## CHAPTER 1

# Localized Chemical Bonding

*Localized chemical bonding* may be defined as bonding in which the electrons are shared by two and only two nuclei. This feature is associated with the structure of organic molecules.[1] Chapter 2 will discuss *delocalized bonding*, in which electrons are shared by more than two nuclei.

## 1.A. COVALENT BONDING[2]

Wave mechanics is based on the fundamental principle that electrons behave as waves (e.g., they can be diffracted). Consequently, a wave equation can be written for electrons, in the same sense that light waves, sound waves, and so on can be described by wave equations. The equation that serves as a mathematical model for electrons is known as the *Schrödinger equation*, which for a one-electron system is:

$$\frac{\delta^2\psi}{\delta x^2}+\frac{\delta^2\psi}{\delta y^2}+\frac{\delta^2\psi}{\delta z^2}+\frac{8\pi^2 m}{h^2}\left(E\;-\;V\right)\;\psi=0$$

where $m$ is the mass of the electron, $E$ is its total energy, $V$ is its potential energy, and $h$ is *Planck's constant*. In physical terms, the function $\Psi$ expresses the square root of the probability of finding the electron at any position defined by the coordinates $x$, $y$, and $z$, where the origin is at the nucleus. For systems containing more than one electron, the equation is similar, but more complicated.

The Schrödinger equation is a differential equation, so solutions to it are themselves equations. The solutions are not differential equations, but simple equations for which graphs can be drawn. Such graphs are essentially three-dimensional (3D) pictures that show the electron density, and these pictures are representations of *orbitals*, which are electron clouds. Most students are familiar with the shapes of the *s* and *p* atomic orbitals (Figure 1.1).[3] Note that each *p* orbital has a *node*, which is a region in space where the probability of finding the electron is

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[1] See Hoffmann, R.; Schleyer, P.v.R.; Schaefer, H.F. III *Angew. Chem. Int. Ed.* ***2008***, *47*, 7164.

[2] This treatment of orbitals is simplified by necessity. For more detailed treatments of orbital theory, as applied to organic chemistry, see Matthews, P.S.C. *Quantum Chemistry of Atoms and Molecules*, Cambridge University Press, Cambridge, ***1986***; Clark, T. *A Handbook of Computational Chemistry*, Wiley, NY, ***1985***; Albright, T.A.; Burdett, J.K.; Whangbo, M. *Orbital Interactions in Chemistry*, Wiley, NY, ***1985***; MacWeeny, R.M. *Coulson's Valence*, Oxford University Press, Oxford, ***1980***; Murrell, J.N.; Kettle, S.F.A; Tedder, J.M. *The Chemical Bond*, Wiley, NY, ***1978***; Dewar, M.J.S.; Dougherty. R.C. *The PMO Theory of Organic Chemistry*, Plenum, NY, ***1975***; Zimmerman, H.E. *Quantum Mechanics for Organic Chemists*, Academic Press, NY, ***1975***; Borden, W.T. *Modern Molecular Orbital Theory for Organic Chemists*, Prentice-Hall, Englewood Cliffs, NJ, ***1975***.

[3] The argument has been proposed that hybrid atomic orbitals should not be taught in a chemistry curriculum. See Grushow, A. *J. Chem. Ed.* ***2011***, *88*, 860.

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*March's Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*, Ninth Edition. Michael B. Smith.

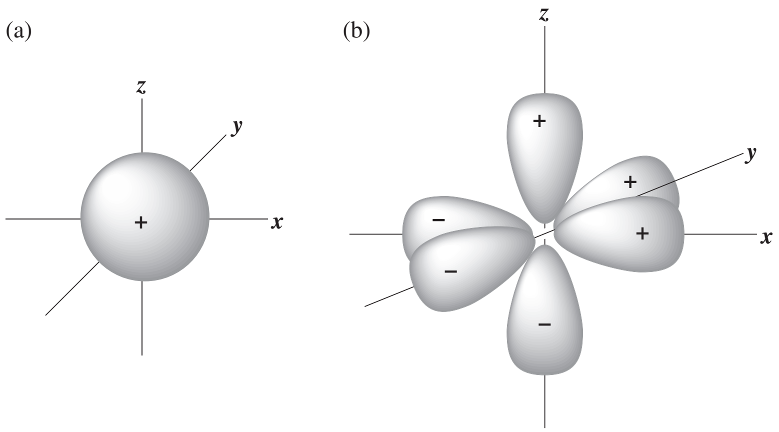

**FIGURE 1.1.** (a) The 1s orbital. (b) The three degenerate 2p orbitals.

extremely small.[4] In Figure 1.1 some lobes of the orbitals are labeled (+) and others (−). These signs do not refer to positive or negative *charges*, since both lobes of an electron cloud must be negatively charged, but rather the signs of the wave function $\Psi$. The wave function always has opposite signs on the two sides of the node, which separates two parts of an orbital and is a point of zero electron density. According to the *Pauli exclusion principle*, no more than two electrons can be present in any orbital, and they must have opposite spins.

The Schrödinger equation can be solved exactly only for one-electron systems, such as the hydrogen atom. Therefore, approximations must be made for molecules. If it could be solved exactly for molecules containing two or more electrons,[5] a precise picture of the shape of the orbitals available to each electron, which is especially for the important ground state, would become available, as well as the energy for each orbital. The two most common general methods of approximation are the molecular-orbital method and the valence-bond method.

In the molecular-orbital method, bonding is considered to arise from the overlap of atomic orbitals. When any number of atomic orbitals overlap, they combine to form an equal number of new orbitals, called *molecular orbitals*. Molecular orbitals differ from atomic orbitals in that an electron cloud effectively surrounds the nuclei of two or more atoms, rather than just one atom. In other words, the electrons are shared by more than one atom rather being localized on a single atom. In localized bonding for a single covalent bond, two one-electron containing atomic orbitals overlap and two molecular orbitals are generated. The so-called *bonding orbital* has a lower energy than the original atomic orbitals. The other orbital is called an *antibonding orbital* and has a higher energy. Orbitals of lower energy fill first. Remember that *any orbital can hold only two electrons*. There can be no gain or loss of electrons. Since the two original atomic orbitals each held one electron, both electrons will reside in the lower-energy *bonding* molecular orbital. The higher energy antibonding orbital remains empty in the ground state.

The overlap of orbitals describe a chemical bond. The greater the overlap of the orbitals, the stronger the bond, but total overlap is prevented by repulsion between the nuclei. In other words, the nuclei cannot superimpose. The strength of the bond is determined by the amount of electron density that resides between the two nuclei. The bond strength is important for the stability of a molecule. One method to determine this parameter is quantum theory

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[4] When wave-mechanical calculations are made according to the Schrödinger equation, the probability of finding the electron in a node is zero, but this treatment ignores relativistic considerations. When such considerations are applied, Dirac has shown that nodes do have a very small electron density: Powell, R.E. *J. Chem. Educ.* ***1968***, *45*, 558. See also, Ellison, F.O.; Hollingsworth, C.A. *J. Chem. Educ.* ***1976***, *53*, 767; McKelvey, D.R. *J. Chem. Educ.* ***1983***, *60*, 112; Nelson, P.G. *J. Chem. Educ.* ***1990***, *67*, 643. For a general review of relativistic effects on chemical structures, see Pyykkö, P. *Chem. Rev.* ***1988***, *88*, 563.

[5] See Roothaan, C.C.J.; Weiss, A.W. *Rev. Mod. Phys.* ***1960***, *32*, 194; Kolos, W.; Roothaan, C.C.J. *Rev. Mod. Phys.* ***1960***, *32*, 219. See Clark, R.G.; Stewart, E.T. *Q. Rev. Chem. Soc.* ***1970***, *24*, 95.

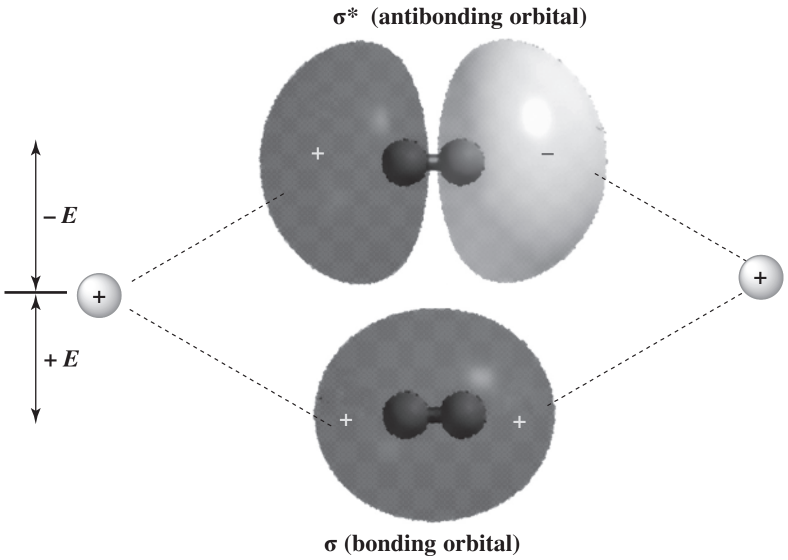

**FIGURE 1.2.** Overlap of two 1s orbitals gives rise to a σ and a σ* orbital.

using the atomic charges and volumes of carbon atoms,[6] which are good descriptors of electron depletion and indicative of the stability and reactivity of a molecule.

Figure 1.2 shows the bonding and antibonding orbitals of diatomic hydrogen (H─H) arise by the overlap of two 1*s* electrons associated with hydrogen atoms. The antibonding orbital has a node between the nuclei, indicating little or no electron density in that area, so it does not contribute to the bond. In molecular orbitals formed by the overlap of two atomic orbitals, the centers of electron density are on the axis common to the two nuclei and they are called σ (*sigma*) orbitals, and the bonds are called σ bonds.[7] The corresponding antibonding orbitals are designated σ* orbitals. Sigma orbitals may be formed by the overlap of any two atomic orbitals, *s*, *p*, *d*, or *f*. However, the two lobes that overlap must have the same sign. In other words, a positive *s*, *p*, *d*, or *f* orbital can form a bond only by overlapping with another positive orbital. Any σ molecular orbital may be represented as approximately ellipsoidal in shape. In chemical structures, a pair of electrons in a bond is represented by a straight line.

Orbitals are frequently designated by their symmetry properties. The σ orbital of hydrogen is often written $\psi_g$. The *g* stands for *gerade*. A *gerade* orbital is one in which the sign on the orbital does not change when it is inverted through its center of symmetry. The σ* orbital is *ungerade* (designated $\psi_u$). An *ungerade* orbital changes sign when inverted through its center of symmetry.

In molecular-orbital calculations, the *linear combination of atomic orbitals* (known as LCAO) generates a wave function from a linear combination of overlapped atomic orbitals. Addition of the atomic orbitals give the bonding molecular orbital:

$$\psi = c_A \psi_A + c_B \psi_B \tag{1-1}$$

The functions $\psi_A$ and $\psi_B$ are the functions for the atomic orbitals of atoms A and B, respectively, and $c_A$ and $c_B$ represent weighting factors. Subtraction is also a linear combination:

$$\psi = c_A \psi_A - c_B \psi_B \tag{1-2}$$

This gives rise to the antibonding molecular orbital.

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[6] Kržan, A.; Mavri, J. *J. Org. Chem.* ***2011***, *76*, 1891.

[7] Shahbazian, S. *Chem. Eur. J.* ***2018***, *24*, 5401.

In the valence-bond method, a wave equation $\psi$ is written for each of the various possible electronic structures that a molecule may have. Each such structure is called a *canonical form*. The total $\psi$ is obtained by summation of all plausible structures, each with its weighting factor:

$$\psi = c_1\psi_1 + c_2\psi_2 + \ldots \tag{1-3}$$

This resembles Eq. (1-1), but here each $\psi$ represents a wave equation for a canonical form and each $c$ is the amount contributed to the total picture by that form.

Values for $c$ are obtained by solving the equation that gives the lowest energy, in agreement with the Lewis structures long familiar to the organic chemist. It is noted that orbital functions can indeed be reconstructed from measured data using several different approaches. However, the results are often less accurate than those achieved with purely theoretical methods.[8]

## 1.B. MULTIPLE VALENCE

An atom with a valence of 1 uses that orbital to form one bond. Atoms with a valence of 2 or more must form bonds by using at least two orbitals. For example, an oxygen atom has two half-filled orbitals so it has a valence of 2. It can form two single bonds by the overlap of these orbitals with the orbitals of two other atoms. A nitrogen atom has three half-filled orbitals and a valence of three. It forms three single bonds.

## 1.C. HYBRIDIZATION

When two equivalent orbitals overlap, a more stable bond known as a $\sigma$-bond is formed. This type of bond contrasts with a bond formed by the overlap of two nonequivalent orbitals, which is less stable. *Only lobes of the same sign can overlap*. The new molecular orbitals are a mixture of the two original orbitals, so they are called *hybrid orbitals*.[9]

In general, nonbonded equivalent orbitals lie as far away from each other as possible because of mutual repulsion. An atom that forms only two $\sigma$ bonds uses two *sp* orbitals, such as mercury in $HgCl_2$, for example. It should be a linear molecule with bond angles of 180° (Cl—Hg—Cl). This kind of hybridization is called *digonal hybridization*. An *sp* hybrid orbital forms a stronger covalent bond than either an *s* or a *p* orbital because it extends out in space in the direction of the other atom's orbital farther than the *s* or the *p* and permits greater overlap. Consider boron with a valence of 3 and the electronic configuration $1s^2 2s^2 2p^1$. Boron has only three valence electrons available to form bonds, hence the valence of 3. Any hybridization model must take this into account. In this case, there are three equivalent hybrid orbitals, each called $sp^2$ (*trigonal hybridization*). There are three $\sigma$ bonds for $sp^2$ hybridization, as shown in Figure 1.3. The three axes are all in one plane and point to the corners of an equilateral triangle as with the known structure of $BF_3$, a planar molecule with bond angles of 120°.

Another type of hybrid orbital is possible for atoms that can form four $\sigma$ bonds, such as carbon. There are four equivalent molecular orbitals connected to a central locus, each called $sp^3$, and mutual electron repulsion leads to a shape in which *the orbitals point to the corners of a regular tetrahedron* (Figure 1.3). A typical molecule is methane, $CH_4$, and assuming that carbon forms four bonds with $sp^3$ hybrid orbitals, the bond angles of methane would thus be expected to be 109°28′. Indeed, those are the angles of a regular tetrahedron. *Note that electrons are not "promoted" in atomic orbitals, as described by the electron promotion model for*

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[8] Schwarz, W.H.E. *Angew. Chem. Int. Ed.* ***2006***, *45*, 1508. For the ball-in-box model, see Pierrefixe, S.C.A.H.; Guerra, C.F.; Bickelhaupt, F.M. *Chem. Eur. J.* ***2008***, *14*, 819; Pierrefixe, S.C.A.H.; Bickelhaupt, F.M. *J. Phys. Chem. A.* ***2008***, *112*, 12816.

[9] See Alabugin, I.V.; Bresch, S.; Gomes, G.d.P. *J. Phys. Org. Chem.* ***2015***, *28*, 147.

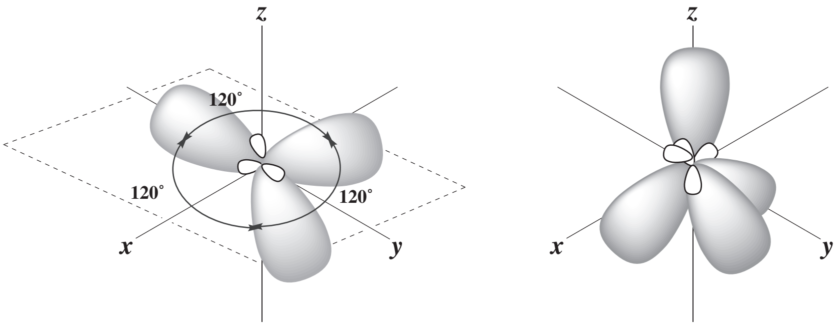

**FIGURE 1.3.** The three $sp^2$ and the four $sp^3$ orbitals.

*bonding*. The bond promotion model is a mathematical device to describe the formation of molecular orbitals using atomic orbitals. Atoms use their available orbitals to form the strongest bonds possible, with the best overlap to form bonds with other atoms. The *VSEPR (valence shell electron pair repulsion) model*[10] can be used to show electron distribution and estimate the 3D shape of molecules formed by second row atoms such as C, N or O.

The hybrid orbitals discussed in this section stem from only one possible approximate solution of the Schrödinger equation. The *s* and the three *p* atomic orbitals used to form $sp^3$ orbitals, for example, can be combined in other equally valid ways. Bickelhaupt and coworkers[8] have proposed an alternative approach to the bonding in carbon that suggests that the maximum coordination number of carbon cannot exceed four because it is too small to allow more than four substituents to approach and form the appropriate bonds.

## 1.D. MULTIPLE BONDS

As noted above, $sp^2$ orbitals are used to form three σ bonds. In general, any carbon atom that is bonded to only three different atoms uses $sp^2$ orbitals for this bonding. Ethene, $H_2C{=}CH_2$ (the old name is ethylene), for example, has three σ bonds (see Figure 1.4), one to each of two hydrogen atoms and one to the other carbon. This orbital overlap description demands that each carbon has another electron in the $2p_z$ orbital that is perpendicular to the plane of the $sp^2$ orbitals. The two parallel $2p_z$ orbitals, one on each of the two adjacent carbon atoms, can overlap sideways to generate a bonding and an antibonding orbital (Figure 1.4). In other words, a new bond is formed, but it is formed by sideways overlap of adjacent *p* orbitals rather than the direct overlap found with σ orbitals. Molecular orbitals formed by the overlap of atomic orbitals whose axes are parallel are called *π orbitals* if they are bonding and *π* orbitals* if they are antibonding.

In this picture of ethene, two different bonds connect the adjacent carbon atoms, a σ bond and a π bond.[11] The stronger σ bond is formed by overlap of the σ orbitals. It is ellipsoidal and symmetrical about the C—C axis. There is sideways overlap of each lobe of the "dumbbell-shaped" π orbitals, one above the plane and one below form the weaker π bond. Maximum overlap of the *p* orbitals is only possible if they are parallel. Since both the σ bond and the π bond connect the two carbon atoms, free rotation is *not* possible about the double bond. Since both carbon atoms in ethylene are $sp^2$ hybridized and each carbon has a planar geometry, the six atoms associated with the double bond ($H_2C{=}CH_2$) are in a plane. The H—C—H bond angles are ~120°. Double bonds are shorter than the corresponding single bonds because maximum stability is obtained when the *p* orbitals overlap as much as possible (Sec. 1.J). Similar to C═C, double bonds between carbon and oxygen (C═O) or nitrogen (C═N) also have one σ and one π orbital.

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[10] Smith, M.B. *Organic Chemistry. An Acid–Base Approach*, 3rd ed., CRC Press, Boca Raton, FL, ***2023***, pp. 48–49.

[11] For an alternative representation, see Pauling, L. *Theoretical Organic Chemistry, The Kekulé Symposium*, Butterworth, London, ***1959***, pp. 2–5; Palke, W.E. *J. Am. Chem. Soc*. **1986**, *108*, 6543.

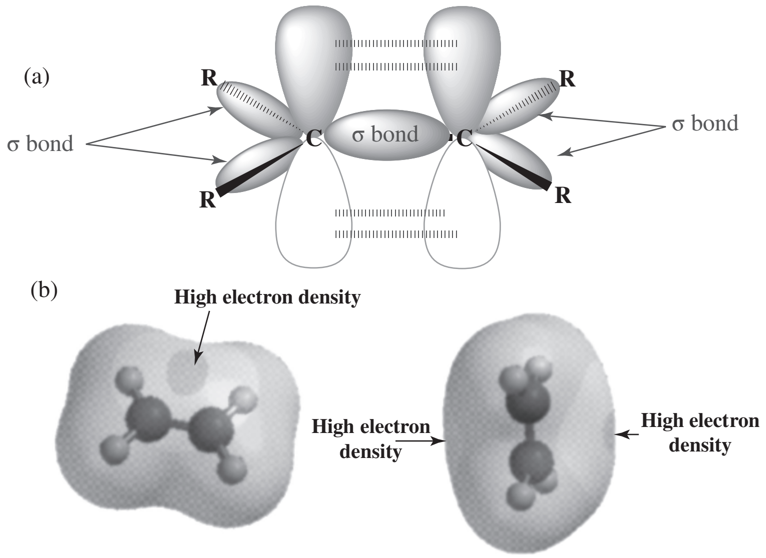

**FIGURE 1.4.** (a) Overlapping *p* orbitals form a π and a π* orbital. The σ orbitals are shown in (a). The electron potential map of ethene in (b) shows the concentration of electron density above and below the plane of the atoms, consistent with a π bond.

When carbon is connected to another carbon atom by a triple bond, as in ethyne ($HC\equiv CH$; the common name is acetylene), each carbon is *sp* hybridized and connected to only two other atoms by a σ bond. Since the two atoms are *sp* hybridized, the four atoms of acetylene are in a straight line (Figure 1.5).[12] Each carbon has two *p* orbitals remaining, with one electron in each. These orbitals are perpendicular to each other and to the $C-C$ axis. The mutually perpendicular *p* orbitals overlap in the manner shown in Figure 1.5a to form two orthogonal π bonds. A triple bond is thus composed of one σ and two π bonds. The electron density map of ethyne in Figure 1.5b shows the higher electron density (the light band around the middle) that surrounds the space between the carbon atoms, consistent with two orthogonal π bonds. Triple bonds between carbon and nitrogen can be represented in a similar manner, $C\equiv N$.

Double and triple bonds in organic molecules usually involve the second-row elements carbon, nitrogen, and oxygen.[13] Third-row elements tend to form weaker π bonds than do the second-row elements,[14] so multiple bonds are less common and the compounds containing them are generally less stable.[15] Compounds with $C=S$ bonds are known, for example, but $C=S$ compounds are generally much less stable than the corresponding $C=O$ compounds (however, see *p*π–*d*π bonding in Sec. 2.H). Stable compounds with $Si=C$ and $Si=Si$ bonds are rare, but examples have been reported,[16] including a pair of *cis* and *trans* $Si=Si$ isomers.[17]

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[12] See Simonetta, M.; Gavezzotti, A., in Patai, S. *The Chemistry of the Carbon–Carbon Triple Bond*, Wiley, NY, ***1978***. pp. 1–56; Dale, J., in Viehe, H.G. *Acetylenes*, Marcel Dekker, NY, ***1969***, pp. 3–96.

[13] For a review of metal–metal multiple bonds, see Cotton, F.A. *J. Chem. Educ.* ***1983***, *60*, 713.

[14] For discussions, see Schmidt, M.W.; Truong, P.N.; Gordon, M.S. *J. Am. Chem. Soc.* ***1987***, *109*, 5217; Schleyer, P.v.R.; Kost, D. *J. Am. Chem. Soc*. ***1988***, *110*, 2105.

[15] For a double bonds between carbon and elements other than C, N, S, or O, see Jutzi, P. *Angew. Chem. Int. Ed.* ***1975***, *14*, 232; Raabe, G.; Michl, J. *Chem. Rev*. ***1985***, *85*, 419 (Si only); Wiberg, N. *J. Organomet. Chem*. ***1984***, *273*, 141 (Si only); Gordon, M.S. *Mol. Struct. Energ*. ***1986***, *1*, 101. For review of $C=P$ and $C\equiv P$ bonds, see Regitz, M. *Chem. Rev*. ***1990***, *90*, 191. Appel, R.; Knoll, F. *Adv. Inorg. Chem*. ***1989***, *33*, 259; Markovski, L.N.; Roanenko, V.D. *Tetrahedron* ***1989***, *45*, 6019.

[16] For $Si=C$ bonds, see West, R. *Pure Appl. Chem*. ***1984***, *56*, 163; Shepherd, B.D.; Campana, C.F.; West, R. *Heteroat. Chem*. ***1990***, *1*, 1.

[17] Michalczyk, M.J.; West, R.; Michl, J. *J. Am. Chem. Soc.* ***1984***, *106*, 821; *Organometallics* ***1985***, *4*, 826.

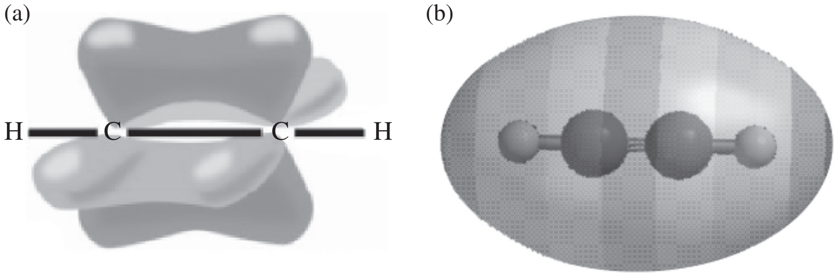

**FIGURE 1.5.** (a) The overlap of mutually perpendicular π orbitals in ethyne to give orthogonal π bonds. (b) Electron potential map of ethyne showing the concentration of electron density between the carbon atoms in red, consistent with two orthogonal π bonds.

There is at least one report of a so-called two-electron, four-center C─C bond for the dimer of tetracyanoethylene.[18] While such multicenter bonding is not formally an example of the multiple bonding described in this section, it constitutes a different type of bonding when compared to the simple C─C bonds described earlier.

## 1.E. PHOTOELECTRON SPECTROSCOPY

The four bonds of methane are equivalent according to most physical and chemical methods of detection. The *nuclear magnetic resonance* (NMR) and the *infrared* (IR) spectra of methane show *no* peaks that can be attributed to different kinds of C─H bonds. In *photoelectron spectroscopy* (PES),[19] a molecule or a free atom is bombarded with vacuum *ultraviolet* (UV) radiation, causing an electron to be ejected. The energy of the ejected electron can be measured, and the difference between the energy of the radiation used and that of the ejected electron is the *ionization potential* of that electron. A molecule that contains several electrons of differing energies can lose any one of them as long as its ionization potential is less than the energy of the radiation used. Since electrons reside in orbitals, a photoelectron spectrum consists of a series of bands, *each corresponding to an orbital of a different energy*. The spectrum gives a direct experimental picture of all orbitals that are present, and they are ejected in ascending order of their energies, if radiation of sufficiently high energy is used.[20] Broad bands usually correspond to strongly bonding electrons and narrow bands to weakly bonding or nonbonding electrons.

Dinitrogen, $N_2$, is a typical diatomic molecule and the electronic structure of the $N_2$ molecule is shown in Figure 1.6 using the LCAO model. In this model, the two 2*s* orbitals of the nitrogen atoms combine to give the two orbitals marked 1 (bonding) and 2 (antibonding), while the six 2*p* orbitals combine to give six orbitals, three of which (marked 3, 4, and 5) are bonding. The three antibonding orbitals (not shown in Figure 1.6) are unoccupied. Using PES, it is possible to probe the validity of this model for bonding. The photoelectron spectrum of $N_2$ is shown in Figure 1.7.[21] Electrons ejected from orbital 1 are not found in Figure 1.7 because the ionization potential of these electrons is greater than the energy of the light used (they can be seen when higher-energy light is used). The broad band in Figure 1.7 corresponds to the four electrons in the degenerate orbitals 3 and 4. The individual peaks within

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[18] Miller, J.S.; Novoa, J.J. *Acc. Chem. Res.* ***2007***, *40*, 189.

[19] See Ballard, R.E. *Photoelectron Spectroscopy and Molecular Orbital Theory*, Wiley, NY, ***1978***; Baker, A.D.; Betteridge, D. *Photoelectron Spectroscopy*, Pergamon, Elmsford, NY, ***1972***. For reviews, see Westwood, N.P.C. *Chem. Soc. Rev*. ***1989***, *18*, 317; Bock, H.; Ramsey, B.G. *Angew. Chem. Int. Ed*. ***1973***, *12*, 734; For the IUPAC descriptive classification of various electron spectroscopy techniques, see Porter, H.Q.; Turner, D.W. *Pure Appl. Chem*. ***1987***, *59*, 1343.

[20] The correlation is not perfect, but the limitations do not seriously detract from the usefulness of the method. The technique is not limited to vacuum UV radiation. Higher energy radiation can also be used.

[21] From Brundle, C.R.; Robin, M.B. in Nachod, F.C.; Zuckerman, J.J. *Determination of Organic Structures by Physical Methods*, Vol. 3, Academic Press, NY, ***1971***, p. 18.

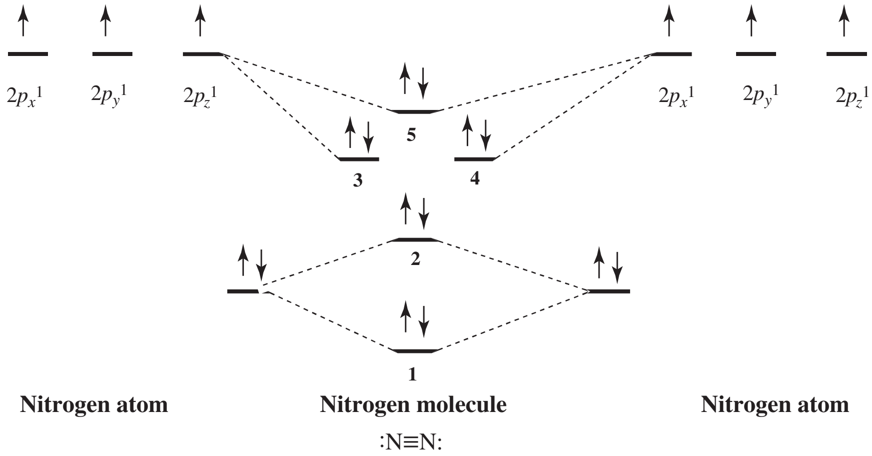

**FIGURE 1.6.** Electronic structure of $N_2$ (inner-shell electrons omitted).

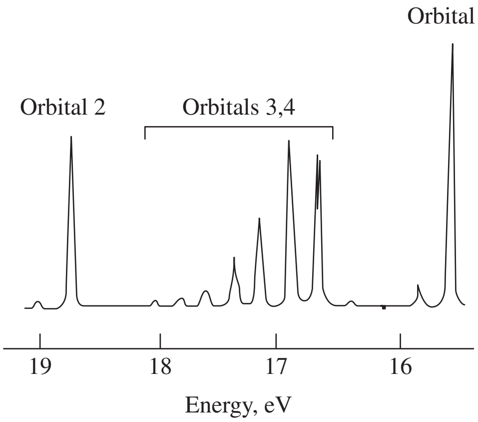

**FIGURE 1.7.** Photoelectron spectrum of $N_2$.[21] *Source:* Reproduced from Brundle, C.R.; Robin M.B. in Nachod, F.C.; Zuckerman, J.J. *Determination of Organic Structures by Physical Methods*, Vol. 1, Academic Press, NY, ***1971***, p. 18/with permission of Elsevier.

this band are caused by different vibrational levels (see Chapter 7). The triple bond of $N_2$ is therefore composed of these two orbitals and orbital 1. The bands corresponding to orbitals 2 and 5 are narrow; hence these orbitals contribute little to the bonding and may be regarded as the two unshared pairs of $\ddot{N} \equiv \ddot{N}$. Note that this result is contrary to that expected from a naive consideration of orbital overlaps shown in Figure 1.6, where it would be expected that the two unshared pairs would be those of orbitals 1 and 2, resulting from the overlap of the filled 2*s* orbitals, and that the triple bond would be composed of orbitals 3, 4, and 5, resulting from overlap of the *p* orbitals. $p_z$

Using PES, the eight valence electrons of methane can be differentiated. The photoelectron spectrum of methane[22] in Figure 1.8 shows two bands,[23] at ~23 and 14 eV, and not the single band expected from the equivalency of the four C─H bonds. The data in Figure 1.8 suggests that carbon uses two available orbitals to form four bonds and the electrons in the bonds are distributed between carbon and the four atoms involved in the bonds. The

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[22] Brundle, C.R.; Robin, M.B.; Basch, H. *J. Chem. Phys.* ***1970***, *53*, 2196; Baker, A.D.; Betteridge, D.; Kemp, N.R.; Kirby, R.E. *J. Mol. Struct.* ***1971***, *8*, 75; Potts, A.W.; Price, W.C. *Proc. R. Soc. London, Ser A* ***1972***, *326*, 165.

[23] A third band, at 290 eV, caused by the 1*s* electrons of carbon, can also found if radiation of sufficiently high energy is used.

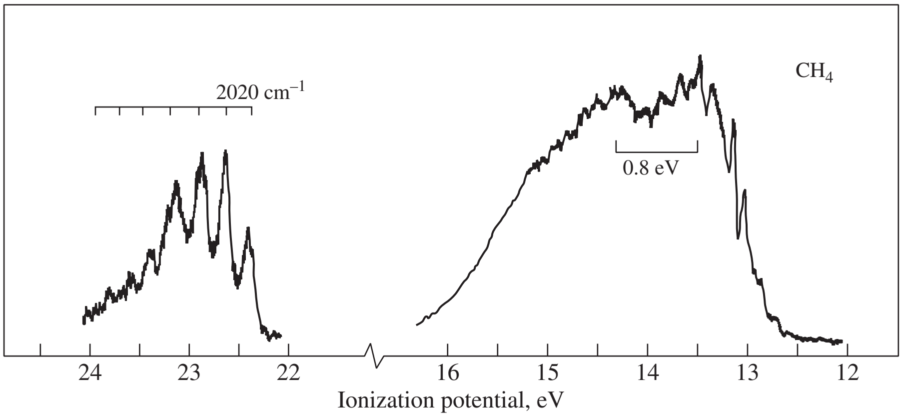

**FIGURE 1.8.** Photoelectron spectroscopy scan of methane.[22] *Source:* Reproduced from Brundle, C.R.; Robin, M.B. *Journal of Chemical Physics* ***1970***, *53*, 2196/with permission of American Institute of Physics.

band at 23 eV comes from two electrons in a low-energy level (called the $a_1$ level), which can be regarded as arising from a combination of the 2*s* orbital of carbon with an appropriate combination of hydrogen 1*s* orbitals. The band at 14 eV comes from six electrons in a triply degenerate level (the $t_2$ level), arising from a combination of the three 2*p* orbitals of carbon with other combinations of 1*s* hydrogen orbitals. As mentioned above, most physical and chemical processes cannot distinguish the different orbitals used in bonding. Although photoelectron spectroscopy shows that multiple orbitals are used for bonding, the four bonds are chemically identical, indistinguishable and considered to be identical. Methane is known to form a tetrahedral array of atoms about carbon, so a model can be used that assumes the four σ bonds are formed by the best overlap of *s* and *p* orbitals of carbon, with the orbital of each of the four atoms approaching at the angles of a regular tetrahedron. Such a tetrahedral approach of the atoms allows the 2*s* and all three 2*p* orbitals of carbon to overlap with the "incoming" atoms to form the best bond possible. This model is consistent with the $sp^3$ hybrid description. Such a model is not real, of course, since an elemental carbon atom does not form bonds with four individual atoms to form a molecule in this manner. However, this model is an alternative to the hybridization model that can be used for methane. The photoelectron spectra of many other organic molecules are known,[24] including monocyclic alkenes, in which bands <10 eV are due to π orbital ionization and those >10 eV originate from ionization of σ orbitals only.[25]

## 1.F. ELECTRONIC STRUCTURES OF MOLECULES

For each molecule, ion, or free radical that has only localized electrons, it is possible to draw a formula called a *Lewis structure* that shows the location of these electrons. Only the valence electrons are shown in the covalent bonds connecting two atoms and any unshared electrons are also shown.[26] Drawing structures correctly in a chemical reaction is important since the position of electrons changes during a reaction. It is necessary to know where the electrons are initially to follow where they are going. To this end, the following rules are followed:

1. The total number of valence electrons in the molecule (or ion or free radical) must be the sum of all outer-shell electrons "contributed" to the molecule by each atom plus those associated with a negative charge. A positive charge indicates a loss of electrons.

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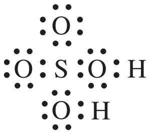
[24] Robinson, J.W. *Practical Handbook of Spectroscopy*, CRC Press, Boca Raton, FL, ***1991***, p. 178.

[25] Novak, I.; Potts, A.W. *Tetrahedron* ***1997***, *53*, 14713.

[26] It has been argued that although the Lewis picture of two electrons making up a covalent bond may work well for organic compounds, it cannot be successfully applied to most inorganic compounds: Jørgensen, C.K. *Top. Curr. Chem.* ***1984***, *124*, 1.

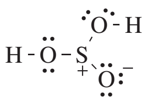
2. Once the number of valence electrons has been ascertained, it is necessary to determine which of them are found in covalent bonds and which are unshared. Unshared electrons (either a single electron or a pair) form part of the outer shell of just one atom, but electrons in a covalent bond are part of the outer shell shared by both atoms of the bond. *Second-row atoms* (B, C, N, O, F) *can have a maximum of eight valence electrons*, and usually have this number, although some cases are known where a second-row atom has only six or seven. Third-row atoms can have more electrons since multiple valences are possible. Thus, for $H_2SO_4$, there are eight shared electrons around sulfur. Each of the four oxygen atoms has eight electrons, but for the two OH units, those oxygen atoms have four shared electrons and four unshared electrons (two electron pairs).

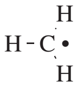


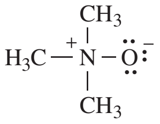
Where there is a choice between a structure that has six or seven electrons around a second-row atom and one in which all such atoms have an octet, the structure based on the octet is generally lower in energy and the one that is observed. In other words, the low-energy structure usually does not have a charge or singly unshared electrons. There are a few exceptions. For molecular $O_2$, the structure $:\dot{O}-\dot{O}:$ has a lower energy than $:\ddot{O}=\ddot{O}:$. Although second-row atoms are limited to eight valence electrons, this is not so for third-row atoms, which can accommodate 10 or even 12 because empty *d* orbitals may be utilized.[27] For example, $PCl_5$ and $SF_6$ are stable compounds, and the hybridization model can be used to explain this fact. In $SF_6$, one *s* and one *p* electron from the ground state $3s^23p^4$ of the sulfur are promoted to empty *d* orbitals, and the six orbitals hybridize to give six $sp^3d^2$ orbitals, which point to the corners of a regular octahedron.

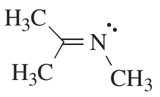
3. It is customary to show the formal charge (FC) on each atom. FC is the difference between the number of valence electrons of an atom in a neutral free state and the number assigned to that atom in a Lewis structure. $FC = V - N - B/2$, where $V$ is the number of valence electrons, $N$ is the number of nonbonding valence electrons, and $B$ is the total number of shared electrons in bonds. An excess of electrons results in a negative charge, and a deficiency results in a positive charge. The total of the FCs on all atoms equals the charge on the whole molecule or ion. Valence is the combining power of an element, as measured by the number of other atoms it can displace or combine with. For second-row atoms it is the number of bonds that can be formed so there are eight electrons around that atom. Valence electrons are the electrons in the outermost shell, or energy level, of an atom. For example, oxygen has six valence electrons and requires two, so it has a valence of two. Similarly, carbon has a valence of four, nitrogen has a valence of three, and fluorine has a valence of one.

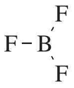
Examples of electronic structures are:











A coordinate-covalent bond (sometimes called a dative bond), represented by an arrow, is one in which both electrons come from the same atom. One atom takes a positive charge and the other atom in

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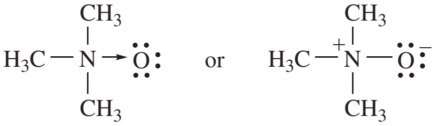
[27] For a review concerning sulfur compounds with a valence shell larger than eight, see Salmond, W.G. *Q. Rev. Chem. Soc.* ***1968***, *22*, 235.

the dative bond takes a negative charge. It is a neutral molecule since the charges cancel. An example is trimethylamine *N*-oxide:



In the electronic picture of trimethylamine *N*-oxide there is a choice of drawing an arrow or charges on the two atoms. If the arrow is used, charges are not assigned to the atoms. If a bond is used, the charges must be assigned to show the charge separation. Compounds such as amine *N*-oxides must be drawn one way or the other. It is usually simpler to use charge separation. It is noted that the electronic descriptions of molecules, especially complex molecules, are much more complicated, in large part due to the ultra-fast dynamics that characterize such molecules. A method of describing molecules has been developed called *attosecond electron dynamics*,[28] which may allow the investigation and understanding of complex ultrafast dynamics in large molecular systems.

## 1.G. ELECTRONEGATIVITY

When two identical atoms have the same substituents, the electron cloud that bonds the two atoms is symmetrical with respect to the plane that is the perpendicular bisector of the bond. Therefore, the electron cloud associated with a C—C bond is symmetrical because the electron density around each carbon atom is the same. When two atoms are not the same, the electron cloud that bonds those two atoms is unsymmetrical. When there are two different atoms and one is more electronegative (the tendency of an atom to acquire electrons) than the other, the electron cloud is distorted toward the more electronegative atom. This attraction is called *electronegativity*[29] and it is greatest for atoms in the upper-right corner of the periodic table and lowest for atoms in the lower-left corner. Therefore, fluorine is more electronegative than carbon and fluorine is more electronegative than iodine. If the C—F bond is examined, there is distortion of the electron cloud associated with the bond distorted toward the more electronegative fluorine atom. In other words, there is a higher probability of finding the electrons near the fluorine than near the carbon. Such a bond is said to be *polarized*. This polarization is represented by giving the fluorine a partial negative charge (shown by the symbol $\delta^-$) and the carbon a partial positive charge (shown by the symbol $\delta^+$).

The distortion of electron density extends to those atoms attached to polarized atoms. In the fragment C—C—C—F, the polarization is observed down the carbon chain: $C^{\delta+}$—$C^{\delta-}$—$C^{\delta+}$—$F^{\delta-}$. The polarization of the C—F unit induces polarization of the attached carbon atoms as shown. This distortion of electron density is called an *induced dipole*. Induced polarization is usually only important for three or four atoms distal to the electronegative atom.

There are several quantitative tables of electronegativity that indicate the direction and extent of electron-cloud distortion for a bond between any pair of atoms. The most popular of these scales, devised by Pauling, is based on bond energies (Sec. 1.L) of diatomic molecules. The data assumes that if the electron distribution were symmetrical in a molecule A—B, the bond energy would be the mean of the energies of A—A and B—B, since in these cases the cloud must be undistorted. If the actual bond energy of A—B is higher than this, as is common, the partial charges attract each other and make a stronger bond, which requires more energy to break.[30] An arbitrary value is assigned to the most electronegative element, fluorine, F = 4.0. The electronegativities of other atoms can then be calculated using the Pauling scale:[31] F = 4.0, O = 3.5, Cl and N = 3.0, Br = 2.8, S, I, and C = 2.5, and H and P = 2.1.

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[28] Nisoli, M.; Decleva, P.; Calegari, F.; Palacios, A.; Martín, F. *Chem. Rev.* ***2017***, *117*, 10760.

[29] For a collection of articles on this topic, see Sen, K.D.; Jørgensen, C.K. *Electronegativity (Vol. 6 of Structure and Bonding)*, Springer, NY, ***1987***. For a review, see Batsanov, S.S. *Russ. Chem. Rev.* ***1968***, *37*, 332. See Poliyzer, P.; Murray, J.S. *J. Phys. Org. Chem*. ***2023***, *36*, e4406.

[30] See Nikitin, K.; O'Gara, R. *Chem. Eur. J.* ***2019***, *25*, 4551.

[31] Taken from Pauling, L. *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, Ithaca, NY, ***1960***, p. 93.

**TABLE 1.1 Some group electronegativities relative to H = 2.176**[37]

| | | | |
|---|---|---|---|
| **$CH_3$** | 2.472 | **$CCl_3$** | 2.666 |
| **$CH_3CH_2$** | 2.482 | **$C_6H_5$** | 2.717 |
| **$CH_2Cl$** | 2.538 | **$CF_3$** | 2.985 |
| **$CBr_3$** | 2.561 | **$C\equiv N$** | 3.208 |
| **$CHCl_2$** | 2.602 | **$NO_2$** | 3.421 |

*Source:* Reproduced from Inamoto, N.; Masuda, S. *Chem. Lett.* ***1982***, 1003/ with permission of The Chemical Society of Japan.

Other treatments[32] have led to scales that are based on different principles, including the Sanderson scale.[33] The average of the ionization potential and the electron affinity has been used,[34] the average one-electron energy of valence-shell electrons in ground-state free atoms,[35] and also the "compactness" of an atom's electron cloud.[27] In some of these treatments electronegativities can be calculated for different valence states, for different hybridizations (e.g., *sp* carbon atoms are more electronegative than $sp^2$, which are still more electronegative than $sp^3$),[36] and even differently for primary, secondary, and tertiary carbon atoms. Also, electronegativity values can be calculated for groups rather than atoms (Table 1.1).[37] A new descriptor Q has been described that, when plotted versus the bond energy, separates nicely a wide variety of bonding types, covalent, polar, and increasingly ionic, metallogenic, electrostatic, and charge-shift bonds, and dispersion interactions.[38]

Electronegativity information can be obtained from NMR spectra. In the absence of a magnetically anisotropic group,[39] the chemical shift of a $^{1}H$ or a $^{13}C$ nucleus is approximately proportional to the electron density around it and hence to the electronegativity of the atom or group to which it is attached. The greater the electronegativity of the atom or group, the lower the electron density around the proton, and the further downfield the chemical shift (relative to tetramethylsilane, TMS, as 0 ppm). This correlation is used to explain the variation of chemical shift of the *ring* protons in the series toluene, ethylbenzene, isopropylbenzene, *tert*-butylbenzene. There is a magnetically anisotropic group here, but its effect should be constant throughout the series. The electron density surrounding the ring protons decreases[40] in the order given.[41] However, this type of correlation is by no means perfect, since all the measurements are made in a powerful field, which itself may affect the electron density distribution. Coupling constants between the two protons of a system $-\mathrm{CH}-\mathrm{CH}-\mathrm{X}$ have also been found to depend on the electronegativity of X.[42]

When the difference in electronegativity between two atoms is great, the electron density in an orbital may be effectively localized on only one nucleus. Such a bond is called an *ionic bond*, which arises naturally out of the previous discussion. It is possible to view polarized covalent bonds as intermediate between ionic and covalent.

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[32] See Huheey, J.E. *Inorganic Chemistry*, 3rd ed., Harper and Row, NY, ***1983***, pp. 146–148; Mullay, J., in Sen, K.D.; Jørgensen, C.K. *Electronegativity (Vol. 6 of Structure and Bonding)*, Springer, NY, ***1987***, p. 9.

[33] The value for Na is from Sanderson, R.T. *J. Am. Chem. Soc.* ***1983***, *105*, 2259; *J. Chem. Educ*. ***1988***, *65*, 112, 223. See Sanderson, R.T. *J. Am. Chem. Soc*. ***1983***, *105*, 2259; *J. Chem. Educ*. ***1988***, *65*, 112, 223.

[34] Hinze, J.; Jaffé, H.H. *J. Am. Chem. Soc.* ***1962***, *84*, 540; Rienstra-Kiracofe, J.C.; Tschumper, G.S.; Schaefer III, H.F.; Nandi, S.; Ellison, G.B. *Chem. Rev*. ***2002***, *102*, 231.

[35] Allen, L.C. *J. Am. Chem. Soc.* ***1989***, *111*, 9003.

[36] Walsh, A.D. *Discuss. Faraday Soc.* ***1947***, *2*, 18; Bergmann, D.; Hinze, J., in Sen, K.D.; Jørgensen, C.K. *Electronegativity (Vol. 6 of Structure and Bonding)*, Springer, NY, 1987, pp. 146–190.

[37] Inamoto, N.; Masuda, S. *Chem. Lett.* ***1982***, 1003. See also, Bratsch, S.G. *J. Chem. Educ*. ***1988***, *65*, 223; Mullay, J. *J. Am. Chem. Soc*. ***1985***, *107*, 7271; Boyd, R.J.; Edgecombe, K.E. *J. Am. Chem. Soc*. ***1988***, *110*, 4182.

[38] Rahm, M.; Hoffmann, R. *J. Am. Chem. Soc.* ***2016***, *138*, 3731.

[39] A magnetically anisotropic group is one that is not equally magnetized along all three axes. The most common such groups are benzene rings (Sec. 2.I) and triple bonds.

[40] This order is opposite to that expected from the field effect (Sec. 1.I). It is an example of the *Baker–Nathan order* (Sec. 2.M).

[41] Moodie, R.B.; Connor, T.M.; Stewart, R. *Can. J. Chem.* ***1960***, *38*, 626.

[42] Williamson, K.L. *J. Am. Chem. Soc.* ***1963***, *85*, 516; Laszlo, P.; Schleyer, P.v.R. *J. Am. Chem. Soc*. ***1963***, 85, 2709; Niwa, J. *Bull. Chem. Soc. Jpn*. ***1967***, 40, 2192.

With this view, the extent of electron-cloud distortion is expressed as the percent ionic character of a bond. In this model, there is a continuous gradation from ionic to covalent bonds.

## 1.H. DIPOLE MOMENT

The *dipole moment*[43] is a property of a molecule that results from charge separations like those discussed above. In polyatomic molecules, each bond has an individual bond moment. A vector showing the magnitude and direction of the shifting of this electron pair is known as a *bond moment*. For one bond, the bond dipole moment (BDM) is determined by the difference in electronegativity between the two atoms, $\mu = q \times d$, where $q$ is the partial charge on either atom times the distance between the charges.[44] In the cgs system, charge is measured in statcoulombs (esu, electrostatic units) and distance in centimeters. The dipole moment ($\mu$) of a molecule is the vectorial addition of individual bond moments.[45] Dipole moment measures a separation of charge. In many cases, dipole moments are additive.[46] Thus, from the dipole moments of toluene and nitrobenzene (Figure 1.9)[47] the moment of *p*-nitrotoluene is predicted to be ~4.36 D and the actual value 4.39 D. However, the moment of *p*-cresol (1.57 D) is different from the predicted value of 1.11 D. In molecules with symmetry such as that in carbon tetrachloride, $CCl_4$, there are individual bond moments but there is no dipole moment for the molecule because the individual moments are canceled out by the symmetry. There is both a magnitude and a direction for the bond moments. In other words, the bond moments for each bond in the tetrahedral array about carbon are in different directions and cancel, so the dipole moment for carbon tetrachloride is 0. The solvent can also influence the dipole moment. *trans*-1,4-dibromo-1,4-dicyanocyclohexane has a zero-dipole moment in the crystal, but it has a nonzero dipole when in solution.[48]

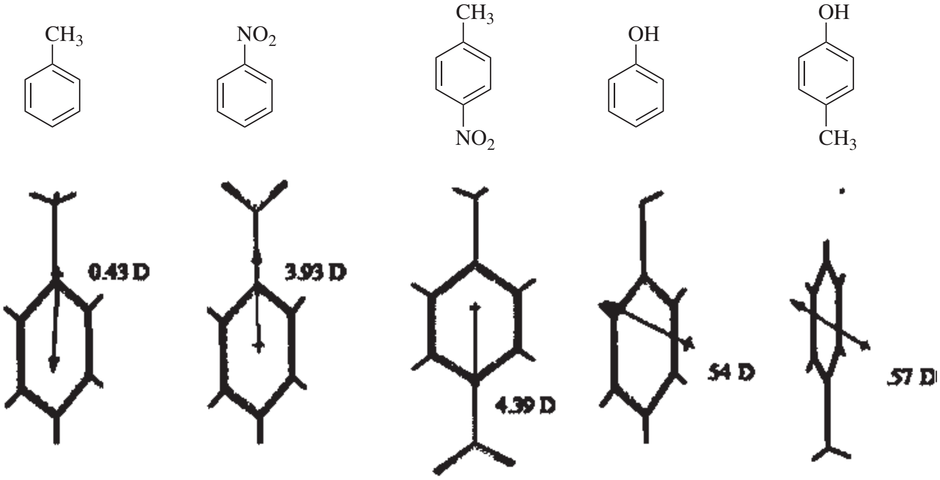

**FIGURE 1.9.** Some dipole moments, in Debye units, measured in benzene. In each 3D model, the arrow indicates the direction of the dipole moment for the molecule, pointing to the negative pole.[49] *Source:* Adapted from Muenter, J.S.; Laurie, V.W. *J. Chem. Phys.* ***1966****, 45*, 855.

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[43] The critical dipole moment to bind an electron is 2.5 D. See Yuan, D.-F.; Liu, Y.; Zhang, Y.-R.; Wang, L.-S. *J. Am. Chem. Soc.* ***2023***, *145*, 5512.

[44] See Structure of organic compounds, Ouellette, R.J.; Rawn, J.D. in *Principles of Organic Chemistry*, Elsevier, ***2015***.

[45] See Exner, O. *Dipole Moments in Organic Chemistry*, Georg Thieme Publishers, Stuttgart, ***1975***; McClellan, A.L. *Tables of Experimental Dipole Moments*, Vol. 1, W.H. Freeman, San Francisco, ***1963***; Vol. 2, Rahara Enterprises, El Cerrito, CA, ***1974***.

[46] For example, see Koudelka, J.; Exner, O. *Collect. Czech. Chem. Commun.* ***1985***, *50*, 188–200.

[47] The values for toluene, nitrobenzene, and *p*-nitrotoluene are from MacClellan, A.L. *Tables of Experimental Dipole Moments*, Vol. 1, W.H. Freeman, San Francisco, ***1963***; Vol. 2, Rahara Enterprises, El Cerrito, CA, ***1974***. The values for phenol and *p*-cresol were determined by Goode, E.V.; Ibbitson, D.A. *J. Chem. Soc*. ***1960***, 4265.

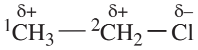
[48] Barón, M.; Stewart, J.J.P. *Can. J. Chem.* ***2020***, *98*, 616.

[49] Muenter, J.S.; Laurie, V.W. *J. Chem. Phys.* ***1966***, *45*, 855.

Because of the small difference between the electronegativity values of carbon and hydrogen, alkanes have very small dipole moments, so small that they are difficult to measure. For this reason, alkanes are nonpolar. For example, the dipole moment of isobutane is 0.132 D[50] and that of propane is 0.085 D.[49] Of course, methane and ethane, because of their symmetry, have no dipole moments.[51] It is noted that simple alkanes with more highly branched carbon skeletons are more stable than their straight-chain isomers,[52] Few organic molecules have dipole moments >7 D. The most polar compound that has been reported is 5,6-diaminobenzene-1,2,3,4-tetracarbonitrile, which has a measured dipole moment of 14.1 D.[53]

## 1.I. INDUCTIVE AND FIELD EFFECTS

The C—C bond in ethane has no polarity because it connects two identical atoms with identical electronegativities. The presence of a more electronegative atom attached to one of the carbon atoms will lead to bond polarization however, with a *dipole* (Secs 1.G and 1.H). The dipole of the C—Cl unit causes an induced dipole for atoms such as C-1 attached to the polarized C-2. Both C-1 and C-2 in chloroethane, for example, are therefore polarized by the presence of the electronegative chlorine atom.



$$\overset{\delta+}{{}^{1}CH_3} - \overset{\delta+}{{}^{2}CH_2} - \overset{\delta-}{Cl}$$

This polarization is the sum of two effects. In the first of these, the C-1 atom is deprived of some of its electron density by the greater electronegativity of Cl, and this effect is partially compensated by drawing the C—C bond electrons closer to itself. The result is a polarization of this bond and a slightly positive charge on the C-2 atom so there is a dipole. The polarization of this bond causes a slight polarization of the attached carbon C-2 and the three methyl C—H bonds. The polarization of one bond caused by the polarization of an adjacent bond due to an induced dipole is known as a through-bond inductive effect. The effect is greatest for adjacent bonds but may also be felt farther away. As a practical matter, the effect is negligible if the polarizing group is more than three bonds away. There is also an effect that a dipole has on a remote reaction center. This effect does not operate through bonds, but directly through space or solvent molecules, and is called a *field effect*.[54] It is often very difficult to separate the two kinds of effect, but several cases have been reported, generally by taking advantage of the fact that the field effect depends on the geometry of the molecule but the inductive effect depends only on the nature of the bonds.

With respect to acidity, an electron-withdrawing substituent in the vicinity of an acidic proton will lower the p$K_a$ (i.e., increase the acidity) so an electron-donating substituent will raise the p$K_a$. The p$K_a$ of butanoic acid is 4.50. In 2-chlorobutanoic acid the chlorine atom is attached to the carbon connected to the carbonyl, the α carbon, and the p$K_a$ is 2.86. In one conformation the acidic proton and the $\delta^-$ chlorine atom are relatively close in space, approximating a five-membered ring, and the acidity is enhanced. In 3-chlorobutanoic acid the chlorine atom is on C-3 and a through-space hydrogen-bonding effect requires a conformation that mimics a six-membered ring so the chorine atom is further away from the OH proton. The diminished effects relative to 2-chlorobutanoic acid lead to a p$K_a$ of 3.99, so it is a weaker acid. In 4-chlorobutanoic acid, the chlorine atom is still further away and a

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[50] Lide, D.R. Jr.; Mann, D.E. *J. Chem. Phys.* ***1958***, *29*, 914.

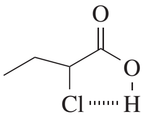
[51] Symmetrical tetrahedral molecules like methane do have extremely small dipole moments, caused by centrifugal distortion effects, but they are so small that they can be ignored for all practical purposes. For $CH_4$ $\mu$ is ~$5.4 \times 10^{-6}$ D: Ozier, I. *Phys. Rev. Lett.* ***1971***, *27*, 1329; Rosenberg, A.; Ozier, I.; Kudian, A.K. *J. Chem. Phys.* ***1972***, *57*, 568.

[52] McKee, W.C.; Schleyer, P.v.R. *J. Am. Chem. Soc.* ***2013***, *135*, 13008.

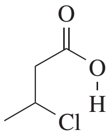
[53] Wudarczyk, J.; Papamokos, G.; Margaritis, V.; Schollmeyer, D.; Hinkel, F.; Baumgarten, M.; Floudas, G.; Mîllen, K. *Angew. Chem. Int. Ed.* ***2016***, *55*, 3220.

[54] Roberts, J.D.; Moreland, W.T. Jr. *J. Am. Chem. Soc.* ***1953***, *75*, 2167.

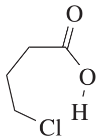
through-space interaction demands an arrangement that approximates a seven-membered ring. The diminished inductive effects lead to a p$K_a$ of 4.50.



2-Chlorobutanoic acid

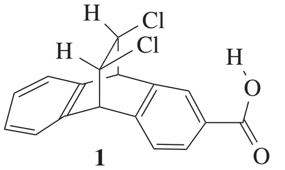


3-Chlorobutanoic acid

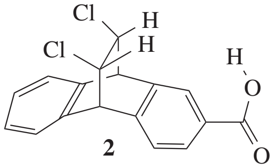


4-Chlorobutanoic acid

p$K_a$ = 6.07



**1**

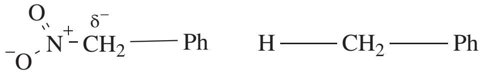


**2**

p$K_a$ = 5.67

In isomers **1** [(9*S*,10*R*,11*S*,12*R*)-11,12-dichloro-9,10-dihydro-9,10-ethanoanthracene-3-carboxylic acid) and **2** [(9*R*,10*S*,11*S*,12*R*)-11,12-dichloro-9,10-dihydro-9,10-ethanoanthracene-2-carboxylic acid],[55] the C—Cl bonds are polarized due to the electronegativity difference between the two atoms. The inductive effect of the chlorine atoms on the position of the electrons in the COOH group (and hence on the acidity, see Chapter 8) should be the same since the same bonds intervene. Because the chlorine atoms are closer in space to the COOH in **1** than they are in **2**, so the field effect is different. A comparison of the acidities of **1** and **2** should reveal whether a field effect is truly operating. When the acid ionizes there is a negative charge associated with the carboxylate group (—COO$^-$). In **1** the chlorines are on the same side of the bridge as the carboxylate (syn isomer). The through-space field effect acts to *destabilize* **1** because the δ$^-$ charge of chlorine is closer to the negative charge of the carboxylate. Placing the negative charges closer together is destabilizing since like charges repel so there is a higher activation energy being needed to reach the transition state for ionization. For **2** the chlorines further from the carboxylate will be less destabilized because the negative charges are further apart so there will be a lower activation energy for ionization compared to the syn isomer. Therefore, **2** will be more acidic than **1** due to the field effect. The evidence obtained from such experiments is overwhelming: field effects are much more important than inductive effects.[56] In most cases, the two types of effect are considered together in this book. They will not be separated but *field effect* will be used to refer to their combined action.[57] Note that the field effect for **1** may be viewed as internal hydrogen bonding (Sec. 3.A).

Functional groups can be classified as electron-withdrawing (−*I*) or electron-donating (+*I*) groups relative to hydrogen. Field effects are always comparison effects. For example, compare the −*I* or +*I* effect of one group with another (usually hydrogen). For example, the $NO_2$ in (nitromethyl)benzene is a −*I* group due to the positive charge on the nitro group, so the methylene carbon attached to the benzene ring has a δ$^-$ dipole. The nitro group draws electrons to itself more than a hydrogen atom would if it occupied the same position in the molecule, as in toluene.



$$^{-}O\text{—}\overset{O}{\overset{\|}{N^{+}}}\text{—}\overset{\delta^-}{CH_2}\text{—}Ph \qquad H\text{—}CH_2\text{—}Ph$$

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[55] See Grubbs, E.J.; Fitzgerald, R.; Phillips, R.E.; Petty, R. *Tetrahedron* ***1971***, *27*, 935.

[56] See Schneider, H.; Becker, N. *J. Phys. Org. Chem.* ***1989***, *2*, 214; Bowden, K.; Ghadir, K.D.F. *J. Chem. Soc., Perkin Trans. 2* ***1990***, 1333. Also see Exner, O.; Fiedler, P. *Collect. Czech. Chem. Commun.* ***1980***, *45*, 1251; Li, Y.; Schuster, G.B. *J. Org. Chem.* ***1987***, *52*, 3975.

[57] There has been some question as to whether it is even meaningful to maintain the distinction between the two types of effect: see Grob, C.A. *Helv. Chim. Acta* ***1985***, *68*, 882; Lenoir, D.; Frank, R.M. *Chem. Ber.* ***1985***, *118*, 753; Sacher, E. *Tetrahedron Lett.* ***1986***, *27*, 4683.

**TABLE 1.2** [58]**Field effects of various groups relative to hydrogen**[a]

| +*I* | −*I* | | |
|---|---|---|---|
| $O^-$ | $NR_3^+$ | COOH | OR |
| $COO^-$ | $SR_2^+$ | F | COR |
| $CR_3$ | $NH_3^+$ | Cl | SH |
| $CHR_2$ | $NO_2$ | Br | SR |
| $CH_2R$ | $SO_2R$ | I | OH |
| $CH_3$ | CN | OAr | $C\equiv CR$ |
| D | $SO_2Ar$ | COOR | Ar |
| | | | $C\equiv CR$ |

[a] The groups are listed approximately in order of decreasing strength for both −*I* and +*I* groups. *Source:* Reproduced from Ceppi, E.; Eckhardt, W.; Grob, C.A. *Tetrahedron Lett.* ***1973***, 3627/with permission of Elsevier.

Thus, in (nitromethyl)benzene, the electrons in the N—C bond are distorted away from the carbon atom to a greater extent than the electrons in the H—C bond of toluene. Similarly, the electrons of the C—Ph bond are more distorted away from the ring in (nitromethyl)benzene than they are in toluene. Therefore, it may be said that, compared with hydrogen, the $NO_2$ group is electron-withdrawing. However, there is no actual donation or withdrawal of electrons but rather electron distortion or electron redistribution. While withdrawing and releasing terms are convenient to use, the terms merely represent a difference in the position of electrons due to inductive effects.

Table 1.2 lists several of the most common −*I* and +*I* groups.[58] It can be seen that compared with hydrogen, most groups are electron-withdrawing. The only electron-donating groups are those with a formal negative charge and atoms of low electronegativity such as Si,[59] Mg, etc., and perhaps the carbon of alkyl groups. Alkyl groups[60] were formerly regarded as electron-donating, but many examples have been found that can be interpreted only by assuming that alkyl groups are electron-withdrawing compared with hydrogen.[61] In accord with this is the value of 2.472 for the group electronegativity of $CH_3$ (Table 1.1) compared with 2.176 for H. This behavior is explained by noting that when an alkyl group is attached to an unsaturated or trivalent carbon (or other atom), its behavior is best explained by assuming it is +*I* (e.g., Secs. 5.Aii, 5.Bi, 8.E, and 11.Bi). Conversely, when it is connected to a saturated atom, the results are not as clear, and alkyl groups seem to be +*I* in some cases and −*I* in others[62] (see also Sec. 8.F). When connected to a positive carbon, alkyl groups are clearly electron-releasing.

The field-effect order of alkyl groups attached to unsaturated systems is tertiary > secondary > primary > $CH_3$, but this order is not always maintained when the groups are attached to saturated systems. Deuterium is electron-donating with respect to hydrogen.[63] Other things being equal, atoms with *sp* bonding generally have a greater electron-withdrawing power than those with $sp^2$ bonding, which in turn have more electron-withdrawing power than those with $sp^3$ bonding.[64] This observation accounts for the fact that aryl, vinylic, and alkynyl groups are −*I*. Field effects always decrease with increasing distance, and in most cases (except when a very powerful +*I* or −*I* group is involved) cause very little difference in a bond four bonds away or more. There is evidence that field effects can be affected by the solvent.[65]

For discussions of field effects on acid and base strength and on reactivity, see Chapters 8 and 9, respectively.

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[58] See also, Ceppi, E.; Eckhardt, W.; Grob, C.A. *Tetrahedron Lett.* ***1973***, 3627.

[59] For a review of field and other effects of silicon-containing groups, see Bassindale, A.R.; Taylor, P.G., in in Patai, S.; Rappoport, Z. *The Chemistry of Organic Silicon Compounds*, pt. 2, Wiley, NY, ***1989***, pp. 893–963.

[60] See Levitt, L.S.; Widing, H.F. *Prog. Phys. Org. Chem.* ***1976***, *12*, 119. See Tandon, R.; Tobias A. Nigst, T.A.; Zipse, H. *Eur. J. Org. Chem.* ***2013***, 5423.

[61] See Sebastian, J.F. *J. Chem. Educ.* ***1971***, *48*, 97.

[62] See Wahl, G.H. Jr.; Peterson, M.R. Jr. *J. Am. Chem. Soc.* ***1970***, *92*, 7238; Minot, C.; Eisenstein, O.; Hiberty, P.C.; Anh, N.T. *Bull. Soc. Chim. Fr.* ***1980***, II–119.

[63] Streitwieser, A. Jr.; Klein, H.S. *J. Am. Chem. Soc.* ***1963***, *85*, 2759.

[64] Bent, H.A. *Chem. Rev.* ***1961***, *61*(275), 281.

[65] See Laurence, C.; Berthelot, M.; Luçon, M.; Helbert, M.; Morris, D.G.; Gal, J. *J. Chem. Soc., Perkin Trans. 2* ***1984***, 705.

## 1.J. BOND DISTANCES[66]

**TABLE 1.3 Bond lengths between *sp*$^3$ carbons in some compounds[58]**

| C—C bond in | Ref. | Bond length, Å |
|---|---|---|
| Diamond | 67 | 1.544 |
| $C_2H_6$ | 68 | 1.5324 ± 0.0011 |
| $C_2H_5Cl$ | 69 | 1.5495 ± 0.0005 |
| $C_3H_8$ | 70 | 1.532 ± 0.003 |
| Cyclohexane | 71 | 1.540 ± 0.015 |
| *tert*-butyl chloride | 72 | 1.532 |
| *n*-butane to *n*-heptane | 73 | 1.531 – 1.534 |
| Isobutane | 74 | 1.535 ± 0.001 |

*Source:* Reproduced from Ceppi, E.; Eckhardt, W.; Grob, C.A. *Tetrahedron Lett.* ***1973***, 3627/with permission of Elsevier.

The bond distances, the distances between atoms, in a molecule are characteristic of the molecule and can give information if compared with the same bond in different molecules. The chief methods of determining bond distances and angles are X-ray diffraction for solids, electron diffraction for gases, and spectroscopic methods, especially microwave spectroscopy. The distance between the atoms of a bond is not constant, since the molecule is always vibrating; the measurements obtained are therefore average values, so that different methods give different results.[75] However, such differences must be considered only when fine distinctions are made.

Measurements vary in accuracy, but indications are that similar bonds have near-constant lengths from one molecule to the next. While exceptions are known,[76] the variation is generally less than 1%. Table 1.3 shows distances for single bonds between two *sp*$^3$ carbons. However, an analysis of C—OR bond distances in >2000 ethers and carboxylic esters (all with *sp*$^3$ carbon) shows that this distance increases with increasing electron withdrawal in the R group and as the C changes from primary to secondary to tertiary.[77] For these compounds, the mean bond lengths of the various types ranged from 1.418 to 1.475 Å. Certain substituents can also influence bond length. The presence of a silyl substituent β to a C—O (ester) linkage can lengthen the C—O, thereby weakening it.[78] This is believed to result from $\sigma$–$\sigma^*$ interactions in which the C—Si $\sigma$ bonding orbital acts as the donor and the C—O $\sigma^*$ orbital acts as the receptor.

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[66] For tables of bond distances and angles, see Allen, F.H.; Kennard, O.; Watson, D.G.; Brammer, L.; Orpen, A.G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* ***1987***, S1–S19 (follows p. 1914); Tables of Interatomic Distances and Configurations in Molecules and Ions *Chem. Soc. Spec. Publ.* No. 11, ***1958***; Interatomic Distances Supplement *Chem. Soc. Spec. Publ.* No. 18, ***1965***; See Topsom, R.D. *Prog. Phys. Org. Chem.* ***1987***, *16*, 85.

[67] Lonsdale, K. *Phil. Trans. R. Soc. London* ***1947***, *A240*, 219.

[68] Bartell, L.S.; Higginbotham, H.K. *J. Chem. Phys.* ***1965***, *42*, 851.

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[71] For tables of interatomic distances, see ref. 66.

[72] Momany, F.A.; Bonham, R.A.; Druelinger, M.L. *J. Am. Chem. Soc.* ***1963***, *85*, 3075. Also see, Lide, Jr., D.R.; Jen, M. *J. Chem. Phys.* ***1963***, *38*, 1504.

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

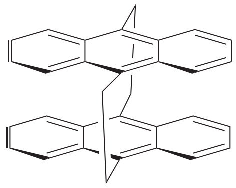
[74] Hilderbrandt, R.L.; Wieser, J.D. *J. Mol. Struct.* ***1973***, *15*, 27.

[75] Burkert, U.; Allinger, N.L. *Molecular Mechanics*. ACS Monograph 177, American Chemical Society, Washington, ***1982***, pp. 6–9; Whiffen, D.H. *Chem. Ber*. ***1971***, *7*, 57–61; Stals, J. *Rev. Pure Appl. Chem*. ***1970***, *20*, 1, pp. 2–5.

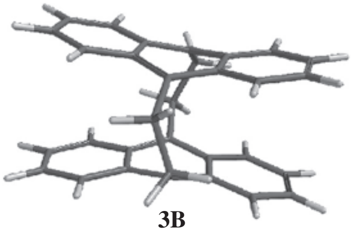
[76] Schleyer, P.v.R.; Bremer, M. *Angew. Chem. Int. Ed.* ***1989***, *28*, 1226.

[77] Allen, F.H.; Kirby, A.J. *J. Am. Chem. Soc.* ***1984***, *106*, 6197; Jones, P.G.; Kirby, A.J. *J. Am. Chem. Soc.* ***1984***, *106*, 6207.

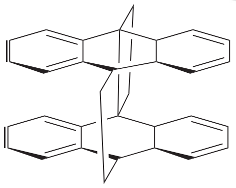
[78] White, J.M.; Robertson, G.B. *J. Org. Chem.* ***1992***, *57*, 4638.



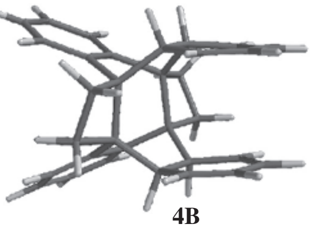
**3A**



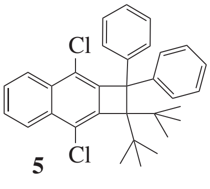
**3B**



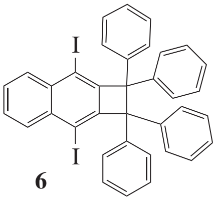
**4A**



**4B**



**5**



**6**

Bond distances for some important bond types are given in Table 1.4.[79] Although a typical C─C single bond has a bond length of ~1.54 Å, certain molecules are known that have significantly longer bond lengths.[80] Calculations have been done for unstable molecules that showed them to have long bond lengths, and an analysis of the X-ray structure for a photoisomer (**4A**) of [2.2]-tetrabenzoparacyclophane, **3A** (also see Sec. 2G), showed a C─C bond length of 1.77 Å (177 pm).[81,82] Note that **3A** is shown as the molecular model **3B** for comparison with photoisomer **4A** and its molecular model **4B**, which has the two four-membered ring moieties. Long bond lengths have been observed in stable molecules such as benzocyclobutane derivatives.[82] A bond length of 1.729 Å (172.9 pm) was reliably measured in 1,1-di-*tert*-butyl-2,2-diphenyl-3,8-dichlorocyclobutan[*b*]naphthalene, **5**.[83] X-ray analysis of several of these derivations confirmed the presence of long C─C bonds, with **6** having a confirmed bond length of 1.734 Å (173.4 pm).[84]

**TABLE 1.4 [79]Bond distances**

| Bond type[a] | | Length, Å (pm) | Typical compounds |
|---|---|---|---|
| **C─C** | | | |
| | $sp^3$–$sp^3$ | 1.53 (153) | |
| | $sp^3$–$sp^2$ | 1.51 (151) | Acetaldehyde, toluene, propene |
| | $sp^3$–$sp$ | 1.47 (147) | Acetonitrile, propyne |
| | $sp^2$–$sp^2$ | 1.48 (148) | Butadiene, glyoxal, biphenyl |
| | $sp^2$–$sp$ | 1.43 (143) | Acrylonitrile, vinylacetylene |
| | $sp$–$sp$ | 1.38 (138) | Cyanoacetylene, butadiyne |
| **C═C** | | | |
| | $sp^2$–$sp^2$ | 1.32 (132) | Ethylene |
| | $sp^2$–$sp$ | 1.31 (131) | Ketene, allenes |
| | $sp$–$sp$[85] | 1.28 (128) | Butatriene, carbon suboxide |

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[79] Except where noted, values are from Allen, F.H.; Kennard, O.; Watson, D.G.; Brammer, L.; Orpen, A.G.; Taylor, R. *J. Chem. Soc. Perkin Trans. 2* ***1987***, S1–S19 (follows p. 1914). In this source, values are given to three significant figures.

[80] Kaupp, G.; Boy, J. *Angew. Chem. Int. Ed.* ***1997***, *36*, 48. Also see Kuroda, Y.; Kobayashi, M.; Taketsugu, T. *Chem. Lett*. ***2019***, *48*, 137.

[81] Ehrenberg, M. *Acta Crystallogr.* ***1966***, *20*, 182.

[82] Toda, F.; Tanaka, K.; Stein, Z.; Goldberg, I. *Acta Crystallogr. Sect. C* ***1996***, *52*, 177.

[83] Toda, F.; Tanaka, K.; Watanabe, M.; Taura, K.; Miyahara, I.; Nakai, T.; Hirotsu, K. *J. Org. Chem.* ***1999***, *64*, 3102.

[84] Tanaka, K.; Takamoto, N.; Tezuka, Y.; Kato, M.; Toda, F. *Tetrahedron* ***2001***, *57*, 3761.

[85] Costain, C.C.; Stoicheff, B.P. *J. Chem. Phys.* ***1959***, *30*, 777.

**TABLE 1.4 (Continued)**

| Bond type[a] | | Length, Å (pm) | Typical compounds | |
|---|---|---|---|---|
| **C≡C**[86] | | | | |
| | *sp*–*sp* | 1.18 (118) | Acetylene | |
| **C—H**[87] | | | | |
| | $sp^3$–**H** | 1.09 (109) | Methane | |
| | $sp^2$–**H** | 1.08 (108) | Benzene, ethylene | |
| | *sp*–**H**[88] | 1.08 (108) | HCN, acetylene | |
| **C—O** | | | | |
| | $sp^3$–**O** | 1.43 (143) | Dimethyl ether, ethanol | |
| | $sp^2$–**O** | 1.34 (134) | Formic acid | |
| **C═O** | | | | |
| | $sp^2$–**O** | 1.21 (121) | Formaldehyde, formic acid | |
| | *sp*–**O**[72] | 1.16 (116) | $CO_2$ | |
| **C—N** | | | | |
| | $sp^3$–**N** | 1.47 (147) | Methylamine | |
| | $sp^2$–**N** | 1.38 (138) | Formamide | |
| **C═N** | | | | |
| | $sp^2$–**N** | 1.28 (128) | Oximes, imines | |
| **C≡N** | | | | |
| | *sp*–**N** | 1.14 (114) | HCN | |
| **C—S** | | | | |
| | $sp^3$–**S** | 1.82 (182) | Methanethiol | |
| | $sp^2$–**S** | 1.75 (175) | Diphenyl sulfide | |
| | *sp*–**S** | 1.68 (168) | $CH_3SCN$ | |
| **C═S** | | | | |
| | *sp*–**S** | 1.67 (167) | $CS_2$ | |
| **C–halogen**[89] | F | Cl | Br | I |
| $sp^3$–halogen | 1.40 (140) | 1.79 (179) | 1.97 (197) | 2.16 (216) |
| $sp^2$–halogen | 1.34 (134) | 1.73 (173) | 1.88 (188) | 2.10 (210) |
| *sp*–halogen | 1.27 (127)[90] | 1.63 (163) | 1.79 (179)[91] | 1.99 (199)[91] |

[a] The values given are average lengths and do not necessarily apply exactly to the compounds mentioned.[91]

*Source:* Reproduced from Allen, F.H.; Kennard, O.; Watson, D.G.; Brammer, L.; Orpen, A.G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* ***1987***, S1-S19/with permission of Royal Society of Chemistry.

A theoretical study has been reported, using computer simulation to apply encapsulation, strapping back, and stiffening to “squeeze” C—C bonds, leading to shorter bonds than would be observed if hybridization and conjugative effects operated alone.[92] The additional strain caused by threefold symmetric geometry constraints is believed to be responsible for this effect rather than changes in hybridization alone, as postulated by others.[93] There are indications that a C—D bond is slightly shorter than a corresponding C—H bond. Thus, electron-diffraction measurements of

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[86] For a full discussion of alkyne bond distances, see Simonetta, M.; Gavezzotti, A. in Patai, S. *The Chemistry of the Carbon–Carbon Triple Bond*, Wiley, NY, ***1978***.

[87] See Henry, B.R. *Acc. Chem. Res.* ***1987***, *20*, 429.

[88] Bartell, L.S.; Roth, E.A.; Hollowell, C.D.; Kuchitsu, K.; Young, J.E. Jr. *J. Chem. Phys.* ***1965***, *42*, 2683.

[89] For reviews of carbon–halogen bonds, see Trotter, J. in Patai, S. *The Chemistry of the Carbon–Halogen Bond*, pt. 1, Wiley, NY, ***1973***, pp. 49–62; Mikhailov, B.M. *Russ. Chem. Rev*. ***1971***, *40*, 983.

[90] Lide, D.R. Jr. *Tetrahedron* ***1962***, *17*, 125.

[91] Rajput, A.S.; Chandra, S. *Bull. Chem. Soc. Jpn.* ***1966***, *39*, 1854.

[92] Huntley, D.R.; Markopoulos, G.; Donovan, P.M.; Scott, L.T.; Hoffmann, R. *Angew. Chem. Int. Ed.* ***2005***, *44*, 7549.

[93] See Tanaka, M.; Sekiguchi, A. *Angew. Chem. Int. Ed.* ***2005***, *44*, 5821.

$C_2H_6$ and $C_2D_6$ showed a C—H bond distance of 1.1122 ± 0.0012 Å (111.22 pm) and a C—D distance of 1.1071 ± 0.0012 Å (110.71 pm).[88]

As seen in Table 1.4, carbon bonds are shortened by increasing *s* character. This is most often explained by the fact that, as the percentage of *s* character in a hybrid orbital increases, the orbital becomes more like an *s* orbital. The orbital is therefore held more tightly by the nucleus than an orbital with less *s* character. However, other explanations have also been offered (Sec. 2.C), and the matter is not completely settled. In general, molecules with one π bond (X═X) have shorter bond distances when compared to single bonds, X—X, and molecules with two π bonds (X≡X) have even shorter bond lengths. Indeed, the bond length clearly decreases in the molecules $H_3C$—$CH_3$, $H_2C$═$CH_2$, and HC≡CH: C—C bond lengths of 1.538 Å, 1.338 Å, and 1.203 Å (153.8, 133.8, and 102.3 pm).[94] There is work that suggests the absence of σ bonds may play a role in producing short bond distances in molecules that contain only π bonds.[95] This suggests that σ bonds prevent π bonds from adopting their optimal shorter distances. Such bonds occur in some organometallic compounds. Bicklehaupt and coworkers[96] reported that the chemical bonding analysis based on the Kohn–Sham molecular orbital theory is incorrect. The C—H bond length decreases from ethane ($R_3C$—H, 1.099 Å) to ethene ($R_2C$—H, 1.091 Å) to ethyne (RC—H, 1.070 Å), and the corresponding C—C single bond lengths decrease along propane ($R_3C$—$CH_3$, 1.533 Å), propene ($R_2C$—$CH_3$, 1.500 Å), and propyne (RC—$CH_3$, 1.456 Å). This is not determined by an increasing amount of *s* character at the carbon atom.[96] It is caused by a diminishing steric (Pauli) repulsion between substituents around the pertinent carbon atom, which leads to a coordination number decrease from $sp^3$ to $sp^2$ to *sp*.[96]

## 1.K. BOND ANGLES

The bond angles of $sp^3$ carbon should be the tetrahedral angle 109°28′ when the four atoms or groups are relatively small and identical, as in methane or carbon tetrachloride (Sec. 1.E). As atoms or groups become larger, bond angles are distorted to accommodate the larger size of the attached units. In most cases the angles deviate a little from the pure tetrahedral value unless two or more units are very large. Examination of methane, bromomethane, and dibromomethane illustrates this phenomenon. The H—C—H bond angles in methane are calculated to be 109°47′, whereas the Br—C—H bond angle in bromomethane is calculated to be 108.08° and the Br—C—Br bond angle in dibromomethane is calculated to be 113.38°. Note that the C—Br bond length is longer than the C—H bond lengths. As the bond angles expand to accommodate the larger atoms, the H—C—H bond angles in bromomethane and dibromomethane must compress to a smaller angle. In 2-bromopropane, the bromine atom also has a methyl group and, the C—C—Br angle in 2-bromopropane is 114.2°.[97]

Variations are generally found from the ideal values of 120° and 180° for $sp^2$ and *sp* carbon, respectively. These deviations occur because of slightly different hybridizations. The four hybrid orbitals formed in a carbon bonded to four other atoms, for example, are generally not exactly equivalent. If each of the four atoms have different electronegativities, each makes its own demand for electrons from the carbon atom.[98] The carbon atom supplies more *p* character when it is bonded to more electronegative atoms, so that in chloromethane, for example, the bond to chlorine has somewhat more than 75% *p* character, which of course requires that the other three bonds have somewhat less, since there are only three *p* orbitals (and one *s*) to be divided among the four hybrid orbitals.[99] Of course, in strained molecules, the bond angles may be greatly distorted from the ideal values (also see Sec. 4.Q).

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[94] Vannes, G.J.H.; Vos, A. *Acta Crystallogr. Sect. B* ***1978***, *B34*, 1947; Vannes, G.J.H.; Vos, A. *Acta Crystallogr. Sect. B*, ***1979***, *B35*, 2593; McMullan, R.K.; Kvick, A. *Acta Crystallogr. Sect. B* ***1992***, *B48*, 726.

[95] Jemmis, E.D.; Pathak, B.; King, R.B.; Schaefer, H.F. III *Chem. Commun.* ***2006***, 2164.

[96] Vermeeren, P.; van Zeist, W.-J.; Hamlin, T.A.; Guerra, C.F.; Bickelhaupt, F.M. *Chem. Eur. J.* ***2021***, *27*, 7074.

[97] Schwendeman, R.H.; Tobiason, F.L. *J. Chem. Phys.* ***1965***, *43*, 201.

[98] For a review of this concept, see Bingel, W.A.; Lüttke, W. *Angew. Chem. Int. Ed.* ***1981***, *20*, 899.

[99] This assumption has been challenged: see Pomerantz, M.; Liebman, J.F. *Tetrahedron Lett.* ***1975***, 2385.

It is important to note that many covalent compounds have definite bond angles. For water, the observed bond angles are 104°27′.[100] For alcohols and ethers the angles are even larger (Sec. 1.K). The bond angles in ammonia, for example, are 106°46′.[100] Although the atoms are continuously vibrating, the mean position is the same for each molecule of a given compound.

The angles of water and ammonia are close to the tetrahedral angle of 109°28′, suggesting that oxygen and nitrogen use $sp^3$ bonding. However, it is commonly accepted that the hybridization is not pure $sp^3$. There is a slight deviation in the bond angles that can be explained by the presence of the unshared electron pair(s), which has a greater steric requirement (Sec. 4.Q) than the electrons in a bond, since there is no second nucleus to draw away some of the electron density and the bonds are thus crowded together. Indeed, most evidence is that unshared pairs have smaller steric requirements than bonds[101] and the unshared pairs have more *s* and the bonds more *p* character than pure $sp^3$ orbitals, making the bonds somewhat more like $p^2$ bonds and reducing the angle. However, these arguments ignore the steric effect of the atoms or groups attached to oxygen or nitrogen. As seen in Table 1.5, oxygen, nitrogen, and sulfur angles generally increase with decreasing electronegativity of the substituents. Note that the explanation given above cannot explain why some of these angles are *greater* than the tetrahedral angle.

**TABLE 1.5 Oxygen, sulfur, and nitrogen bond angles in some compounds[79]**

| Angle | Value | Compound | Ref. |
|---|---|---|---|
| **H—O—H** | 104°27′ | Water | 102 |
| **C—O—H** | 107–109° | Methanol | 71 |
| **C—O—C** | 111°43′ | Dimethyl ether | 103 |
| **C—O—C** | 124 ± 5° | Diphenyl ether | 104 |
| **H—S—H** | 92.1° | Hydrogen sulfide | 91 |
| **C—S—H** | 99.4° | Methanethiol | 91 |
| **C—S—C** | 99.1° | Dimethyl sulfide | 105 |
| **H—N—H** | 106°46′ | Ammonia | 102 |
| **H—N—H** | 106° | Methylamine | 106 |
| **C—N—H** | 112° | Methylamine | 94 |
| **C—N—C** | 108.7° | Trimethylamine | 107 |

*Source:* Adapted from Allen, F.H.; Kennard, O.; Watson, D.G.; Brammer, L.; Orpen, A.G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* ***1987***, S1-S19 (follows p. 1914).

## 1.L. BOND ENERGIES[108]

There are two kinds of bond energy. The energy necessary to cleave a bond to give the constituent radicals is called the *dissociation energy, D*.[109] For example, *D* for $H_2O \rightarrow HO + H$ is 118 kcal mol$^{-1}$ (494 kJ mol$^{-1}$). However, this is not

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[100] Bent, H.A. *Chem. Rev.* ***1961***, *61*, 275, see p. 277.

[101] See Blackburne, I.D.; Katritzky, A.R.; Takeuchi, Y. *Acc. Chem. Res.* ***1975***, *8*, 300; Vierhapper, F.W.; Eliel, E.L. *J. Org. Chem.* ***1979***, *44*, 1081; Gust, D.; Fagan, M.W. *J. Org. Chem.* ***1980***, *45*, 2511. For other views, see Lambert, J.B.; Featherman, S.I. *Chem. Rev*. ***1975***, *75*, 611; Breuker, K.; Kos, N.J.; van der Plas, H.C.; van Veldhuizen, B. *J. Org. Chem.* ***1982***, *47*, 963.

[102] Bent, H.A. *Chem. Rev.* ***1961***, *61*(275), 277.

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[105] Iijima, T.; Tsuchiya, S.; Kimura, M. *Bull. Chem. Soc. Jpn.* ***1977***, *50*, 2564.

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[108] Blanksby, S.J.; Ellison, G.B. *Acc. Chem. Res.* ***2003***, *36*, 255; For reviews including methods of determination, see Wayner, D.D.M.; Griller, D. *Adv. Free Radical Chem. (Greenwich, Conn.)* ***1990***, *1*, 159; Kerr, J.A. *Chem. Rev*. ***1966***, *66*, 465.

[109] For a study of predissociation bond dissociation energies, see Morse, M.D. *Acc. Chem. Res.* ***2019***, *52*(1), 119.

taken as the energy of the O—H bond in water, since *D* for H—O → H + O is 100 kcal mol$^{-1}$ (418 kJ mol$^{-1}$). The average of these two values, 109 kcal mol$^{-1}$ (456 kJ mol$^{-1}$), is taken as the *bond energy, E*. In diatomic molecules, of course, *D* = *E*.

The *D* values may be easy or difficult to measure, and they can be estimated by various techniques.[110] When properly applied, "Pauling's original electronegativity equation accurately describes homolytic bond dissociation enthalpies of common covalent bonds, including highly polar ones, with an average deviation of (1.5 kcal mol$^{-1}$ [≈6.3 kJ mol$^{-1}$] from literature values)."[111] Whether measured or calculated, there is no question as to what *D* values mean. With *E* values the matter is not so simple. For methane, the total energy of conversion from $CH_4$ to C + 4H (at 0 K) is 393 kcal mol$^{-1}$ (1644 kJ mol$^{-1}$).[112] Consequently, *E* for the C—H bond in methane is 98 kcal mol$^{-1}$ (411 kJ mol$^{-1}$) at 0 K. The more usual practice is not to measure the heat of atomization, which is the energy necessary to convert a compound to its atoms, directly but to calculate it from the heat of combustion. Such a calculation is shown in Figure 1.10.

Heats of combustion are very accurately known for hydrocarbons.[113] For methane the value at 25 °C is 212.8 kcal mol$^{-1}$ (890.4 kJ mol$^{-1}$), which leads to a heat of atomization of 398.0 kcal mol$^{-1}$ (1665 kJ mol$^{-1}$) or a value of *E* for the C—H bond at 25 °C of 99.5 kcal mol$^{-1}$ (416 kJ mol$^{-1}$). This method is fine for molecules like methane in which all the bonds are equivalent, but for more complicated molecules assumptions must be made. Thus, for ethane the heat of atomization at 25 °C is 676.1 kcal mol$^{-1}$ or 2829 kJ mol$^{-1}$ (Figure 1.10), but it must be decided how much of this energy is due to the C—C bond and how much to the six C—H bonds. Since there is no way of obtaining this information, an assumption must be made. If the assumption is made that *E* for each of the C—H bonds is the same as *E* for the C—H bond in methane (99.5 kcal mol$^{-1}$ or 416 kJ mol$^{-1}$), then 6×99.5 (or 416) = 597.0 (or 2498), leaving 79.1 kcal mol$^{-1}$ (331 kJ mol$^{-1}$) for the C—C bond. However, a similar calculation for propane gives a value of 80.3 (or 336) for the C—C bond, and for isobutane, the value is 81.6 (or 341). A consideration of heats of atomization of isomers also illustrates the difficulty. The *E* values for the C—C bonds in pentane, isopentane, and neopentane, similarly calculated from heats of atomization, are (at 25 °C) 81.1, 81.8, and 82.4 kcal mol$^{-1}$ (339, 342, and 345 kJ mol$^{-1}$), respectively, even though all of them have 12 C—H bonds and four C—C bonds. The bond dissociation enthalpies for bridgehead C—H bonds has been determined.[114] The allylic C—H bond dissociation energy of cyclopropene was measured to be 104.4 kcal mol$^{-1}$ (435 kJ mol$^{-1}$), and there is evidence that the radical is nonaromatic.[115]

|  |  |  |  |  | **kcal** | **kJ** |
|---|---|---|---|---|---|---|
| $C_2H_{6\,(gas)}$ | $+ 3.5\ O_2$ | = | $2\ CO_{2\,(gas)}$ | $+\ 3\ H_2O_{(liq)}$ | +372.9 | +1560 |
|  | $2\ CO_{2\,(gas)}$ | = | $2\ C_{(graphite)}$ | $+\ 2\ O_{2\,(gas)}$ | –188.2 | –787 |
|  | $3\ H_2O_{(liq)}$ | = | $3\ H_{2\,(gas)}$ | $+\ 1.5\ O_{2\,(gas)}$ | –204.9 | –857 |
|  | $3\ H_{2\,(gas)}$ | = | $6\ H_{(gas)}$ |  | –312/5 | –1308 |
|  | $2\ C_{(graphite)}$ | = | $2\ C_{(gas)}$ |  | –343.4 | –1437 |
|  | $C_2H_{6\,(gas)}$ | = | $6\ H_{(gas)}$ | $+\ 2\ C_{(gas)}$ | –676.1 kcal | –2829 kJ |

**FIGURE 1.10.** Calculation of the heat of atomization of ethane at 25 °C.

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[110] Cohen, N.; Benson, S.W. *Chem. Rev.* ***1993***, *93*, 2419; Korth, H.-G.; Sicking, W. *J. Chem. Soc., Perkin Trans. 2* ***1997***, 715.

[111] Matsunaga, N.; Rogers, D.W.; Zavitsas, A.A. *J. Org. Chem.* ***2003***, *68*, 3158.

[112] For the four steps, *D* values are 101 to 102, 88, 124, and 80 kcal mol$^{-1}$ (423–427, 368, 519, and 335 kJ mol$^{-1}$), respectively, though the middle values are much less reliable than the other two: Knox, B.E.; Palmer, H.B. *Chem. Rev.* ***1961***, *61*, 247; Brewer, R.G.; Kester, F.L. *J. Chem. Phys*. ***1964***, *40*, 812; Linevsky, M.J. *J. Chem. Phys*. ***1967***, *47*, 3485.

[113] See Cox, J.D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*, Academic Press, NY, ***1970***, Domalski, E.S. *J. Phys. Chem. Ref. Data* ***1972***, *1*, 221–277; Stull, D.R.; Westrum Jr., E.F.; Sinke, G.C. *The Chemical Thermodynamics of Organic Compounds*, Wiley, NY, ***1969***.

[114] Fattahi, A.; Lis, L.; Tehrani, Z.A.; Marimanikkuppam, S.S.; Kass, S.R. *J. Org. Chem.* ***2012***, *77*, 1909.

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These differences have been attributed to various factors caused by the introduction of new structural features. Thus isopentane (2-methylbutane) has a tertiary carbon whose C—H bond does not have exactly the same amount of *s* character as the C—H bond in pentane, which for that matter contains secondary carbons not possessed by methane. It is known that *D* values, which *can* be measured, are not the same for primary, secondary, and tertiary C—H bonds (see Table 5.2). There is also the steric factor (Sec. 4.Q). Hence it is certainly incorrect to use the value of 99.5 kcal mol$^{-1}$ (416 kJ mol$^{-1}$) from methane as the *E* value for all C—H bonds. Several empirical equations have been devised that account for these factors; the total energy can be computed[116] if the proper set of parameters (one for each structural feature) is inserted. Of course, these parameters are originally calculated from the known total energies of some molecules that contain the structural feature.

The literature contains charts that take hybridization into account so a $sp^3$ C—H bond does not have the same energy as a $sp^2$ C—H bond.[117] Bond dissociation energies, both calculated and experientially determined, are constantly being refined. Improved values are available for the O—O bond of peroxides,[118] the C—H bond in alkyl amines,[119] the N—H bond in aniline derivatives,[120] the N—H bond in protonated amines,[121] the O—H bond in phenols,[122] the C—H bond in alkenes,[123] amides, and ketones,[124] and in $CH_2X_2$ and $CH_3X$ derivatives (X = COOR, C=O, SR, $NO_2$, etc.),[125] the O—H and S—H bonds of alcohols and thiols,[126] and the C—Si bond of aromatic silanes.[127] Solvent plays a role in the *E* values. When phenols bearing electron-releasing groups are in aqueous media, calculations show that the bond dissociation energies decrease due to hydrogen-bonding interactions with water molecules, while electron-withdrawing substituents on the phenol increase the bond dissociation energies.[128] The bond dissociation energy of 1-phenylcyclopropane was determined to be 93.0 kcal mol$^{-1}$ (389.1 kJ mol$^{-1}$).[129]

Certain generalizations can be derived from bond energy data.

1. There is a correlation of bond strengths with bond distances. In general, *shorter bonds are stronger bonds*. Since it is known that increasing *s* character shortens bonds (Sec. 1.J), it follows that bond strengths increase with increasing *s* character. Calculations show that ring strain has a significant effect on bond dissociation energy, particularly the C—H bond of hydrocarbons, because it forces the compound to adopt an undesirable hybridization.[130]
2. Bonds to atoms moving down the periodic table become weaker. Compare C—O and C—S, or the carbon–halogen bonds C—F, C—Cl, C—Br, and C—I. This is a consequence of the first generalization, since bond distances must increase going down the periodic table because the number of inner electrons increases. However, it is noted that "high-level *ab initio* molecular orbital calculations confirm that the effect of alkyl substituents on R—X bond dissociation energies varies according to the nature of X (the stabilizing influence

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[116] For a review, see Cox, J.D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*, Academic Press, NY, ***1970***, pp. 531–597. See also, Gasteiger, J.; Jacob, P.; Strauss, U. *Tetrahedron* ***1979***, *35*, 139.

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of the ionic configurations to increase in the order Me < Et < *i*-Pr < *t*-Bu), accounting for the *increase* (rather than expected decrease) in the R—X bond dissociation energies with increasing alkylation in the R—$OCH_3$, R—OH, and R—F molecules. This effect of X has been explained in terms of the increasing contribution of the ionic $R^+X^-$ configuration for electronegative X substituents."[131]

3. Double bonds are both shorter and stronger than the corresponding single bonds, but not twice as strong, because π overlap is less than σ overlap. This means that a σ bond is stronger than a π bond. The difference in energy between a single bond, say C—C, and the corresponding double bond is the amount of energy necessary to cause rotation around the double bond.[132]

Calculations suggest that covalent bond strength and equilibrium bond length are not determined by maximum overlap of the σ valence orbitals, as described in previous sections.[133] Rather, orbital interactions, Pauli repulsion, and quasiclassical electrostatic attraction determine both.

Solvents are thought to play a role in the bond dissociation energy of molecules, as noted for phenol above, and also for intermediates (see Chapter 5). It has been assumed that the solvation enthalpies were small and they have been largely ignored in calculations involving various reactions. Solvent effects on the bond dissociation energy of a molecule may arise from the difference in solvation enthalpies between the molecule and the key intermediate. For radical reactions that involve polar molecules, the radical–solvent interaction may be larger.[134]

The relation of energy and bond length has been discussed.[135] It is noted that the bond energy of the C—S bond[136] is 61 kcal $mol^{-1}$ (255 kJ $mol^{-1}$), that of the C—N bond[137] is 69–75 kcal $mol^{-1}$ (290–315 kJ $mol^{-1}$), and a reported value for the O—O bond[138] is 42.9 kcal $mol^{-1}$ (179.6 ± 4.5 kJ $mol^{-1}$).

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