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Organic Chemistry

for Students of Medicine and Biology

Chief editor

Xia Shuzhen, Luo Yiming

Vice-chief editor

Li Guiling, Yu Yu

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Preface

In order to meet the development of all-English or bilingual teaching of organic chemistry in medical colleges of our country, we are now grouped to edit this book. The sequence of chapters and related contents in this book are consistent to the sixth edition of *Organic Chemistry* in Chinese which is published by People's Medical Publishing House as a NHO's programming book material. We have applied "three basic contents—basic theories, basic knowledge, basic skills" and "five features—thoughtful, scientific, advanced, heuristic, adaptable" to this book. That means precise demonstrations, clear arrangements, visual illuminations and fluent language. The whole book is arranged in a proper and gradual sequence to avoid destroying the coherence or connections of chapters and furthermore unnecessary repetition.

The organization of this book is by functional group, beginning with the simple (alkanes) and progressing to the more complex. Within this organization, however, there is also an emphasis on explaining the fundamental mechanistic similarities of reactions.

The essays at the end of chapters (except chapters 1 and 13) present interesting applications of organic chemistry relevant to the main chapter subject. Including topics from science, biological science, medicine, and day-to-day life, these applications enliven and reinforce the material presented in each chapter. We have contributed our effort to make this book as effective, clear and readable as possible, to show the beauty and logic of organic chemistry; and to make the subject interesting to learn.

The authors thank Miss Hu Zhangcheng, Miss Yang Ou and Mr. Wang Xinhua, who are all editors from Huazhong University of Science and Technology Press. Their encouragement, excellent work made it possible to put the final manuscript into book form.

Finally, we express our indebtedness to our students who gave the reason for beginning the courage to continue, and the fortitude to complete the project.

We are sincerely grateful to them all.

Authors
November 20, 2005

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Chapter 1 Introduction

Nearly all bonds that bind atoms together to form organic compounds are of covalent type. So it is important to grasp the basic principles of chemical structure and bonding applicable to organic molecules for learning organic chemistry. This chapter describes the theory of covalent bond and that of acids and bases.

1.1 Organic Compounds and Organic Chemistry

Organic Chemistry according to its original definition dealt only with those substances of natural organic origin — that is, products from plants or animals. It was thought by early chemists that the production of an organic compound involved the “vital force” of a living organism. The science of chemistry was thus separated into two broad divisions—inorganic and organic. In 1828, however, the German chemist Friedrich Wöhler heated some ammonium cyanate, NH_4OCN , and obtained urea:



For the first time the vital force theory began to be questioned. Certainly nothing could be more organic than urea, for it is excreted in the urine of mammals, and ammonium cyanate was prepared from two inorganic substances, potassium cyanate(KOCN) and ammonium sulfate($(\text{NH}_4)_2\text{SO}_4$). By the mid-1800s, a great deal of evidence was against the vitalistic theory and it had become clear that the same basic scientific principles are applicable to all compounds. The only distinguishing characteristic of organic compounds is that all contain the element carbon. As is often the case, names persist even though they are no longer descriptive. Today, compounds containing carbon are called **organic compounds**. They contain occasionally oxygen, nitrogen, sulfur, phosphorus, halogen and metals. **Organic chemistry** is the study of organic compounds.

Organic molecules constitute the chemical bricks of life. Fats, sugars, proteins, and the nucleic acids are compounds in which the principal component is carbon. So are countless substances that we take for granted in everyday use. Virtually all the clothes that we wear are made of organic molecules — some of natural fibers, such as cotton and silk, others artificial, such as polyester. Toothbrushes, toothpaste, soaps, shampoos, deodorants, perfumes — all contain organic compounds, as do furniture, carpets, the plastic in light fixtures and cooking utensils, paintings, food, and countless other items.

Organic substances have improved the quality of our lives, yet the uncontrolled disposal of organic chemicals has polluted the environment, causing deterioration of animal and plant life, as well as injury

and disease to humans. If we are to create useful molecules and learn to control their effects, we need a knowledge of their properties and an understanding of their behavior. We must be able to apply the principles of organic chemistry.

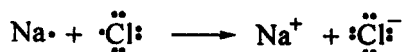
You and your classmates come to this course with a variety of backgrounds and interests. Most of you plan to be professionals in a biological, technical, or allied health field. Knowledge of chemistry is essential to a true understanding of everything from DNA replication to drug discovery to nutrition to engineering. Indeed, the chemical properties and principles you learn in this course will pervade almost every aspect of your private and professional lives. In this text, we provide you with both the principles and applications of chemistry that will help you in your professional practice and enrich your everyday life as well.

1.2 Bonding in Organic Compound

1.2.1 Ionic Bonding and Covalent Bonds

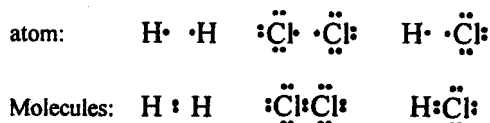
To explain how and why elements combine to form compounds, we have a model that relates the electronic structure of atoms and ions to their properties. This model can be extended to compounds. Chemical bonds are the forces that hold the atoms together. Two classes (really limited cases) of chemical bonds will be discussed that describe the forces that hold all of the atoms together in ionic and covalent compound.

Ionic bonding is the bonding that results from the electrostatic attraction between positively charged cation and negatively charged anion. The formation of binary ionic compounds can be represented by using **Lewis electron-dot symbols** to show how electrons are lost from metals and gained by nonmetals.



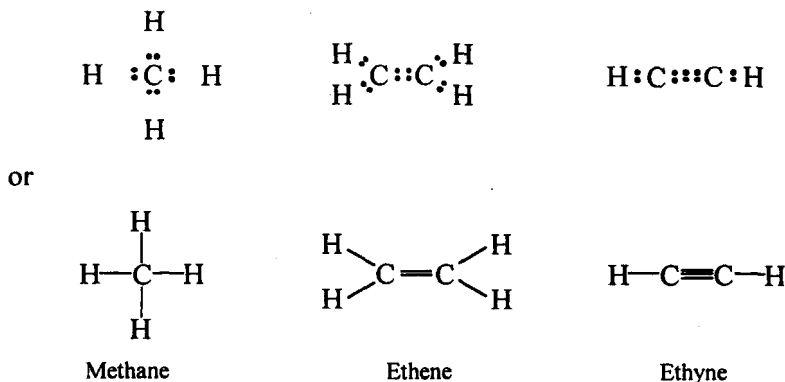
Covalent bonds involve the sharing of electron pairs between atoms of similar electronegativity, unlike ionic bonds, which does the completing transfer of electrons form. Because of the similarity in electronegativity, neither atom can relieve the other of its outer-shell electrons, as the case in ionic bonding, instead, each atom's nucleus is electrically attracted to the mutually shared electron pair, and a bond results.

In the simplest kind of covalent bond formation, each atom involved provides one electron to the bond. A shared pair of electrons results, becoming part of the outer shell of each atom. Consider, for example, hydrogen, chlorine, and hydrogen chloride, which are represented below by electron-dot formulas showing both bonding and nonbonding outer-shell electrons.



Usually, electron sharing occurs in a way that provides one or both atoms in the bond with the outer-shell configuration of a noble gas (in these cases two outer-shell electrons for hydrogen and eight for chlorine) — **the octet rule**.

The Lewis electron-dot symbol notation can be used to describe the covalent bonds in molecule. Two types of pairs of electrons are shown in these structures. Bonding pairs of electrons are shared between two atoms. Lone or nonbonding pairs of electrons are on one atom and not shared. Drawings of this type are known as Lewis structures. Representations of covalent bonds using Lewis symbols show shared electrons as dots (lines) between atoms and unshared electrons as dots. For example,

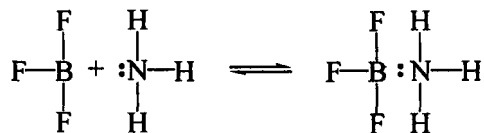


In the example given for the formation of a covalent bond, each atom contributes one electron.

Problem 1-1 Draw both Lewis electron-dot and line-bond structures for the following molecules:

- (1) CH_3CN (2) CH_3OH (3) CH_3NH_2 (4) NO_3^-

This equality of electron donation is not universal in covalent bonding. Covalent bonds can also be formed by having one atom contribute both electrons. The reaction between boron trifluoride and ammonia is illustrated:



The N atom in NH_3 contributes both electrons and is called **the donor atom**. The B atom in BF_3 brings no electrons to the “marriage”, and is therefore called **the acceptor atom**. Bonds formed between donor and acceptor atoms are called **coordinate covalent**. It should be emphasized, however, that once a coordinate covalent bond is formed, it is indistinguishable from the covalent bond; the N—B bond is covalent.

In coordinate covalent bonding, the donor atom suffers some loss of negative charge because of displacement of the electron cloud toward the acceptor atom. Coincidentally, the acceptor atom gains some negative charge by virtue of this displacement. If we assume by convention that this electronic displacement is just sufficient to distribute the shared electrons equally between the two atoms, then it is possible to assign integral charge values to the two atoms. These values are called **formal charges**.

Formal charges must be distinguished from the ionic charges assigned to electrically independent species like Ba^{2+} and F^- . When two molecules combine by coordinate covalent bonding, the donor atom acquires δ^+ unit of formal charge and the acceptor atom acquires δ^- unit of formal charge for each coordinate covalent bond formed.

1.2.2 Valence Bond Theory and Hybridization

A. Valence Bond Theory

The Valence Bond Method is a quantum mechanical expression of the Lewis concept of the shared electron pair. It considers the bond to be formed from the interaction of atomic orbital as the atoms approach each other. There can be one electron in each atomic orbital, or two electrons in one atomic orbital and none in the other. The two electrons must have opposite spins. As the atomic orbital begin to overlap, the two electrons come under the influence of the two nuclei, and are localized between these nuclei. The nuclei are attracted by the electrons and approach each other until the bond distance is reached. When the orbitals overlap, the electrons become indistinguishable; one can no longer say which electron came from which atom.

B. Atomic Structure of Carbon

The chemical properties of an element depend on the electron configuration of the outer shell.

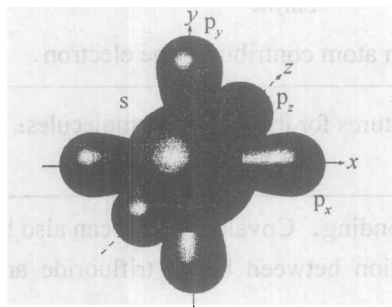


Figure 1-1 Electronic Structure of Carbon

Carbon has four electrons in its outer shell, two in the $2s$ orbital and one each in the $2p_x$ and $2p_y$ orbital. One would expect carbon, with this configuration, to be divalent, since the $2s$ orbital is filled and only the $2p_x$ and $2p_y$ orbitals have an unpaired electron to share. Carbon's tetravalent is explained by promoting one $2s$ electron to a $2p$ orbital, creating four unpaired electrons during bonding. Since bond formation is an energy-releasing process and formation of four bonds creates a stable octet in carbon's outer shell, the total process is energetically favorable. Figure 1-1 shows the shapes and geometric orientations of the four half-filled orbitals in carbon's outer shell.

C. Hybrid Orbital

In nearly all organic compounds, carbon exhibits a covalence of four. Let's start with a simple case and consider methane, CH_4 . Carbon has four electrons in its valence shell ($2s^2 2p^2$) and can form four bonds to hydrogens. What are the four C—H bonds in methane like? Because carbon uses two kinds of orbitals ($2s$ and $2p$) to form the bonds, we might expect methane to have two kinds of C—H bonds. In fact, however, all four C—H bonds in methane are identical and are spatially oriented toward the four corners of a regular tetrahedron. How can we explain this?

sp^3 hybrids Linus Pauling, who showed that an s orbital and three p orbitals could combine, or **hybridize**, to form four equivalent atomic orbitals with tetrahedral orientation, provided an answer in 1931. Shown in Figure 1-2, these tetrahedrally oriented orbitals are called **sp^3 hybrids**. Note that the superscript 3 in the name sp^3 tells how many of each type of atomic orbital combine to form the hybrid,

not how many electrons occupy it.

The concept of hybridization explains how carbon forms four equivalent tetrahedral bonds but doesn't explain why it does so. The shape of the hybrid orbital suggests the answer. When an s orbital hybridizes with three p orbitals, the resultant hybrid orbitals are unsymmetrical about the nucleus. One of the two lobes is much larger than the other (Figure 1-2) and can therefore overlap better with another orbital when it forms a bond. As a result, sp^3 hybrid orbitals form stronger bonds than unhybridized s or p orbitals do.

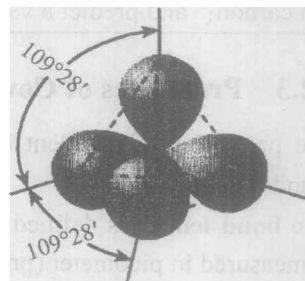


Figure 1-2 Four Tetrahedral sp^3 Orbitals of the Carbon Atom

sp^2 hybrids When we discussed sp^3 hybrid orbital previously, we said that all four of carbon's valence-shell atomic orbitals combine to form four equivalent sp^3 hybrids. Imagine instead that the 2s orbital combines with only two of the three available 2p orbitals. Three hybrid orbitals called sp^2 hybrids result, and one unhybridized 2p orbital remains unchanged. The three sp^2 orbitals lie in a plane at angles of 120° to one another, with the remaining p orbital perpendicular to the sp^2 plane, as shown in Figure 1-3.

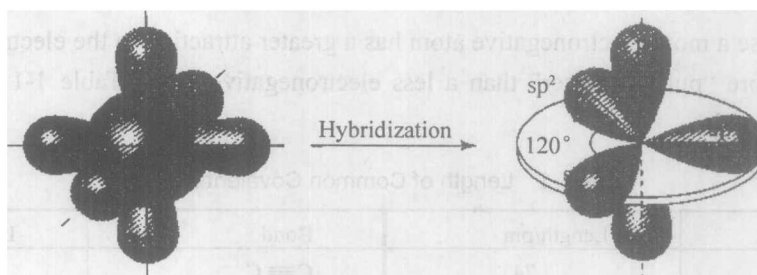


Figure 1-3 sp^2 Hybridized Carbon Atom

sp hybrids In addition to forming single and double bonds by sharing two and four electrons, respectively, carbon can form triple bonds by sharing six electrons. To account for triple bonds, such as that in acetylene, C_2H_2 , we need a third kind of hybrid orbital — an sp hybrid.

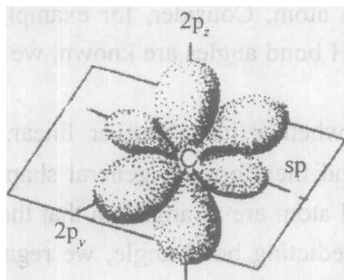


Figure 1-4 sp Hybridized Carbon Atom

Imagine that, instead of combining with two or three 2p orbitals, the carbon 2s orbital hybridizes with only a single 2p orbital. Two sp hybrid orbitals result, and two p orbitals remain unchanged. The two sp orbitals are linear, or 180° apart on the x-axis, and the remaining two p orbitals are perpendicular on the y-axis and the z-axis, as shown in Figure 1-4.

Problem 1-2 Draw a line-bond structure for propyne, $\text{CH}_3\text{C}\equiv\text{CH}$, indicate the hybridization of each carbon; and predict a value for each bond angle.

1.2.3 Properties of Covalent Bonds

The properties of covalent bonds involve physical quantities — bond length, bond angle, bond energy and bond polarity.

The bond length is defined as the distance between the centers of bonded nuclei. Bond length is usually measured in picometer (pm), $1 \text{ pm} = 10^{-10}$ centimeter.

Bond lengths between atoms of a given type decrease with the amount of multiple bonding. Thus, bond lengths for carbon-carbon bonds are in the order $\text{C}-\text{C} > \text{C}=\text{C} > \text{C}\equiv\text{C}$.

Bond lengths tend to increase with the size of the bonded atoms. This effect is most dramatic as we proceed down the periodic table. Thus, a $\text{C}-\text{H}$ bond is shorter than a $\text{C}-\text{F}$ bond, which is shorter than a $\text{C}-\text{Cl}$ bond. Since bond length is the distance between the centers of bonded atoms, it is reasonable that larger atoms should form longer bonds.

When we make comparisons within a given row of the periodic table, bonds of a certain type (single, double, or triple) between a given atom and a series of other atoms become shorter with increasing electronegativity. Thus, the $\text{C}-\text{F}$ bond in $\text{H}_3\text{C}-\text{F}$ is shorter than the $\text{C}-\text{C}$ bond in $\text{H}_3\text{C}-\text{CH}_3$. This effect occurs because a more electronegative atom has a greater attraction to the electrons of the bonding partner, and therefore “pulls it closer” than a less electronegative atom. Table 1-1 lists the length of common covalent bonds.

Table 1-1 Length of Common Covalent Bonds

Bond	Length/pm	Bond	Length/pm
$\text{H}-\text{H}$	74	$\text{C}\equiv\text{C}$	120
$\text{C}-\text{H}$ (Alkane)	110	$\text{C}-\text{O}$ (Alcohol)	143
$\text{C}-\text{C}$	154	$\text{C}=\text{O}$	122
$\text{C}=\text{C}$ (Alkene)	133	$\text{C}-\text{N}$ (Amine)	147
$\text{C}\equiv\text{C}$ (Benzene)	139	$\text{O}-\text{H}$ (Alcohol)	96

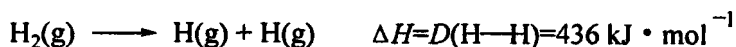
The bond angle is the angle between two bonds to the same atom. Consider, for example, the compound methane, CH_4 . When the $\text{C}-\text{H}$ bond length and $\text{H}-\text{C}-\text{H}$ bond angles are known, we know the structure of methane.

The bond angles within a molecule determine its shape — whether it is bent or linear. Two generalizations allow us to predict the approximate bond angles, and therefore the general shapes, of many simple molecules. The first is that the groups bond to a central atom are arranged so that they are as far apart as possible. In applying this rule for the purpose of predicting bond angle, we regard all groups as identical. Thus the groups that surround carbon in CH_3Cl (methyl chloride) are treated as identical, even though in reality the $\text{C}-\text{Cl}$ bond is considerably longer than the $\text{C}-\text{H}$ bonds. Although the bond angles show minor deviations from the exact tetrahedral bond angle of 109.5° , methyl

chloride in fact has the general tetrahedral shape. Molecules, then, assume the tetrahedral structure, when four groups are arranged about a central atom. Since carbon is tetravalent, this is an extremely important geometry for many organic compounds.

The second generalization about molecular structure applies to molecules with unshared electron pairs. In predicting the geometry of a molecule, an unshared electron pair can be considered as a bond without an atom at one end. This rule allows us to handle, for example, the geometry of ammonia. In view of this rule, ammonia, NH_3 , has four groups about the central nitrogen, three hydrogens and an electron pair. To a first approximation, these groups adopt the tetrahedral geometry with the electron pair occupying one corner of the tetrahedron. (This geometry is sometimes called **pyramidal**, or pyramid-like, geometry.)

Bond dissociation energy or bond energy (D) is the energy required to break one mole of bonds in a gaseous species. The thermochemical equation that describes the bond dissociation for H_2 is



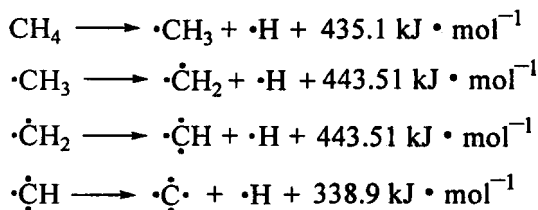
Bond energies are always endothermic and thus have a positive sign; it takes energy to break a bond.

Covalent bonds form between many different elements. Clearly, not all types of covalent bonds are of equal strength; each involves different nuclei and electrons in different orbitals. Bond strengths are very important, because species with strong bonds are generally stable.

Table 1-2 shows a number of important bond energies. For diatomic molecules, these numbers are measured exactly. A problem arises in measuring exact bond energies in polyatomic molecules because the other atoms influence the energy required to break a bond. Consider the bond energy for each $\text{C}-\text{H}$ bond in methane.

Table 1-2 Bond Energy

Covalent bond	Bond energy $D/(\text{kJ} \cdot \text{mol}^{-1})$	Covalent bond	Bond energy $D/(\text{kJ} \cdot \text{mol}^{-1})$	Covalent bond	Bond energy $D/(\text{kJ} \cdot \text{mol}^{-1})$
$\text{F}-\text{F}$	159.0	$\text{S}-\text{S}$	266.0	$\text{CH}=\text{C}-\text{H}$	522.5
$\text{Cl}-\text{Cl}$	242.7	$\text{S}-\text{H}$	339.0	$\text{C}_6\text{H}_5\text{CH}_2-\text{H}$	355.2
$\text{Br}-\text{Br}$	192.3	$\text{C}-\text{H}$	414.0	$\text{C}=\text{C}$	611.0
$\text{I}-\text{I}$	150.8	$\text{C}-\text{C}$	348.0	$\text{C}\equiv\text{C}$	837.0
$\text{H}-\text{H}$	436.0	$\text{C}-\text{N}$	293.0	$\text{C}=\text{N}$	615.0
$\text{H}-\text{F}$	569.0	$\text{C}-\text{O}$	351.0	$\text{C}\equiv\text{N}$	891.0
$\text{H}-\text{Cl}$	431.0	$\text{C}-\text{F}$	439.0	$\text{C}=\text{O}$	799.0
$\text{H}-\text{Br}$	368.0	$\text{C}-\text{Cl}$	328.0	$\text{N}=\text{N}$	418.0
$\text{H}-\text{I}$	296.8	$\text{C}-\text{Br}$	276.0	$\text{N}\equiv\text{N}$	946.0
$\text{N}-\text{H}$	389.0	$\text{C}-\text{I}$	238.0	$\text{S}=\text{O}$	523.0
$\text{N}-\text{O}$	201.0	$\text{C}-\text{S}$	259.0	$\text{HO}-\text{H}$	464.5
$\text{O}-\text{H}$	463.0	$\text{C}_6\text{H}_5-\text{H}$	431.0	$\text{D}-\text{D}$	444.1
$\text{O}-\text{O}$	146.0	$\text{CH}_2=\text{CH}-\text{H}$	431.0		



The values are not the same because the species in which we are breaking the bonds are not the same. Since bond energies depend on the environment of the bonded atoms, Table 1-2 gives average bond energies for all cases other than the diatomic molecules. While not exact, these numbers are fairly accurate since most bonds between the same two atoms are of similar strengths.

The values of bond energies span a fairly wide range. The C—H bond is more than twice as strong as the O—F bond. In comparing bond strengths between the same two atoms, double and triple bonds are stronger than single bonds, as expected, from their multiple sharing of electrons.

Polar covalent bond Atoms with equal or nearly equal electronegativities form covalent bonds in which both atoms exert equal or nearly equal pulls on the bonding electrons. This type of covalent bond is called a **nonpolar bond**. In organic molecules, carbon-carbon bonds and carbon-hydrogen bonds are the most common types of nonpolar bond.

In covalent compounds like H_2O , HCl , CH_3OH , or $\text{H}_2\text{C}=\text{O}$, one atom has a substantially greater electronegativity than the others. The more electronegative atom has a greater attraction to the bonding electrons — not enough of an attraction for the atom to break off as an ion, but enough so that this atom takes the larger share of electron density. The result is a **polar covalent bond**, a bond with an uneven distribution of electron density. The degree of polarity of a bond depends partly on the difference in electronegativities of the two atoms bonded together and partly on other factors, such as the size of the atoms. The larger the difference in electronegativities of the two atoms bonded together, the larger polarity of covalent bond. Table 1-3 shows electronegativities of important elements. We may think of chemical bonds as a continuum from nonpolar covalent bonds to ionic bonds. Within this continuum, we speak of the increasing ionic character of the bonds.

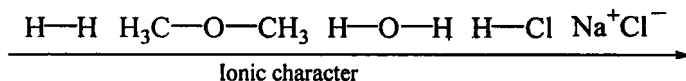
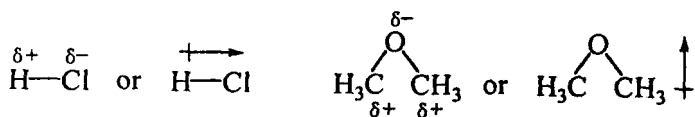


Table 1-3 Electronegativities of Important Elements

H						
2.2						
Li	Be	B	C	N	O	F
0.98	1.57	2.04	2.55	3.04	3.44	3.98
Na	Mg	Al	Si	P	S	Cl
0.93	1.31	1.61	1.90	2.19	2.58	3.16
K	Ca					Br
0.82	1.00					2.96
						I
						2.66

The distribution of electrons in a polar-molecule may be symbolized by partial charges: δ^+ (partial positive) and δ^- (partial negative). Another way of representing the different electron densities within a molecule is by a crossed arrow (\rightarrow) that points from the partially positive end of a molecule to the partially negative end.



Bond Moment If a polar bond, such as an O—H bond, is subjected to an electric field, the bond feels a certain amount of “turning force”. This force is simply the push of the electric field to the aligned bond in the field. A more polar bond feels more force than a less polar bond. The **bond moment**, a measure of the polarity of a bond, may be calculated from the value of the force field by that bond.

Problem 1-3 Use the δ^+/δ^- convention to indicate the direction of expected polarity for each of the bonds shown:

- (1) Br—CH₃ (2) H₂N—CH₃ (3) H—NH₂
 (4) HO—CH₃ (5) BrMg—CH₃ (6) F—CH₃

The bond moment is defined as $\mu = e \times d$, where e is the charge (in electrostatic units) and d is the distance between the charges (in meter), and is reported in units called Debyes (D). Bond moments range from 0.4 D for the nonpolar C—H bond to 3.5 D for the highly polar C≡N bond (see Table 1-4). The bond moment for a particular bond is relatively constant from compound to compound.

Table 1-4 Bond Moment for Common Covalent Bonds

Bond	Bond moment/D	Bond	Bond moment/D
C—H	0.4	C—Cl	1.46
N—H	1.31	C—Br	1.35
O—H	1.51	C—I	1.19
C—N	0.22	C=O	2.3
C—O	0.74	C≡N	3.5
C—F	1.41		

Polar Molecule The dipole moment μ is the vector sum of the bond moments in a molecule. Because vector addition takes into account the direction as well as the magnitude of the bond moments, the dipole moment is a measure of the polarity of the molecule as a whole.

The dipole moments for a few organic compounds are listed in Table 1-5. Note that the dipole moment of CCl₄ is zero, even though each C—Cl bond has a moment of 1.46 D. The reason for this apparent anomaly is that the CCl₄ molecule is symmetrical; in the vector addition, the bond moments cancel and result in a vector sum of zero. Carbon dioxide is another molecule with bond moments but no dipole moment. Again, this is a case of a symmetrical molecule in which the bond moments cancel. On the other hand, the bond moments of a water molecule do not cancel, and water has a dipole moment.