetry of the basis set of atomic orbitals used to generate the molecular orbitals.[135] This means that the molecular orbitals must be either symmetric or antisymmetric with respect to the symmetry operations provided for by the symmetry group of the atomic orbitals.[136] If we consider each C–H σ bond formed by overlap of an sp^3 orbital on a carbon atom with a 1s orbital on a hydrogen atom to be an MO, then clearly each of these MOs lacks the full symmetry of the basis set of s and p atomic orbitals.

There are two ways to correct our treatment of methane by inclusion of symmetry-correct MOs. The first approach is to consider the descriptions of C–H bonds to be **localized molecular orbitals** (LMOs)—that is, molecular orbitals that have electron density on only a portion of a molecule. We can then consider these LMOs to be the basis set of orbitals for a new MO calculation to determine the symmetry-correct, **delocalized MOs** for the

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[135] The term *basis set* refers to the set of atomic orbitals used to construct the molecular orbitals.

[136] The terms *symmetric* and *antisymmetric* mean that the result of any symmetry operation will be an orbital of the same type and in the same location as before the transformation. If the orbital is symmetric with respect to that transformation, then the orbital produced will also have + and − lobes in the same locations as before; if the orbital is antisymmetric, then the resulting orbital will have + lobes where − lobes were, and vice versa. All MOs must be either symmetric or antisymmetric. If a symmetry operation that corresponds to an element of symmetry of the basis set of atomic orbitals transforms a lobe to a position in space in which there was not a lobe beforehand, that MO is said to be **asymmetric** (without symmetry) and is not allowable as a symmetry-correct MO for the molecule. These topics will be discussed in more detail in Chapters 4 and 11.

FIGURE 1.16

Mixing of atomic orbitals on carbon with hydrogen $1s$ orbitals to make molecular orbitals of methane. (Adapted from reference 138.)

molecule. [126,137–139] The second, more direct approach is to calculate delocalized methane molecular orbitals directly from the unhybridized orbitals: a carbon $2s$ orbital, three carbon $2p$ orbitals, and four hydrogen $1s$ orbitals. Both procedures produce four delocalized molecular orbitals, each of which has the full symmetry of the original basis set of tetrahedral methane. [140]

The resulting molecular orbitals for methane are listed in equations 1.40–1.43, where H_1 is the hydrogen $1s$ orbital on hydrogen 1, and so on. [126] Figure 1.16 shows a qualitative MO energy level diagram, and Figure 1.17 represents the three-dimensional electron contour plot for the orbitals. [141] We see that one MO (ϕ_1) represents a bonding interaction of the carbon $2s$ orbital with all four of the hydrogen $1s$ orbitals, while the other orbitals each have both bonding and some antibonding interactions. Therefore, ϕ_1 is lower in energy than the other three. These figures make clear that there are two different energy levels for the bonding electrons, so two PES bands would be predicted. We conclude, therefore, that the customary view of sp^3 hybridization, while useful for predicting geometries, does not provide the most direct explanation for the PES results.

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[137] Flurry, R. L., Jr. *J. Chem. Educ.* **1976**, *53*, 554; Cohen, I.; Del Bene, J. *J. Chem. Educ.* **1969**, *46*, 487.

[138] Hoffman, D. K.; Ruedenberg, K.; Verkade, J. G. *J. Chem. Educ.* **1977**, *54*, 590.

[139] Dewar, M. J. S.; Dougherty, R. C. *The PMO Theory of Organic Chemistry*; Plenum Press: New York, 1975; p. 21 ff.

[140] Note that the four molecular orbitals are not tetrahedral in shape. Rather, each is either symmetric or antisymmetric with respect to the symmetry operations of the T_d point group.

[141] Graphics with semiempirical MO calculations using a CACheTM WorkSystem. For a more complete discussion of the molecular orbitals of methane, see Jorgensen, W. L.; Salem, L. *The Organic Chemist's Book of Orbitals*; Academic Press: New York, 1973; p. 68.
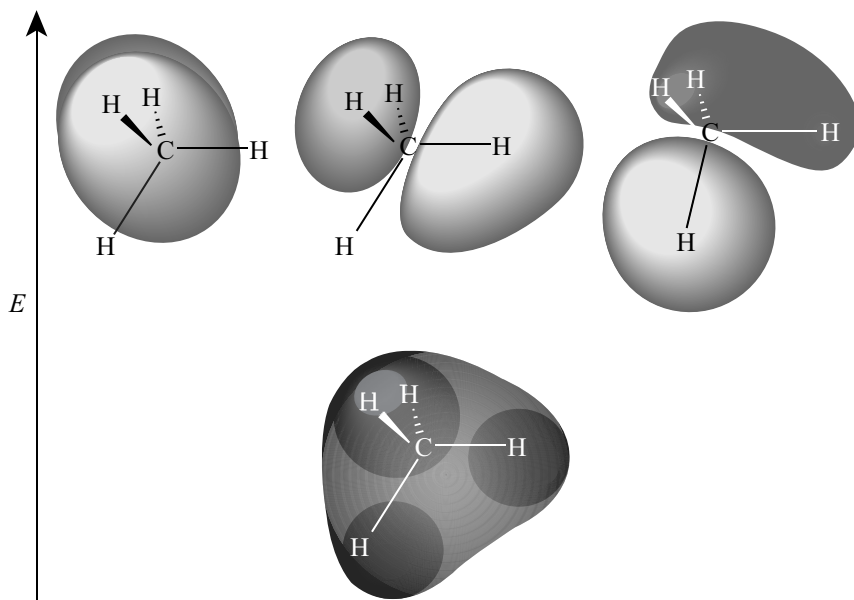
FIGURE 1.17
Bonding MOs for methane.

$$\phi_1 = 0.545\,C_{2s} + 0.272(H_1 + H_2 + H_3 + H_4) \tag{1.40}$$

$$\phi_2 = 0.545\,C_{2p_x} + 0.272\,(H_1 + H_2 - H_3 - H_4) \tag{1.41}$$

$$\phi_3 = 0.545\,C_{2p_y} + 0.272(H_1 - H_2 + H_3 - H_4) \tag{1.42}$$

$$\phi_4 = 0.545\,C_{2p_z} + 0.272(H_1 - H_2 - H_3 + H_4) \tag{1.43}$$

We must now address a fundamental question. Are there C–H bonds in methane? The answer from MO theory is clearly no. Population of the four bonding molecular orbitals with four pairs of electrons leads to a bonding interaction *among* the carbon atom and all of the hydrogen atoms (not just *between* carbon and the individual hydrogens). Thus, we should say that there is *bonding* in MO theory, but there are not distinct *bonds* formed by separate electron pairs localized between two atoms.

It is important to recognize that this conclusion is not a repudiation of valence bond theory.[142] As Shaik and Hiberty pointed out, a correct valence bond theory description of the bonding in methane produces a result that is entirely consistent with the PES result.[116] Rather, the PES result is a reminder that illustrations of C–H bonds formed by overlap of hydrogen $1s$ and carbon sp^3 orbitals should not be considered pictures of reality.

Valence Shell Electron Pair Repulsion Theory

We have seen that the tetrahedral shape of methane is consistent with a bonding model based on sp^3 hybrid orbitals on carbon. We should not conclude, however, that the geometry is a result of sp^3 hybridization. We

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[142] Pauling argued that the photoelectron spectrum of methane is consistent with sp^3 hybridization for methane. Pauling, L. *J. Chem. Educ*. **1992**, *69*, 519. See also the discussion by Simons, J. *J. Chem. Educ*. **1992**, *69*, 522.

could have predicted the geometry just as well from the Lewis structure of methane simply by using **valence shell electron pair repulsion** (VSEPR) **theory**.[143–145] The VSEPR method does not require the use of atomic or molecular orbitals; it is simply a solution to a problem in which the mutually repulsive points (electron pairs) are arranged as far apart from each other as possible on the surface of a sphere.[146]

To use the VSEPR theory to predict the geometry of methane, we simply ask the following question: What is the most stable arrangement for four pairs of electrons bonded to a central atom? The tetrahedral arrangement provides for the maximum distance between each electron pair and the other three electron pairs, so we expect this arrangement to be the most stable.[147] A simple method to calculate the bond angles of the resulting regular tetrahedron was pointed out by Ferreira.[148] Methane does not have a molecular dipole moment, even though each C–H bond might be slightly polar. Any bond dipole moment corresponding to one C–H bond aligned with the x-axis must therefore be canceled by the vector sum of the projections of the other three C–H bond dipole moments along the x-axis. Thus, the cosine of an H–C–H bond angle must be $1/3$, so the bond angle must be $109°28'$.

The VSEPR approach can easily be extended to ethane. Since each carbon atom has four substituents and since the electronegativity of carbon is close to that of hydrogen, we would predict the local geometry about each carbon atom to be tetrahedral as in methane. The H–C–H bond angles at each carbon atom should remain 109.5°, as should the H–C–C bond angles. The C–C bond would be longer than the C–H bonds because the covalent radius of a carbon atom is greater than that of a hydrogen atom. This prediction is consistent with the experimental geometry reported for ethane, as shown in Figure 1.18.[29]

Now let us consider methyl chloride. The covalent radius of chlorine (Table 1.2) is about 0.22 Å greater than that of carbon, so the C–Cl bond distance should be about 1.76 Å. Thus, we predict the molecular geometry of methyl chloride to be as shown in Figure 1.19(a). Spectroscopic data suggest, however, that the structure is like that shown in Figure 1.19(b). [29,149] While the C–Cl bond length is reasonable, the H–C–H bond angle is greater than 109.5°, and the H–C–Cl angle is smaller than 109.5°.

We can rationalize the difference between prediction and experiment with VSEPR theory by noting that the electronegativity of chlorine is greater than that of carbon (Table 1.12). In a methane C–H bond, the carbon atom and the hydrogen atom attract the electron pair approximately equally. In CH_3Cl, however, the electrons in the C–Cl bond will be pulled toward the

$l_{C\text{-}H} = 1.093 Å$
$l_{C\text{-}C} = 1.534 Å$
$\angle_{H\text{-}C\text{-}H} = 109.45°$

FIGURE 1.18

Experimental geometry of ethane.

[143] For a discussion of VSEPR, see Gillespie, R. J. *J. Chem. Educ.* **1963**, *40*, 295; Bent, H. A. *Chem. Rev.* **1961**, *61*, 275; Burdett, J. K. *Chem. Soc. Rev.* **1978**, *7*, 507. See also reference 8.

[144] Gillespie, R. J. *Chem. Soc. Rev.* **1992**, *21*, 59.

[145] Hall, M. B. *J. Am. Chem. Soc.* **1978**, *100*, 6333.

[146] The model may be more intuitively useful if we visualize the electron points as three-dimensional objects with shapes similar to those calculated for hybrid atomic orbitals. See Gillespie, R. J. *J. Chem. Educ.* **1963**, *40*, 295.

[147] The origin of the repulsion is thought to result from the Pauli exclusion principle and not from Coulombic repulsion of the electron pairs. For a discussion, see Allen, L. C. *Theor. Chim. Acta (Berlin)* **1972**, *24*, 117.

[148] Ferreira, R. *J. Chem. Educ.* **1998**, *75*, 1087.

[149] See also Wiberg, K. B. *J. Am. Chem. Soc.* **1979**, *101*, 1718 and references therein.

(a) Predicted

Cl
|←——1.76 Å
H─ˑᵐᵐᶜC
H   H ⎬—1.09 Å

<H—C—H = ca. 109.5°

<H—C—Cl = ca. 109.5°

(b) Experimental

Cl
|←——1.781 Å
H─ˑᵐᵐᶜC
H   H ⎬—1.096 Å

<H—C—H = 110°52'
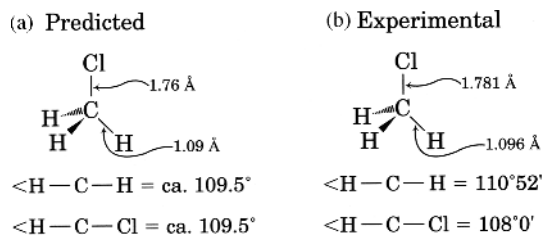
<H—C—Cl = 108°0'

FIGURE 1.19

(a) Qualitative prediction of CH_3Cl geometry. (b) Experimental data.

chlorine atom and away from the carbon atom. In terms of VSEPR theory, points on a sphere representing pairs of electrons used for bonding to electronegative groups can be considered less repulsive to other points (electron pairs) than are points corresponding to bonds to less electronegative atoms.[144] This should decrease the Cl–C–H bond angle, as is observed. In turn, the carbon atom will pull electron density from the hydrogen atoms attached to it. Since electron density associated with the C–H bonds has been increased near the carbon nucleus, the repulsion between pairs of C–H bonds is now increased, at least by comparison with C–H bond repulsion by the C–Cl bond. Therefore, the H–C–H bond angle is expanded relative to that of methane.

Variable Hybridization and Molecular Geometry

The qualitative VSEPR explanation of the geometry of methyl chloride can be made quantitative by a modification of the concept of hybridized atomic orbitals (Figure 1.20). Because methyl chloride is less symmetric than methane, we envision the hybrid orbitals on carbon to be different in energy.[150] Carbon 2p orbitals are higher in energy than 2s orbitals (Figure 1.8) because electrons in a 2p orbital are further from the carbon nucleus than electrons in a 2s orbital. Because the chlorine will pull some electron density away from the less electronegative carbon atom, these electrons will be further from the carbon nucleus and will best be described as being in an orbital having less s character and more p character than sp^3.[151–153] As a result, there must be more s character in the carbon orbitals used for the three C–H bonds, so the H–C–H bond angles are expanded from 109.5° to 110.5°.

To make this bonding description quantitative, it is useful to describe an sp^n orbital in terms of its **hybridization index**, n, and its **hybridization parameter**, λ, defined as $\lambda^2 = n$. Now the fractional s character of the ith orbital is given by the expression $1/(1 + \lambda_i^2)$.[154,155] For example, the fraction of
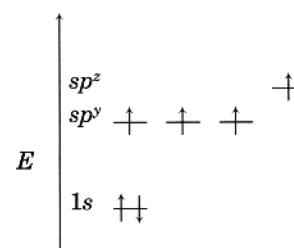

sp^z

sp^y +   +   +   +

E

$1s$ +|+

FIGURE 1.20

Hybridization of carbon proposed for CH_3Cl.

[150] For further reading, see (a) Breslow, R. *Organic Reaction Mechanisms*, 2nd ed.; W. A. Benjamin: Menlo Park, CA, 1969; p. 3; (b) Coulson, C. A.; Stewart, E. T. in Patai, S., Ed. *The Chemistry of Alkenes*, Vol. 1; Wiley-Interscience: London, 1964; p. 98 ff.

[151] The fundamental principle is that the more s character in a carbon orbital, the more electronegative is that orbital: Walsh, A. D. *Discuss. Faraday Soc.* **1947**, *2*, 18; *J. Chem. Soc.* **1948**, 398.

[152] Bent, H. A. *Chem. Rev.* **1961**, *61*, 275.

[153] The lower energy of s orbitals results because their average distance from the nucleus is less than is the average distance from the nucleus for p orbitals of the same principal quantum number. See reference 118a.

[154] Coulson, C. A. *J. Chem. Soc.* **1955**, 2069.

[155] (a) Mislow, K. *Introduction to Stereochemistry*; W. A. Benjamin: New York, 1966; pp. 13–23; (b) reference 113a, p. 195 ff.

s character of an sp^3 hybrid orbital is $1/(1+3) = 1/4$. Since the total s character of all the hybrid orbitals must sum to 1, equation 1.44 holds:

$$\sum_i \frac{1}{1 + \lambda_i^2} = 1 \tag{1.44}$$

Similarly, the total p character of the hybrid orbitals must equal the number of p orbitals involved in the hybridization. For an sp^3-hybridized carbon, equation 1.45 applies, where $\lambda_i^2/(1 + \lambda_i^2)$ is the fractional p character of the ith hybrid orbital.

$$\sum_i \frac{\lambda_i^2}{(1 + \lambda_i^2)} = 3 \tag{1.45}$$

Hybridization parameters can be related to molecular geometry. The interorbital angle θ_{ab} between hybrid orbitals from carbon to atom a and to atom b can be determined from equation 1.46.[156] If atoms a and b are identical, then equation 1.47 applies.

$$1 + \lambda_a \lambda_b \cos\theta_{ab} = 0 \tag{1.46}$$

$$1 + \lambda_a^2 \cos\theta_{aa} = 0 \tag{1.47}$$

Note that these equations predict that the interorbital angle will increase with greater s character, which is consistent with the increase in bond angle from $109.5°$ to $120°$ to $180°$ as the hybridization changes from sp^3 to sp^2 to sp, respectively.

For a monosubstituted methane such as methyl chloride, denoted here as CA_3B, there are only two different bond angles: θ_{aa} and θ_{ab}. They are related by the expression[157]

$$3\sin^2\theta_{ab} = 2\left(1 - \cos\theta_{aa}\right) \tag{1.48}$$

so knowledge of only one of these bond angles is sufficient to calculate the other. In the case of methyl chloride, the H–C–Cl bond angle is $108°$, so we can calculate the H–C–H bond angle.

$$\cos\theta_{aa} = 1 - \frac{3\sin^2\theta_{ab}}{2} \tag{1.49}$$

We find that $\theta_{aa} = 110.5°$. The value of λ_a^2 can now be calculated from the formula

$$\lambda_a^2 = -\frac{1}{\cos\theta_{aa}} = 2.80 \tag{1.50}$$

---

[156] For strained molecules, such as those with small rings, the interorbital bond angle may not be the same as that of the internuclear bond angle. See the discussions of bent bonds later in this chapter.

[157] If there are two sets of identical ligands, CA_2B_2, there will be three bond angles: θ_{aa}, θ_{ab}, and θ_{bb}. They are related by the formula $\cos\theta_{ab} = -\cos 2\theta_{aa} \cos 2\theta_{bb}$. For further details and examples, see reference 155a.

Thus, the orbitals used to bond hydrogen to carbon in methyl chloride are $sp^{2.80}$. Since the total s character in all four orbitals to carbon must sum to 1.00, equation 1.51 holds.

$$3\left(\frac{1}{1+2.80}\right) + \frac{1}{1+\lambda_b^2} = 1 \qquad (1.51)$$

Rearranging equation 1.51 and solving for λ_b^2 gives a value of 3.75. Therefore, the C–Cl bond uses a $sp^{3.75}$ hybrid orbital on carbon.

The association of tetravalent carbon with sp^3 hybridization is so entrenched in organic chemistry that it may be surprising that C–C–C bond angles are 109.47° only for carbon atoms with four identical substituents. The C–C–C angle of propane is 112.4°,[158] and the C–C–C angles in pentane, hexane, and heptane are similar.[159] A survey of 3431 X-ray crystallography measurements by Boese, Schleyer, and their co-workers revealed a range of C–C–C bond angles from 74.88° to 159.66°, with the mean being 113.5° ± 4.5°.[160] These researchers also demonstrated that the mean angle C–C–X in a series of ethyl derivatives varies with the electronegativity of the group X, with compounds having a more electronegative X (e.g., F, OH) having smaller C–C–X angles than compounds with less electronegative X groups (e.g., Na, Li).[161]

Now let us consider CH_2Cl_2. Myers and Gwinn determined from the microwave spectra of isotopically substituted methylene chloride that the C–Cl distance is 1.772 Å and the C–H distance is 1.082 Å. The Cl–C–Cl angle was determined to be 111°47′, while the H–C–H angle was found to be 112°0′.[162] Using equation 1.50, we calculate λ_{Cl}^2 to be 2.69, so the C–Cl bonding uses a carbon orbital that is an $sp^{2.69}$ hybrid. Using equation 1.44, we calculate λ_H^2 to be 3.37. That corresponds to an H–C–H angle of 107°, but the experimental value is 112°. Clearly, there is an inconsistency between the experimental values and our expectation based on the principles of variable hybridization.

One approach to this problem is to reexamine our intuitive model of a covalent bond as a straight line between two atoms. We must consider the possibility that the C–Cl or C–H bonds (or both) may actually be curved.[163] Figure 1.21 shows the proposed curved bond structure for CH_2Cl_2. We can reconcile the apparent conflict between geometry and hybridization parameters if we define the **internuclear bond angle** to be the angle measured by the shortest distance between pairs of nuclei and define the **interorbital bond angle** to be the angle the hybrid orbitals make as they leave the carbon atom. The experimental geometry provides internuclear bond angles, while the
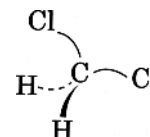

FIGURE 1.21
Curved bond representation of CH_2Cl_2.

[158] Lide, D. R., Jr. *J. Chem. Phys.* **1960**, *33*, 1514.

[159] Bonham, R. A.; Bartell, L. S.; Kohl, D. A. *J. Am. Chem. Soc.* **1959**, *81*, 4765.

[160] Boese, R.; Bläser, D.; Niederprüm, N.; Nüsse, M.; Brett, W. A.; Schleyer, P. v. R.; Bühl, M.; Hommes, N. J. R. v. E. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 314.

[161] Because the C–C–X bond angle also varied with rotation about the C–X bond, electronegativity was judged not to be the only determinant of bond angles. A role was also described for hyperconjugation, a concept that will be discussed in later chapters.

[162] Myers, R. J.; Gwinn, W. D. *J. Chem. Phys.* **1952**, *20*, 1420.

[163] An alternative possibility is that the hybrid orbitals in CH_2Cl_2 involve some d orbital character, but Myers and Gwinn (reference 162) discounted this possibility because of the much higher energy of d orbitals.
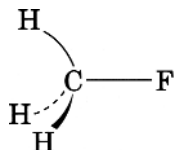
FIGURE 1.22
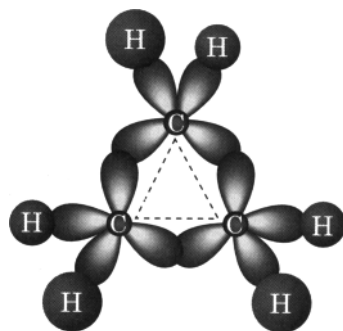
Curved bond paths suggested for CH_3F. (Reproduced from reference 167.)

FIGURE 1.23

Relationship between internuclear and interorbital angles in cyclopropane. (Adapted from reference 150a.)

variable hybridization analysis considers interorbital bond angles. Thus, the H–C–H and Cl–C–Cl inter*nuclear* angles could both be greater than 109°, but the inter*orbital* angles could still be 107°.

Curved bonds have also been proposed for CH_3F. Because of the greater electronegativity of fluorine than chlorine, we might expect the C–F bond to utilize even more p character on carbon than does the C–Cl bond in CH_3Cl. This should decrease the H–C–F bond angle even more than the H–C–Cl angle in CH_3Cl. However, the H–C–F bond angle in CH_3F is found to be 108.9°.[164] Wiberg and co-workers have explained this apparent anomaly by suggesting that there is considerable curvature in the C–H bonds, as shown in Figure 1.22.[165,166] The H–C–F angle made by the C–F bond path and by one of the C–H bond paths *as they leave the carbon atom* is estimated to be 106.7°, which is, as expected, smaller than the H–C–Cl bond angle in methyl chloride.[167,168]

The idea of curved bonds in methylene chloride and methyl fluoride may seem unfamiliar, but this explanation has long been invoked to describe bonding in cyclopropane.[169] The experimental values for the C–C and C–H bond lengths are 1.510 Å and 1.089 Å, respectively, and the H–C–H angle is 115.1°.[170] The hybridization of the orbital on carbon used for C–H bonding is computed to be $sp^{2.36}$, making the hybridization used for C–C bonds $sp^{2.69}$. In turn, that value predicts a C–C–C *interorbital* value of 111.8°.[171] Since this is considerably larger than the 60° internuclear angle required for an equilateral triangle, we conclude that the orbitals used for C–C bonding overlap considerably outside the internuclear lines (the dashed lines in Figure 1.23).

The hybridization parameter is useful as a tool to describe molecular bonding, but it is not a parameter that can be measured directly. It can be determined indirectly, however, through the study of physically observable values that correlate with it.[172] It is generally accepted that NMR coupling constants involving hydrogen depend on the close approach of an electron to the nucleus and so provide a measure of the density of bonding electrons at the nucleus.[173] Since s orbitals but not p orbitals have electron density at the nucleus, the coupling constant is a probe of the s character of the bond at the two nuclei in the C–H bond. Equation 1.52 shows a useful empirical relation-

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[164] Clark, W. W.; De Lucia, F. C. *J. Mol. Struct.* **1976**, *32*, 29.

[165] The curved bond line follows the path of maximum electron density from one atom to another and is known as a **bond path**. See Runtz, G. R.; Bader, R. F. W.; Messer, R. R. *Can. J. Chem.* **1977**, *55*, 3040. For a discussion, see Krug, J. P.; Popelier, P. L. A.; Bader, R. F. W. *J. Phys. Chem.* **1992**, *96*, 7604.

[166] Wiberg, K. B. *Acc. Chem. Res.* **1996**, *29*, 229.

[167] Wiberg, K. B.; Hadad, C. M.; Breneman, C. M.; Laidig, K. E.; Murcko, M. A.; LePage, T. J. *Science* **1992**, *252*, 1266.

[168] For a discussion of theories concerning the stability and geometry of carbon atoms with two, three, or four fluorine substituents, see Wiberg, K. B.; Rablen, P. R. *J. Am. Chem. Soc.* **1993**, *115*, 614.

[169] For a leading reference to some theoretical treatments for the bonding in cyclopropane, see Hamilton, J. G.; Palke, W. E. *J. Am. Chem. Soc.* **1993**, *115*, 4159.

[170] Bastiansen, O.; Fritsch, F. N.; Hedberg, K. *Acta Crystallogr.* **1964**, *17*, 538.

[171] The bond path angle for the C–C–C bonds in cyclopropane was determined to be 78° on the basis of the theory of atoms in molecules (reference 38).

[172] For a discussion and references, see Ferguson, L. N. *Highlights of Alicyclic Chemistry*, Part 1; Franklin Publishing Company: Palisade, NJ, 1973; p. 52 ff.

[173] Crăciun, L.; Jackson, J. E. *J. Phys. Chem. A* **1998**, *102*, 3738.

TABLE 1.14   Correlation of Rate Constants of Proton Exchange with $J_{13_{C-H}}$

Compound	Relative Rate[a]	$J_{13_{C-H}}$
Cyclopropane	7.0×10^4	161
Cyclobutane	28.0	134
Cyclopentane	5.7	128
Cyclohexane	1.00	123, 124
Cycloheptane	0.76	123
Cyclooctane	0.64	122

[a]See reference 172.

ship between the NMR coupling constant for ^{13}C and H ($J_{13_{C-H}}$) and the hybridization parameter.[155,174,175]

$$J_{13_{C-H}}(\text{cps}) = \frac{500}{1 + \lambda_a^2} \tag{1.52}$$

We expect electron density at hydrogen to be related to the acidity of a C–H bond, and Streitwieser and co-workers demonstrated a correlation between $J_{13_{C-H}}$ and the kinetic acidities (the rates of exchange of C–H protons for tritium catalyzed by cesium cyclohexylamide). The data in Table 1.14 show a good correlation of $\log k_{rel}$ (rate constant relative to that of cyclohexane) with $J_{13_{C-H}}$ as shown in equation 1.53.[172]

$$\log k_{rel} = 0.129\, J_{13_{C-H}} - 15.9 \tag{1.53}$$

An explanation for the correlation of acidity with $J_{13_{C-H}}$ is that both are related to the hybridization of the carbon orbital used for C–H bonding. Because s orbitals are lower in energy than p orbitals, a hybrid orbital with more s character will be lower in energy and thus have electron density closer to the nucleus than will a hybrid with less s character. This lower energy orbital will be more electronegative and will be better able to stabilize a negative charge when a proton is removed in an acid–base reaction.[152]

It must be reemphasized that hybridization is only a conceptual and a mathematical model that allows us to calculate molecular parameters. Changing hybridization is simply modifying that original model to suit a current need, just as the concept of hybridization represents only a change to the model of atomic energy levels. Variable hybridization should not be considered more fundamental than the VSEPR model, just more mathematical. The ability to make quantitative predictions of molecular geometry and physical properties makes the variable hybridization model quite useful for some problems. On the other hand, the VSEPR model is also valuable as an intuitive basis for qualitatively correct predictions. As is so often the case, we need not decide which of two complementary models to adopt for all situations; we need only to determine which best serves our purposes in a particular case.

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[174] Muller, N.; Pritchard, D. E. *J. Chem. Phys.* **1959**, *31*, 1471 found that better correlations were obtained when calculated atomic charges were included in the equation.

[175] Liberles, A. *J. Chem. Educ.* **1977**, *54*, 479 used hybridization parameters to show that lone pairs in *sp* hybrid orbitals have a greater local dipole moment than do lone pairs in any other hybrids.

1.4 COMPLEMENTARY DESCRIPTIONS OF THE DOUBLE BOND

The σ,π Description of Ethene

FIGURE 1.24

Depiction of carbon with sp^2 hybridization.

Let us next consider alternative descriptions of the carbon–carbon double bond. Nearly all introductory organic chemistry textbooks describe the double bond in terms of the σ,π formulation.[176] The simplest example of such bonding is ethene, in which one of the two carbon–carbon bonds is said to be a σ bond formed through overlap of an sp^2 hybrid orbital (Figure 1.24) on each of the carbon atoms, while the second carbon–carbon bond is described as a π bond, made by overlap of two parallel $2p$ orbitals on the carbon atoms (Figure 1.25). To be more complete, we say that overlap of the two sp^2 hybrids produces both a σ bonding and a σ^* antibonding orbital. Similarly, overlap of the two p orbitals produces both a π bonding and a π^* antibonding molecular orbital, with energies shown qualitatively in Figure 1.25. A pictorial representation of the carbon–carbon σ and π bonds is shown in Figure 1.26. This description of the carbon–carbon double bond is very familiar, but is it correct? Frenking and Krapp described π bonding as one of the "unicorns in the world of chemical bonding models."[177] By that they mean that everyone knows what a unicorn looks like even though no one has ever seen one.

The σ,π model does have qualitative utility because it correctly predicts the carbon–carbon bond length of ethene to be shorter than the carbon–carbon bond length of ethane. The reason is that the overlap of sp^2 orbitals (which have more s character and are therefore closer to the carbon nucleus than are sp^3 hybrids) makes a shorter bond, and the two atoms should be pulled even closer by the π bond. On the other hand, the interorbital angle between two sp^2 hybrid orbitals on the same carbon atom is 120°, so the simple σ,π model predicts the H–C–H and H–C–C bond angles to be 120° (Figure 1.27). Figure 1.28 shows the geometry of ethene determined from spectroscopic measurements, and the H–C–H bond angles are 117°, not 120°.[29] Most organic chemists are not bothered by this discrepancy between prediction and experiment. We usually argue that the geometry of ethene is an anomaly and that other alkenes would obey our predicted bond angles. We will return to the ethene geometry shortly, but first let us consider another model for the bonding of ethene.

The Bent Bond Description of Ethene

A much older description of ethene is known as the bent bond formulation.[178] The double bond is described as the result of overlap of two sp^3 hybrid orbitals on *each* of the two carbon atoms, as shown in Figure 1.29. This model also predicts that ethene should be a planar molecule, but it predicts H–C–H bond angles of 109.5°—which is even further from the observed 117° than was the prediction based on sp² hybridization. Furthermore, except for cyclopropane, we feel uncomfortable about drawing molecular pictures with bonds that
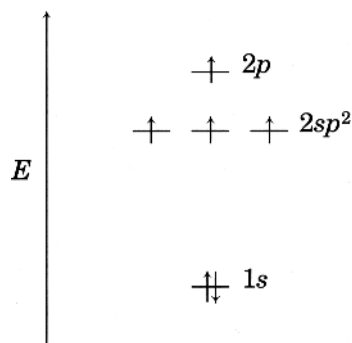
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[176] One text that presented the bent bond formulation was Roberts, J. D.; Stewart, R.; Caserio, M. C. *Organic Chemistry*; W. A. Benjamin: Menlo Park, CA, 1971.

[177] Frenking, G.; Krapp, A. *J. Comput. Chem.* **2007**, *28*, 15.

[178] Bent bonds are also known as banana bonds or τ (tau) bonds. For a discussion of the utility of this model in explaining molecular conformation and reactivity, see Wintner, C. E. *J. Chem. Educ.* **1987**, *64*, 587 and references therein.
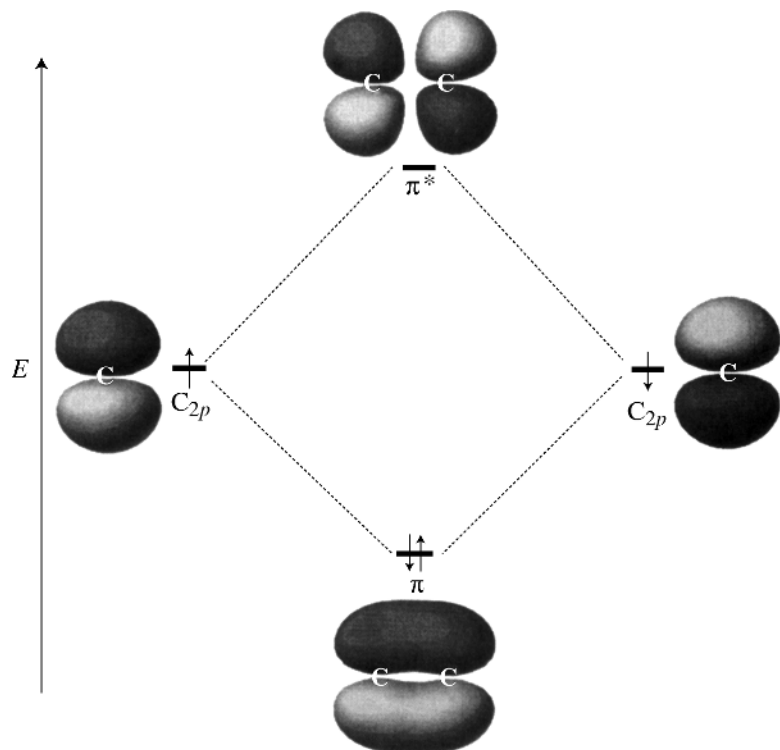
FIGURE 1.25
Energies of ethene π and π^* orbitals.

curve in space as do those in Figure 1.29. Nevertheless, one advocate of the bent bond description was Linus Pauling, who wrote:

> There may be chemists who would contend that one innovation of great significance has been made—the introduction of the σ,π description of the double bond and the triple bond and of conjugated systems, in place of the bent bond description. I contend that the σ,π description is less satisfactory than the bent bond description, that this innovation is only ephemeral, and that the use of the σ,π description will die out before long....[179]
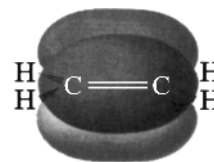
FIGURE 1.26
The σ,π formulation for ethene.

Predictions of Physical Properties with the Two Models

Geometry of Alkenes

Although Pauling's prediction has not yet come true, there are advantages in using the bent bond formulation. One advantage is conceptual simplicity. If the sp^3 hybridization model can give the correct answer, why use a whole family of explanations (sp^3, sp^2, and sp) for bonding questions? A practical advantage is the ease of construction of physical models. Some molecular model kits designed for introductory organic chemistry courses use bent bonds as the physical model of the double bond. Such models give acceptable structural geometries, require fewer parts in the model set, and are easier for novices to use than are model kits that attempt to represent π bonds. Still another advantage is that the bent bond formulation seems to provide more quantitative answers than does the σ,π formulation. Consider the measure-
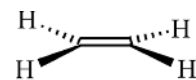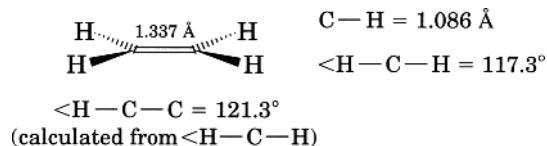

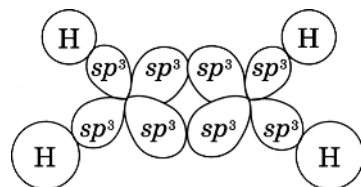$$\text{<H—C—H} = 120°$$
$$\text{<H—C—C} = 120°$$

FIGURE 1.27
Predicted geometry of ethene.

[179] Pauling, L. in *Theoretical Organic Chemistry, The Kekulé Symposium*; Butterworths Scientific Publications: London, 1959; p. 1.

H······ 1.337 Å ······H
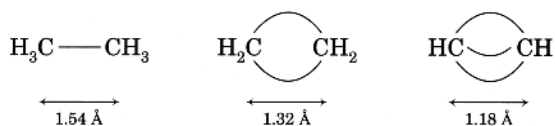
H——————H

C — H = 1.086 Å

<H — C — H = 117.3°

<H — C — C = 121.3°
(calculated from <H — C — H)

FIGURE 1.28

Experimental geometry of ethene.

FIGURE 1.29

Overlap of sp^3 hybrid orbitals in the bent bond description of ethene.

FIGURE 1.30

Quantitative predictions of the bent bond formulation.

ment of the carbon–carbon distances illustrated in Figure 1.30. Taking the C–C bond length of ethane, l.54 Å, as the length of an arc formed by overlap of sp^3 orbitals outside the internuclear line, Pauling calculated that ethene should have an internuclear distance of 1.32 Å, quite close to the experimental value.[30] Similarly, three bent bonds arranged as 1.54 Å arcs directed 109.47° apart produce a C–C internuclear distance of 1.18 Å for ethyne, which is essentially the same as the experimental value.[180] The σ,π formulation makes no quantitative prediction about the length of the double or triple bond.

H_3C —— CH_3 H_2C CH_2 HC CH

1.54 Å   1.32 Å   1.18 Å

Acidities of Hydrocarbons

The alkanes, alkenes, and alkynes are not usually considered to be acidic, but it is possible to measure rates and equilibria of proton removal in solution and in the gas phase (Chapter 7). Table 1.15 shows some experimental data for acidities as indicated by ΔH°_{acid}, the enthalpy change for detachment of a proton from the hydrocarbon in the gas phase, showing that the ethyne is more acidic than ethene, which in turn is more acidic than ethane.

We explain these results by considering the relative stabilities of the carbanions formed by removal of a proton from each structure. In the σ,π formulation, the hybridization of the carbon orbital with the nonbonded electron pair changes from sp^3 to sp^2 to sp as a proton is removed ethane to ethene to ethyne, respectively (Figure 1.31). Again, the more s character in an

TABLE 1.15   Gas Phase Acidities of C₂ Hydrocarbons

Compound	ΔH°_{acid} (kcal/mol)
Ethane	420.1 ± 2.0
Ethane	409.4 ± 0.6
Ethyne	378.5 ± 0.2

Source: Reference 181.

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[180] Robinson, E. A.; Gillespie, R. J. *J. Chem. Educ.* **1980**, *57*, 329 described these calculations as well as the use of molecular models with bent bonds to measure the internuclear distances.

[181] Data from the compilation by Bartmess, J. E. in Mallard, W. G.; Linstrom, P. J., Eds. *NIST Webbook, NIST Standard Reference Database Number 69*; National Institute of Standards and Technology: Gaithersburg, MD (http://webbook.nist.gov).
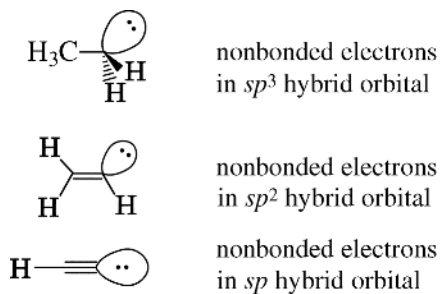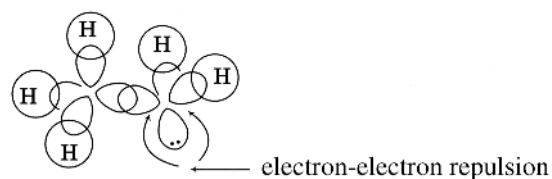
FIGURE 1.31

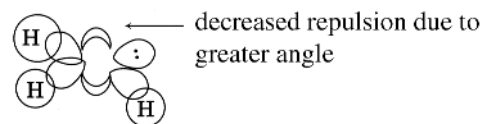σ,π rationalization of carbanion stabilities. (Charges are not shown.)

atomic orbital, the greater is the electron attracting power of that orbital, and the more stable should be an anion produced by removing a proton and leaving a nonbonded pair of electrons in that orbital.[152] Thus, the order of carbanion stability should be $(sp)C:^- > (sp^2)C:^- > (sp^3)C:^-$, which is the same as the ranking of hydrocarbon acidities: $(sp)C–H > (sp^2)C–H > (sp^3)C–H$.

The same phenomena can be rationalized with the bent bond formulation by noting the effect of curved C–C bonds on the electron pair repulsions around each carbon atom. As Figure 1.32 shows, formation of bent bonds in ethene pulls the electrons closer to the center of the C–C internuclear line; in turn, this decreases the repulsion between the electron pair comprising the C–H bond in question and the electron pairs comprising the bent C–C bonds. That means that the C–H electrons see a less shielded carbon nucleus, so they are attracted more strongly to the carbon nucleus. An unshared pair of electrons left behind by removal of a proton from ethene, as shown in Figure 1.32(b), is much more stable than is a pair of electrons left behind by removal of a proton from ethane, as shown in Figure 1.32(a). For the same reason, a nonbonded pair of electrons is more stable on a triple bonded carbon, as shown in Figure 1.32(c), than on a double bonded carbon. Thus, the bent bond formulation can rationalize these experimental observations, at least qualitatively, as well as can the σ,π description.
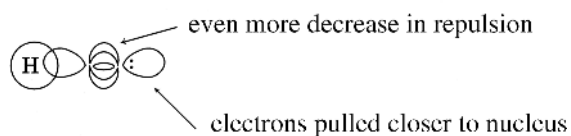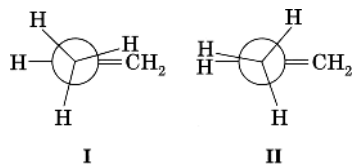
(a) Ethane

electron-electron repulsion

(b) Ethene

decreased repulsion due to greater angle

(c) Ethyne

even more decrease in repulsion

electrons pulled closer to nucleus

FIGURE 1.32

Bent bond rationalization of acidities. (Charges are not shown.)

FIGURE 1.33

Conformations of propene: σ,π description. (Adapted from reference 182.)

Conformations of Propene

Let us now consider which bonding model is more amenable to qualitative predictions of molecular conformation. Specifically, what should be the preferred conformation of propene? Walters noted that two conformers of propene (designated as I and II) can be visualized as Newman projections observed by sighting down the C3–C2 bond (Figure 1.33).[182,183] In conformer I, a C–H bond eclipses a carbon–carbon double bond. In conformer II, a C–H bond eclipses a C–H bond. Assuming that there is greater electron density in a double bond than in a C–H single bond, we would expect conformer II to be more stable. Experimentally, however, conformer I was found to be more stable by about 2 kcal/mol.[184]

If we depict the same Newman projections with bent bonds, as shown in Figure 1.34, we see that conformer II now represents essentially an all-eclipsed conformation. Thus, it is easily predicted to be less stable than I, which is an all-staggered arrangement. If utility is the main criterion for adopting conceptual models, then this result would seem to argue persuasively for using the bent bond formulation.[185,186] The bent bond model leads directly to a correct prediction of conformational stability, but the σ,π model does not.[187]

Pauling's prediction that the use of the σ,π description will wane may yet come true. In recent years some theoreticians have determined that calculations of molecular structure are in better agreement with the bent bond description than with the σ,π description. Figure 1.35(a) shows calculated contour lines of a carbon orbital in a plane that is perpendicular to the molecular plane of ethene, and Figure 1.35(b) shows contour lines for an orbital in a plane containing the carbon atoms of cyclopropane. Clearly, much of the orbital lies outside the internuclear bond line in each case. It is generally agreed that the bonds in cyclopropane are bent; the picture from this theoretical calculation reinforces the view that they are bent in ethene also.

This conclusion was reinforced by a number of investigations. The title of one publication was "Double Bonds Are Bent Equivalent Hybrid (Banana) Bonds."[188] Another study concluded that "the GVB description of the double bond in (C_2F_4) is *not* the traditional picture of σ and π bonds but rather a representation in terms of two bent bonds."[189] Still another paper comparing

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[182] Walters, E. A. *J. Chem. Educ.* **1966**, *43*, 134.

[183] Newman projections and other stereochemical representations will be discussed in Chapter 2.

[184] Herschbach, D. R.; Krisher, L. C. *J. Chem. Phys.* **1958**, *28*, 728.

[185] The emphasis in the present discussion is on the application of two very simple conceptual models to a particular problem. High level calculations provide a much deeper analysis of the conformations of propene and other molecules. For a discussion, see Bond, D.; Schleyer, P. v. R. *J. Org. Chem.* **1990**, *55*, 1003.

[186] Proponents of the σ,π formulation could argue that taking additional factors into account would correct the initial prediction that conformer II is more stable. When faced with discrepancies between prediction and experiment, the proponents of a particular conceptual model often take the position that consideration of additional factors would favor their model.

[187] This discussion implicitly treats the methyl group as interacting with the vinyl group only through steric interactions. This assumption ignores the electronic interactions inherent in any molecular entity. See, for example, Mo, Y.; Peyerimhoff, S. D. *J. Chem. Phys.* **1998**, *109*, 1687.

[188] Palke, W. E. *J. Am. Chem. Soc.* **1986**, *108*, 6543.

[189] GVB is a type of theoretical calculation. Schultz, P. A.; Messmer, R. P. *J. Am. Chem. Soc.* **1988**, *110*, 8258.
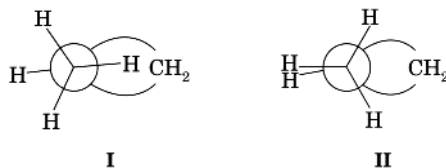
FIGURE 1.34

Conformations of propene: bent bond formulation. (Adapted from reference 182.)

the bent bond and σ,π models concluded that ". . . from an energetical point of view, both constructions provide an equally good starting point for the treatment of correlation effects beyond the one-electron configuration."[190] Another study concluded that "our results yield bent bonds as the favored bonding description, showing that the σ,π bond descriptions of multiple bonds are artifacts of approximations to the full independent-particle equations." [191] For systems that exhibit resonance, such as benzene and the allyl radical, these authors stated the conclusion even more succinctly: "bent bonds are better."[192,193]

The distinction between the bent bond and σ,π formulations of the double bond is not as clear-cut as the discussion above might suggest. Although the results depend on the level of theory used, the two models predict essentially the same result at higher levels of analysis.[194] As Schultz and Messmer put it, "no experiment can possibly distinguish between a σ,π double bond and double bent bonds in any system, and therefore neither can be proven to be 'right' in an absolute sense; both are approximate descriptions."[191] The σ,π model for the double bond and the bent bond description should each be taken as viable *starting points* to describe molecular structure but not as complete descriptions.[30,195] Each approach has its advantages and disadvantages. It is important that we consider both methods and that we know why we choose one over the other when we talk about organic chemistry.
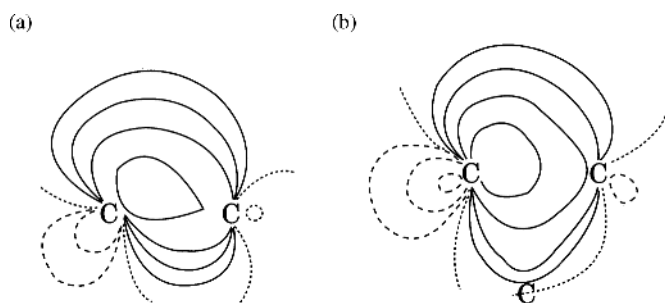
FIGURE 1.35

Contour lines for a bonding orbital on one carbon in (a) ethene and (b) cyclopropane. (Adapted from reference 169.)

[190] Karadakov, P. B.; Gerratt, J.; Cooper, D. L.; Raimondi, M. *J. Am. Chem. Soc.* **1993**, *115*, 6863.

[191] Schultz, P. A.; Messmer, R. P. *J. Am. Chem. Soc.* **1993**, *115*, 10925.

[192] Schultz, P. A.; Messmer, R. P. *J. Am. Chem. Soc.* **1993**, *115*, 10943.

[193] For a different view, see Carter, E. A.; Goddard W. A. III. *J. Am. Chem. Soc.* **1988**, *110*, 4077.

[194] Gallup, G. A. *J. Chem. Educ.* **1988**, *65*, 671 and references therein.

[195] England, W. *J. Chem. Educ.* **1975**, *52*, 427; Palke, W. E. *J. Am. Chem. Soc.* **1986**, *108*, 6543.

1.5 CHOOSING MODELS IN ORGANIC CHEMISTRY

Conceptual, mathematical, and physical models are essential tools in organic chemistry because they help rationalize the results of experiments (observables) with theory (nonobservables). Yet the paradox is that these models may be most useful to us when they are oversimplified to the point of being incorrect in some way. Without a straight line or pair of dots to represent a chemical bond, we would find it difficult to describe chemistry in a practical way. Yet in some cases we find it advantageous to draw those lines curved instead of straight, and sp^3 hybrid orbitals cannot be relied on even to predict all of the properties of methane. A more detailed description of that line and of those orbitals can be made only with the help of computers and high level mathematics.

If any one of our models is asked to give a more correct answer to a problem, it quickly becomes more complex. Electronegativity is useful in a qualitative sense, but attempts to make it more quantitative lead to different conclusions about what it means and how it should be determined. Elementary VB theory and MO theory are intuitively reasonable, but further development obscures the simple mental pictures each provides. We feel a need to retain these simple pictures, therefore, even when we know that they cannot be totally accurate.

One solution to the use of oversimplified models in organic chemistry is to hybridize complementary conceptual models, just as we hybridize the two Kekulé structures for benzene in our minds in order to understand and describe aromaticity. The σ,π and bent bond descriptions represent a pair of models that serve as useful beginning points or approaches to the description of the double bond. Visualizing a hybrid of these two mental pictures may be more nearly correct than is thinking in terms of either model alone.

Perhaps another metaphor may be useful. In the end, our models must be described in a language of some kind, but having *a* language to describe something does not necessarily make that explanation complete.[196] If we view complementary models as different languages to describe chemistry, we find it better to be multilingual—to be able to converse in many languages, to translate from one language to another, and to think in more than one language. If we have only one approach, then we are only computers doing what we have been programmed to do. Progress in chemistry requires the ability to see relationships in a new way, and that requires education, not just training.[197]

Problems

1.1. Kuhn (reference 3) wrote that scientists "are little better than laymen at characterizing the established bases of their field." Briefly summarize the physical phenomena that support your belief in atomic and molecular theory.

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[196] For provocative comments on language and models, see Bent, H. A. *J. Chem. Educ.* **1984**, *61*, 774. In particular, Bent noted that "indeed, to be useful, *a model must be wrong, in some respects*—else it would be the thing itself. The trick is to see—with the help of a teacher—*where it's right*."

[197] One aspect of this idea is what Turro (reference 24) called "organic thinking," which is one of the ways that the study of organic chemistry transfers to other areas:

An important value of learning organic chemistry is the mastering of "organic thinking," an approach to intellectual processing whereby the "sameness" of many families of structures and reactions is revealed.

1.2. Find a popular or scientific article that refers to observations of a single atom or atoms.

    a. What is the nature of the experiment?

    b. What observations are made directly with the human senses?

1.3. a. Consider two geometries for methane other than the regular tetrahedron. Show how each alternative geometry is inconsistent with the known number of isomers of some derivative of methane.

    b. Consider at least four structures with the molecular formula C_6H_6 and show how each is inconsistent with the known number of isomers of benzene substitution products having a given molecular formula.

    c. In parts a and b of this problem, you assumed that the structure of a derivative (e.g., bromobenzene) is essentially the same as that of the parent structure (e. g., benzene). Is that assumption valid? For example, how can we know that methane is not planar, even though chloromethane is roughly tetrahedral?

1.4. Use the values in Table 1.3 to determine the van der Waals volume and surface area for each of the pentanes. Verify that for n-pentane the values are correctly predicted by the formulas $V_W = 6.88 + 10.23 \ N_C$ and $A_W = 1.54 + 1.35 \ N_C$, where N_C is the number of carbon atoms in the molecule.

1.5. The heat of formation of corannulene (**2**) in the crystal state is 81.81 kcal/mol. Its heat of sublimation has been calculated to be 29.01 kcal/mol. What is the ΔH_f° of **2** in the vapor phase?

2
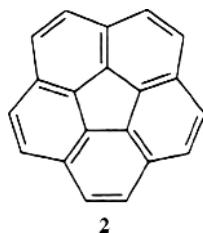
1.6. A proposed system for the conversion and storage of solar energy was based on the photochemical isomerization of norbornadiene (**3**) to quadricyclane (**4**) during sunny periods, with catalytic conversion of **4** to **3** and release of energy at a later time. The heats of hydrogenation of **3** and **4** (both in the liquid phase) to norbornane are −68.0 kcal/mol and −92.0 kcal/mol, respectively. What is the potential for energy storage, in kcal/mol, for the photochemical conversion of **3** to **4**?
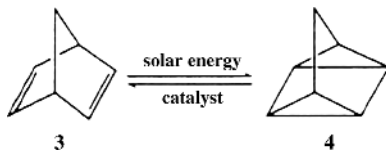

1.7. The standard heat of combustion of 4,4-dimethyl-1,3-cyclohexanedione was determined to be −1042.90 kcal/mol. Its standard heat of sublimation is +23.71 kcal/mol. What is the ΔH_f° (gas phase) of this compound?

1.8. The heat of hydrogenation of phenylethyne was found to be −66.12 kcal/mol, and the heat of formation of phenylethane is 7.15 kcal/mol. What is the ΔH_f° of phenylethyne?

1.9. a. The heat of formation of 2,5-thiophenedicarboxylic acid at 298.15 K is −772.4 2.2 kJ/mol. Its heat of sublimation is 139.8 ± 0.4 kJ/mol. What is the ΔH_f° of the compound in the gas phase?

    b. The heat of formation of liquid 2-acetylthiophene at 298.15 K is −118.0 ± 1.7 kJ/mol, while that of crystalline 3-acetylthiophene is −129.1 ± 1.4 kJ/mol.

The heat of vaporization of 2-acetylthiophene at 298.15 K is 58.8 ± 1.2 kJ/mol, and the heat of sublimation of 3-acetylthiophene at 298.15 K is 74.6 ± 1.1 kJ/mol. What is the difference in the gas phase heats of formation of these two compounds?

1.10. *cis*-3-Methyl-2-pentene has a ΔH_f° that is 1.65 kcal/mol more negative than that of 2-ethyl-1-butene. The ΔH_r of 2-ethyl-1-butene with trifluoroacetic acid is −10.66 kcal/mol. Predict the heat of reaction of *cis*-3-methyl-2-pentene with trifluoroacetic acid under the same conditions.

1.11. The heat of hydrogenation of *cis*-1,3,5-hexatriene to hexane is −81 kcal/mol, while that of the trans isomer is −80.0 kcal/mol. Under the same conditions the heat of hydrogenation of 1,5-hexadiene is −60.3 kcal/mol. What would be the heat of hydrogenation for just the middle double bond of the cis and trans isomers of 1,3,5-hexatriene?

1.12. Calculate ΔH_f° for heptane using both equations 1.9 and 1.12. How do these predictions compare with literature values?

1.13. The dipole moments of CH_3F, CH_3Cl, CH_3Br, and CH_3I are reported to be 1.81, 1.87, 1.80, and 1.64 D, respectively.[69]

   a. Calculate the partial charge on the halogen in each of the methyl halides (assuming that the halogen bears the partial negative charge and that the partial positive charge is centered on the carbon atom) using the C–X bond lengths listed in Table 1.1.

   b. What trend, if any, do you see in the dipole moments of the methyl halides? How do you rationalize this result?

1.14. For what category of atoms could Allen or Nagle but not Pauling electronegativity values be determined?

1.15. The C–C–C bond angle of propane is reported to be 112.4°. What is the hybridization of the orbitals on C2 used for C–C and C–H bonding?

1.16. Both experimental and theoretical studies indicate that the C1–C2 bond length (*l*) and the C1–C2–C3 bond angle (α) in molecules having the following general structure are strongly correlated. (The C1–C2–C3′ and the C1–C2–C3″ bond angles are also α.) One study found that they could be related by the equation

$$l = 2.0822 - 0.0049\,\alpha \tag{1.54}$$

where distances are in Å and angles are in degrees.
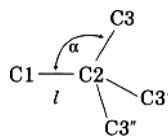
   a. What does this equation indicate about the change in bond length expected when the adjacent angle changes to a value greater than or less than 109.5°?

   b. Rationalize the form of equation 1.54 in terms of both variable hybridization theory and VSEPR theory.

1.17. a. Arrange the following compounds in order of increasing length of C–H bonds and rationalize your answer: ethane, ethene, ethyne, cyclopropane, and cyclobutane.

   b. Arrange these compounds in order of increasing length of C–C single bonds and explain your answer: ethane, 2-methylpropane, 2-methylpropene, 1,3-butadiene, 1,3-butadiyne, 1-butene-3-yne.

1.18. a. Use the bent bond description of double bonds to rationalize that the H–C–H bond angles in ethene are 117° and not 109.5°.

b. Modify your explanation to predict the H–C–H angle of formaldehyde. Specifically, should it be larger or smaller than the H–C–H angle of ethene?

1.19. Consider again ethene and formaldehyde, this time analyzing the double bond in each as a two-membered ring. Calculate the fractional s character and hybridization parameter for the C–H bond in each.

1.20. a. Consider the formula $J_{13_{C-H}} = 5.7 \times (\% \ s) - 18.4 \ \text{Hz}$. Determine whether this formula is equivalent to that in equation 1.52, and explain your reasoning.

b. Muller and Pritchard (reference 174) determined that the lengths of C–H bonds correlate with values of $J_{13_{C-H}}$ according to equation 1.55:

$$r_{C-H} = 1.1597 - 4.17 \times 10^{-4} J_{13_{C-H}} \tag{1.55}$$

Use equations 1.52 and 1.55 to relate the length of a C–H bond directly to λ^2.

1.21. Analyze cyclopropane, cyclobutane, and cyclopentane according to both the bent bond (using sp^3 hybrid orbitals) and variable hybridization descriptions.

a. For each compound, use the literature value for the H–C–H bond angle to calculate the fractional s and p character of the carbon orbitals used for C–H bonds, then use the result to calculate the interorbital C–C–C bond angle. How do the calculated values differ from the literature values of the internuclear bond angles? What does that tell you about the nature of the strain in the molecule? What does that suggest to you about the chemical properties of cyclobutane (e.g., reaction with electrophiles).

b. What does each model suggest to you about the acidities of the C–H bonds? How do the literature data for the acidity of cyclopropane agree with the predictions?

1.22. McNelis and Blandino noted that the sum of the six bond angles (109.5° degrees each) around a tetrahedral carbon atom is 657° and postulated that the bond angles in other tetraligant species should sum to that same value.[198] For example, the H–C–F bond angle in fluoromethane was reported to be 109° 2′ (Table 1.1). Since there are three H–C–F and three H–C–H angles, the "657" method predicts the H–C–H bond angle to be $\frac{1}{3}(657° - 3 \times 109.03°) = 110°$.

a. How does this result compare with an experimental value?

b. Does the predictive ability of the "657" method depend on the extent to which the geometry at a carbon atom is nearly tetrahedral? If so, determine the range of $\angle_{H-C-F}$ values for which the "657" method produces a predicted H–C–H angle that is less than 10° different from the value calculated using the trigonometric relationships.

1.23. The C–H coupling constants for ethane, ethene, and ethyne are 125.2, 156, and 249 Hz, respectively. Do these values correlate with the gas phase acidity values in Table 1.15? If so, use the correlation to estimate the gas phase acidity of cyclopropane ($J_{13_{C-H}} = 161$).

1.24. In bicyclo[1.1.0]butane (**5**), the $^{13}C - {}^1H$ coupling constant for the bridgehead C–H groups is 202 Hz. Calculate the % s character in the bond from carbon to hydrogen at this position. Would you expect the acidity of the bridgehead protons to be greater or less than that of the protons in acetylene?

5
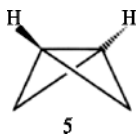
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[198] McNelis, E.; Blandino, M. *New J. Chem.* **2001**, *25*, 772. More precisely, $6 \times 109.47° = 656.82°$.

1.25. If λ is a function of molecular geometry and $J_{13_{C-H}}$ is also a function of λ, then is not $J_{13_{C-H}}$ really a function of geometry? Is λ an observable? If not, do we need to define λ at all?

1.26. On page 32 we saw experimental evidence that some familiar views of hybridization are at best oversimplified. In view of this result, can you justify the continued use of hybridized orbitals as a conceptual model in organic chemistry?

1.27. Greenberg and Liebman have stated that "we believe organic chemistry is essentially a pictorial and not a mathematical science."[199] Do you agree with this statement? Do you think organic chemistry should be a mathematical science? Do you believe it will become so in the future?

1.28. Respond to Coulson's observation about the nature of theory in chemistry:

> Sometimes it seems to me that a bond between two atoms has become so real, so tangible, so friendly that I can almost see it. And then I awake with a little shock: for a chemical bond is not a real thing: it does not exist: no one has ever seen it, no-one ever can. It is a figment of our own imagination. . . . Here is a strange situation. The tangible, the real, the solid, is explained by the intangible, the unreal, the purely mental.[154]

1.29. Respond to Roald Hoffmann's statement that

> . . .much that goes into the acceptance of theories has little to do with rationalization and prediction. Instead, I will claim, what matters is a heady mix of factors in which psychological attitudes figure prominently.[200]

Hoffmann also wrote that

> . . .explanations are almost always stories. Indeed, moralistic and deterministic stories. For to be satisfying they don't just say $A \rightarrow B \rightarrow C \rightarrow D$, but $A \rightarrow B \rightarrow C \rightarrow D$ *because* of such and such properties of A, B and C. The implicit strong conviction of causality, justified by seemingly irrefutable reason, may be dangerously intoxicating. This is one reason why I wouldn't like scientists and engineers to run this world.[200]

Do you think scientists who understand the limitations of human knowledge discussed in this chapter would be better able to run the world than Hoffmann imagines?

1.30. Weisberg argues that there is a trade-off between precision and generality in the models that scientists use and that "sacrificing precision in model descriptions can often add explanatory depth to the models picked out by these descriptions."[201] Cite examples from this chapter that are consistent with Weisberg's statement. Are any examples inconsistent with Weisberg's conclusion?

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[199] Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic Press: New York, 1978; p. 37.

[200] Hoffmann, R. *Am. Sci.* **2003**, *91*, 9.

[201] Weisberg, M. *Philos. Sci.* **2004**, *71*, 1071