

Chapter 2

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2.1 The Makeup of Organic Compounds

To understand the nature and reactivity of organic molecules, we first look at the “pieces” of such molecules, atoms and chemical bonds. Most of the millions of known natural and synthetic organic compounds are combinations of a relatively small number of elements, namely carbon (C), hydrogen (H), oxygen (O), nitrogen (N), sulfur (S), phosphorus (P), silicon (Si), as well as the halogens fluorine (F), chlorine (Cl), bromine (Br), and iodine (I). The chief reason for the almost unlimited number of stable organic molecules that can be built from this limited number of elements is the ability of carbon to form stable carbon-carbon bonds. All kinds of three-dimensional *carbon skeletons* can therefore be made, even when the carbon atoms are also bound to *heteroatoms*, elements other than carbon and hydrogen. Such parts of molecules containing heteroatoms are of particular interest because they are often the site of specific interactions and reactivities. Thus, they are commonly referred to as *functional groups* or *functionalities*.

Fortunately, despite the extremely large number of existing organic chemicals containing all kinds of functional groups, knowledge of a few governing rules about the nature of the elements and chemical bonds already enable us to understand important relationships between the structure of a given compound and its properties and reactivities. In large part, these attributes then determine the compound’s behavior in the environment.

Elemental Composition, Molecular Formula, and Molar Mass

When describing a compound, we first specify the elements it contains, or its *elemental composition*. For example, butyl chloride consists of carbon, hydrogen, and chlorine. We then specify how many atoms of each of element are present in one molecule, the compound’s *molecular formula*. Butyl chloride contains four carbon atoms, nine hydrogen atoms, and one chlorine atom, thus its molecular formula is C_4H_9Cl . We can then calculate the *molecular mass* or *molecular weight* of the compound, which is the sum of all the atoms’ masses present in the molecule. The average atomic masses of elements of interest to us in organic molecules are given in Table 2.1 in units of m_u (unified atomic mass unit). This unit is approximately equal to 1.6605×10^{-27} kg. Using these atomic mass values, we obtain an *average* molecular mass of $92.57 m_u$ for butyl chloride.

Complicating matters a bit is the natural occurrence of *stable isotopes*, atoms that have the same number of protons and electrons but different numbers of neutrons in the nucleus, thus giving rise to different atomic masses. Table 2.2 enumerates examples of common elements present in organic chemicals exhibiting stable isotopes with significant natural abundances. Thus, the atomic masses given in Table 2.1 represent averaged values of the naturally occurring isotopes of a given element (e.g., average carbon is 1.1% at $13 m_u$ + 98.9% at $12 m_u = 12.011 m_u$).

To find the molar mass of a pure substance, we take 1 mole, Avogadro’s number $N_A = 6.022 \times 10^{23}$, of identical molecules. For butyl chloride, this amount weighs 92.57 grams. Therefore, 1 mole (abbreviation 1 mol) of any pure substance always

Table 2.1 Atomic Mass, Electronic Configuration, and Typical Number of Covalent Bonds of the Most Important Elements Present in Organic Molecules

Name ^a	Element		Mass ^b (m_u)	Number of Electrons in Shell					Net Charge of Kernel	Number of Covalent Bonds ^c
	Symbol	Number		K	L	M	N	O		
Hydrogen	H	1	1.008	1					1+	1
Helium	He	2		2					0	
Carbon	C	6	12.011	2	4				4+	4
Nitrogen	N	7	14.007	2	5				5+	3, (4) ^d
Oxygen	O	8	15.999	2	6				6+	2, (1) ^e
Fluorine	F	9	18.998	2	7				7+	1
Neon	Ne	10		2	8				0	
Silicon	Si	14	28.0855	2	8	4			4+	4
Phosphorus	P	15	30.974	2	8	5			5+	3, 5
Sulfur	S	16	32.06	2	8	6			6+	2, 4, 6, (1) ^e
Chlorine	Cl	17	35.453	2	8	7			7+	1
Argon	Ar	18		2	8	8			0	
Bromine	Br	35	79.904	2	8	18	7		7+	1
Krypton	Kr	36		2	8	18	8		0	
Iodine	I	53	126.905	2	8	18	18	7	7+	1
Xenon	Xe	54		2	8	18	18	8	0	

^aThe underlined elements are noble gases.^bAbundance-averaged mass values of the naturally occurring isotopes.^cNumber of covalent bonds commonly occurring in organic molecules.^dPositively charged atom.^eNegatively charged atom.

contains the same amount of molecules and weighs in grams what the *average* molecule weighs in m_u . We should point out, however, that the ensemble of individual molecules of a given compound, for example with the molecular formula C_4H_9Cl , covers a range of different masses. For butyl chloride, 95.6% of the molecules contain 4 ^{12}C atoms, whereas 4.4% have 1 ^{13}C and 3 ^{12}C atoms. Similarly, 75.8% of all molecules contain a ^{35}Cl and 24.2% a ^{37}Cl atom. Hence, by neglecting the 2H isotope, 72.5% have a molecular formula of $^{12}C_4^1H_9^{35}Cl$, 3.3% $^{13}C^1H^{35}Cl$ (1 m_u higher),

Table 2.2 Isotope Ratios of Elements Exhibiting Stable Isotopes at Significant Abundances Present in Organic Molecules

Element	Isotope Ratios	Element	Isotope Ratio
Hydrogen	$^2H: ^1H = 0.00015:1$	Silicon	$^{29}Si: ^{28}Si = 0.051:1$ $^{30}Si: ^{28}Si = 0.034:1$
Carbon	$^{13}C: ^{12}C = 0.011:1$	Sulfur	$^{34}S: ^{32}S = 0.044:1$
Nitrogen	$^{15}N: ^{14}N = 0.0037:1$	Chlorine	$^{37}Cl: ^{35}Cl = 0.32:1$
Oxygen	$^{18}O: ^{16}O = 0.0020:1$	Bromine	$^{81}Br: ^{79}Br = 0.98:1$

23.1% $^{12}\text{C}^1\text{H}^{37}\text{Cl}$ ($2 m_u$ higher), and 1.1% $^{13}\text{C}^1\text{H}^{37}\text{Cl}$ ($3 m_u$ higher). Molecules containing different isotopes of a given element may exhibit somewhat different reactivities, particularly at positions where a reaction occurs. Therefore, measurements of the exact stable isotope composition of a given compound, referred to as compound specific stable isotope analysis (CSIA), may be very useful in assessing transformation processes in the environment (see Chapter 27).

Given the molecular formula, we now describe how the different atoms are connected to each other. The description of the exact connection of the various atoms, the connectivity, is commonly referred to as the *structure* of the compound. Depending on the number and types of atoms, many different ways to interconnect a given set of atoms may exist, yielding different structures. Such related compounds are referred to as *isomers*. Furthermore, as we subsequently discuss, several compounds can have atoms connected in exactly the same order (i.e., they exhibit the same structure), but the spatial arrangement differs. Such compounds are called *stereoisomers*. Sometimes, the term structure is used to denote both the connectivity as well as the spatial arrangement of the atoms. The term *constitution* of a compound is then sometimes introduced to solely describe the connectivity.

Electron Shells of Elements Present in Organic Compounds

Before we can examine how many different structures exist for a given molecular formula (e.g., $\text{C}_4\text{H}_9\text{Cl}$), we need to recall some of the rules concerning the number and nature of bonds that each of the various elements present in organic molecules may form. To this end, we first examine the electronic configuration of the atoms involved (see also Table 2.1).

The configuration of electrons of an atom is often described by the notion of electron shells of varying energies. Electrons in shells farther from the nucleus exhibit higher average energies and travel farther from the nucleus than those in inner shells. The shell closest to the nucleus (K-shell) holds two electrons (see elements in first row of periodic table). The second shell (L-shell) holds up to eight (see second row of periodic table); the third shell (M-shell) can ultimately hold eighteen, but a stable configuration is reached when the shell is filled with eight electrons (see argon structure). Electrons in the outermost shell, the *valence shell*, are called valence electrons, whereas the remainder of the atom is referred to as the *kernel*. If the outer shell is filled, as with argon and the other noble gases (helium, neon, krypton, xenon, and radon), the atom is especially nonreactive. Thus, the number of valence electrons of a particular atom chiefly determines the chemical nature of an element. Some significant differences between elements exhibiting the same number of valence electrons do exist, such as between nitrogen and phosphorus or oxygen and sulfur. The differences between such elements are due in large part to the different energetic status of the electrons in the various shells and are further addressed in subsequent discussions.

Therefore, much of the chemistry of the elements present in organic molecules is understandable in terms of a simple model describing the tendencies of the atoms to attain such “filled-shell” conditions by gaining, losing, or most importantly sharing

electrons. Among the elements present in organic molecules, hydrogen requires two electrons to fill its valence shell; one it supplies, and the other it must get elsewhere. Other important atoms of organic chemistry require eight valence electrons, which is called an octet configuration (see Table 2.1).

Covalent Bonding

Organic molecules customarily complete the octet in their valence shell by sharing electrons with other atoms, thus forming so-called *covalent bonds*. Each single covalent bond is composed of a pair of electrons, in most cases one electron contributed by each of the two bonded atoms. The covalent bond may thus be characterized as a mutual deception. By contributing only one electron to the bond, each atom “feels” it has both electrons in its outer shell. Thus, we visualize the bonds in an organic compound structure as electron pairs localized between two positive atomic nuclei; the electrostatic attraction of the nuclei to the electrons holds the atoms together. The simple physical law of the attraction of opposite charges and the repulsion of like charges is the most basic force in chemistry, and it explains many chemical phenomena.

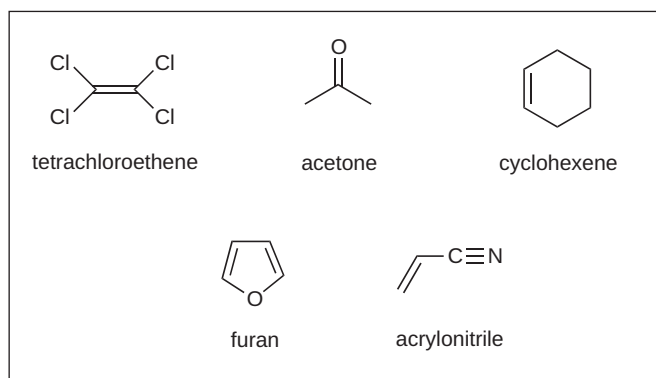
Using the simple concept of electron sharing to complete an octet in a valence shell, we can now easily deduce from Table 2.1 that in a neutral organic molecule, H, F, Cl, Br, and I (monovalent atoms) should form one bond, O and S (bivalent atoms) form two bonds, N and P (trivalent atoms) form three bonds, and C and Si (tetravalent atom) form four bonds. These valency rules are valid for the majority of cases that are of interest to us. Notable exceptions are S and P (see Table 2.11 and examples given in Chapter 3).

We are now ready to draw all the possible *structural isomers* for butyl chloride by simply applying these valency rules. Table 2.3 shows the four different possibilities. With this example, we also take the opportunity to get acquainted with some of the common conventions used to symbolize molecular structures. The first convention (type 1 in Table 2.3) differentiates shared and unshared valence electron pairs. Straight lines denote shared electrons forming covalent bonds, while pairs of dots represent the unshared electrons. This representation clearly shows the nuclei and all of the electrons we must visualize. To simplify this first convention, all lines indicating bonds to hydrogen as well as the dots for unshared (nonbonding) electrons are frequently not shown (type 2). For further convenience, we may in many cases, eliminate all the bond lines without loss of clarity, as illustrated by type 3. In this convention, parentheses indicate branching. Finally, especially when dealing with compounds exhibiting a large number of carbon atoms, another convention is simply to sketch the carbon skeleton (type 4 in Table 2.3). Each line is thus a skeletal bond and is assumed to have carbons at each end, unless another element is shown. Furthermore, no carbon-hydrogen bonds are indicated but are assumed present as required to make up full bonding (four bonds) at each carbon atom. To distinguish the various carbon-carbon bonds, bond lines are placed at about 120° , roughly resembling the true physical bond angle (see Fig. 2.2). Finally, an approach called SMILES (Simplified Molecular-Input Line-Entry System) can be used to write out each structure in a manner normalized for computing (see U.S. EPA, 2009; Weininger, 1988).

Table 2.3 Different Conventions (types 1-4 and SMILES) Symbolizing the Molecular Structures of the Four Butyl Chloride (or Chlorobutanes) Isomers

type 1	type 2	type 3	type 4	SMILES
	$\text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{Cl}$	$\text{H}_3\text{CCH}_2\text{CH}_2\text{CH}_2\text{Cl}$		<chem>CCCCCl</chem>
	$\text{H}_3\text{C}-\text{CH}_2-\underset{\text{Cl}}{\text{CH}}-\text{CH}_3$	$\text{H}_3\text{CCH}_2\text{CH}(\text{Cl})\text{CH}_3$		<chem>CCC(Cl)C</chem>
	$\text{H}_3\text{C}-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2-\text{Cl}$	$\text{H}_3\text{CCH}(\text{CH}_3)\text{CH}_2\text{Cl}$		<chem>CC(C)CCl</chem>
	$\text{H}_3\text{C}-\underset{\text{CH}_3}{\overset{\text{Cl}}{\text{C}}}-\text{CH}_3$	$(\text{H}_3\text{C})_3\text{CCl}$		<chem>CC(C)(Cl)C</chem>

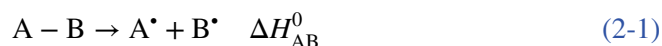
So far, we have dealt only with single bonding between two atoms. Many cases exist, however, in which atoms with more than one “missing” electron in their outer shell form *double bonds* or sometimes even *triple bonds*, when two atoms share either two or even three pairs of electrons to complete the octet in their valence shells. A few examples of compounds exhibiting double or triple bonds are given in Fig. 2.1 (using structural convention type 4). We note that a double line between the corresponding atoms indicates a double bond, and, logically, a triple bond has three parallel lines. Ring structures, with or without double bonds, are usually composed predominantly of carbon atoms, but they may also contain heteroatoms (i.e., elements other than carbon or hydrogen such as N, O, S, Si).

**Figure 2.1** Some simple molecules (type 4 from Table 2.3) exhibiting double and triple bonds.

At this point, it is important to point out again that structural isomers may exhibit very different properties and reactivities (e.g., butyl chloride isomers in Table 1.1 and the following examples). This should remind us that even small distinctions in the arrangement of a molecule may translate into either quite similar but also very different environmental behavior. Therefore, we now review what it is about compound structure that dictates chemical nature and reactivity.

Bond Energies (Enthalpies) and Bond Lengths: The Concept of Electronegativity

Here we address an important aspect of chemical bonding, the strength of a chemical bond in organic molecules. We should have a general idea of the energy involved in holding atoms together in a covalent bond. The most convenient measure of bond energy is indicated by the bond *dissociation enthalpy*, ΔH_{AB}^0 . For a diatomic molecule, this is defined as the *heat change* of the *gas phase* reaction:



where each atom retains its original electron at constant pressure and temperature (e.g., 1.013 bar and 25°C). Here, ΔH_{AB}^0 also contains the differences in translational, rotational (only AB), and vibrational (only AB) energies between *educt* (A–B) and *products* (A[•], B[•]). Unfortunately, it is not possible to directly measure bond dissociation (or formation) enthalpies for each of the different bonds present in a molecule containing more than one bond. They must be determined indirectly, commonly through thermochemical studies of evolved heat (calorimetric measurements) in reactions such as combustion. These studies yield only enthalpies of overall reactions, where several bonds are broken and formed. The individual bond dissociation (or formation) enthalpies have then to be deduced from this data in various ways. The results are commonly shown in tables as average strengths for a particular type of bond, valid for gas phase reactions at 25°C and 1.013 bar. Table 2.4 summarizes average bond enthalpies (and bond lengths) of some important covalent bonds.

From these data, some general conclusions about covalent bonds in organic molecules can be drawn. Bond lengths between elements in the second row of periodic table (C, N, O, F) with hydrogen are all around 1 Å (0.1 nm). Bonds involving larger atoms (S, P, Cl, Br, I) are longer and weaker. Double and triple bonds are shorter and stronger than the corresponding single bonds. We also notice that the bond enthalpies of double and triple bonds are often somewhat less than twice and three times the values of the single atom bonds. An important exception are C = O bonds.

To get an appreciation of the magnitude of bond energies, it is illustrative to compare bond enthalpies to the energy of molecular motion (translational, vibrational, and rotational), which at room temperature is typically a few tens to not much more than one hundred kilojoules per mole. As can be seen in Table 2.4, most bond energies in organic molecules are much larger than this, and, therefore, organic compounds are generally stable to thermal disruption at ambient temperatures. At high temperatures, however, the energy of intramolecular motion increases and can then exceed certain

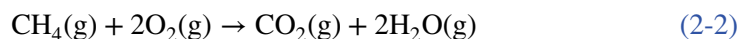
Table 2.4 Average Bond Lengths^a and Bond Enthalpies of Some Important Covalent Bonds

Bond	Length (Å)/ Enthalpy (kJ mol ⁻¹)	Bond	Length (Å)/ Enthalpy (kJ mol ⁻¹)	Bond	Length (Å)/ Enthalpy (kJ mol ⁻¹)
<i>Diatomic Molecules</i>					
H–H	0.74/436	F–F	1.42/155	O=O	1.21/498
H–F	0.92/566	Cl–Cl	1.99/243	N≡N	1.10/946
H–Cl	1.27/432	Br–Br	2.28/193		
H–Br	1.41/367	I–I	2.67/152		
H–I	1.60/298				
<i>Covalent Bonds in Organic Molecules</i>					
<i>Single Bonds^b</i>					
H–C	1.11/415	C–C	1.54/348	C–F	1.35/486
H–N	1.00/390	C–N	1.47/306	C–Cl	1.78/339
H–O	0.96/465	C–O	1.41/360	C–Br	1.94/281
H–S	1.33/348	C–S	1.81/275	C–I	2.14/216
<i>Double and triple bonds</i>					
C=C	1.34/612	C=O ^d	1.20/737	C≡C	1.16/838
C=N	1.28/608	C=O ^e	1.20/750	C≡N	1.16/888
C=S ^c	1.56/536	C=O ^f	1.16/804		

^aBond length in Å (1 Å = 0.1 nm).^bBond lengths are given for bonds in which none of the partner atoms is involved in a double or triple bond. If so, bond lengths are somewhat shorter.^cIn carbon disulfide; ^d in aldehydes; ^e in ketones; and ^f in carbon dioxide.

bond energies. This leads to a thermally induced disruption of bonds, a process that is commonly referred to as pyrolysis (heat splitting).

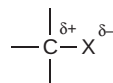
We note here that the persistence of organic compounds in the environment is due to the relatively high activation energy needed to break bonds and not because the atoms in a given molecule are present in their lowest possible energetic state. Hence, many organic compounds are nonreactive for kinetic, not thermodynamic reasons. We discuss the energetics and kinetics of chemical reactions in Chapter 21. Here, a simple example helps to illustrate this point. From daily experience, we know that heat can be gained from burning natural gas, gasoline, or wood. We also know that all these fuels are virtually inert under environmental conditions until we light a match and provide the necessary initial activation energy to break bonds. Once the reaction has started, enough heat is liberated to keep it going. The amount of heat liberated can be estimated from the bond enthalpies given in Table 2.4. For example, when burning methane gas in a stove, the process that occurs is the reaction of the hydrocarbon, methane, with oxygen to yield CO₂ and H₂O:



In this gas phase reaction, we break four C–H and two O=O “double” bonds, and we make two C=O and four O–H bonds. Therefore, when converting 1 mole of methane,

we have to invest $(4 \times 415) + (2 \times 498) = +2656 \text{ kJ mol}^{-1}$, and we gain $(2 \times 804) + (4 \times 465) = -3468 \text{ kJ mol}^{-1}$. The estimated heat of reaction at 25°C for the reaction in Eq. 2-2 is -812 kJ mol^{-1} (the experimental value is -802 kJ mol^{-1}), an impressive amount of energy. We recall from basic chemistry that, by convention, we use a minus sign to indicate that the reaction is *exothermic* (from the greek *exo* for outside), which occurs when heat is given off to the outside. A positive sign is assigned to the heat of reaction if the reaction consumes heat by taking energy into the product structures. These reactions are called *endothermic* (from the greek *endon* for within).

Electronegativity. Among the elements present in organic molecules, we intuitively and correctly predict that the smaller the atom allowing a closer approach of the bonding electrons to the positively charged nucleus, and the higher the net charge of the kernel (see Table 2.1), the greater the atom's tendency to attract additional electrons. As indicated in Table 2.5, this attraction for the electrons, or *electronegativity*, increases with increasing kernel charge, as within a row in the periodic table (e.g., from C to F), and decreases with increasing kernel size, as within a column (e.g., from F to I). When visualizing a chemical bond, it is appropriate then to imagine that the "electron cloud" or averaged electron position located between the two nuclei is generally distorted toward the atom that is more *electronegative*. This results in the accumulation of a negative charge at one end of the bond (denoted as δ^-) and, correspondingly, a deficiency at the other end (denoted as δ^+):



The most commonly used quantitative scale to express *electronegativity* (Table 2.5) was devised by Pauling (1960). On this scale, a value of 4.0 is arbitrarily assigned to the most electronegative atom, fluorine, and a value of 1.0 to lithium. The difference in

Table 2.5 Electronegativity of Atoms According to the Scale Devised by Pauling (1960)

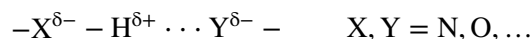
Charge of Kernel					Increasing Size of Kernel
+1	+4	+5	+6	+7	
H 2.2					↓
	C 2.5	N 3.0	O 3.5	F 4.0	
		P 2.2	S 2.5	Cl 3.0	
			Si 1.9	Br 2.8	
				I 2.5	

electronegativity between two atoms A and B is calculated from the extra bond energy in A–B versus the mean bond energies of A–A and B–B in which the electrons should be equally shared (see Table 2.4). The reason for deriving relative electronegativities based on bond energies is that we interpret the extra bond strength in such a bond between involving atoms of different electronegativity to be due to the attraction of the partial positive and negative charges.

From Table 2.5, we can see that carbon is slightly more electronegative than hydrogen, according to Pauling's scale. However, the electron-attracting power of an atom in isolation differs from that attached to electron-attracting or electron-donating substituents in an organic molecule. For example, many experimental observations indicate that carbon in CH₃ is significantly less electronegative than hydrogen. We may rationalize this by recognizing that each additional hydrogen contributes some electron density to the carbon and successively reduces that central atom's electronegativity. In conclusion, we should be aware that the electronegativity values in Table 2.5 represent only a rough scale of the relative electron-attracting power of the elements. Therefore, in bonds between atoms of similar electronegativity, the direction and extent of polarization also depends on the type of substitution at the two atoms.

Let us further discuss the importance of charge separation in bonds involving atoms of different electronegativity, for example, C and N, O, or Cl. The extent of partial ionic character in such *polar* covalent bonds is a key factor in determining a compound's partitioning behavior and reactivity in the environment. The polarization in bonds is important in directing the course of chemical reactions in which either these bonds themselves or other bonds in the vicinity are broken. For example, our earlier illustration of the combustion of methane (Eq. 2-2) demonstrates that enthalpy can be gained when nonpolar bonds, as commonly encountered in organic molecules, are broken and polar bonds are formed, such as those in carbon dioxide and water. Furthermore, the partial charge separation makes each bond between dissimilar atoms a *dipole*. The (vector) sum of all bond dipoles in a structure yields the total dipole moment of the molecule, an entity that can be measured. However, the dipole moments of individual bonds are most important with respect to the interactions of a given compound with its molecular surroundings.

Hydrogen Bonding. One special result of the polarization of bonds to hydrogen is *hydrogen bonding*. As indicated in Table 2.1, hydrogen does not possess any inner electrons isolating its nucleus from the bonding electrons. Thus, in bonds of hydrogen with highly electronegative atoms, the bonding electrons are drawn strongly to the electronegative atom, leaving the proton exposed at the outer end of the covalent bond. This relatively bare proton can now attract another electron-rich center, especially heteroatoms with nonbonding electrons, and form a *hydrogen bond* as schematically indicated by the dotted line:



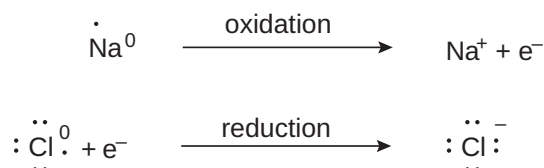
In organic molecules, this most often occurs if X and Y represent nitrogen or oxygen. If the electron-rich center forms part of the same molecule, one speaks of an

intra-molecular hydrogen bond. If the association involves two different molecules, it is referred to as an *inter*-molecular hydrogen bond. Although such hydrogen bonds are relatively weak (15 to 20 kJ mol⁻¹) as compared to covalent bonds, they are of enormous importance with respect to the spatial arrangements and interactions of molecules.

Oxidation State of Atoms in an Organic Molecule

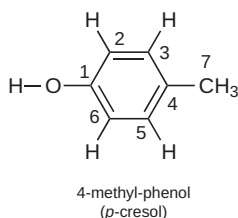
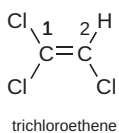
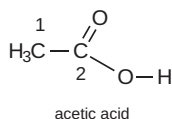
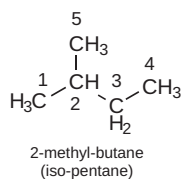
When dealing with transformation reactions, it is important to know whether or not electrons have been transferred between the reactants. Reactions that involve the transfer of electrons between different chemical species are generally referred to as *redox reactions*. The terms *oxidation* and *reduction* refer, respectively, to the loss and gain of electrons at an atom or ion. To evaluate the number of electrons transferred, we conveniently examine the (formal) oxidation states of all atoms involved in the reaction. Of particular interest to us is the oxidation state of carbon, nitrogen, and sulfur in a given organic molecule, as these are the elements most frequently involved in organic redox reactions. Of particular interest to the energy production of all organisms is the oxidation state of carbon atoms.

An oxidation state of zero is assigned to the uncharged element; a loss of *Z* electrons leads to an oxidation state of +*Z*. Similarly, a gain of *Z* electrons leads to an oxidation state of -*Z*. A simple example is the oxidation of sodium by chlorine, resulting in the formation of sodium chloride:



In ionic redox reactions, as shown in the oxidation of sodium by chlorine, a full electron transfer occurs. In covalent bonds, electrons are shared and one formally assigns possession of the electron pair to the more electronegative atom of the two bonded atoms. Therefore, to calculate the oxidation state of atoms in an organic molecule, add 0 for each bond to an identical atom, -1 for each bond to a less electronegative atom or for each negative charge on the atom, and +1 for each bond to a more electronegative atom or for each positive charge. In C-S, C-I and even C-P bonds, the electrons are attributed to the heteroatom although the electronegativities of these heteroatoms are very similar to that of carbon. Finally, we should also point out that roman instead of arabic numbers are frequently used to express the oxidation state of a covalently bound atom. Recall that the elements carbon (-IV to +IV), nitrogen (-III to +V), and sulfur (-II to +VI) may be present in organic molecules in various oxidation states, while others exhibit primarily (e.g., O; -II) or exclusively only one oxidation state (e.g., H, F, Cl, Br, I; all -I). Box 2.1 illustrates how to determine the oxidation state of carbon in some organic molecules. Examples of the oxidation states of nitrogen and sulfur in various functional groups are given in Fig. 2.11.

Box 2.1 Determining the Oxidation States of Carbon Atoms Present in Organic Molecules



Determine the oxidation state of each carbon present in (a) iso-pentane, (b) acetic acid, (c) trichloroethene, and (d) 4-methylphenol (*p*-cresol). In organic molecules, hydrogen always assumes an oxidation state of +I, chloride of –I, and oxygen, in most cases, of –II.

(a) The carbons of the methyl groups (C_1 , C_4 , C_5) are bound to three hydrogens and one carbon, hence their oxidation state is $3(-I) + (0) = -III$. The methylene group (C_3) is bound to two hydrogens and two carbons which yields $2(-I) + 2(0) = -II$. Finally, the methine group (C_2) exhibits an oxidation state of $(-I) + 3(0) = -I$.

(b) As in (a), the oxidation state of the carbon of the methyl group (C_1) is –III, while one of the carboxylic carbon (C_2) is $(+II) + (+I) + (0) = +III$. Hence the “average oxidation state” of carbon in acetic acid is 0.

(c) In trichloroethene, the oxidation states of the two carbons are $2(+I) + 0 = +II$ for (C_1) and $(-I) + (+I) + 0 = 0$ for (C_2).

(d) The carbons present in the benzene ring exhibit oxidation states of $(+I) + 2(0) = +I$ (C_1), $(-I) + 2(0) = -I$ for (C_2 , C_3 , C_5 , C_6), and $3(0) = 0$ for (C_4). The oxidation state of the methyl carbon (C_7) is again –III.

The Spatial Arrangement of Atoms in Organic Molecules

To describe the steric arrangement of the atoms in a molecule, in addition to bond lengths, we need to know something about the angles between the bonds, sizes of the atoms, and their freedom to move within the molecule (e.g., rotations about bonds).

Bond Angles. A simple but very effective rule that we can apply when considering *bond angles* in molecules is that the electrons accept the closeness to one another because of pairing, meaning that they spin and orbit in opposite directions. However, each pair of electrons, shared or unshared, wants to stay as far as possible from other pairs of electrons. For further details on the valence shell electron pair repulsion (VSEPR) theory see Pfennig and Frock (1999). In the case of a carbon atom with four single bonds, the bonds will generally point toward the corners of a *tetrahedron*. In the symmetrical case, this is when a carbon is bound to four identical *substituents* (i.e., atoms or groups of atoms as –H in CH_4 , or –Cl in CCl_4 , or – CH_3 in $C(CH_3)_4$), the bond angles are 109.5° . In most cases, however, each carbon atom is bound to different substituents, which leads to minor variations in the bond angles, as illustrated in Fig. 2.2. For *saturated* carbon atoms, that is, carbon atoms not involved in a double or triple bond, the C–C–C bond angles are typically about 112° , except for ring

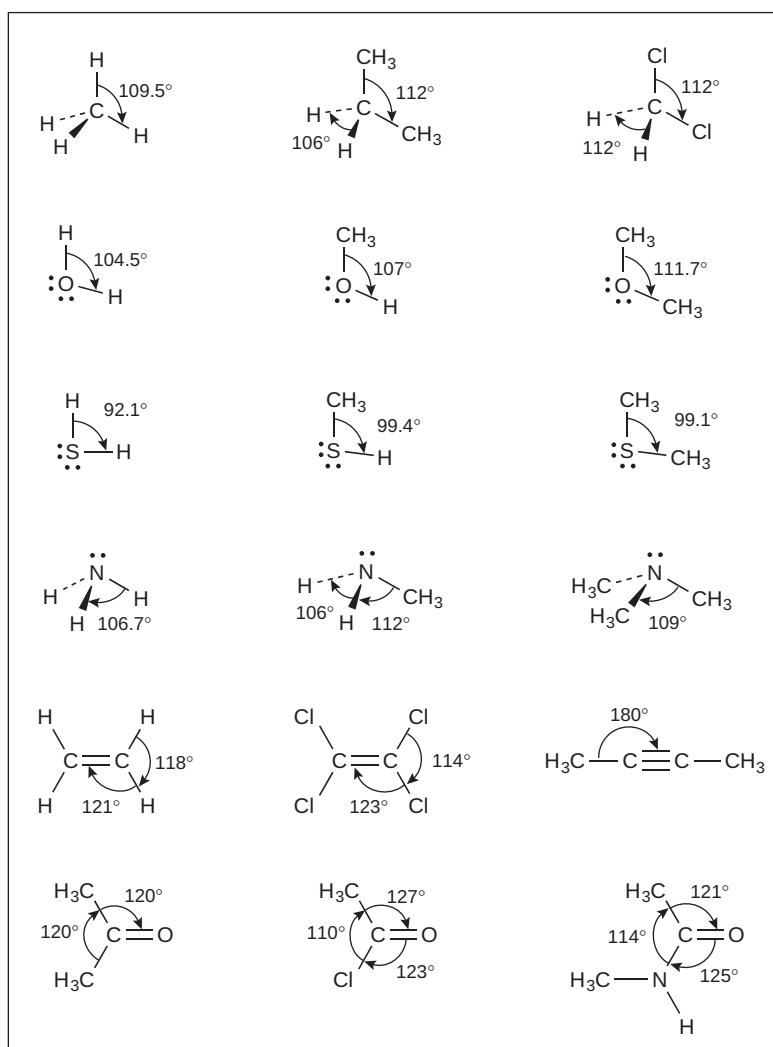


Figure 2.2 Examples of bond angles in some simple molecules. Data from Hendrickson et al. (1970) and March (1992).

systems containing less than six ring atoms, where bond angles may be considerably smaller. With respect to the heteroatoms N, O, P, and S, we see from the examples given in Fig. 2.2 that nonbonded electron pairs behave as if they point to imaginary substituents, provided that the heteroatoms are also only single-bonded to other atoms, thus giving rise to a bent or pyramidal geometry.

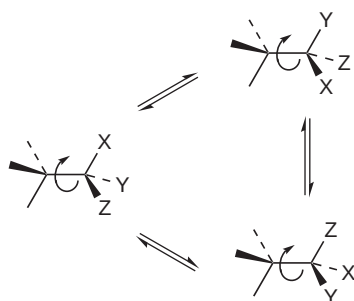


Figure 2.3 Rotation about a σ -bond leading to various spatial arrangements of the atoms in a molecule.

Stereoisomerism. The association of electrons in a single, or sigma (σ), bond allows rotation about the axis of the linkage (Fig. 2.3). Such rotation does not disrupt the bonding electron pair (i.e., it does not break the bond), and therefore under ambient temperatures, the substituents attached to two carbons bonded by a sigma bond are usually not “frozen” in position with respect to one another. Thus, the spatial arrangement of groups of atoms connected by such a single bond may change from time to time owing to such rotation. However, such geometric distributions of the atoms in the structure are usually not analytically separable from one another as the energy required for interconversion is rather small, leading to interconversions

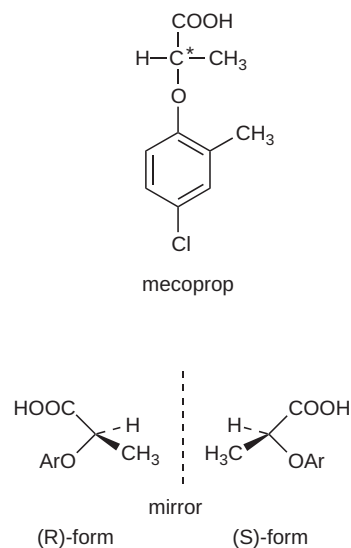


Figure 2.4 The two enantiomers of the herbicide mecoprop. The asymmetric carbon center is indicated by the asterisk; Ar denotes the aromatic substituent.

during separation. Nevertheless, even if fast rotations about a single bond occur, *stereoisomerism* is possible. *Stereoisomers* are compounds made up of the same atoms bonded by the same sequence of bonds, but having different three-dimensional structures that are not superimposable.

When considering stereoisomerism, one commonly distinguishes between two different cases. First, molecules that are alike in every respect but are *mirror images* of each other are not superimposable. We refer to such molecules as being *chiral*. In general, any object for which the image and mirror image are distinguishable (e.g., our left and right hands) is denoted to be chiral. For example, if in a molecule a carbon atom is bound to four different substituents, as is the case in the functional group of the herbicide mecoprop (Fig. 2.4), two structural isomers are possible. In this context, one sometimes refers to such a carbon atom as a center of chirality. Mirror image isomers are called *enantiomers* or *optical isomers* because they rotate the plane of polarized light in opposite directions. They can be analytically separated. In general, enantiomers have identical properties in a symmetrical molecular environment, but their behavior may differ quite significantly in a chiral environment. Most importantly, they may react at very different rates with other chiral species. This is the reason why many compounds are biologically active, whereas their enantiomers are not. For example, the “R-form” of mecoprop (see Fig. 2.4) is an active herbicide, whereas the “S-form” is rather biologically inactive (Bosshardt, 1988).

The second type of stereoisomerism encompasses all other cases in which the three-dimensional structures of two isomers exhibiting the same connectivity among the atoms are not superimposable. Such stereoisomers are referred to as *diastereomers*. They may arise due to different structural factors. One possibility is the presence of more than one chiral moiety. For example, many natural products contain two to ten asymmetric centers per molecule, and molecules of compound classes such as polysaccharides and proteins contain hundreds. Thus, organisms may build large molecules that exhibit highly stereoselective sites that are important for many biochemical reactions including the transformation of organic pollutants.

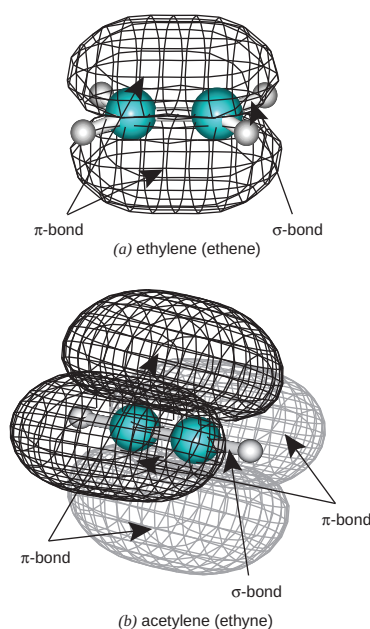
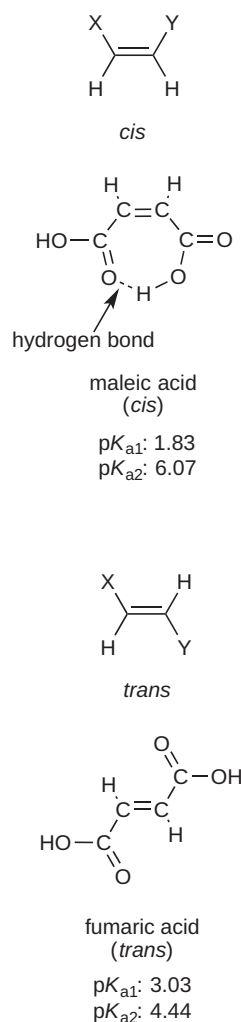


Figure 2.5 Simplified picture of the electron clouds of the π -electrons of a (a) double and (b) triple bond.

Another important form of diastereoisomerism results from restricted rotation of bonds such as those encountered with double bonds and ring structures. When considering the geometry of a *double bond*, we imagine a combination of two different types of bonds between two atoms. One of the bonds would be equivalent to a single bond, that is, a bond in which the pair of electrons occupies the region around the axis between the doubly bonded atoms. We can picture the second bond, which is called a π -bond (e.g., carbon-carbon, carbon-oxygen, carbon-nitrogen, carbon-sulfur, nitrogen-oxygen), by imaging the two bonding π -electrons to be present in an “electron cloud” located above and below a plane in which the axes of all other bonds, including unshared electron pairs, lie. Figure 2.5a illustrates such electron clouds for ethylene (ethane). The atoms closest to a carbon-carbon double bond are in a plane with bond angles of about 120° (see Fig. 2.2). Rotation about the axis would mean that we would have to break this bond. In triple-bond compounds, as in the case for acetylene (ethyne), two π -bond electron clouds exist orthogonal to each other, thus leading to a linear (bond angles = 180°) configuration (Fig. 2.5b).



Let us now consider a compound $XHC=CHY$ in which $X, Y \neq H$. In this case, two isomers exist, sometimes also called *geometric* isomers, which are distinct and, in principle, analytically separable as no rotation occurs about the C–C bond (Fig. 2.6). To distinguish between the two isomers, one commonly uses the terms *cis* and *trans* to describe the relative position of two *substituents* (atoms or groups other than hydrogen). The term *cis* is used if the two substituents are on the same side of the double bond, and the term *trans* signifies they are “across” from one another. As with other types of isomerism, closely related compounds may exhibit quite different properties. For example, the boiling points of *cis*- and *trans*-1,2-dichloroethene ($X=Y=Cl$) are 60 and 48°C respectively. More pronounced differences in properties between *cis/trans* isomers are observed when interactions between two substituents (e.g., intramolecular hydrogen bonding) occur in the *cis* but not in the *trans* form, as is encountered with maleic and fumaric acid (Fig. 2.6). These two compounds are so different that they have been given different names. For example, their melting points differ by more than 150°C, and their aqueous solubilities vary by more than a factor of 100. Also, the acidity constants (pK_a values in Fig. 2.6; see Section 4.3) are significantly different because the hydrogen bonding possible in maleic acid facilitates the dissociation of the first proton by stabilizing the negative charge. However, because of the hydrogen bond, dissociation of the second proton is less favorable as compared to fumaric acid.

The organization of atoms into a ring containing less than ten carbons also prevents free rotation. Consequently, *cis* and *trans* isomers are also possible in such ring systems. The *cis* isomer has two substituents on the same side of the ring (i.e., above or below); the *trans* isomer exhibits a substituent on either side (Fig. 2.7). In ring systems with more than two substituted carbons, more isomers are possible. For examples, 1,2,3,4,5,6-hexachlorocyclohexane (HCH) has eight possible isomers, three of which (α -, β -, and γ -isomers) are important from an environmental point of view as they are considered Persistent Organic Pollutants (POPS; see Section 3.2).

Figure 2.6 *Cis/trans* isomerism at double bonds exhibiting two substituents.

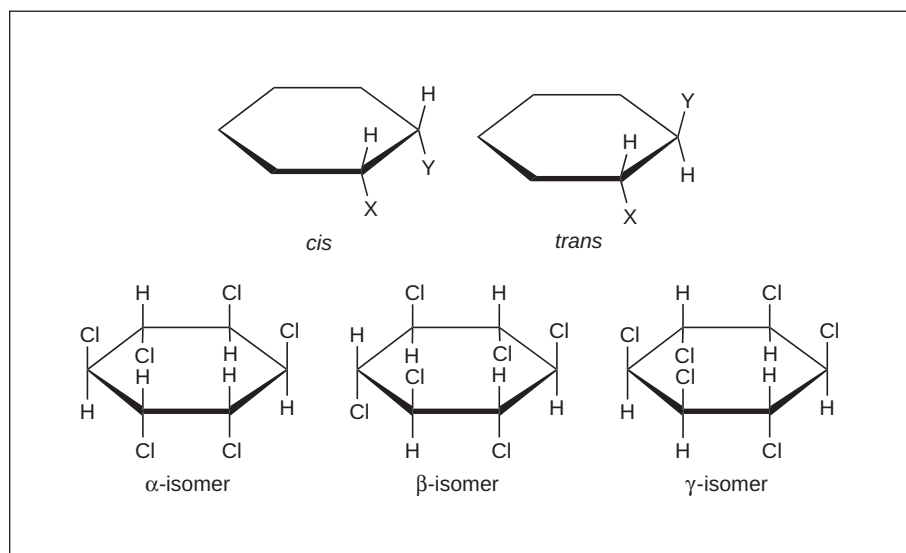


Figure 2.7 Geometric isomers in ring systems with two (*cis/trans*) or more substituted carbons (α -, β -, γ -isomers of 1,2,3,4,5,6-hexachlorocyclohexane (HCH)).

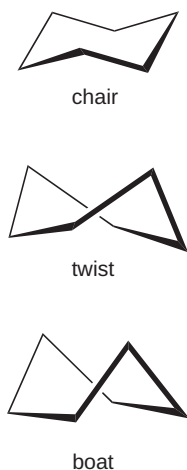
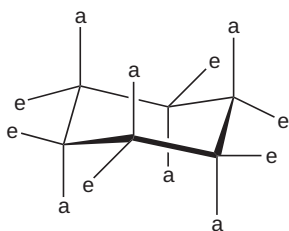


Figure 2.8 Different possible conformations of a six-membered ring (e.g., cyclohexane).



At this point, we reiterate that the relative positions of atoms in many structures are continuously changing. The term “*different conformations*” of a molecule is used if two different three-dimensional arrangements of the atoms in a molecule are rapidly interconvertible, as is the case if free rotations about sigma bonds are possible. If rotation is not possible, we speak of different *configurations*, which represent isomers that can be analytically separated. Obviously, the conformations with the lowest energy, the most stable forms, are the ones in which a molecule will preferentially exist. In the case of six-membered rings such as cyclohexane, three stable conformations exist, known as the chair, twist, and boat form (Fig. 2.8).

Depending on the type of substituents, usually one of the forms is the most stable one. In the case of the HCH isomers (Fig. 2.7), this is the chair form. Taking a closer look at the chair form, we see that six of the bonds linking substituents to the ring are directed differently than the other six (see margin).

The six axial bonds (a) are directed upwards or downwards from the “plane” of the ring, while the other six equatorial bonds (e) are more within the “plane.” Conversion of one chair form into another converts all axial bonds into equatorial bonds and vice versa. In monosubstituted cyclohexanes, for steric reasons, the more stable form is usually the one with the substituent in the equatorial position. If there is more than one substituent, the situation is more complicated since we have to consider more combinations of substituents, which may interact. Often the more stable form is the one with more substituents in the equatorial positions. For example, in the α -isomer of HCH (Fig. 2.7), four chlorines are equatorial (aaeeee), and in the β -isomer, all substituents are equatorial. The structural arrangement of the β -isomer also greatly inhibits degradation reactions; the steric arrangement of the chlorine atoms is unfavorable for dehydrochlorination and reductive dechlorination (see Chapter 23 and Bachmann et al., 1988).

Delocalized Electrons, Resonance, and Aromaticity

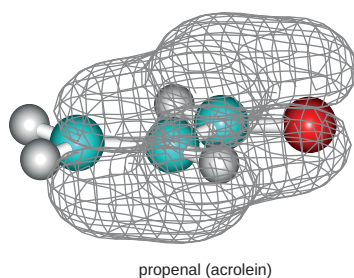
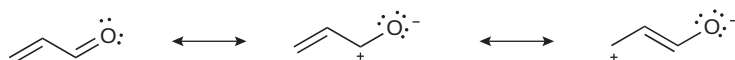


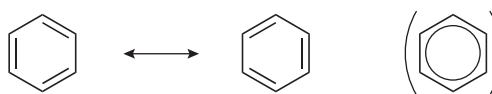
Figure 2.9 Schematic picture of π -electron delocalization in propenal (acrolein). The blue balls represent the carbon atoms, the gray ones the hydrogen atoms, and the red one the oxygen atom.

Having reviewed the spatial orientation of different chemical bonds and the consequences on the steric arrangement of the atoms in an organic molecule, we now proceed to discuss special situations in which electrons move throughout a region covering more than two atoms. The resulting bonds are often referred to as “*delocalized chemical bonds*.” From an energetic point of view, this diminished constraint on the positions of these electrons in the bonds results in their having lower energy and, as a consequence, the molecule exhibits greater stability. For us, the most important case of delocalization is encountered in molecules exhibiting multiple π -bonds, spaced so they can interact with one another. We refer to such a series of π -bonds as *conjugated*. To effectively interact, π -bonds must be adjacent to each other, and the σ -bonds of all atoms involved must *lie in one plane*. In such a conjugated system, we can qualitatively visualize the π -electrons to be smeared over the whole region, as is illustrated for propenal ($\text{CH}_2=\text{CH}-\text{CHO}$, also known as acrolein) in Fig. 2.9.

If we try to visualize propenal’s structure by indicating the extreme possible positions of these conjugated electrons, we write:

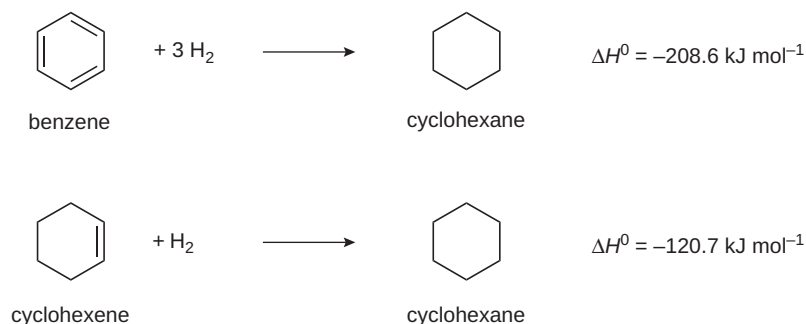


The double-sided arrows do not signify that the three structures are interconvertible, but rather that the location of the four electrons is best thought of as a weighted average of extreme possibilities. This freedom in electron positioning results in what we call delocalization, and the visualization of a given molecule by a set of localized or “static” structures is called the *resonance* (from the Latin *resonantia* meaning echo) method for representing a structure. The relative contribution of the extremes to the overall resonance structure is determined by their relative stabilities. The stabilizing effect of delocalization is most pronounced in *aromatic systems*. The best-known aromatic system is that of benzene, which has three conjugated double bonds in a six-membered ring:



Again, each of the static structures alone does not represent the molecule, but the molecule is a hybrid of these structures. Thus, the electrons in the conjugated π -bonds of benzene are sometimes denoted with a circle. In *substituted benzenes* (i.e., benzenes in which hydrogen is substituted by another atom or group of atoms), depending on the type and position of the substituents, the different resonance forms may exhibit somewhat different stabilities and contribute differently to the overall structure.

A quantitative estimate of the stabilization or *resonance energy* of benzene, which cannot be directly measured, may be obtained by determining the heat evolved when hydrogen is added to benzene and cyclohexene to yield cyclohexane:



If each of the double bonds in benzene were identical to the one in cyclohexene, the heat of hydrogenation of benzene would be three times the heat evolved during hydrogenation of cyclohexene. The values previously given show a large discrepancy between the “expected” ($-120.7 \times 3 = -362 \text{ kJ mol}^{-1}$) and the measured ($-208.6 \text{ kJ mol}^{-1}$) ΔH^0 value. Hence, benzene is about 150 kJ mol^{-1} more stable than would be expected if no resonance interactions among the π -electrons existed. Large stabilization energies are not only observed in components containing a benzene ring but, in general, in all *cyclic* π -bond systems with $4n + 2$ (i.e., 6, 10, 14...) electrons. In the early days of organic chemistry, it was recognized that the benzene ring is particularly unreactive compared to acyclic (noncyclic) compounds containing conjugated double bonds. The quality that renders such ring systems especially stable was and

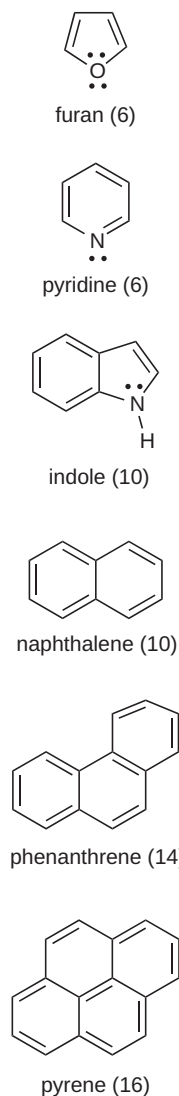
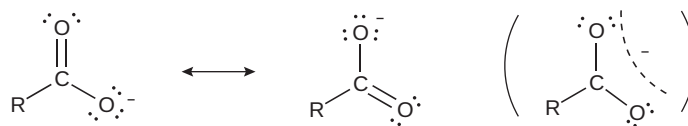


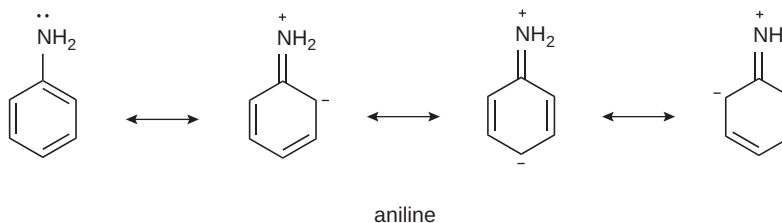
Figure 2.10 Some additional examples of aromatic ring systems in organic compounds (in parentheses number of π -electrons).

still is referred to as *aromaticity*. Some additional examples of aromatic ring systems are given in Fig. 2.10. Aromatic compounds containing heteroatoms contribute either one (e.g., pyridine) or two electrons (e.g., furan, indole) to the conjugated π -electron systems. Also, some polycyclic compounds are referred to as polycyclic *aromatic* compounds, although they are not aromatic throughout their structure in a strict sense (e.g., pyrene has 16 electrons in its π -bond system).

As was already indicated for propenal and the five-membered *heteroaromatic* rings (e.g., furan, Fig. 2.10), resonance may also be important between nonbonded electrons on a single atom and a π -bond system. For example, an unshared electron pair of oxygen greatly contributes to the stabilization of the carboxylate anion, thus rendering the proton of a carboxylic acid group quite acidic (see also Fig. 2.6):



Similarly, two unshared electrons of the nitrogen in aniline are in resonance with the aromatic π -electron system:



This delocalization has a significant impact on the acid/base properties of anilines as compared to the aliphatic amino compounds, giving them much higher pK_a values (see Chapter 4, Section 4.4). In summary, delocalization of electrons enhances stability, and we can visualize delocalized bonding by using the resonance method. In Part V, we learn more about the effects of resonance on chemical equilibrium and the kinetics of chemical reactions of organic compounds.

Common Functional Groups

Finally, a key feature of organic compounds involves the presence of functional groups, i.e., those parts of a molecule that exhibit one or several heteroatoms. These parts of a compound's structure are frequently the site of specific interactions with other molecules and are points at which reactions are initiated. As we see in Chapter 3, many chemicals of particular environmental concern contain halogen atoms, that is, fluorine, chlorine, bromine and iodine. Besides the halogens, oxygen, nitrogen, and sulfur atoms are common heteroatoms present in organic molecules. Figure 2.11 provides an overview of some simple functional groups exhibiting one or several of these elements that we frequently encounter throughout the book. The oxidation states of

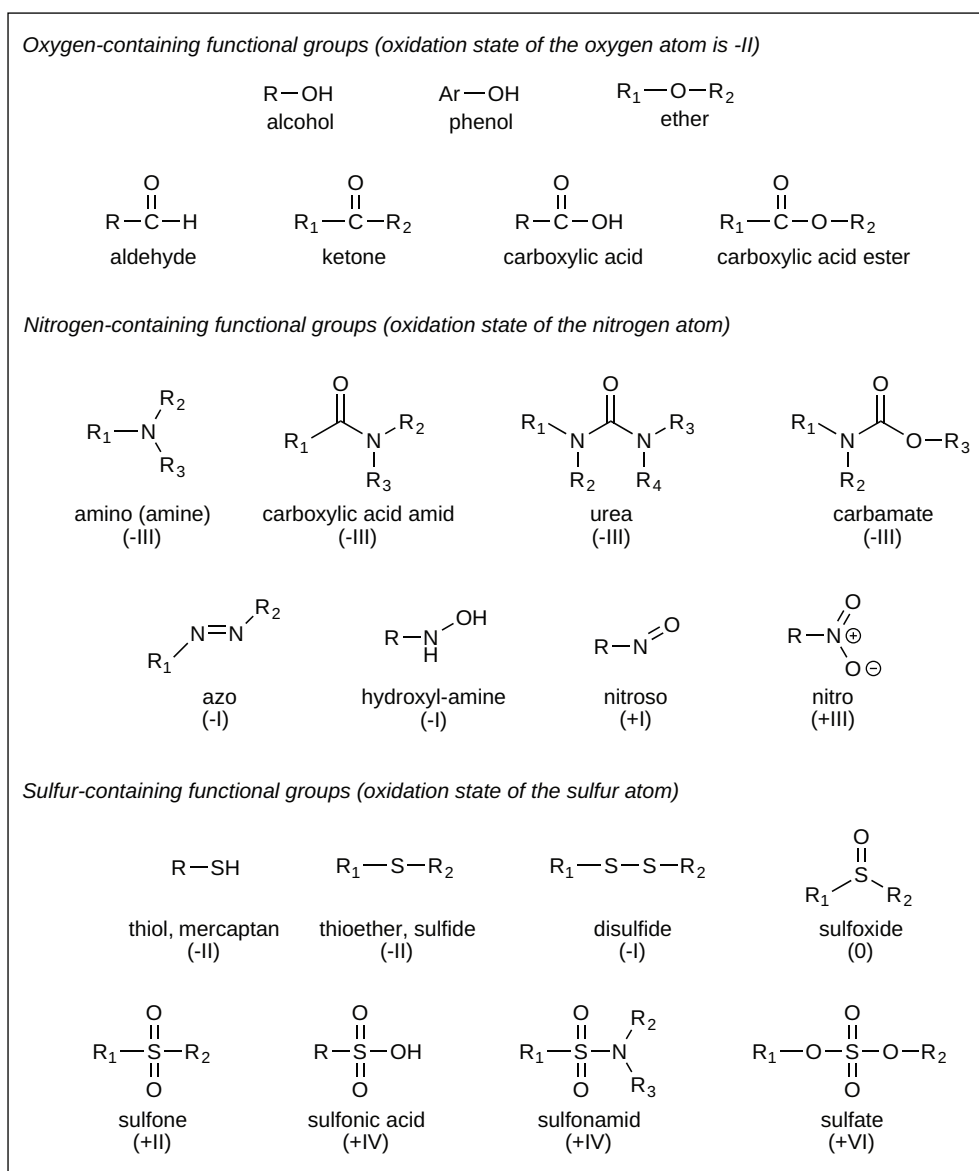


Figure 2.11 Some functional groups (“functionalities”) commonly found in organic compounds.

the N and S heteroatoms are indicated, and R- denotes a part of the molecule that is bound to the functional group at a carbon atom. Sometimes Ar- is used to specify that this carbon is part of an aromatic ring.

2.2 Intermolecular Forces Between Uncharged Molecules

The forces between like and unlike molecules determine how a given compound is distributed in the environment. For example, such intermolecular forces strongly influence how readily a compound evaporates from its pure liquid or solid phase into the gas phase, how much it likes to be dissolved in water, or how it partitions from water

or air into organic phases such as natural organic matter or biological media. Therefore, we need to understand how the chemical structure of the compound dictates what kind of molecular interactions it is capable of undergoing. In this section, we discuss qualitatively the forces that exist between uncharged molecules. If molecules carry a formal negative or positive charge, such as with acids or bases, we also need to consider *electrostatic interactions*. In all cases, we rely on the simple principal that opposite charges are attractive whereas like charges are repulsive.

The sum of all intermolecular forces between *uncharged molecules* is always attractive. These affinities generally result from the electron-deficient regions in a molecule attracting electron-rich counterparts in neighboring molecules or atoms in surfaces. The total affinity of molecules for one another comes from the summation of all attractions. The resulting interactions (Fig. 2.12) can be divided into two categories:

(1) “*Nonspecific*” interactions that exist between any kinds of molecules, no matter what chemical structure these molecules may have. These nonspecific interactions are generally referred to as *van der Waals (vdW)* interactions. They are a superposition of the following components:

(i) Attractions between *time-varying, uneven electron distributions* in adjacent molecules are the origin of *London dispersive forces*. The intensity of such unevenness in a particular molecule or material is related to its polarizability, the tendency of its charge distribution to be distorted by an external electric field. As a result, the strength of intermolecular attraction energies arising from these time-varying dipoles is proportional to the product of the polarizabilities of each of the interacting sets of atoms.

(ii) Dipole-induced dipole interactions are the source of *Debye energies*. Dipoles exist within chemical structures because of the juxtaposition of atoms with different electronegativities (e.g., an oxygen bonded to a carbon atom). When such a permanent dipole moment in one chemical is juxtaposed to material with a time-averaged even electron distribution, then the first molecule causes an uneven electron distribution to form in the second material. The strength of the resultant intermolecular attraction is proportional to the dipole moment’s product of the first molecule and the second molecule’s polarizability.

(iii) Dipole–dipole interactions are the cause of *Keesom energies*. In this case, permanent dipoles in each substance cause the molecules to orient so that the two dipoles face each other in a head-to-tail fashion. The strengths of these attractions are proportional to the product of the dipole moments of the two interacting molecules and depend on the orientation of the interacting partners.

(2) *Specific* interactions (Fig. 2.12d) result from particular molecular structures that enable relatively strong local attractions between permanently electron-poor parts of a chemical structure (e.g., the hydrogen attached to an oxygen) and corresponding permanently electron-rich sites of another molecule (e.g., the nonbonded electrons of atoms like oxygen and nitrogen). These specific interactions, which we

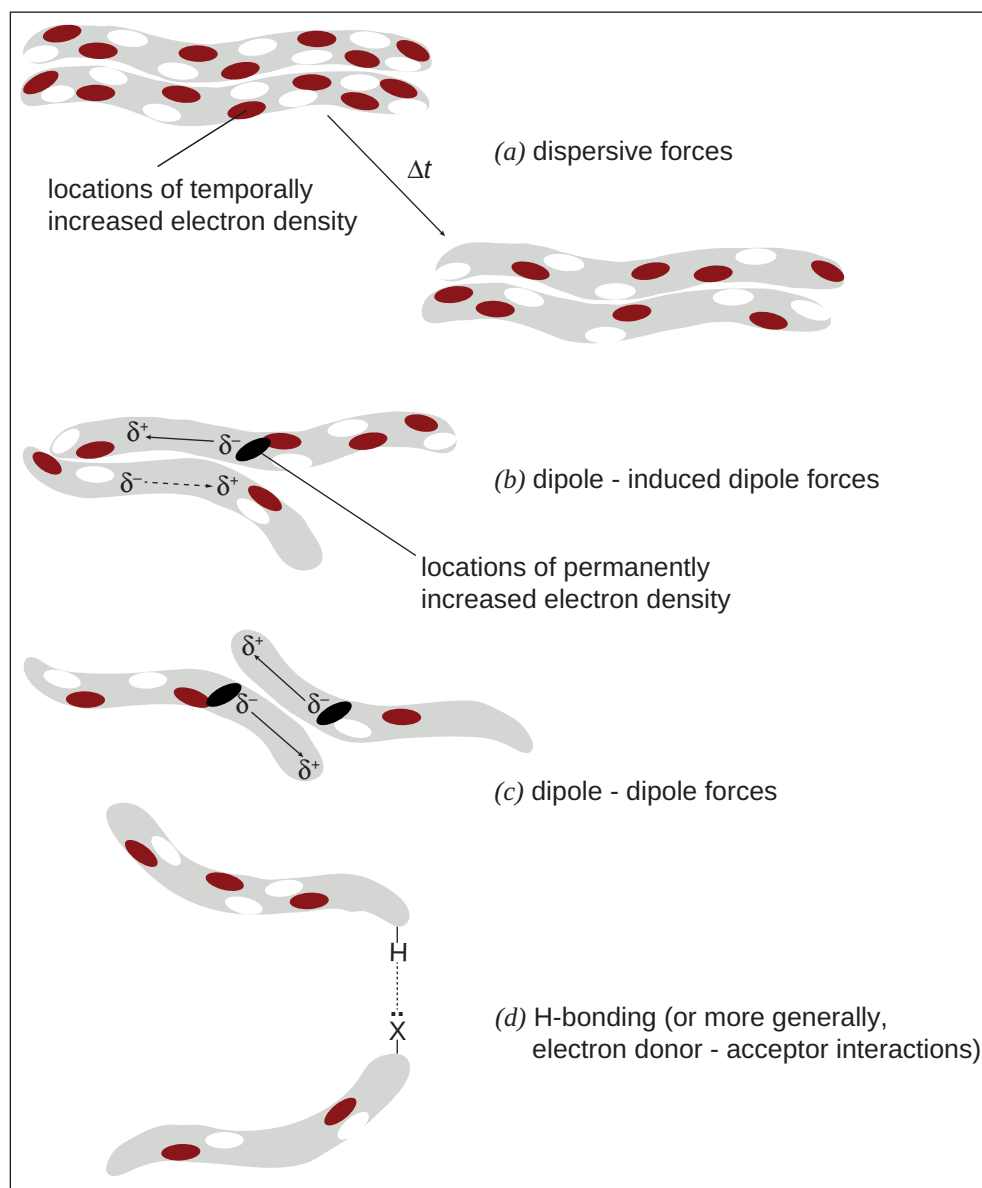


Figure 2.12 Illustration of the various molecular interactions arising from uneven electron distributions: (a) dispersive forces, (b) dipole-induced dipole forces, (c) dipole-dipole forces, and (d) electron acceptor-electron donor forces.

refer to as *polar* interactions are, of course, only possible between molecules that exhibit complementary structural moieties, which occurs if one moiety acts as an *electron acceptor* (often also referred to as *H-donor*) and the other one as an *electron donor* (or *H-acceptor*). Hence, polar interactions can be classified as *electron donor-acceptor* (EDA) or *hydrogen donor-acceptor* (HDA) interactions.

The ability or inability of a given compound to undergo specific interactions can be used to divide organic chemicals into different categories of apolar, monopolar, or bipolar, which are further explained in Box 2.2. The apolar compounds interact chiefly by vdW forces. The monopolar compounds have in addition either H-donor (electron acceptor) or H-acceptor (electron donor) properties, and the bipolar compounds

Box 2.2 Classification of Organic Compounds According to Their Ability to Undergo Particular Molecular Interactions

Compounds that undergo only vdW interactions (London, Debye, and Keesom interactions) are commonly referred to as *apolar*. Examples include alkanes, chlorinated benzenes, and PCBs.

If a chemical exhibits a functionality that has either donor or acceptor characters but not both, we call such a compound *monopolar*. Examples include structures with an ether function, --C--O--C-- (an electron donor or H-acceptor), a keto group, $>\text{C=O}$ (an electron donor or H-acceptor), or an aromatic ring carrying electron withdrawing substituents (an electron acceptor).

Some molecules contain moieties like amino (--NH_2), hydroxyl (--OH), and carboxyl groups (--COOH) that exhibit both donor and acceptor properties. We refer to these compounds as *bipolar*.

For large, complex compounds, it is often not obvious how the whole compound should be classified. Such compounds may exhibit functional groups that participate in locally strong polar interactions. However, due to the large size of the molecule, the overall behavior of the compound is dominated by vdW-interactions. It has, therefore, become common practice to divide the world of chemicals into only two categories, namely, *polar* and *nonpolar* compounds. The nonpolar chemicals include all those chemicals whose molecular interactions are dominated by vdW forces.

exhibit both. This classification will ultimately be useful when we want to determine whether we should include various factors for quantifying the contributions of these forces in our estimates of the energies controlling specific absorption or adsorption associations in which we are interested.

Finally, we note that in the absence of electron donor-acceptor interactions, the London dispersive energy, which increases with increasing molecular size, is the dominant contributor to the overall attraction of many molecules to their surroundings. Therefore, understanding this type of intermolecular interaction and its dependency on chemical structure allows us to establish a baseline for chemical attractions. If molecules exhibit stronger attractions than expected from these interactions, other intermolecular forces are likely important. To see the superposition of these additional interactions and their effect on various partitioning phenomena, we examine the role of dispersive forces as well as of polar interactions in more detail in Chapter 7, where we derive models to quantify these interactions.

2.3 Questions and Problems

Special note: Problem solutions are available on the book's website. Solutions to problems marked with an asterisk are available for everyone. Unmarked problems have solutions only available to teachers, practitioners, and others with special permission.

Questions

Q 2.1

Which are the most common elements encountered in organic chemicals? What is a *heteroatom* in an organic molecule?

Q 2.2

Explain the simplest model used to describe the tendency of the various elements present in organic chemicals to undergo covalent bonding. For which elements is this simple model not strictly applicable?

Q 2.3

Which elements present in organic compounds exhibit stable isotopes. What is the relative abundance of these isotopes?

Q 2.4

What does the *structure* of a given compound describe? What are *structural isomers*?

Q 2.5

What types of covalent bonds exist between the atoms present in organic molecules? What factors determine the strength of covalent bonds? Give some examples of very strong and very weak bonds.

Q 2.6

Which atoms present in organic molecules may exhibit different *oxidation states*? What are the possible oxidation states of these elements? Explain in words how you assign the oxidation states to the different atoms present in a given molecule.

Q 2.7

What is *stereoisomerism*? What type of stereoisomerism exists? Give some examples of different types of stereoisomers.

Q 2.8

In what context do you use the terms, *cis* and *trans*? In what context do you use *ortho*, *meta*, and *para*?

Q 2.9

Explain the terms “delocalized electrons,” “resonance,” and “aromaticity.” Give examples of compounds for which these terms apply.

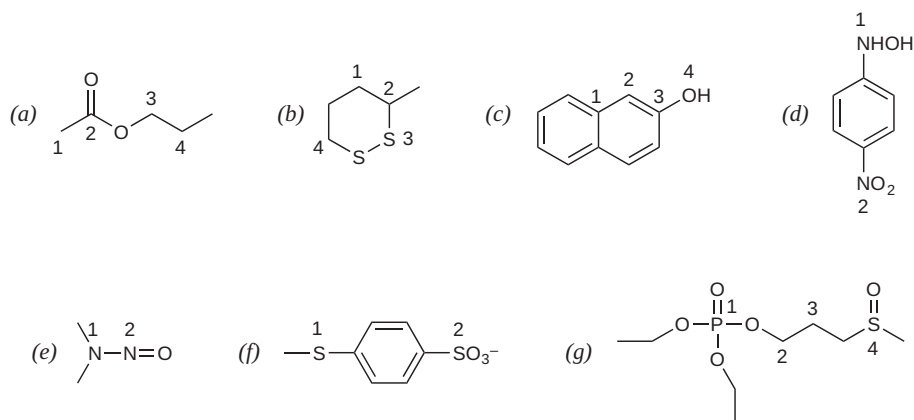
Q 2.10

What is an apolar, monopolar, and a bipolar organic compound? Give some examples of functional groups that are monopolar, and some examples that make a compound bipolar.

Problems

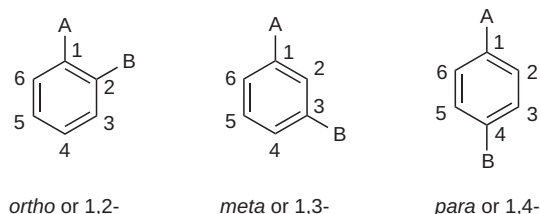
P 2.1 Determining the Oxidation State of Atoms in an Organic Molecule

Determine the oxidation states of the numbered atoms in the following organic molecules:



P 2.2 Assessing the Number of Isomers of Substituted Benzenes

Recall that di-substituted benzenes have three isomers, in that the two substituents may be in *ortho*-, *meta*-, or *para*-position relative to each other:

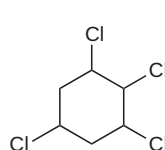


Depending on the nature of the two substituents, the three isomers may have quite similar or very different properties.

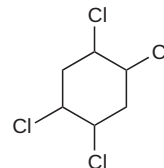
Write down all possible *tri*-substituted benzenes for the following situations (a) all substituents are the same (AAA), (b) only two of the substituents are the same (AAB), (c) all three substituents are different (ABC).

P 2.3 Assessing the Number of Stereoisomers in Substituted Cyclohexanes

Write down all possible stereoisomers of 1,2,3,5- and 1,2,4,5- tetrachlorocyclohexane. Which of them are chiral, that is, which ones exist as pairs of enantiomers?



1,2,3,5-tetrachlorocyclohexane



1,2,4,5-tetrachlorocyclohexane

2.4 Bibliography

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