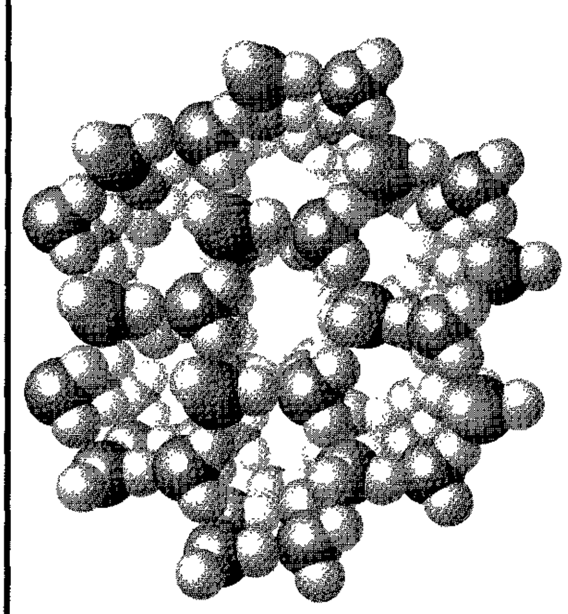

CHAPTER 3

Simple Bonding Theory

We now turn from the use of quantum mechanics and its description of the atom to an elementary description of molecules. Although most of the discussion of bonding in this book uses the molecular orbital approach to chemical bonding, simpler methods that provide approximate pictures of the overall shapes and polarities of molecules are also very useful. This chapter provides an overview of Lewis dot structures, valence shell electron pair repulsion (VSEPR), and related topics. The molecular orbital descriptions of some of the same molecules are presented in Chapter 5 and later chapters, but the ideas of this chapter provide a starting point for that more modern treatment. General chemistry texts include discussions of most of these topics; this chapter provides a review for those who have not used them recently.

Ultimately, any description of bonding must be consistent with experimental data on bond lengths, bond angles, and bond strengths. Angles and distances are most frequently determined by diffraction (X-ray crystallography, electron diffraction, neutron diffraction) or spectroscopic (microwave, infrared) methods. For many molecules, there is general agreement on the bonding, although there are alternative ways to describe it. For some others, there is considerable difference of opinion on the best way to describe the bonding. In this chapter and Chapter 5, we describe some useful qualitative approaches, including some of the opposing views.

3-1 LEWIS ELECTRON-DOT DIAGRAMS

Lewis electron-dot diagrams, although very much oversimplified, provide a good starting point for analyzing the bonding in molecules. Credit for their initial use goes to G. N. Lewis,[1] an American chemist who contributed much to thermodynamics and chemical bonding in the early years of the 20th century. In Lewis diagrams, bonds between two atoms exist when they share one or more pairs of electrons. In addition, some molecules have nonbonding pairs (also called lone pairs) of electrons on atoms.

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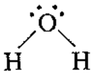
[1] G. N. Lewis, *J. Am. Chem. Soc.*, **1916**, *38*, 762; *Valence and the Structure of Atoms and Molecules*, Chemical Catalogue Co., New York, 1923.

These electrons contribute to the shape and reactivity of the molecule, but do not directly bond the atoms together. Most Lewis structures are based on the concept that eight **valence electrons** (corresponding to *s* and *p* electrons outside the noble gas core) form a particularly stable arrangement, as in the noble gases with s^2p^6 configurations. An exception is hydrogen, which is stable with two valence electrons. Also, some molecules require more than eight electrons around a given central atom.

A more detailed approach to electron-dot diagrams is presented in Appendix D.

Simple molecules such as water follow the **octet rule**, in which eight electrons surround the oxygen atom. The hydrogen atoms share two electrons each with the oxygen, forming the familiar picture with two bonds and two lone pairs:



Shared electrons are considered to contribute to the electron requirements of both atoms involved; thus, the electron pairs shared by H and O in the water molecule are counted toward both the 8-electron requirement of oxygen and the 2-electron requirement of hydrogen.

Some bonds are double bonds, containing four electrons, or triple bonds, containing six electrons:

$$:\ddot{O}=C=\ddot{O}: \qquad H-C\equiv C-H$$

3-1-1 RESONANCE

In many molecules, the choice of which atoms are connected by multiple bonds is arbitrary. When several choices exist, all of them should be drawn. For example, as shown in Figure 3-1, three drawings (resonance structures) of CO_3^{2-} are needed to show the double bond in each of the three possible C—O positions. In fact, experimental evidence shows that all the C—O bonds are identical, with bond lengths (129 pm) between double-bond and single-bond distances (116 pm and 143 pm respectively); none of the drawings alone is adequate to describe the molecular structure, which is a combination of all three, not an equilibrium between them. This is called **resonance** to signify that there is more than one possible way in which the valence electrons can be placed in a Lewis structure. Note that in resonance structures, such as those shown for CO_3^{2-} in Figure 3-1, the electrons are drawn in different places but the atomic nuclei remain in fixed positions.

The species CO_3^{2-}, NO_3^-, and SO_3, are **isoelectronic** (have the same electronic structure). Their Lewis diagrams are identical, except for the identity of the central atom.

When a molecule has several resonance structures, its overall electronic energy is lowered, making it more stable. Just as the energy levels of a particle in a box are lowered by making the box larger, the electronic energy levels of the bonding electrons are lowered when the electrons can occupy a larger space. The molecular orbital description of this effect is presented in Chapter 5.

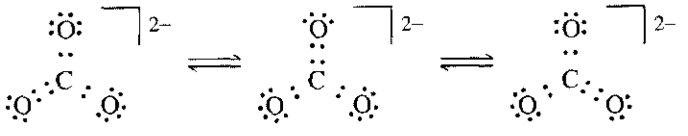


FIGURE 3-1 Lewis Diagrams for CO_3^{2-}.

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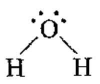

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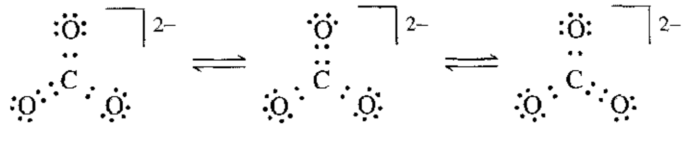


FIGURE 3-1 Lewis Diagrams for CO_3^{2-}.

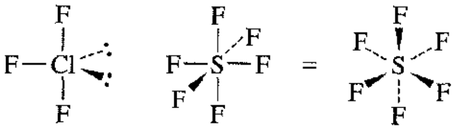


FIGURE 3-2 Structures of ClF_3 and SF_6.

3-1-2 EXPANDED SHELLS

When it is impossible to draw a structure consistent with the octet rule, it is necessary to increase the number of electrons around the central atom. An option limited to elements of the third and higher periods is to use *d* orbitals for this expansion, although more recent theoretical work suggests that expansion beyond the *s* and *p* orbitals is unnecessary for most main group molecules.[2] In most cases, two or four added electrons will complete the bonding, but more can be added if necessary. Ten electrons are required around chlorine in ClF_3 and 12 around sulfur in SF_6 (Figure 3-2). The increased number of electrons is described as an expanded shell or an expanded electron count.

There are examples with even more electrons around the central atom, such as IF_7 (14 electrons), $[TaF_8]^{3-}$ (16 electrons), and $[XeF_8]^{2-}$ (18 electrons). There are rarely more than 18 electrons (2 for *s*, 6 for *p*, and 10 for *d* orbitals) around a single atom in the top half of the periodic table, and crowding of the outer atoms usually keeps the number below this, even for the much heavier atoms with *f* orbitals energetically available.

3-1-3 FORMAL CHARGE

Formal charges can be used to help in the assessment of resonance structures and molecular topology. The use of formal charges is presented here as a simplified method of describing structures, just as the Bohr atom is a simple method of describing electronic configurations in atoms. Both of these methods are incomplete and newer approaches are more accurate, but they can be useful as long as their limitations are kept in mind.

Formal charges can help in assigning bonding when there are several possibilities. This can eliminate the least likely forms when we are considering resonance structures and, in some cases, suggests multiple bonds beyond those required by the octet rule. It is essential, however, to remember that formal charge is only a tool for assessing Lewis structures, not a measure of any actual charge on the atoms.

Formal charge is the apparent electronic charge of each atom in a molecule, based on the electron-dot structure. The number of valence electrons available in a free atom of an element minus the total for that atom in the molecule (determined by counting lone pairs as two electrons and bonding pairs as one assigned to each atom) is the formal charge on the atom:

$$\text{Formal charge} = \begin{pmatrix}\text{number of valence}\\ \text{electrons in a free}\\ \text{atom of the element}\end{pmatrix} - \begin{pmatrix}\text{number of unshared}\\ \text{electrons on the atom}\end{pmatrix} - \begin{pmatrix}\text{number of bonds}\\ \text{to the atom}\end{pmatrix}$$

In addition,

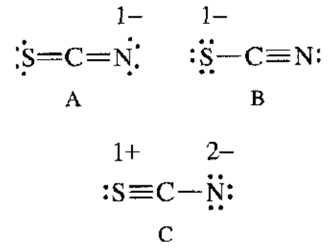
$$\text{Charge on the molecule or ion} = \text{sum of all the formal charges}$$

---

[2] L. Suidan, J. K. Badenhoop, E. D. Glendening, and F. Weinhold, *J. Chem. Educ.*, **1995**, *72*, 583; J. Cioslowski and S. T. Mixon, *Inorg. Chem.*, **1993**, *32*, 3209; E. Magnusson, *J. Am. Chem. Soc.*, **1990**, *112*, 7940.

Structures minimizing formal charges, placing negative formal charges on more electronegative (in the upper right-hand part of the periodic table) elements, and with smaller separation of charges tend to be favored. Examples of formal charge calculations are given in Appendix D for those who need more review. Three examples, SCN^-, OCN^-, and CNO^-, will illustrate the use of formal charges in describing electronic structures.

EXAMPLES



$$\underset{A}{:\ddot{S}=C=\overset{1-}{\ddot{N}}:} \qquad \underset{B}{:\overset{1-}{\ddot{S}}-C\equiv N:} \qquad \underset{C}{:\overset{1+}{S}\equiv C-\overset{2-}{\ddot{N}}:}$$

FIGURE 3-3 Resonance Structures of Thiocyanate, SCN^-.

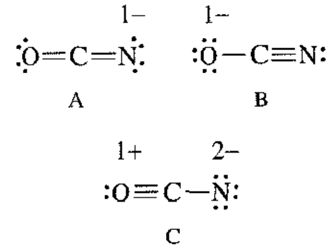
SCN^- In the thiocyanate ion, SCN^-, three resonance structures are consistent with the electron-dot method, as shown in Figure 3-3. Structure A has only one negative formal charge on the nitrogen atom, the most electronegative atom in the ion, and fits the rules well. Structure B has a single negative charge on the S, which is less electronegative than N. Structure C has charges of 2− on N and 1+ on S, consistent with the relative electronegativities of the atoms but with a larger charge and greater charge separation than the first. Therefore, these structures lead to the prediction that structure A is most important, structure B is next in importance, and any contribution from C is minor.

The bond lengths in Table 3-1 are consistent with this conclusion, with bond lengths between those of structures A and B. Protonation of the ion forms HNCS, consistent with a negative charge on N in SCN^-. The bond lengths in HNCS are those of double bonds, consistent with the structure H—N=C=S.

TABLE 3-1
Table of S—C and C—N Bond Lengths (pm)

	S—C	C—N
SCN^-	165	117
HNCS	156	122
Single bond	181	147
Double bond	155	128 (approximate)
Triple bond		116

SOURCE: A. F. Wells, *Structural Inorganic Chemistry*, 5th ed., Oxford University Press, New York, 1984, pp. 807, 926, 934–936.



$$\underset{A}{:\ddot{O}=C=\overset{1-}{\ddot{N}}:} \qquad \underset{B}{:\overset{1-}{\ddot{O}}-C\equiv N:} \qquad \underset{C}{:\overset{1+}{O}\equiv C-\overset{2-}{\ddot{N}}:}$$

FIGURE 3-4 Resonance Structures of Cyanate, OCN^-.

OCN^- The isoelectronic cyanate ion, OCN^- (Figure 3-4), has the same possibilities, but the larger electronegativity of O makes structure B more important than in thiocyanate. The protonated form contains 97% HNCO and 3% HOCN, consistent with structure A and a small contribution from B. The bond lengths in OCN^- and HNCO in Table 3-2 are consistent with this picture, but do not agree perfectly.

TABLE 3-2
Table of O—C and C—N Bond Lengths (pm)

	O—C	C—N
OCN^-	113	121
HNCO	118	120
Single bond	143	147
Double bond	119	128 (approximate)
Triple bond	113	116

SOURCE: A. F. Wells, *Structural Inorganic Chemistry*, 5th ed., Oxford University Press, New York, 1984, pp. 807, 926, 933–934; R. J. Gillespie and P. L. A. Popelier, *Chemical Bonding and Molecular Geometry*, Oxford University Press, New York, 2001, p. 117.

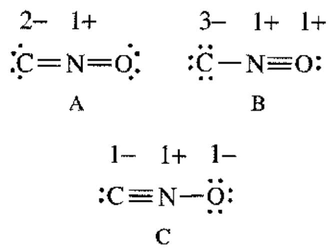


FIGURE 3-5 Resonance Structures of Fulminate, CNO^-.

CNO^- The isomeric fulminate ion, CNO^- (Figure 3-5), can be drawn with three similar structures, but the resulting formal charges are unlikely. Because the order of electronegativities is $C < N < O$, none of these are plausible structures and the ion is predicted to be unstable. The only common fulminate salts are of mercury and silver; both are explosive. Fulminic acid is linear HCNO in the vapor phase, consistent with structure C, and coordination complexes of CNO^- with many transition metal ions are known with MCNO structures.[3]

EXERCISE 3-1

Use electron-dot diagrams and formal charges to find the bond order for each bond in POF_3, SOF_4, and SO_3F^-.

Some molecules have satisfactory electron-dot structures with octets, but have better structures with expanded shells when formal charges are considered. In each of the cases in Figure 3-6, the observed structures are consistent with expanded shells on the central atom and with the resonance structure that uses multiple bonds to minimize formal charges. The multiple bonds may also influence the shapes of the molecules.

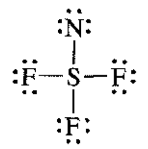
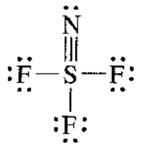
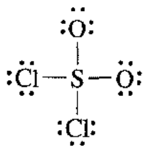
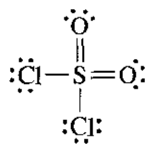
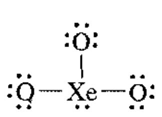
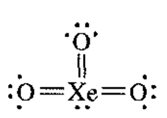
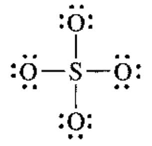
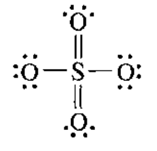
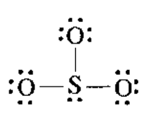
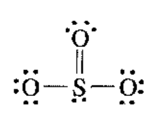
	Octet			*Expanded*			
Molecule		*Atom*	*Formal Charge*		*Atom*	*Formal Charge*	*Expanded to:*
SNF_3		S N	2+ 2−		S N	0 0	12
SO_2Cl_2		S O	2+ 1−		S O	0 0	12
XeO_3		Xe O	3+ 1−		Xe O	0 0	14
SO_4^{2-}		S O	2+ 1−		S O	0 0,1−	12
SO_3^{2-}		S O	1+ 1−		S O	0 0,1−	10

FIGURE 3-6 Formal Charge and Expanded Shells.

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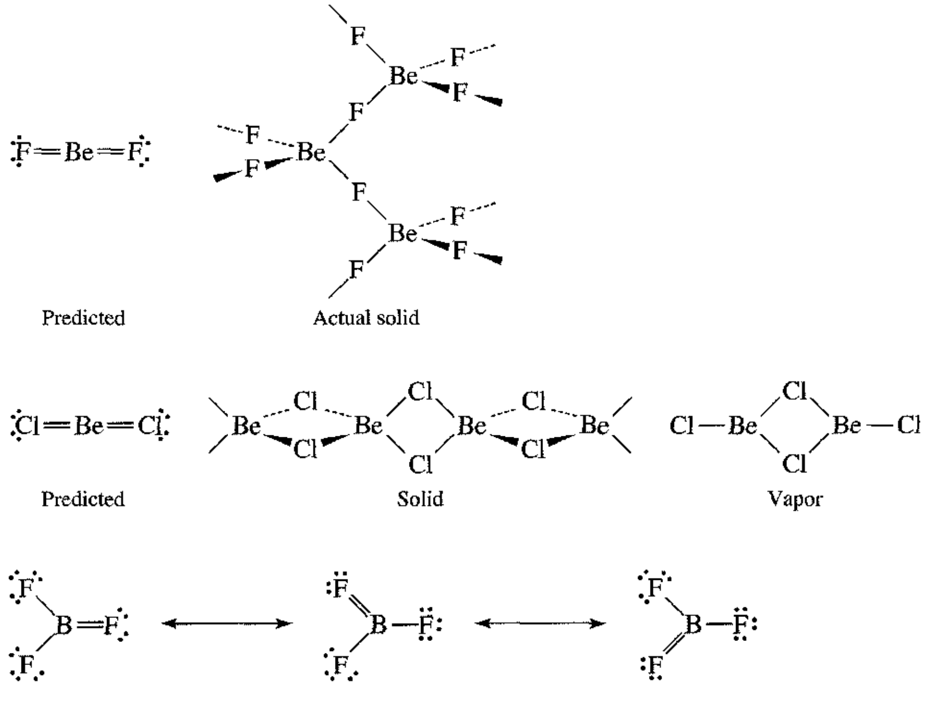
[3] A. G. Sharpe, "Cyanides and Fulminates," in *Comprehensive Coordination Chemistry*, G. Wilkinson, R. D. Gillard, and J. S. McCleverty, eds., Pergamon Press, New York, 1987, Vol. 2, pp. 12–14.

3-1-4 MULTIPLE BONDS IN Be AND B COMPOUNDS

A few molecules, such as BeF_2, $BeCl_2$, and BF_3, seem to require multiple bonds to satisfy the octet rule for Be and B, even though we do not usually expect multiple bonds for fluorine and chlorine. Structures minimizing formal charges for these molecules have only four electrons in the valence shell of Be and six electrons in the valence shell of B, in both cases less than the usual octet. The alternative, requiring eight electrons on the central atom, predicts multiple bonds, with BeF_2 analogous to CO_2 and BF_3 analogous to SO_3 (Figure 3-7). These structures, however, result in formal charges ($2-$ on Be and $1+$ on F in BeF_2, and $1-$ on B and $1+$ on the double-bonded F in BF_3), which are unlikely by the usual rules.

It has not been experimentally determined whether the bond lengths in BeF_2 and $BeCl_2$ are those of double bonds, because molecules with clear-cut double bonds are not available for comparison. In the solid, a complex network is formed with coordination number 4 for the Be atom (see Figure 3-7). $BeCl_2$ tends to dimerize to a 3-coordinate structure in the vapor phase, but the linear monomer is also known at high temperatures. The monomeric structure is unstable; in the dimer and polymer, the halogen atoms share lone pairs with the Be atom and bring it closer to the octet structure. The monomer is still frequently drawn as a singly bonded structure with only four electrons around the beryllium and the ability to accept more from lone pairs of other molecules (Lewis acid behavior, discussed in Chapter 6).

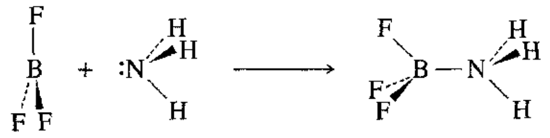
Bond lengths in all the boron trihalides are shorter than expected for single bonds, so the partial double bond character predicted seems reasonable in spite of the formal charges. Molecular orbital calculations for these molecules support significant double bond character. On the other hand, they combine readily with other molecules that can


Predicted
Actual solid
Predicted
Solid
Vapor
Predicted

The B—F bond length is 131 pm;
the calculated single-bond length is 152 pm.

FIGURE 3-7 Structures of BeF_2, $BeCl_2$, and BF_3. (Reference: A. F. Wells, *Structural Inorganic Chemistry*, 5th ed., Oxford University Press, Oxford, England, 1984, pp. 412, 1047.)

contribute a lone pair of electrons (Lewis bases), forming a roughly tetrahedral structure with four bonds:



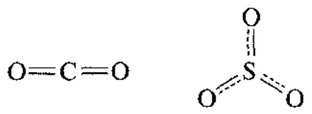
Because of this tendency, they are frequently drawn with only six electrons around the boron.

Other boron compounds that do not fit simple electron-dot structures include the hydrides, such as B_2H_6, and a large array of more complex molecules. Their structures are discussed in Chapters 8 and 15.

3-2 VALENCE SHELL ELECTRON PAIR REPULSION THEORY

Valence shell electron pair repulsion theory (VSEPR) provides a method for predicting the shape of molecules, based on the electron pair electrostatic repulsion. It was described by Sidgwick and Powell[4] in 1940 and further developed by Gillespie and Nyholm[5] in 1957. In spite of this method's very simple approach, based on Lewis electron-dot structures, the VSEPR method predicts shapes that compare favorably with those determined experimentally. However, this approach at best provides approximate shapes for molecules, not a complete picture of bonding. The most common method of determining the actual structures is X-ray diffraction, although electron diffraction, neutron diffraction, and many types of spectroscopy are also used.[6] In Chapter 5, we will provide some of the molecular orbital arguments for the shapes of simple molecules.

Electrons repel each other because they are negatively charged. The quantum mechanical rules force some of them to be fairly close to each other in bonding pairs or lone pairs, but each pair repels all other pairs. According to the VSEPR model, therefore, molecules adopt geometries in which their valence electron pairs position themselves as far from each other as possible. A molecule can be described by the generic formula AX_mE_n, where A is the central atom, X stands for any atom or group of atoms surrounding the central atom, and E represents a lone pair of electrons. The **steric number** (**SN** $= m + n$) is the number of positions occupied by atoms or lone pairs around a central atom; lone pairs and bonds are nearly equal in their influence on molecular shape.



Carbon dioxide is an example with two bonding positions (SN = 2) on the central atom and double bonds in each direction. The electrons in each double bond must be between C and O, and the repulsion between the electrons in the double bonds forces

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[4] N. V. Sidgwick and H. M. Powell, *Proc. R. Soc.*, **1940**, *A176*, 153.

[5] R. J. Gillespie and R. S. Nyholm, *Q. Rev. Chem. Soc.*, **1957**, *XI*, 339, a very thorough and clear description of the principles, with many more examples than are included here; R. J. Gillespie, *J. Chem. Educ.*, **1970**, *47*, 18.

[6] G. M. Barrow, *Physical Chemistry*, 6th ed., McGraw-Hill, New York, 1988, pp. 567–699; R. S. Drago, *Physical Methods for Chemists*, 2nd ed., Saunders College Publishing, Philadelphia, 1977, pp. 689–711.

a linear structure on the molecule. Sulfur trioxide has three bonding positions (SN = 3), with partial double bond character in each. The best positions for the oxygens in this molecule are at the corners of an equilateral triangle, with O—S—O bond angles of 120°. The multiple bonding does not affect the geometry because it is shared equally among the three bonds.

The same pattern of finding the Lewis structure and then matching it to a geometry that minimizes the repulsive energy of bonding electrons is followed through steric numbers four, five, six, seven, and eight, as shown in Figure 3-8.

The structures for two, three, four, and six electron pairs are completely regular, with all bond angles and distances the same. Neither 5- nor 7-coordinate structures can have uniform angles and distances, because there are no regular polyhedra with these numbers of vertices. The 5-coordinate molecules have a trigonal bipyramidal structure, with a central triangular plane of three positions plus two other positions above and below the center of the plane. The 7-coordinate molecules have a pentagonal bipyramidal structure, with a pentagonal plane of five positions and positions above and below

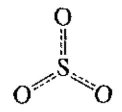
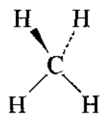
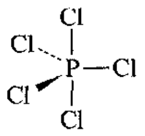
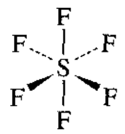
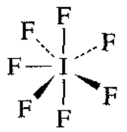
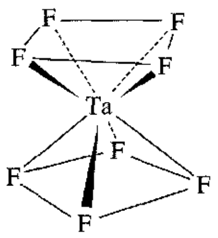
Steric Number	*Geometry*	*Examples*	*Calculated Bond Angles*	
2	Linear	CO_2	180°	$O{=}C{=}O$
3	Planar triangular (trigonal)	SO_3	120°	
4	Tetrahedral	CH_4	109.5°	
5	Trigonal bipyramidal	PCl_5	120°, 90°	
6	Octahedral	SF_6	90°	
7	Pentagonal bipyramidal	IF_7	72°, 90°	
8	Square antiprismatic	$TaF_8{}^{3-}$	70.5°, 99.6°, 109.5°	

FIGURE 3-8 VSEPR Predictions.

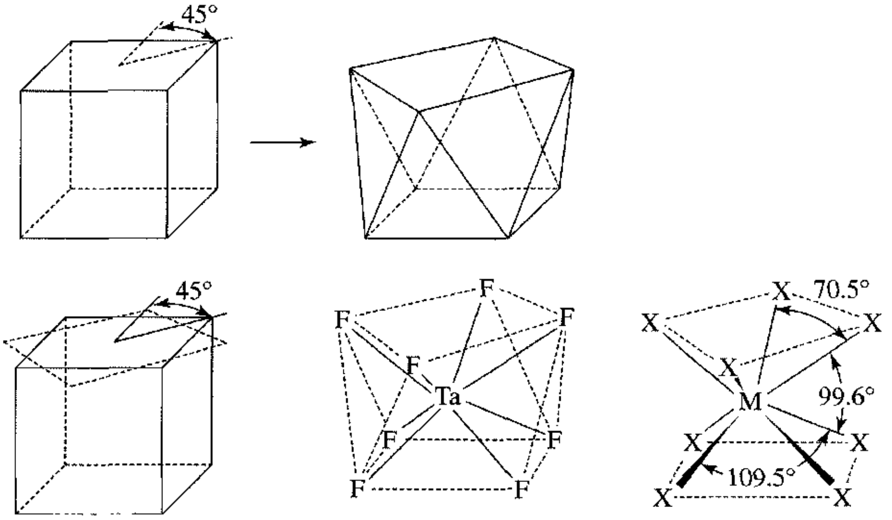


FIGURE 3-9 Conversion of a Cube into a Square Antiprism.

the center of the plane. The regular square antiprism structure ($SN = 8$) is like a cube with the top and bottom faces twisted 45° into the antiprism arrangement, as shown in Figure 3-9. It has three different bond angles for adjacent fluorines. $[TaF_8]^{3-}$ has square antiprism symmetry, but is distorted from this ideal in the solid.[7] (A simple cube has only the 109.5° and 70.5° bond angles measured between two corners and the center of the cube, because all edges are equal and any square face can be taken as the bottom or top.)

3-2-1 LONE PAIR REPULSION

We must keep in mind that we are always attempting to match our explanations to experimental data. The explanation that fits the data best should be the current favorite, but new theories are continually being suggested and tested. Because we are working with such a wide variety of atoms and molecular structures, it is unlikely that a single, simple approach will work for all of them. Although the fundamental ideas of atomic and molecular structures are relatively simple, their application to complex molecules is not. It is also helpful to keep in mind that for many purposes, prediction of exact bond angles is not usually required. To a first approximation, lone pairs, single bonds, double bonds, and triple bonds can all be treated similarly when predicting molecular shapes. However, better predictions of overall shapes can be made by considering some important differences between lone pairs and bonding pairs. These methods are sufficient to show the trends and explain the bonding, as in explaining why the H—N—H angle in ammonia is smaller than the tetrahedral angle in methane and larger than the H—O—H angle in water.

Steric number = 4

The isoelectronic molecules CH_4, NH_3, and H_2O (Figure 3-10) illustrate the effect of lone pairs on molecular shape. Methane has four identical bonds between carbon and each of the hydrogens. When the four pairs of electrons are arranged as far from each other as possible, the result is the familiar tetrahedral shape. The tetrahedron, with all H—C—H angles measuring 109.5°, has four identical bonds.

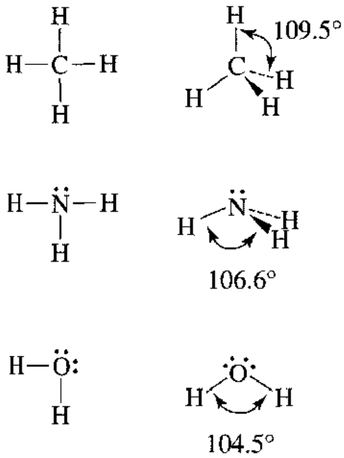


FIGURE 3-10 Shapes of Methane, Ammonia, and Water.

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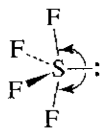
[7] J. L. Hoard, W. J. Martin, M. E. Smith, and J. F. Whitney, *J. Am. Chem. Soc.*, **1954**, *76*, 3820.

Ammonia also has four pairs of electrons around the central atom, but three are bonding pairs between N and H and the fourth is a lone pair on the nitrogen. The nuclei form a trigonal pyramid with the three bonding pairs; with the lone pair, they make a nearly tetrahedral shape. Because each of the three bonding pairs is attracted by two positively charged nuclei (H and N), these pairs are largely confined to the regions between the H and N atoms. The lone pair, on the other hand, is concentrated near the nitrogen; it has no second nucleus to confine it to a small region of space. Consequently, the lone pair tends to spread out and to occupy more space around the nitrogen than the bonding pairs. As a result, the H—N—H angles are 106.6°, nearly 3° smaller than the angles in methane.

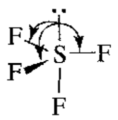
The same principles apply to the water molecule, in which two lone pairs and two bonding pairs repel each other. Again, the electron pairs have a nearly tetrahedral arrangement, with the atoms arranged in a V shape. The angle of largest repulsion, between the two lone pairs, is not directly measurable. However, the lone pair–bonding pair (*lp-bp*) repulsion is greater than the bonding pair–bonding pair (*bp-bp*) repulsion, and as a result the H—O—H bond angle is only 104.5°, another 2.1° decrease from the ammonia angles. The net result is that we can predict approximate molecular shapes by assigning more space to lone electron pairs; being attracted to one nucleus rather than two, the lone pairs are able to spread out and occupy more space.

Steric number = 5

For trigonal bipyramidal geometry, there are two possible locations of lone pairs, axial and equatorial. If there is a single lone pair, for example in SF_4, the lone pair occupies an equatorial position. This position provides the lone pair with the most space and minimizes the interactions between the lone pair and bonding pairs. If the lone pair were axial, it would have three 90° interactions with bonding pairs; in an equatorial position it has only two such interactions, as shown in Figure 3-11. The actual structure is distorted by the lone pair as it spreads out in space and effectively squeezes the rest of the molecule together.



Equatorial lone pair

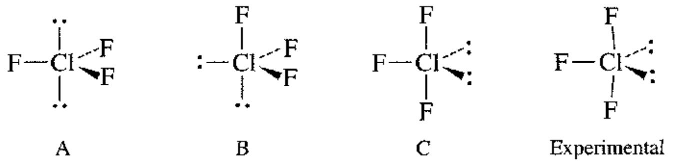


Axial lone pair

FIGURE 3-11 Structure of SF_4.

ClF_3 provides a second example of the influence of lone pairs in molecules having a steric number of 5. There are three possible structures for ClF_3, as shown in Figure 3-12. Lone pairs in the figure are designated *lp* and bonding pairs are *bp*.

In determining the structure of molecules, the lone pair–lone pair interactions are most important, with the lone pair–bonding pair interactions next in importance. In addition, interactions at angles of 90° or less are most important; larger angles generally have less influence. In ClF_3, structure B can be eliminated quickly because of



	Calculated			*Experimental*
	A	*B*	*C*	
lp-lp	180°	90°	120°	cannot be determined
lp-bp	6 at 90°	3 at 90° 2 at 120°	4 at 90° 2 at 120°	cannot be determined
bp-bp	3 at 120°	2 at 90° 1 at 120°	2 at 90°	2 at 87.5° Axial Cl—F 169.8 pm Equatorial Cl—F 159.8 pm

FIGURE 3-12 Possible Structures of ClF_3.

the 90° *lp-lp* angle. The *lp-lp* angles are large for A and C, so the choice must come from the *lp-bp* and *bp-bp* angles. Because the *lp-bp* angles are more important, C, which has only four 90° *lp-bp* interactions, is favored over A, which has six such interactions. Experiments have confirmed that the structure is based on C, with slight distortions due to the lone pairs. The lone pair–bonding pair repulsion causes the *lp-bp* angles to be larger than 90° and the *bp-bp* angles less than 90° (actually, 87.5°). The Cl—F bond distances show the repulsive effects as well, with the axial fluorines (approximately 90° *lp-bp* angles) at 169.8 pm and the equatorial fluorine (in the plane with two lone pairs) at 159.8 pm.[8] Angles involving lone pairs cannot be determined experimentally. The angles in Figure 3-12 are calculated assuming maximum symmetry consistent with the experimental shape.

Additional examples of structures with lone pairs are illustrated in Figure 3-13. Notice that the structures based on a trigonal bipyramidal arrangement of electron pairs around a central atom always place any lone pairs in the equatorial plane, as in SF_4, BrF_3, and XeF_2. These are the shapes that minimize both lone pair–lone pair and lone pair–bonding pair repulsions. The shapes are called teeter-totter or seesaw (SF_4), distorted T (BrF_3), and linear (XeF_2).

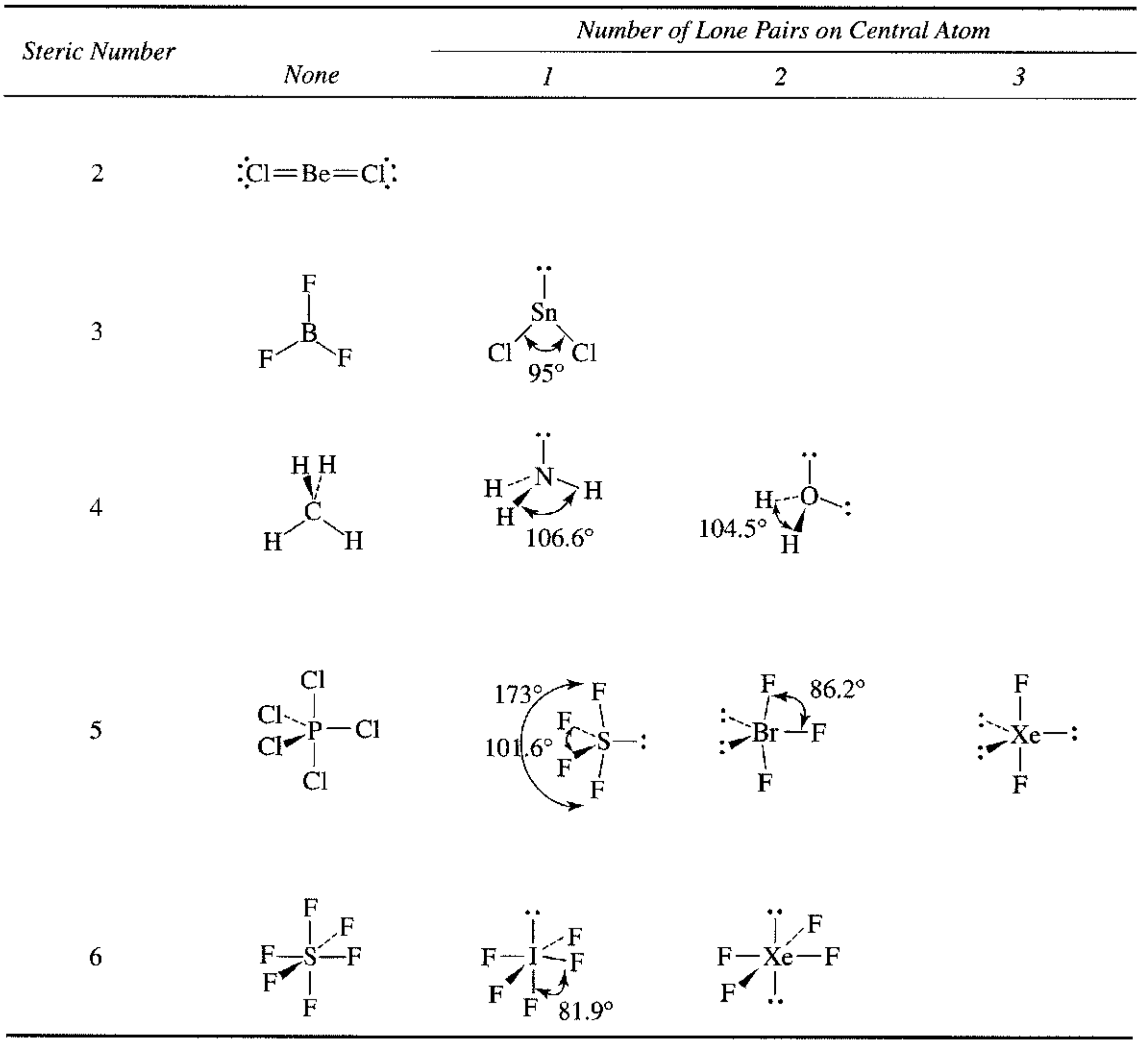


FIGURE 3-13 Structures Containing Lone Pairs.

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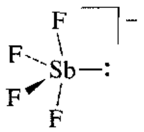
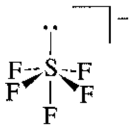
[8] A. F. Wells, *Structural Inorganic Chemistry*, 5th ed., Oxford University Press, New York, 1984, p. 390.

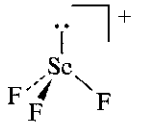
EXAMPLES



SbF_4^- has a single lone pair on Sb. Its structure is therefore similar to SF_4, with a lone pair occupying an equatorial position. This lone pair causes considerable distortion, giving an F—Sb—F (axial positions) angle of 155° and an F—Sb—F (equatorial) angle of 90°.



SF_5^- has a single lone pair. Its structure is based on an octahedron, with the ion distorted away from the lone pair, as in IF_5.



SeF_3^+ has a single lone pair. This lone pair reduces the F—Se—F bond angle significantly, to 94°.

EXERCISE 3-2

Predict the structures of the following ions. Include a description of distortions from the ideal angles (for example, less than 109.5° because . . .).

NH_2^- NH_4^+ I_3^- PCl_6^-

3-2-2 MULTIPLE BONDS

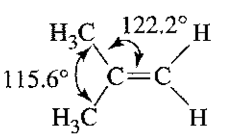


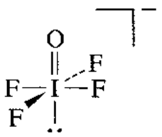
FIGURE 3-14 Bond Angles in $(CH_3)_2C{=}CH_2$.

The VSEPR model considers double and triple bonds to have slightly greater repulsive effects than single bonds because of the repulsive effect of π electrons. For example, the $H_3C—C—CH_3$ angle in $(CH_3)_2C{=}CH_2$ is smaller and the $H_3C—C{=}CH_2$ angle is larger than the trigonal 120° (Figure 3-14).[9]

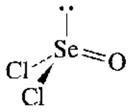
Additional examples of the effect of multiple bonds on molecular geometry are shown in Figure 3-15. Comparing Figures 3-14 and 3-15 indicates that multiple bonds tend to occupy the same positions as lone pairs. For example, the double bonds to oxygen in SOF_4, ClO_2F_3, and XeO_3F_2 are all equatorial, as are the lone pairs in the matching compounds of steric number 5, SF_4, BrF_3, and XeF_2. Also, multiple bonds, like lone pairs, tend to occupy more space than single bonds and to cause distortions that in effect squeeze the rest of the molecule together. In molecules that have both lone pairs and multiple bonds, these features may compete for space; examples are shown in Figure 3-16.

EXAMPLES

HCP, like HCN, is linear, with a triple bond: $H—C{\equiv}P$.



IOF_4^- has a single lone pair on the side opposite the oxygen. The lone pair has a slightly greater repulsive effect than the double bond to oxygen, as shown by the average O—I—F angle of 89°. (Because oxygen is less electronegative than fluorine, the extra repulsive character of the I═O bond places it opposite the lone pair.)



$SeOCl_2$ has both a lone pair and double bonding to the oxygen. The lone pair has a greater effect than the double bond to oxygen; the Cl—Se—Cl angle is reduced to 97° by this effect, and the Cl—Se—O angle is 106°.

EXERCISE 3-3

Predict the structures of the following. Indicate the direction of distortions from the regular structures.

$XeOF_2$ $ClOF_3$ $SOCl_2$

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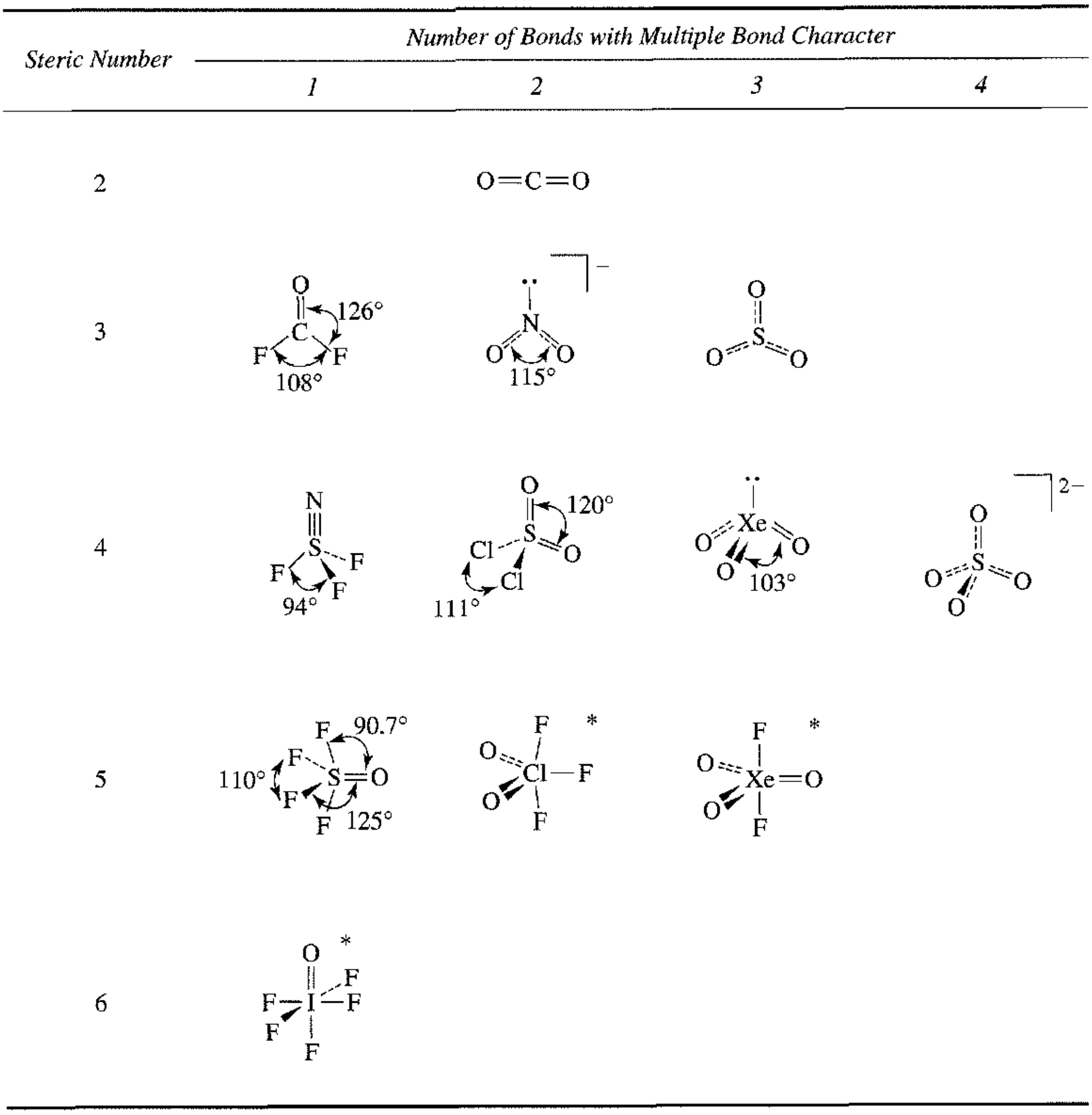
[9] R. J. Gillespie and I. Hargittai, *The VSEPR Model of Molecular Geometry*, Allyn & Bacon, Boston, 1991, p. 77.



* The bond angles of these molecules have not been determined accurately. However, spectroscopic measurements are consistent with the structures shown.

FIGURE 3-15 Structures Containing Multiple Bonds.

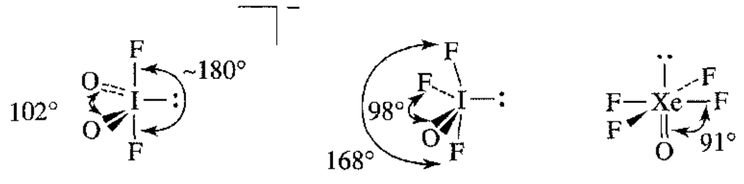


FIGURE 3-16 Structures Containing Both Lone Pairs and Multiple Bonds.

3-2-3 ELECTRONEGATIVITY AND ATOMIC SIZE EFFECTS

Electronegativity was mentioned earlier as a guide in the use of formal charge arguments. It also can play an important role in determining the arrangement of outer atoms around a central atom and in influencing bond angles. The effects of electronegativity and atomic size frequently parallel each other, but in the few cases in which they have opposite effects, electronegativity seems to prevail. Table 3-3 contains data that we can use in this discussion.

TABLE 3-3
Electronegativity (Pauling Units)

1	2	12	13	14	15	16	17	18
H 2.300								He 4.160
Li 0.912	Be 1.576		B 2.051	C 2.544	N 3.066	O 3.610	F 4.193	Ne 4.787
Na 0.869	Mg 1.293		Al 1.613	Si 1.916	P 2.253	S 2.589	Cl 2.869	Ar 3.242
K 0.734	Ca 1.034	Zn 1.588	Ga 1.756	Ge 1.994	As 2.211	Se 2.424	Br 2.685	Kr 2.966
Rb 0.706	Sr 0.963	Cd 1.521	In 1.656	Sn 1.824	Sb 1.984	Te 2.158	I 2.359	Xe 2.582
Cs 0.659	Ba 0.881	Hg 1.765	Tl 1.789	Pb 1.854	Bi (2.01)	Po (2.19)	At (2.39)	Rn (2.60)

SOURCE: J. B. Mann, T. L. Meek, and L. C. Allen, *J. Am. Chem. Soc.*, **2000**, *122*, 2780, Table 2.

Electronegativity scales

The concept of electronegativity was first introduced by Linus Pauling in the 1930s as a means of describing bond energies. Bond energies of polar bonds (formed by atoms with different electronegativities) are larger than the average of the bond energies of the two homonuclear species. For example, HCl has a bond energy of 428 kJ/mol, compared to a calculated value of 336 kJ/mol, the average of the bond energies of H_2 (432 kJ/mol) and Cl_2 (240 kJ/mol). From data like these, Pauling calculated electronegativity values that could be used to predict other bond energies. More recent values have come from other molecular properties and from atomic properties, such as ionization energy and electron affinity. Regardless of the method of calculation, the scale used is usually adjusted to give values near those of Pauling to allow better comparison. Table 3-4 summarizes approaches used for determining different scales.

TABLE 3-4
Electronegativity Scales

Principal Authors	*Method of Calculation or Description*
Pauling[10]	Bond energies
Mulliken[11]	Average of electron affinity and ionization energy
Allred & Rochow[12]	Electrostatic attraction proportional to Z^*/r^2
Sanderson[13]	Electron densities of atoms
Pearson[14]	Average of electron affinity and ionization energy
Allen[15]	Average energy of valence shell electrons, configuration energies
Jaffé[16]	Orbital electronegativities

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[10] L. Pauling, *The Nature of the Chemical Bond*, 3rd ed., 1960, Cornell University Press, Ithaca, NY; A. L. Allred, *J. Inorg. Nucl. Chem.*, **1961**, *17*, 215.

[11] R. S. Mulliken, *J. Chem. Phys.*, **1934**, *2*, 782; **1935**, *3*, 573; W. Moffitt, *Proc. R. Soc. (London)*, **1950**, *A202*, 548; R. G. Parr, R. A. Donnelly, M. Levy, and W. E. Palke, *J. Chem. Phys.*, **1978**, *68*, 3801–3807; R. G. Pearson, *Inorg. Chem.*, **1988**, *27*, 734–740; S. G. Bratsch, *J. Chem. Educ.*, **1988**, *65*, 34–41, 223–226.

[12] A. L. Allred and E. G. Rochow, *J. Inorg. Nucl. Chem.*, **1958**, *5*, 264.

[13] R. T. Sanderson, *J. Chem. Educ.*, **1952**, *29*, 539; **1954**, *31*, 2, 238; *Inorganic Chemistry*, Van Nostrand-Reinhold, New York, 1967.

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

[15] L. C. Allen, *J. Am. Chem. Soc.*, **1989**, *111*, 9003; J. B. Mann, T. L. Meek, and L. C. Allen, *J. Am. Chem. Soc.*, **2000**, *122*, 2780; J. B. Mann, T. L. Meek, E. T. Knight, J. F. Capitani, and L. C. Allen, *J. Am. Chem. Soc.*, **2000**, *122*, 5132.

[16] J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.*, **1962**, *84*, 540; *J. Phys. Chem.*, **1963**, *67*, 1501; J. E. Huheey, *Inorganic Chemistry*, 3rd ed., Harper & Row, New York, 1983, pp. 152–156.

Appendix B-4 shows electronegativity values for a larger set of elements. Any set can be used for the prediction of bond angles and molecular shape; specific sets are more useful for the calculation of properties for which they are designed. A graphic representation of electronegativity is in Figure 8-1.

Calculation of electronegativities from bond energies requires averaging over a number of compounds to cancel out experimental uncertainties and other minor effects. Methods that use ionization energies and other atomic properties can be calculated more directly. The electronegativities reported here and in Appendix B-4 are suitable for most uses, but the actual values for atoms in molecules may differ from this average, depending on their electronic environment.

Many of those interested in electronegativity agree that it depends on the structure of the molecule as well as the atom. Jaffé used this idea to develop a theory of the electronegativity of *orbitals* rather than *atoms*. Such theories are useful in detailed calculations of properties that change with subtle changes in structure, but we will not discuss this aspect further. The differences between values from the different scales are relatively small, except for those of the transition metals.[17] All will give the same results in qualitative arguments, the way most chemists use them.

Remember that all electronegativities are measures of an atom's ability to attract electrons from a neighboring atom *to which it is bonded.* A critique of all electronegativity scales, and particularly Pauling's, describes conditions that all scales should meet and many of their deficiencies.[18]

With the exception of helium and neon, which have large calculated electronegativities and no known stable compounds, fluorine has the largest value, and electronegativity decreases toward the lower left corner of the periodic table. Hydrogen, although usually classified with Group 1 (IA), is quite dissimilar from the alkali metals in its electronegativity, as well as in many other properties, both chemical and physical. Hydrogen's chemistry is distinctive from all the groups.

Electronegativities of the noble gases can be calculated more easily from ionization energies than from bond energies. Because the noble gases have higher ionization energies than the halogens, other calculations have suggested that the electronegativities of the noble gases may match or even exceed those of the halogens[19] (Table 3-3). The noble gas atoms are somewhat smaller than the neighboring halogen atoms (for example, Ne is smaller than F) as a consequence of a greater effective nuclear charge. This charge, which is able to attract noble gas electrons strongly toward the nucleus, is also likely to exert a strong attraction on electrons of neighboring atoms; hence, the high electronegativities predicted for the noble gases are reasonable.

Electronegativity and bond angles

Many bond angles can be explained by either electronegativity or size arguments. Molecules that have a larger difference in electronegativity values between their central and outer atoms have smaller bond angles. The atom with larger electronegativity draws the electrons toward itself and away from the central atom, reducing the repulsive effect of those bonding electrons. The compounds of the halogens in Table 3-5 show this effect; the compounds containing fluorine have smaller angles than those containing chlorine, which in turn have smaller angles than those containing bromine or iodine. As a result, the lone pair effect is relatively larger and forces smaller bond angles. The same result is obtained if size is considered; as the size of the outer atom increases in the $F < Cl < Br < I$ series, the angle increases.

[17] J. B. Mann, T. L. Meek, E. T. Knight, J. F. Capitani, and L. C. Allen, *J. Am. Chem. Soc.*, **2000**, *122*, 5132.

[18] L. R. Murphy, T. L. Meek, A. L. Allred, and L. C. Allen, *J. Am. Chem. Soc.*, **2000**, *122*, 5867.

[19] L. C. Allen and J. E. Huheey, *J. Inorg. Nucl. Chem.*, **1980**, *42*, 1523.

TABLE 3-5
Bond Angles and Lengths

Molecule	*Bond Angle (°)*	*Bond Length (pm)*	*Molecule*	*Bond Angle (°)*	*Bond Length (pm)*	*Molecule*	*Bond Angle (°)*	*Bond Length (pm)*	*Molecule*	*Bond Angle (°)*	*Bond Length (pm)*
H_2O	104.5	97	OF_2	103.3		OCl_2	110.9				
H_2S	92	135	SF_2	98	159	SCl_2	103	201			
H_2Se	91	146									
H_2Te	90	169									
NH_3	106.6	101.5	NF_3	102.2	137	NCl_3	106.8	175			
PH_3	93.8	142	PF_3	97.8	157	PCl_3	100.3	204	PBr_3	101	220
AsH_3	91.83	151.9	AsF_3	96.2	170.6	$AsCl_3$	97.7	217	$AsBr_3$	97.7	236
SbH_3	91.3	170.7	SbF_3	87.3	192	$SbCl_3$	97.2	233	$SbBr_3$	95	249

SOURCE: N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, 2nd ed., Butterworth-Heinemann, Oxford, 1997, pp. 557, 767; A. F. Wells, *Structural Inorganic Chemistry*, 5th ed., Oxford University Press, Oxford, 1987, pp. 705, 793, 846, and 879.

For the molecules containing hydrogen, neither the electronegativity nor the size argument works well. NH_3 should have the largest angle in the series of nitrogen compounds based on the electronegativity argument and the smallest angle based on the size argument; instead, it has nearly the same angle as NCl_3. Similar problems are found for H_2O, H_2S, PH_3, AsH_3, and SbH_3. The two effects seem to counterbalance each other, resulting in the intermediate angles.

Similar arguments can be made in situations in which the outer atoms remain the same but the central atom is changed. For example, consider the hydrogen series and the chlorine series in Table 3-5. For these molecules, the electronegativity and size of the central atom need to be considered. As the central atom becomes more electronegative, it pulls electrons in bonding pairs more strongly toward itself. This effect increases the concentration of bonding pair electrons near the central atom, causing the bonding pairs to repel each other more strongly, increasing the bond angles. In these situations, the compound with the most electronegative central atom has the largest bond angle.

The size of the central atom can also be used to determine the angles in the series. When the central atom is larger, all the electron pairs are naturally at greater distances from each other. However, the effect is greater for the bonded pairs, which are pulled away from the central atom by outer atoms. This leads to a relatively larger repulsive effect by the lone pairs and decreasing angles in the order $O > S > Se > Te$ and $N > P > As > Sb$.

EXERCISE 3-4

Which compound has the smallest bond angle in each series?

a. OSF_2 $OSCl_2$ $OSBr_2$ (halogen—S—halogen angle)
b. $SbCl_3$ $SbBr_3$ SbI_3
c. PI_3 AsI_3 SbI_3

3-2-4 LIGAND CLOSE-PACKING

Another approach to bond angles has been developed by Gillespie.[20] The **ligand close-packing** (LCP) model uses the distances between the outer atoms in molecules as a guide. For a series of molecules with the same central atom, the nonbonded distances between the outer atoms are consistent, but the bond angles and bond lengths change. For example, a series of BF_2X and BF_3X compounds, where X = F, OH, NH_2, Cl, H, CH_3, CF_3, and PH_3, have B—F bond distances of 130.7 to 142.4 pm and F—B—F

[20] R. J. Gillespie, *Coord. Chem. Rev.*, **2000**, *197*, 51.

TABLE 3-6
Ligand Close-Packing Data

Molecule	*Coordination Number of* B	B—F *Distance (pm)*	FBF *Angle (°)*	F···F *Distance (pm)*
BF_3	3	130.7	120.0	226
BF_2OH	3	132.3	118.0	227
BF_2NH_2	3	132.5	117.9	227
BF_2Cl	3	131.5	118.1	226
BF_2H	3	131.1	118.3	225
BF_2BF_2	3	131.7	117.2	225
BF_4^-	4	138.2	109.5	226
$BF_3CH_3^-$	4	142.4	105.4	227
$BF_3CF_3^-$	4	139.1	109.9	228
BF_3PH_3	4	137.2	112.1	228
BF_3NMe_3	4	137.2	111.5	229

SOURCE: R. J. Gillespie and P. L. A. Popelier, *Chemical Bonding and Molecular Geometry*, Oxford University Press, New York, 2001, Table 5.3, p. 119; R. J. Gillespie, *Coord. Chem. Rev.*, **2000**, *197*, 51.

bond angles of 105.4° to 120.0°, but the nonbonded F···F distances remain nearly constant at 225 to 229 pm. Examples are shown in Table 3-6. Gillespie and Popelier have also described several other approaches to molecular geometry, together with their advantages and disadvantages.[21]

3-3
POLAR MOLECULES

Whenever atoms with different electronegativities combine, the resulting molecule has polar bonds, with the electrons of the bond concentrated (perhaps very slightly) on the more electronegative atom; the greater the difference in electronegativity, the more polar the bond. As a result, the bonds are dipolar, with positive and negative ends. This polarity causes specific interactions between molecules, depending on the overall structure of the molecule.

Experimentally, the polarity of molecules is measured indirectly by measuring the dielectric constant, which is the ratio of the capacitance of a cell filled with the substance to be measured to the capacitance of the same cell with a vacuum between the electrodes. Orientation of polar molecules in the electric field partially cancels the effect of the field and results in a larger dielectric constant. Measurements at different temperatures allow calculation of the **dipole moment** for the molecule, defined as

$$\mu = Qr$$

where Q is the charge on each of two atoms separated by a distance, r.[22] Dipole moments of diatomic molecules can be calculated directly. In more complex molecules, vector addition of the individual bond dipole moments gives the net molecular dipole moment. However, it is usually not possible to calculate molecular dipoles directly from bond dipoles. Table 3-7 shows experimental and calculated dipole moments of chloromethanes. The values calculated from vectors use C—H and C—Cl bond dipoles of 1.3 and 4.9×10^{-30} C m, respectively, and tetrahedral bond angles. Part of the discrepancy arises from bond angles that differ from the tetrahedral, but the column

[21] R. J. Gillespie and P. L. A. Popelier, *Chemical Bonding and Molecular Geometry*, Oxford University Press, New York, 2001, pp. 113–133.

[22] The SI unit for dipole moment is coulomb meter (C m), but a commonly used unit is the debye (D). 1 D = 3.338×10^{-30} C m.

TABLE 3-7
Dipole Moments of Chloromethanes

Molecule	*Experimental (D)*	*Calculated (D)*	
		Calculated from Vectors	*Calculated by PC Spartan*
CH_3Cl	1.87	1.77	1.51
CH_2Cl_2	1.60	2.08	1.50
$CHCl_3$	1.01	1.82	1.16

SOURCE: Experimental data, *Handbook of Chemistry and Physics*, 66th ed., CRC Press, Cleveland, OH, 1985–86, p. E-58 (from NBS table NSRDS-NBS 10); Spartan, see footnote 23.

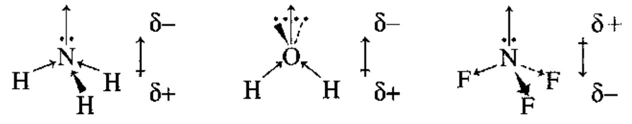
of data from PC Spartan,[23] a molecular modeling program, shows the difficulty of calculating dipoles. Clearly, calculating dipole moments is more complex than simply adding the vectors for individual bond moments, but we will not consider that here. For most purposes, a qualitative approach is sufficient.

The dipole moments of NH_3, H_2O, and NF_3 (Figure 3-17) reveal the effect of lone pairs, which can be dramatic. In ammonia, the averaged N — H bond polarities and the lone pair all point in the same direction, resulting in a large dipole moment. Water has an even larger dipole moment because the polarities of the O — H bonds and the two lone pairs results in polarities all reinforcing each other. On the other hand, NF_3 has a very small dipole moment, the result of the polarity of the three N — F bonds opposing polarity of the lone pair. The sum of the three N — F bond moments is larger than the lone pair effect, and the lone pair is the positive end of the molecule. In cases such as those of NF_3 and SO_2, the direction of the dipole is not easily predicted because of the opposing polarities. SO_2 has a large dipole moment (1.63 D), with the polarity of the lone pair prevailing over that of the S — O bonds.

Molecules with dipole moments interact electrostatically with each other and with other polar molecules. When the dipoles are large enough, the molecules orient themselves with the positive end of one molecule toward the negative end of another because of these attractive forces, and higher melting and boiling points result. Details of the most dramatic effects are given in the discussion of hydrogen bonding later in this chapter and in Chapter 6.

On the other hand, if the molecule has a very symmetric structure or if the polarities of different bonds cancel each other, the molecule as a whole may be nonpolar, even though the individual bonds are quite polar. Tetrahedral molecules such as CH_4 and CCl_4 and trigonal molecules and ions such as SO_3, NO_3^-, and CO_3^{2-} are all nonpolar. The C — H bond has very little polarity, but the bonds in the other molecules and ions are quite polar. In all these cases, the sum of all the polar bonds is zero because of the symmetry of the molecules, as shown in Figure 3-18.

Nonpolar molecules, whether they have polar bonds or not, still have intermolecular attractive forces acting on them. Small fluctuations in the electron density in such



Net dipole, 1.47 D Net dipole, 1.85 D Net dipole, 0.23 D

Calculated, 1.85 D Calculated, 1.86 D Calculated, 0.32 D

FIGURE 3-17 Bond Dipoles and Molecular Dipoles.

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[23] Spartan is obtainable from Wavefunction, Inc., 18401 Von Karman Ave, Suite 370, Irvine, CA 92612; see http://www.wavefun.com.

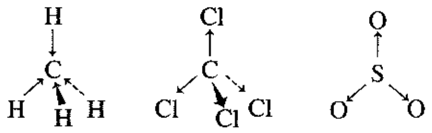

FIGURE 3-18 Cancellation of Bond Dipoles due to Molecular Symmetry.

Zero net dipole for all three

molecules create small temporary dipoles, with extremely short lifetimes. These dipoles in turn attract or repel electrons in adjacent molecules, setting up dipoles in them as well. The result is an overall attraction among molecules. These attractive forces are called **London** or **dispersion forces**, and make liquefaction of the noble gases and nonpolar molecules such as hydrogen, nitrogen, and carbon dioxide possible. As a general rule, London forces are more important when there are more electrons in a molecule, because the attraction of the nuclei is shielded by inner electrons and the electron cloud is more polarizable.

3-4 HYDROGEN BONDING

Ammonia, water, and hydrogen fluoride all have much higher boiling points than other similar molecules, as shown in Figure 3-19. In water and hydrogen fluoride, these high boiling points are caused by hydrogen bonds, in which hydrogen atoms bonded to O or F also form weaker bonds to a lone pair of electrons on another O or F. Bonds between hydrogen and these strongly electronegative atoms are very polar, with a partial positive charge on the hydrogen. This partially positive H is strongly attracted to the partially negative O or F of neighboring molecules. In the past, the attraction among these molecules was considered primarily electrostatic in nature, but an alternative molecular orbital approach, which will be described in Chapters 5 and 6, gives a more complete description of this phenomenon. Regardless of the detailed explanation of

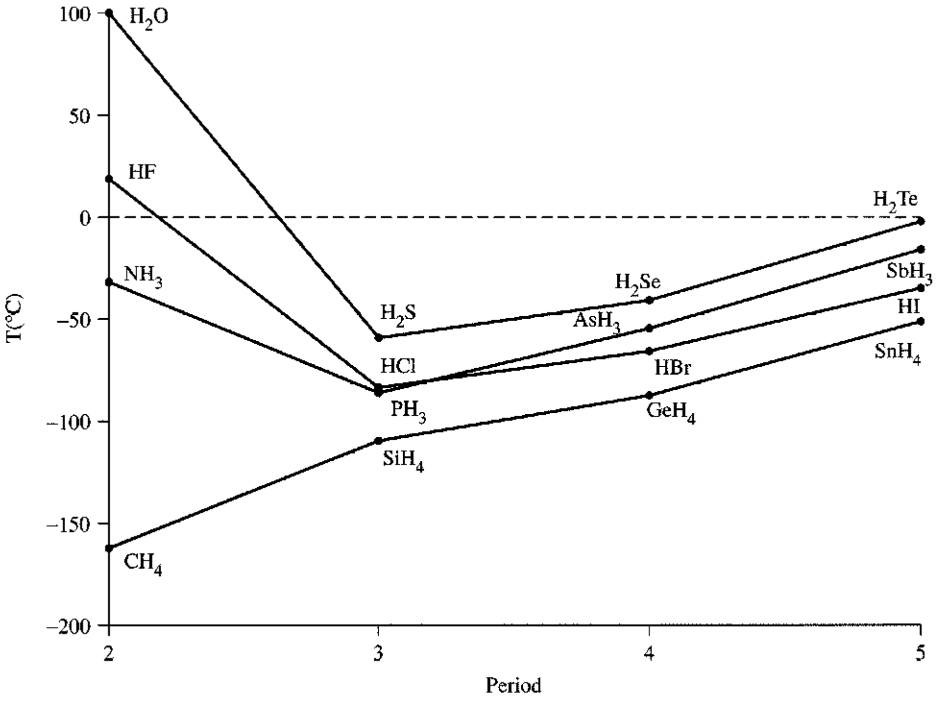

FIGURE 3-19 Boiling Points of Hydrogen Compounds.

the forces involved in hydrogen bonding, the strongly positive H and the strongly negative lone pairs tend to line up and hold the molecules together. Other atoms with high electronegativity, such as Cl, can also form hydrogen bonds in strongly polar molecules such as chloroform, $CHCl_3$.

In general, boiling points rise with increasing molecular weight, both because the additional mass requires higher temperature for rapid movement of the molecules and because the larger number of electrons in the heavier molecules provides larger London forces. The difference in temperature between the actual boiling point of water and the extrapolation of the line connecting the boiling points of the heavier analogous compounds is almost 200° C. Ammonia and hydrogen fluoride have similar but smaller differences from the extrapolated values for their families. Water has a much larger effect, because each molecule can have as many as four hydrogen bonds (two through the lone pairs and two through the hydrogen atoms). Hydrogen fluoride can average no more than two, because HF has only one H available.

Hydrogen bonding in ammonia is less certain. Several experimental studies[24] in the gas phase fit a model of the dimer with a "cyclic" structure, although probably asymmetric, as shown in Figure 3-20(b). Theoretical studies depend on the method of calculation, the size of the basis set used (how many functions are used in the fitting), and the assumptions used by the investigators, and conclude that the structure is either linear or cyclic, but that in any case it is very far from rigid.[25] The umbrella vibrational mode (inverting the NH_3 tripod like an umbrella in a high wind) and the interchange mode (in which the angles between the molecules switch) appear to have transitions that allow easy conversions between the two extremes of a dimer with a near-linear N—H—N hydrogen bond and a centrosymmetric dimer with C_{2h} symmetry. Linear N—H—N bonds seem more likely in larger clusters, as confirmed by both experiment and calculation. There is no doubt that the ammonia molecule can accept a hydrogen and form a hydrogen bond through the lone pair on the nitrogen atom with H_2O, HF, and other polar molecules, but it does not readily donate a hydrogen atom to another molecule. On the other hand, hydrogen donation from nitrogen to carbonyl oxygen is common in proteins and hydrogen bonding in both directions to nitrogen is found in the DNA double helix.

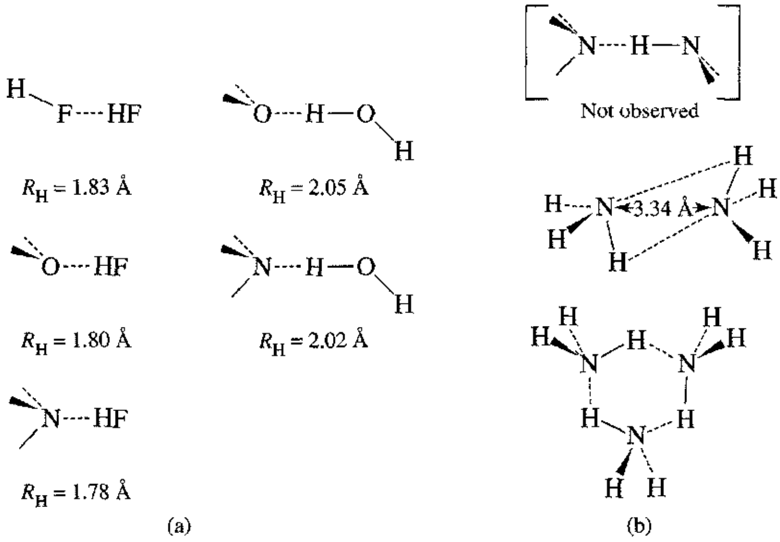

FIGURE 3-20 Dimer Structures in the Gas Phase. (a) Known hydrogen-bonded structures. R_H = hydrogen bond distance. (b) Proposed structures of the NH_3 dimer and trimer.

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[24] D. D. Nelson, Jr., G. T. Fraser, and W. Klemperer, *Science*, **1987**, *238*, 1670; M. Behrens, U. Buck, R. Fröchtenicht, and M. Hartmann, *J. Chem. Phys.*, **1997**, *107*, 7179; F. Huisken and T. Pertsch, *Chem. Phys.*, **1988**, *126*, 213.

[25] J. S. Lee and S. Y. Park, *J. Chem. Phys.*, **2001**, *112*, 230; A. van der Avoird, E. H. T. Olthof, and P. E. S. Wormer, *Faraday Discuss.*, **1994**, *97*, 43, and references therein.

Water has other unusual properties because of hydrogen bonding. For example, the freezing point of water is much higher than that of similar molecules. An even more striking feature is the decrease in density as water freezes. The tetrahedral structure around each oxygen atom with two regular bonds to hydrogen and two hydrogen bonds to other molecules requires a very open structure with large spaces between ice molecules (Figure 3-21). This makes the solid less dense than the more random liquid water surrounding it, so ice floats. Life on earth would be very different if this were not so. Lakes, rivers, and oceans would freeze from the bottom up, ice cubes would sink, and ice fishing would be impossible. The results are difficult to imagine, but would certainly require a much different biology and geology. The same forces cause coiling of protein and polynucleic acid molecules (Figure 3-22); a combination of hydrogen bonding with other dipolar forces imposes considerable secondary structure on these large molecules. In Figure 3-22(a), hydrogen bonds between carbonyl oxygen atoms and hydrogens attached to nitrogen atoms hold the molecule in a helical structure. In Figure 3-22(b), similar hydrogen bonds hold the parallel peptide chains together; the bond angles of the chains result in the pleated appearance of the sheet formed by the peptides. These are two of the many different structures that can be formed from peptides, depending on the side-chain groups R and the surrounding environment.

Another example is a theory of anesthesia by non–hydrogen bonding molecules such as cyclopropane, chloroform, and nitrous oxide, proposed by Pauling.[26] These molecules are of a size and shape that can fit neatly into a hydrogen-bonded water structure with even larger open spaces than ordinary ice. Such structures, with molecules trapped in holes in a solid, are called **clathrates**. Pauling proposed that similar hydrogen-bonded microcrystals form even more readily in nerve tissue because of the presence of other solutes in the tissue. These microcrystals could then interfere with the transmission of nerve impulses. Similar structures of methane and water are believed to

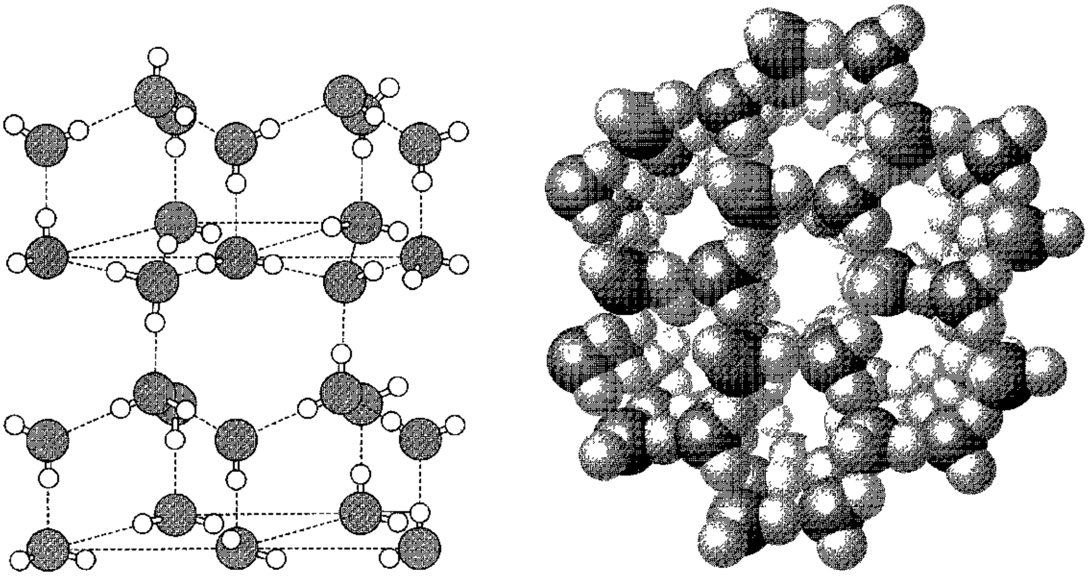

FIGURE 3-21 Two Drawings of Ice. (a) From T. L. Brown and H. E. LeMay, Jr., *Chemistry, The Central Science*, Prentice Hall, Englewood Cliffs, NJ, 1988, p. 628. Reproduced with permission. The rectangular lines are included to aid visualization; all bonding is between hydrogen and oxygen atoms. (b) Copyright © 1976 by W. G. Davies and J. W. Moore, used by permission; reprinted from *Chemistry*, J. W. Moore, W. G. Davies, and R. W. Collins, McGraw-Hill, New York, 1978. All rights reserved.

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[26] L. Pauling, *Science*, **1961**, *134*, 15.

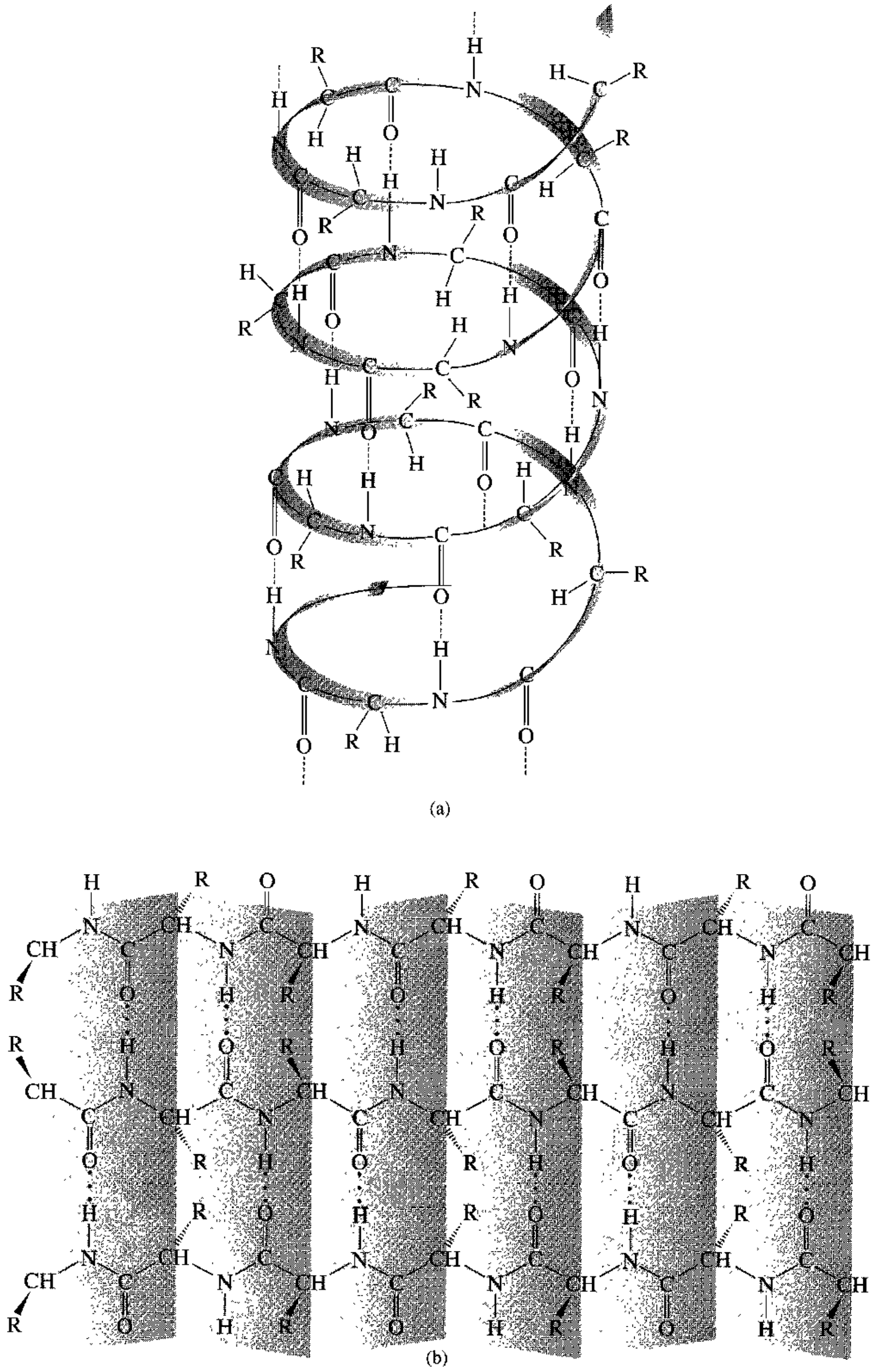

FIGURE 3-22 Hydrogen-Bonded Protein Structures. (a) A protein α helix. Peptide carbonyls and N—H hydrogens on adjacent turns of the helix are hydrogen-bonded. (From T. L. Brown and H. E. LeMay, Jr., *Chemistry, the Central Science*, Prentice Hall, Englewood Cliffs, NJ, 1988, p. 946. Reproduced with permission.) (b) The pleated sheet arrangement. Each peptide carbonyl group is hydrogen-bonded to a N—H hydrogen on an adjacent peptide chain. (Reproduced with permission from L. G. Wade, Jr., *Organic Chemistry*, Prentice Hall, Englewood Cliffs, NJ, 1988, pp. 1255–1256.)

hold large quantities of methane in the polar ice caps. The amount of methane in such crystals can be so great that they burn if ignited.[27]

More specific interactions involving the sharing of electron pairs between molecules are discussed in Chapter 6 as part of acid–base theories.

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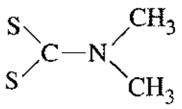
[27] L. A. Stern, S. H. Kirby, W. B. Durham, *Science*, **1996**, *273*, 1765 (cover picture), 1843.

GENERAL REFERENCES

Good sources for bond lengths and bond angles are the references by Wells, Greenwood and Earnshaw, and Cotton and Wilkinson cited in Chapter 1. Appendix D provides a review of electron-dot diagrams and formal charges at the level of most general chemistry texts. Alternative approaches to these topics are available in most general chemistry texts, as are descriptions of VSEPR theory. One of the best VSEPR references is still the early paper by R. J. Gillespie and R. S. Nyholm, *Q. Rev. Chem. Soc.* **1957**, *XI*, 339–380. More recent expositions of the theory are in R. J. Gillespie and I. Hargittai, *The VSEPR Model of Molecular Geometry*, Allyn & Bacon, Boston, 1991, and R. J. Gillespie and P. L. A. Popelier, *Chemical Bonding and Molecular Geometry: From Lewis to Electron Densities*, Oxford University Press, New York, 2001. Molecular orbital arguments for the shapes of many of the same molecules are presented in B. M. Gimarc, *Molecular Structure and Bonding*, Academic Press, New York, 1979, and J. K. Burdett, *Molecular Shapes*, John Wiley & Sons, New York, 1980.

PROBLEMS

3-1 The dimethyldithiocarbamate ion, $[S_2CN(CH_3)_2]^-$, has the following skeletal structure:



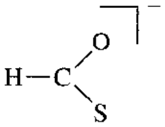
a. Give the important resonance structures of this ion, including any formal charges where necessary. Select the resonance structure likely to provide the best description of this ion.

b. Repeat for dimethylthiocarbamate, $[OSCN(CH_3)_2]^-$.

3-2 Several resonance structures are possible for each of the following ions. For each, draw these resonance structures, assign formal charges, and select the resonance structure likely to provide the best description for the ion.

a. Selenocyanate ion, $SeCN^-$

b. Thioformate ion,



c. Dithiocarbonate, $[S_2CO]^{2-}$ (C is central)

3-3 Draw the resonance structures for the isoelectronic ions NSO^- and SNO^-, and assign formal charges. Which ion is likely to be more stable?

3-4 Three isomers having the formula N_2CO are known: ONCN (nitrosyl cyanide), ONNC (nitrosyl isocyanide), and NOCN (isonitrosyl cyanide). Draw the most important resonance structures of these isomers, and determine the formal charges. Which isomer do you predict to be the most stable (lowest energy) form? (Reference: G. Maier, H. P. Reinsenauer, J. Eckwert, M. Naumann, and M. De Marco, *Angew. Chem., Int. Ed.*, **1997**, *36*, 1707.)

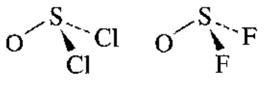
3-5 Predict and sketch the structure of the (as yet) hypothetical ion IF_3^{2-}.

3-6 Select from each set the molecule or ion having the smallest bond angle, and briefly explain your choice:

a. NH_3, PH_3, or AsH_3

b. O_3^+, O_3, or O_3^-

c.



(halogen—S—halogen angle)

d. NO_2^- or O_3

e. ClO_3^- or BrO_3^-

3-7 Sketch the most likely structure of PCl_3Br_2 and explain your reasoning.

3-8 Give Lewis dot structures and sketch the shapes of the following:

a. $SeCl_4$ **b.** I_3^-
c. $PSCl_3$ (P is central) **d.** IF_4^-
e. PH_2^- **f.** TeF_4^{2-}
g. N_3^- **h.** $SeOCl_4$ (Se is central)
i. PH_4^+ **j.** NO^-

3-9 Give Lewis dot structures and sketch the shapes of the following:

a. ICl_2^- **b.** H_3PO_3 (one H is bonded to P)
c. BH_4^- **d.** $POCl_3$
e. IO_4^- **f.** $IO(OH)_5$
g. $SOCl_2$ **h.** $ClOF_4^-$
i. XeO_2F_2 **j.** $ClOF_2^+$

3-10 Give Lewis dot structures and sketch the shapes of the following:

a. SOF_6 (one F is attached to O) **b.** POF_3
c. ClO_2 **d.** NO_2
e. $S_2O_4^{2-}$ (symmetric, with an S—S bond)
f. N_2H_4 (symmetric, with an N—N bond)

3-11 **a.** Compare the structures of the azide ion, N_3^-, and the ozone molecule, O_3.
b. How would you expect the structure of the ozonide ion, O_3^-, to differ from that of ozone?

3-12 Give Lewis dot structures and shapes for the following:

a. $VOCl_3$ **b.** PCl_3 **c.** SOF_4
d. ClO_2^- **e.** ClO_3^- **f.** P_4O_6

(P_4O_6 is a closed structure with overall tetrahedral arrangement of phosphorus atoms; an oxygen atom bridges each pair of phosphorus atoms.)

3-13 Consider the series NH_3, $N(CH_3)_3$, $N(SiH_3)_3$, and $N(GeH_3)_3$. These have bond angles at the nitrogen atom of 106.6°, 110.9°, 120°, and 120°, respectively. Account for this trend.

3-14 Explain the trends in bond angles and bond lengths of the following ions:

	X—O *(pm)*	O—X—O *Angle*
ClO_3^-	149	107°
BrO_3^-	165	104°
IO_3^-	181	100°

3-15 Compare the bond orders expected in ClO_3^- and ClO_4^- ions.

3-16 Give Lewis dot structures and sketch the shapes for the following:

a. PH_3 **b.** H_2Se **c.** SeF_4
d. PF_5 **e.** ICl_4^- **f.** XeO_3
g. NO_3^- **h.** $SnCl_2$ **i.** PO_4^{3-}
j. SF_6 **k.** IF_5 **l.** ICl_3
m. $S_2O_3^{2-}$ **n.** BF_2Cl

3-17 Which of the molecules or ions in Problem 3-16 are polar?

3-18 Carbon monoxide has a larger bond dissociation energy (1072 kJ/mol) than molecular nitrogen (945 kJ/mol). Suggest an explanation.

3-19 **a.** Which has the longer axial P—F distance, $PF_2(CH_3)_3$ or $PF_2(CF_3)_3$? Explain briefly.
b. Al_2O has oxygen in the center. Predict the approximate bond angle in this molecule and explain your answer.

c. Predict the structure of CAl_4. (Reference: X. Li, L-S. Wang, A. I. Boldyrev, and J. Simons, *J. Am. Chem. Soc.*, **1999**, *121*, 6033.)

3-20 For each of the following bonds, indicate which atom is more negative. Then rank the series in order of polarity.
a. C—N **b.** N—O **c.** C—I **d.** O—Cl **e.** P—Br **f.** S—Cl

3-21 Explain the following:
a. PCl_5 is a stable molecule, but NCl_5 is not.
b. SF_4 and SF_6 are known, but OF_4 and OF_6 are not.

3-22 Provide explanations for the following:
a. Methanol, CH_3OH, has a much higher boiling point than methyl mercaptan, CH_3SH.
b. Carbon monoxide has slightly higher melting and boiling points than N_2.
c. The *ortho* isomer of hydroxybenzoic acid [$C_6H_4(OH)(CO_2H)$] has a much lower melting point than the *meta* and *para* isomers.
d. The boiling points of the noble gases increase with atomic number.
e. Acetic acid in the gas phase has a significantly lower pressure (approaching a limit of one half) than predicted by the ideal gas law.
f. Mixtures of acetone and chloroform exhibit significant negative deviations from Raoult's law (which states that the vapor pressure of a volatile liquid is proportional to its mole fraction). For example, an equimolar mixture of acetone and chloroform has a lower vapor pressure than either of the pure liquids.

3-23 L. C. Allen has suggested that a more meaningful formal charge can be obtained by taking into account the electronegativities of the atoms involved. Allen's formula for this type of charge, referred to as the Lewis-Langmuir (L-L) charge, of an atom, A, bonded to another atom, B, is

$$\text{L-L charge} = \frac{\text{(US) group}}{\text{number of A}} - \frac{\text{number of unshared}}{\text{electrons on A}} - 2\sum_{B} \frac{\chi_A}{\chi_A + \chi_B}\begin{pmatrix}\text{number of bonds}\\ \text{between A and B}\end{pmatrix}$$

where χ_A and χ_B designate the electronegativities. Using this equation, calculate the L-L charges for CO, NO^-, and HF and compare the results with the corresponding formal charges. Do you think the L-L charges are a better representation of electron distribution? (Reference: L. C. Allen, *J. Am. Chem. Soc.*, **1989**, *111*, 9115.)

3-24 Predict the structure of $I(CF_3)Cl_2$. Do you expect the CF_3 group to be in an axial or equatorial position? Why? (Reference: R. Minkwitz and M. Merkei, *Inorg. Chem.*, **1999**, *38*, 5041.)

3-25 Two ions isoelectronic with carbon suboxide, C_3O_2, are N_5^+ and $OCNCO^+$. Whereas C_3O_2 is linear, both N_5^+ and $OCNCO^+$ are bent at the central nitrogen. Suggest an explanation. Also predict which has the smaller outer atom—N—outer atom angle and explain your reasoning. (References: I. Bernhardi, T. Drews, and K. Seppelt, *Angew. Chem., Int. Ed.*, **1999**, *38*, 2232; K. O. Christe, W. W. Wilson, J. A. Sheehy, and J. A. Boatz, *Angew. Chem., Int. Ed.*, **1999**, *38*, 2004.)

3-26 The thiazyl dichloride ion, $NSCl_2^-$, has recently been reported. This ion is isoelectronic with thionyl dichloride, $OSCl_2$.
a. Which of these species has the smaller Cl—S—Cl angle? Explain briefly.
b. Which do you predict to have the longer S—Cl bond? Why? (Reference: E. Kessenich, F. Kopp, P. Mayer, and A. Schulz, *Angew. Chem., Int. Ed.*, **2001**, *40*, 1904.)

3-27 Although the C—F distances and the F—C—F bond angles differ considerably in $F_2C{=}CF_2$, F_2CO, CF_4, and F_3CO^- (C—F distances: 131.9 to 139.2 pm; F—C—F bond angles: 101.3° to 109.5°), the F···F distance in all four structures is very nearly the same (215 to 218 pm). Explain, using the LCP model of Gillespie. (Reference: R. J. Gillespie, *Coord. Chem. Rev.*, **2000**, *197*, 51.)