Chapter 1

CHEMICAL STRUCTURE AND BONDING

Probably many students have already acquired some knowledge in a beginner's chemistry course. Nevertheless, it would be expedient to recall in this opening chapter some information on general chemistry and the structural theory of organic chemistry that will be helpful in studying the entire course.

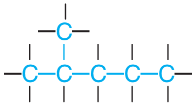
1.1. THE STRUCTURAL THEORY OF ORGANIC COMPOUNDS

In the mid-nineteenth century (1858–1860), F.A. Kekulé (in Germany) and A.S. Couper (in Scotland) independently formulated the basis of one of the most fundamental theories in modern organic chemistry, the structural theory. It comprises two main ideas.

- Atoms in organic compounds form a definite number of bonds. A measure of bonding ability of atoms is known today as *valence*. Thus, a carbon atom forms four bonds when it is linked to other atoms and is tetravalent. Nitrogen forms usually three bonds and is trivalent, oxygen forms two bonds and is divalent, hydrogen and halogens are univalent.


tetravalent atom   trivalent atom   divalent atom   univalent atoms

- Carbon atoms can bond to each other to form extended chains of atoms linked together.


chains of carbon atoms

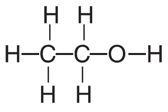
At that time, in 1861, the Russian chemist A. Butlerov made an outstanding contribution to organic chemistry when he developed new ideas in this field. The main of them stated:

> The chemical nature of a complex particle is determined by the nature of its elementary constituent parts, their number and chemical structure.

Butlerov stated that all the atoms in a molecule interact with one another, and a mutual influence is the strongest between directly linked atoms. It was Butlerov who introduced the term *chemical structure* into chemistry.

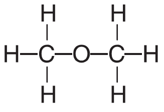
Butlerov's theory of chemical structure gave a rational explanation of isomerism.

There are many compounds that have the same molecular formula, but they differ in physical and chemical properties due to their different molecular structure. Such compounds are called *isomers* (from the Greek *isos* – equal, and *meros* – part). One of the simplest examples of isomeric compounds is a pair of *ethanol* and *dimethyl ether* with the molecular formula C_2H_6O. The former is a liquid, the latter is a gas at room temperature (their boiling points are 78 and –25 °C, respectively). Ethanol reacts with sodium, dimethyl ether does not. It is quite enough to look at the structural formulas for these compounds to reveal their difference.



$$\begin{array}{ccccccccc} & & H & & H & & & & \\ & & | & & | & & & & \\ H & - & C & - & C & - & O & - & H \\ & & | & & | & & & & \\ & & H & & H & & & & \end{array}$$

ethanol



$$\begin{array}{ccccccccc} & & H & & & & H & & \\ & & | & & & & | & & \\ H & - & C & - & O & - & C & - & H \\ & & | & & & & | & & \\ & & H & & & & H & & \end{array}$$

dimethyl ether

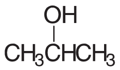
This is an example of constitutional isomerism when isomers differ from each other in their functional groups. Isomers can also differ in the position of the same functional group at the same carbon skeleton (positional isomers are, for example, isomeric alcohols 1-propanol and 2-propanol shown below). But the main reason for constitutional isomerism consists in the great variety of carbon skeletons. Thus, hydrocarbons C_4H_{10} represent the simplest example of skeleton isomerism.

The term *structural isomerism* is often used but it has a broader sense than constitutional isomerism. Really, structural isomers differ in *all* details of their structure including spatial arrangement of atoms (Chapter 10).

Positional isomers

$CH_3CH_2CH_2OH$

1-propanol



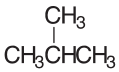
$$\begin{array}{c} \mathrm{OH} \\ | \\ \mathrm{CH_3CHCH_3} \end{array}$$

2-propanol

Skeleton isomers

$CH_3CH_2CH_2CH_3$

butane



$$\begin{array}{c} \mathrm{CH_3} \\ | \\ \mathrm{CH_3CHCH_3} \end{array}$$

isobutane

The structural theory originated by Kekulé, Couper, and Butlerov was extended into three dimensions by the Dutch physico-chemist J.H. van‘t Hoff[1] and J.A. Le Bel (from France). In 1874, they independently proposed that four atoms to which carbon is bonded do not lie in one plane, but sit at the corners of a tetrahedron, with carbon in the centre (Fig. 1.1).

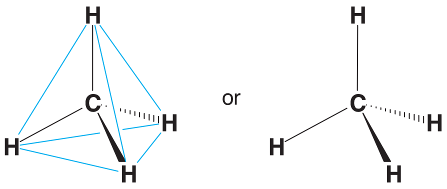


Figure 1.1. The tetrahedral structure of methane.

To show the three-dimensional arrangement of groups around the central carbon the following conventions are generally used: normal lines represent bonds in the plane of the paper, heavy wedged line represents a bond coming towards the viewer, and a dashed line represents a bond moving away from the viewer.

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[1] Jacobus Hendricus van't Hoff (1852–1911), the first Nobel Prize winner in Chemistry (1901). His famous paper on stereochemistry, *The Position of Atoms in Space*, was published when he was 22 years old.

After the discovery of the electron (in 1897), the atomic theory penetrated into organic chemistry very intensively. Developments of quantum mechanics were also applied to organic chemistry, thus forming by the 1930's the basis of the modern understanding of the subject. These concepts are considered in greater detail in the following sections.

1.2. THE STRUCTURE OF ATOMS

An atom consists of a positively charged nucleus surrounded by negatively charged electrons. The nucleus, in its turn, consists of protons, carriers of the total positive charge, and neutral particles called neutrons (except the light isotope of hydrogen). Both particles are equal in mass, whereas the mass of the electron is about 1/1840 of the mass of the proton.

The number of protons determines the charge of the nucleus and identifies the atom as belonging to an individual element. In a neutral atom the positive charge of the nucleus is balanced by the negative charge of the electrons. The atomic number of an element is the number of protons (or electrons), and the mass number is the total of protons and neutrons.

Electrons are of the most interest to chemistry because their number and arrangement accounts for constitution and chemical properties of molecules. Above all, we will consider electron arrangement in carbon and hydrogen and then elements frequent in organic molecules, such as oxygen, nitrogen, sulfur, and halogens.

1.2.1. Atomic Orbitals

Electrons are located in certain regions of space called orbitals.

The orbital is a region of space where the probability of finding an electron is large, about 95% of its time.

In other words, this is the region within which the electron density is the greatest. According to the *Pauli exclusion principle*, each orbital can contain a maximum of two electrons but they must be of opposite spin.

An electron spins about its axis and spin orientation is usually shown by arrows, either ↑ or ↓. Thus, two spin-paired electrons would be designated ↑↓.

Electrons occupy different shells (energy levels) designated by the numbers 1, 2, 3, and so on. The total number of orbitals in a given shell is n^2 where n is the shell's number. The farther the shell is from the nucleus, the greater the energy of those electrons is (Table 1.1).

Table 1.1. Distribution of electrons in the first three shells

Shell number	*Energy increasing*	*Orbitals' number of each type*			*Electron capacity of the filled shell*
		s	*p*	*d*	
1	⇩	1	0	0	2
2		1	3	0	8
3		1	3	5	18

Orbitals also differ in their shapes. There are four types of orbitals, specified *s*, *p*, *d*, and *f*. Only *s* and *p* orbitals will be concerned since they are the most important in organic chemistry. Taking into account both the size and the shape of orbitals, we designate them 1*s*, 2*s*, 2*p*, 3*s*, and so on. The *s* orbitals are spherical in shape. The three *p* orbitals are dumb-bell-shaped and oriented in such a way as to point mutually at right angles (Cartesian coordinates with the axes *x*, *y*, and *z*). They are sometimes called the $2p_x$, $2p_y$, and $2p_z$ orbitals to emphasize their directional character. The shapes of the *s* and *p* orbitals are shown in Fig. 1.2.

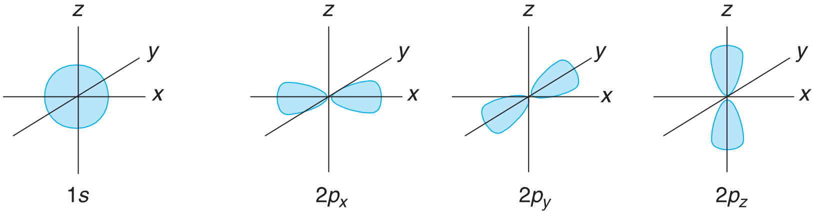


Figure 1.2. The shapes of the *s* and *p* atomic orbitals.
The nucleus is at the origin of the three coordinate axes.

The 2*s* and 3*s* orbitals have the same shape as the 1*s* orbital, but they are bigger and higher in energy. Similarly, the 3*p* orbital has the same shape as 2*p* one.

1.2.2. Electronic Configuration

A description of the orbitals that electrons occupy in an atom is called electronic configuration. The most stable state (so called ground-state) of an atom is that in which the electrons are at the lowest energy level, that is, in shells which are closest to the nucleus. To arrive at electronic configuration of any atom we should follow a few simple rules:

- Orbitals of the lowest energy are filled first. This is the *aufbau principle* (from the German *Aufbau* – building up);
- The Pauli exclusion principle mentioned above;
- The orbitals of a given shell are first filled with one electron each, and then with a second. This is known as the *Hund's rule*.

The application of these rules indicates a 1*s* configuration of hydrogen. Electronic configuration of helium, the next element after hydrogen, will consequently be $1s^2$. Six electrons of a ground-state carbon atom are arranged to give a $1s^22s^22p_x2p_y$ orbital configuration (a simpler form is usually preferred, without sub-division of *p* orbitals, but it is less informative). These and other examples are shown in Table 1.2.

In representations of electronic configuration, a superscript is used to indicate the number of electrons at a particular orbital. Remember that numerals in front of the orbital symbols indicate the shell's number.

1.3. THE NATURE OF CHEMICAL BONDING

An understanding of the nature of a chemical bond is one of the major aims of chemistry. W. Kössel (a German physicist) and G.N. Lewis (an American physico-

Table 1.2. Ground-state electronic configuration of some elements

Element	*Atomic number*	*Electronic configuration*	
		*Spin-orbital plotting**	*Written form*
Hydrogen	1	$1s$ ↑	$1s$
Carbon	6	$2p$ ↑ ↑ — $2s$ ↑↓ $1s$ ↑↓	$1s^2 2s^2 2p^2$
Nitrogen	7	$2p$ ↑ ↑ ↑ $2s$ ↑↓ $1s$ ↑↓	$1s^2 2s^2 2p^3$
Oxygen	8	$2p$ ↑↓ ↑ ↑ $2s$ ↑↓ $1s$ ↑↓	$1s^2 2s^2 2p^4$
Sulfur	16	$3p$ ↑↓ ↑ ↑ $3s$ ↑↓ $2p$ ↑↓ ↑↓ ↑↓ $2s$ ↑↓ $1s$ ↑↓	$1s^2 2s^2 2p^6 3s^2 3p^4$

* Coloured lines represent orbitals. Empty $3d$ shell for the sulfur atom is not shown.

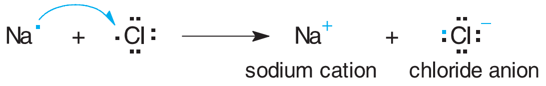
chemist) developed the first, but still useful, theory of bonding in 1916. The point of the theory consists in high chemical stability of noble gases. This, in its turn, may be explained by very stable electronic configuration of the atoms that have a filled outermost shell (with two or eight electrons for helium and neon, respectively). According to this idea, other atoms tend to attain such configuration. This could be achieved either by complete transfer of electron (or electrons), called valence electrons, from one atom to another or by sharing electrons between atoms.

Thus, Kössel and Lewis suggested two main types of chemical bonds: the ionic and covalent bonds. Both will be reviewed.

1.3.1. Ionic Bonds

The transfer of one or more valence electrons from one atom to another results in ionic (or electrovalent) bond formation. This kind of bonding is not typical for organic compounds; nevertheless it will be briefly discussed.

The reaction between sodium and chlorine atoms to form sodium chloride is a simple example of the ionic bond formation:



The atom that gives up the electron(s) becomes positively charged, a cation. Such atoms are said to be electropositive. The atom that accepts the electron(s) is converted into an anion. Such atoms are said to be electronegative. In terms of the Lewis–Kössel theory both atoms acquire the electronic configuration of a noble gas (argon).

In general, an ionic bond is formed between two atoms that differ greatly in their electronegativity.

Electronegativity is the ability of an atom to attract valence electrons.

Electronegativity cannot be measured directly, but can be calculated from some atom's physical characteristics. Of different scales of electronegativity, the most widespread is the Pauling's[1] scale that is given in tabulated form (Table 1.3) where the principal elements of organic compounds (so-called *organogens*) are coloured.

Table 1.3. Electronegativities of some elements (after Pauling)

H 2.1							He
Li 1.0	Be 1.6	B 2.0	C 2.5*	N 3.0	O 3.5	F 4.0	Ne
Na 0.9	Mg 1.2	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar
K 0.8	Ca 1.0					Br 2.8	Kr
						I 2.6	Xe

* This is the value for saturated carbon. Double-bonded and triple-bonded carbons have electronegativity values of 2.65 and 2.8, respectively.

Strictly speaking, the ionic bond may only conditionally be assigned to a bond. In a solid state, an ionic compound represents a crystal lattice with a definite arrangement of ions but it is impossible to say that any particular ion is connected to another particular ion. In solution, the ions exist separately being surrounded with molecules of a solvent.

1.3.2. Covalent Bonds

A covalent bond is another kind of bonding when two atoms have the same electronegativity or they differ in electronegativity not too much. Such atoms are bound by *sharing* electron pairs instead of transferring electrons. A combination of atoms joined together by covalent bonds is called a *molecule*.

From this point of view, it is impossible to imagine a molecule of sodium chloride or other ionic compound. A crystal of NaCl represents a single giant «molecule».

Molecular orbital theory. The nature of covalent bonds is the central concept in the study of organic chemistry. How are these bonds formed? The molecular orbital theory gives a satisfactory explanation for the question.

Molecules may be represented by the electron-dot (or Lewis) structures where the valence electrons are shown as the dots. But more convenient are dash (or line-bond) structures in which a dash represents a pair of shared electrons (for more

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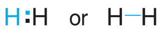
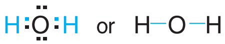
[1] Linus Pauling (1901–1994), an American physicist, chemist, and biochemist; Nobel Prize winner (1954 in chemistry, 1963 in World Peace).

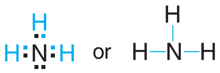
details see Section 1.5). Pairs of nonbonding valence electrons are often neglected, but it is necessary to keep them in mind. Examples are shown below:



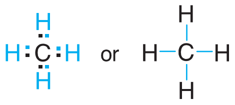
hydrogen (H_2)



water (H_2O)



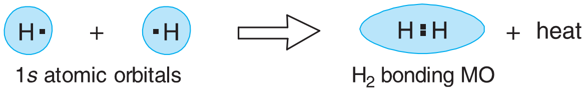
ammonia (NH_3)



methane (CH_4)

In molecules, the atomic orbitals interact with each other by overlap to form a new set of orbitals, each of them is called a *molecular orbital* (MO). The total number of molecular orbitals always equals the number of atomic orbitals. Let us consider the covalent bond formation in the hydrogen molecule.

It is convenient to imagine that the MO is localized in the region of two nuclei. When filled with electrons, the MO represents a covalent bond and the shared electron pair is attracted to both nuclei rather than to a separate atom:



This situation is energetically favourable because this MO is lower in energy than two initial atomic orbitals. The low-energy orbital is called a *bonding* MO. The second, higher-energy MO is unfilled and no bond could result. This orbital is called an *antibonding* MO (Fig. 1.3).

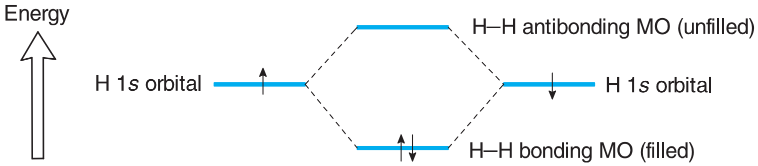


Figure 1.3. Energic diagram of the levels of the atomic and molecular orbitals for the H_2 molecule.

Problem 1.1. Draw a schematic representation of the formation of a bromine molecule from two bromine atoms.

The bond in the hydrogen molecule has maximum electron density along the line joining two nuclei (the internuclear axis) and is circularly symmetric with respect to it. Such a bond is referred to as a *sigma* (σ) *bond*. It may also be formed by similar head-on overlap of other atomic orbitals, for example, an *s* and a *p* or two *p* orbitals, as shown in Fig. 1.4.

These general considerations will now be applied to bonding in carbon compounds.

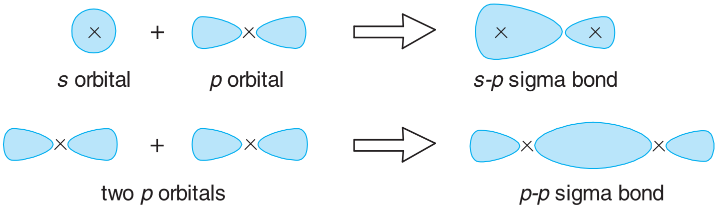


Figure 1.4. The formation of sigma bonds by head-on overlap of atomic *s* and *p* orbitals. The nuclei are shown with the sign **x**.

1.4. BONDING IN CARBON COMPOUNDS

The ground-state electronic configuration of the carbon atom is $1s^22s^22p_x2p_y$, that means two of four electrons in its valence shell are paired (in the 2*s* orbital) and two are unpaired (in different 2*p* orbitals). We might expect the formation of only two covalent bonds between carbon and other atoms, for example hydrogens, giving rise to CH_2 molecule. Meanwhile, it is known for a long time that carbon is tetravalent and the simplest organic compound is CH_4 – methane.

1.4.1. *sp*³ Hybridization

To form four bonds, carbon must adopt another electronic configuration in which all valence electrons would be unpaired. It can be achieved by the transfer of an electron from the 2*s* to the $2p_z$ orbital to form an *excited-state* configuration, $1s^22s2p_x$-$2p_y2p_z$, as shown in Fig. 1.5. The transfer requires consumption of a certain amount of energy because of slightly higher energy of a *p* orbital than an *s* orbital. This energy loss is then compensated during formation of two additional σ bonds.

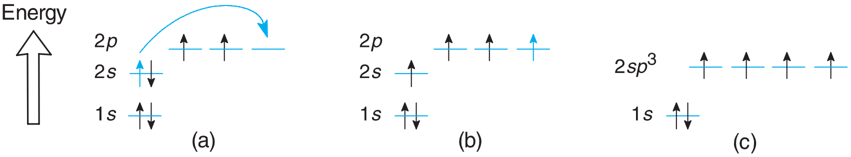


Figure 1.5. Electronic configuration of ground-state (a), excited-state (b), and *sp*³-hybridized carbon (c).

Another problem requires an explanation: Why does an excited-state carbon form four *equivalent* bonds in spite of the fact that its orbitals with valence electrons (a 2*s* and three 2*p*) differ in shape and energy?

L. Pauling (in 1931) gave the answer by the concept of the *orbital hybridization*. It was suggested that an *s* orbital and three *p* orbitals are mathematically mixed, or hybridized, to form four equivalent atomic orbitals called *sp*³ *hybrids*:

$$\text{one } 2s \text{ orbital} + \text{three } 2p \text{ orbitals} \longrightarrow \text{four } 2sp^3 \text{ hybrid orbitals}$$

New orbitals have the same energy: less than that of the 2*p* orbitals but greater than that of the 2*s* orbital (Fig. 1.5, *c*). The four hybrid orbitals are of the same shape resembling *p* orbitals, except that the dumb-bell is lop-sided and one of the lobes is much larger than the other (Fig. 1.6). This gives rise to better overlap with another orbital in bond formation and, as a result, sp^3 hybrid orbitals form stronger bonds than unhybridized *s* or *p* orbitals do.

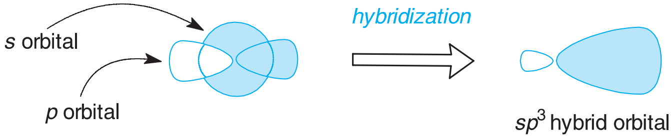


Figure 1.6. The formation of an sp^3 hybrid orbital by overlap of a *p* orbital with part of an *s* orbital.

Hybrid orbitals are located symmetrically in space at the vertices of a regular tetrahedron as shown in Fig. 1.7. All of the angles between any two bonds formed in this case are around 109.5°. This is the so-called *tetrahedral angle* that can slightly deviate (±2°) from the standard value when different atoms are attached to carbon.

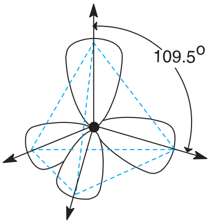


Figure 1.7. The tretrahedral configuration of an sp^3-hybridized carbon. A dot in the center represents a nucleus of the carbon atom. Small lobes of the orbitals are omitted for simplicity.

This type of hybridization is the most common electronic state of carbon, which forms σ bonds to other atoms: hydrogen, carbon, oxygen, nitrogen, and so on.

Problem 1.2. Draw a three-dimensional structure of chloroform, $CHCl_3$. What bond angles would you expect for all of the bonds in the molecule?

1.4.2. *sp*² Hybridization

There is another possibility to hybridize carbon atomic orbitals. For example, the 2*s* orbital and only two of the three 2*p* orbitals can be combined to produce three equivalent *sp*² *hybrid* orbitals:

$$\text{one } 2s \text{ orbital} + \text{two } 2p \text{ orbitals} \longrightarrow \text{three } 2sp^2 \text{ hybrid orbitals}$$

These hybrid orbitals lie in a plane at angles of 120° to each other. The remaining 2*p* orbital is perpendicular to the plane of the sp^2 orbitals, as shown in Fig. 1.8, *a*. The figure also shows how two such hybridized carbon atoms in ethylene molecule form not only a σ bond by sp^2-sp^2 head-on overlap, but also an additional bond by a *p–p* lateral, or sideways overlap. The latter produces a bonding orbital with maximum electron density outside the line joining the two carbon nuclei. This bond is called a *pi* (π) *bond*. A combination of the σ and π bonds results in the formation of a carbon–carbon *double bond*.

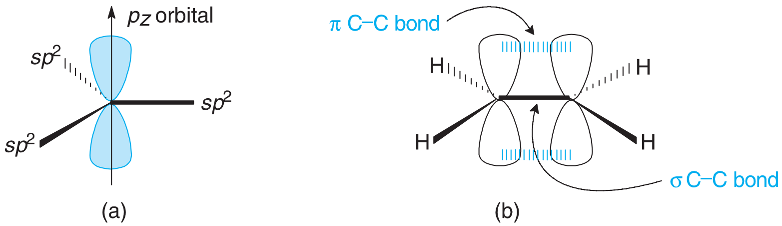


Figure 1.8. The sp^2-hybridized carbon (a) and the schematic orbital formula of ethylene (b). Hybridized orbitals are shown by their axes only.

Problem 1.3. Write a dash formula for propene, $CH_3CH{=}CH_2$. Indicate the type of hybridization for each carbon and predict each bond angle.

1.4.3. *sp* Hybridization

The third type of carbon hybridization consists in mixing the 2*s* orbital and only one 2*p* orbital to produce two equivalent *sp hybrid* orbitals:

$$\text{one } 2s \text{ orbital} + \text{one } 2p \text{ orbital} \longrightarrow \text{two } 2sp \text{ hybrid orbitals}$$

The two *sp* hybrid orbitals are oriented at 180° to each other, while the remaining unhybridized two *p* orbitals are both mutually perpendicular and also perpendicular to the hybrid orbitals (Fig. 1.9, *a*).

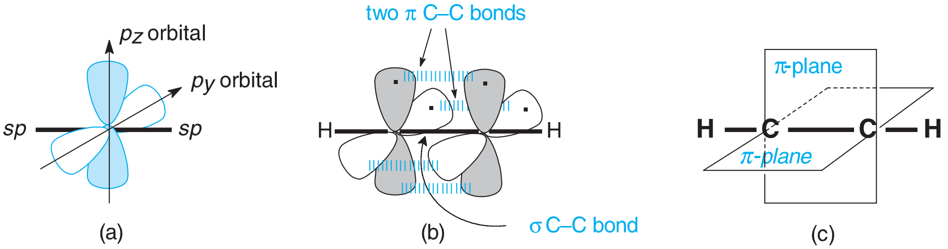


Figure 1.9. The *sp*-hybridized carbon (a), the schematic orbital formula of acetylene (b), and two mutually perpendicular π planes that formed two π bonds. The orbitals involved in the C–H and C–C single bonds are omitted for clarity.

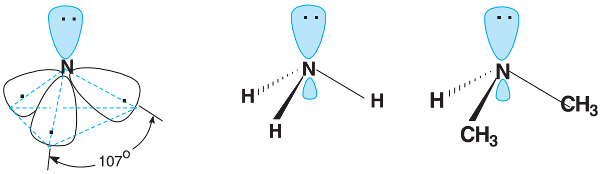
In acetylene, C_2H_2, the *sp* orbitals of each carbon head-on overlap to form a σ bond. In addition, two pairs of the *p* orbitals overlap to form two π bonds, as shown in Fig. 1.9, *b* and *c*. Thus, the net effect is formation of a carbon-carbon *triple bond*.

1.4.4. Hybridization of Other Atoms

The description of covalent bonding can be applied to other elements, first of all nitrogen and oxygen being present very often in organic compounds. Their hybridization will be described by the simplest examples.

Nitrogen hybridization. Ground-state nitrogen atom has the electronic configuration $1s^22s^22p_x2p_y2p_z$. It might form three σ bonds with hydrogens, for example, using its half-filled 2*p* orbitals. In this case, ammonia would have all N–H bonds at right angles which are typical for unhybridized *p* orbitals. In fact, all H–N–H bond angles in ammonia are 107° (Fig. 1.10, *a*), differing slightly from the tetrahedral value of 109.5°.

Such geometry of ammonia can be explained by sp^3 hybridization of nitrogen. The molecule is pyramidal, nearly tetrahedral, where *non-bonding* electrons (called also a *lone pair* of electrons) occupy one of the four sp^3 hybrid orbitals; the remaining three orbitals form three σ bonds to hydrogen atoms, as illustrated in Fig. 1.10. Another reason for hybridization lies in better overlap of a hybrid orbital compared to unhybridized one.

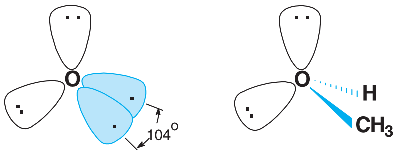


(a) (b) (c)

Figure 1.10. The sp^3-hybridized nitrogen (a), the pyramidal structures of ammonia (b) and seconddary amine (c). Hybrid orbitals filled with a lone pair of electrons are shown in colour.

Nitrogen hybridization and bonding in amines, from the primary, RNH_2, to the tertiary ones, R_3N, are quite similar to those of ammonia, except that one, two, or three sp^3-hybridized carbons of the R groups form σ bonds to nitrogen (Fig. 1.10, *c*).

Oxygen hybridization. An oxygen atom has the ground-state electronic configuration $1s^22s^22p_x^{\,2}2p_y2p_z$ and is therefore divalent. For the same reasons described for nitrogen in ammonia, oxygen in water and some organic compounds, such as alcohols, ROH, or ethers, ROR′, is also sp^3-hybridized (Fig. 1.11).



(a) (b)

Figure 1.11. The sp^3-hybridized oxygen (a) and the structure of methanol (b). The bonding orbitals and σ bonds are shown in colour.

Important classes of organic compounds, such as aldehydes, ketones, and carboxylic acids, comprise an sp^2-hybridized double-bonded oxygen atom. It will be discussed in appropriate chapters.

Problem 1.4. What geometry would you predict for the compounds: (a) trimethylamine, $(CH_3)_3N$; (b) dimethyl ether, CH_3OCH_3? Draw three-dimensional structures of them.

1.5. THE REPRESENTATION OF STRUCTURAL FORMULAS

A molecular formula gives, with a few exceptions, no information on a structure of an organic compound. Even if a molecular formula corresponds to only one structure, organic chemists prefer structural or condensed structural formulas to show the functional group present. Thus, you never find the formula of methanol as CH_4O, but CH_3OH, as well as formic acid is usually written as HCOOH rather than CH_2O_2.

Structural formulas are, of course, the most informative ones. They show all atoms and their arrangement in a molecule. There are several types representing the structure. In the *dash formula* covalent bonds are depicted by dashes (Fig. 1.12, *a*). Two dots are sometimes used in the *dot formula* replacing the dash for representation of valence electrons. But for complicated structures, drawing each bond and atom is too time-consuming, therefore simplified formulas are often used.

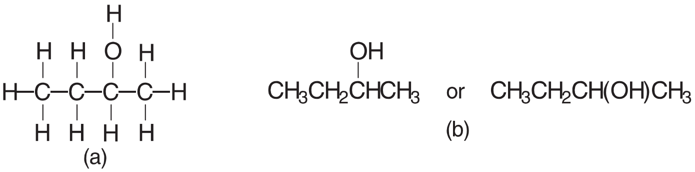


Figure 1.12. The dash formula (a) and the condensed formulas (b) for 2-butanol.

In the *condensed formula*, C–H and C–C bonds (but only single bonds) are not shown, and atoms attached to a particular carbon are written immediately after that carbon (Fig. 1.12, *b*). Such formulas are widely used in organic chemistry.

Problem 1.5. Write condensed formulas for all the structural isomers of $C_4H_{10}Br$.

The *skeletal formulas* are the easiest to write because they show only the molecular framework. In this case, carbon atoms and hydrogen atoms attached to them are omitted but other atoms (O, N, Cl, etc.) must be written. Each crossing and ending of the lines is understood to have a carbon. The number of hydrogens at each carbon can be easily calculated taking into account a valence of carbon that is always equal to four. This type of representation is most helpful in cyclic structures. Examples are given in Fig. 1.13. Of course, it is not forbidden to use a mixed type of representation as shown by the example of cumene in the figure.

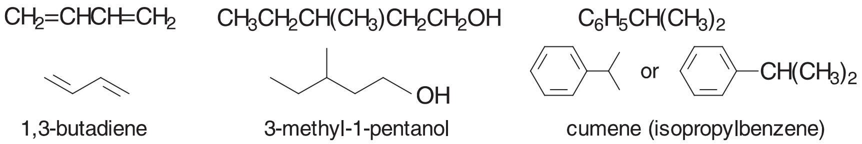


Figure 1.13. Different types of a structure representation: the condensed formulas (the upper row) and the skeletal formulas (the lower row).

Problem 1.6. Convert the following molecular formulas into any structural formula (more than one structure is possible for some compounds): (a) CH_5N; (b) C_3H_6; (c) C_3H_7Cl; (d) C_4H_{10}; (e) C_3H_8O.

1.6. SHAPE OF MOLECULES AND MOLECULAR MODELS

Organic molecules are generally not planar but three-dimensional objects. This results from tetrahedral configuration of saturated carbon atoms, that is, ones bonded to four other atoms (Fig. 1.7). Molecular shape often plays an important role in many chemical reactions; this role is crucial in biochemical processes.

Two parameters characterize the shape of a molecule, namely bond angles and bond lengths. The former have been discussed in Sec. 1.4. The bond length represents the distance between nuclei of atoms bonded. It depends on the atoms that form the bond and a type of bonding, but for the same type of bonding between the same atoms it remains nearly constant. For example, a C–H bond and a single C–C bond is 109 and 154 pm in length, respectively. Bond lengths for some covalent bonds are given in Appendix 1.

In the SI units, bond lengths are expressed in picometres (pm) or in nanometres (nm), i. e. 10^{-12} or 10^{-9} m, respectively. But most chemists (and textbooks) still use the angstrom unit (Å), which is 10^{-10} m. The conversion gives 1 Å = 100 pm = 0.1 nm.

Taking into account bond angles and bond lengths, it is possible to build three-dimensional models of organic molecules, or *molecular models*. Several kinds of models are commercially available; three of them are essentially used (Fig. 1.14).

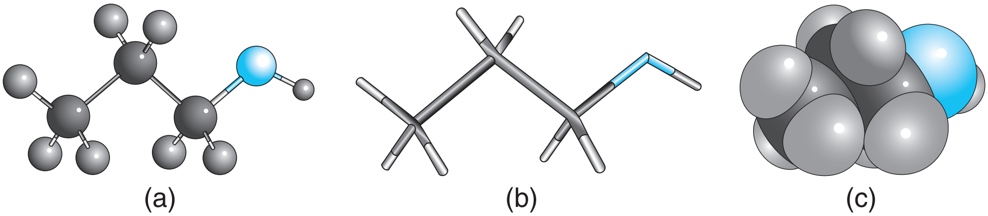


Figure 1.14. Three types of molecular models of 1-propanol, $CH_3CH_2CH_2OH$: ball-and-stick (a), stick (b), and space-filling (c). The oxygen atom is shown in colour.

Ball-and-stick models are visually effective for students' use. Stick, or skeletal models (called also the Dreiding models) show precise bond angles and lengths as well as interatomic distances in a molecule. Space-filling models, as it follows from the name, demonstrate the space occupied by atoms and can thus show interaction and crowding of atoms in a molecule.

If you cannot find a set of models, you can make «ball-and-stick models» with your own hand from readily available materials. Use several matches for bonds and plasticine or any pliable material for atoms.

Additional Problems

1.7. Give the ground-state electronic configuration for the following: (a) Cl atom; (b) Na atom; (c) cation Na^+; (d) hydride ion, H^-.

1.8. Identity all the bonds in sodium ethoxide, CH_3CH_2ONa, that contains both ionic and covalent bonds.

1.9. Indicate a type of bonding (covalent or ionic) in the following compounds: (a) C_2H_6; (b) CH_3Cl; (c) CH_3OH; (d) $CaCl_2$; (e) Br_2; (f) HCl.

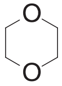
1.10. Indicate the type of hybridization for each carbon in the following compounds:

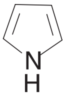
(a) $CH_2{=}CH_2$; (d) CH_3CH_2OH;
(b) $(CH_3)_2CHCH(CH_3)_2$; (e) $CH_2{=}CHCH{=}O$;
(c) $CH_2{=}CHCH{=}CH_2$; (f) $CH_3CH_2C{\equiv}N$.

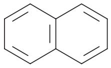
1.11. Select compound(s) in which *all* carbon atoms are *sp*^{2}-hybridized:

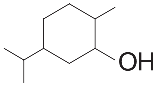
(a) $CH_3CH{=}CHCH{=}CH_2$; (d) $CH_2{=}CHC{\equiv}CH$;
(b) $CH_2{=}CHCl$; (e) $CH_2{=}CHCH{=}O$;
(c) $CH_2{=}C(CH_3){-}CH{=}CH_2$; (f) $CH_2{=}CCl{-}CH{=}CH_2$.

1.12. Convert the following skeletal formulas into molecular formulas:

(a)


(b)


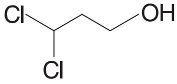
(c)


(d)


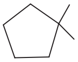
1.13. Rewrite each of the condensed formulas given below, as dash formulas and as skeletal formulas:

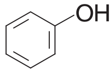
(a) $CH_3CH_2CH(CH_3)CH(CH_3)_2$; (d) $H_2N(CH_2)_3NH_2$;
(b) $CH_3CHBrCHBrCH_3$; (e) $CH_2{=}C(CH_3)CH{=}CH_2$;
(c) $CH_3CH(OH)CH_2CH_3$; (f) $C_6H_5OCH_2CH_3$.

1.14. Write condensed formulas for each of the following skeletal formulas:

(a)


(b)


(c)


(d)


1.15. Convert the following molecular formulas into *cyclic* skeletal formulas (there is more than one possibility in each case): (a) C_4H_8; (b) C_3H_6O; (c) C_4H_7Cl.