

Introduction

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References Text Books:

1. John McMurry "Organic Chemistry" 9th Edition Cengage Learning, USA (2016).
2. R.T. Morrison, R.N. Boyd and S.K. Bhattacharjee "Organic Chemistry" 7th Edition Pearson Education Inc. India (2011).

Organic chemistry, then, is the study of carbon compounds. But why is carbon special? Why, of the more than 50 million presently known chemical compounds, do most of them contain carbon? The answers to these questions come from carbon's electronic structure and its consequent position in the periodic table (**Figure 1-1**). As a group 4A element, carbon can share four valence electrons and form four strong covalent bonds. Furthermore, carbon atoms can bond to one another, forming long chains and rings. Carbon, alone of all elements, is able to form an immense diversity of compounds, from the simple methane, with one carbon atom, to the staggeringly complex DNA, which can have more than *100 million* carbons.

Group 1A												8A					
H	2A											3A	4A	5A	6A	7A	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															

Figure 1-1 The position of carbon in the periodic table. Other elements commonly found in organic compounds are shown in the colors typically used to represent them.

Of course, not all carbon compounds are derived from living organisms. Modern chemists have developed a remarkably sophisticated ability to design and synthesize new organic compounds in the laboratory medicines, dyes, polymers, and a host of other substances. Organic chemistry touches the lives of everyone; its study can be a fascinating undertaking.

Atomic Structure: The Nucleus

As you probably know from your general chemistry course, an atom consists of a dense, positively charged nucleus surrounded at a relatively large distance by negatively charged electrons (**Figure 1-2**). The nucleus consists of subatomic particles called protons, which are positively charged, and neutrons, which are electrically neutral. Because an atom is neutral overall, the number of positive protons in the nucleus and the number of negative electrons surrounding the nucleus are the same.

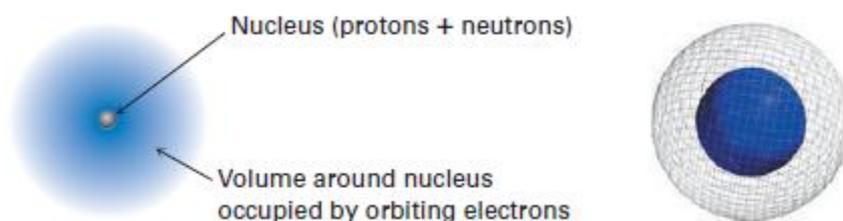


Figure 1-2 A schematic view of an atom. The dense, positively charged nucleus contains most of the atom's mass and is surrounded by negatively charged electrons. The three dimensional view on the right shows calculated electron-density surfaces. Electron density increases steadily toward the nucleus and is 40 times greater at the blue solid surface than at the gray mesh surface.

Atomic Structure: Orbitals

An orbital describes the volume of space around a nucleus that an electron is most likely to occupy. You might therefore think of an orbital as looking like a photograph of the electron taken at a slow shutter speed.

In such a photo, the orbital would appear as a blurry cloud, indicating the region of space where the electron has been. This electron cloud doesn't have a sharp boundary, but for practical purposes we can set its limits by saying that an orbital represents the space where an electron spends 90% to 95% of its time.

What do orbitals look like? There are four different kinds of orbitals, denoted *s*, *p*, *d*, and *f*, each with a different shape. Of the four, we'll be concerned primarily with *s* and *p* orbitals because these are the most common in organic and biological chemistry. An *s* orbital is spherical, with the nucleus at its center; a *p* orbital is dumbbell-shaped; and four of the five *d* orbitals are clover leaf-shaped, as shown in **Figure 1-3**. The fifth *d* orbital is shaped like an elongated dumbbell with a doughnut around its middle.

The orbitals in an atom are organized into different **electron shells**, centered on the nucleus and having successively larger size and energy. Different shells contain different numbers and kinds of orbitals, and each orbital within a shell can be occupied by two electrons.

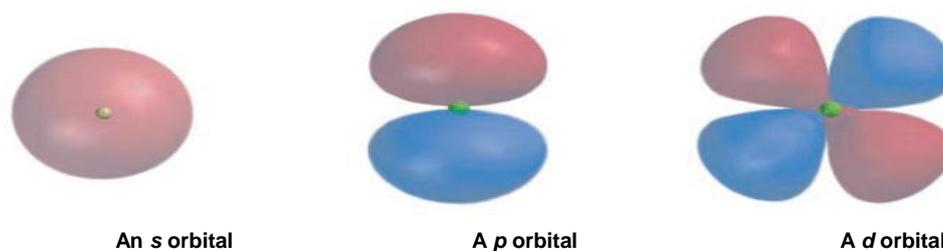


Figure 1-3 Representations of *s*, *p*, and *d* orbitals. An *s* orbital is spherical, a *p* orbital is dumbbell shaped, and four of the five *d* orbitals are cloverleaf-shaped. Different lobes of *p* and *d* orbitals are often drawn for convenience as teardrops, but their actual shape is more like that of a doorknob, as indicated.

The first shell contains only a single *s* orbital, denoted $1s$, and thus holds only 2 electrons. The second shell contains one $2s$ orbital and three $2p$ orbitals and thus holds a total of 8 electrons. The third shell contains a $3s$ orbital, three $3p$ orbitals, and five $3d$ orbitals, for a total capacity of 18 electrons. These orbital groupings and their energy levels are shown in **Figure 1-4**.

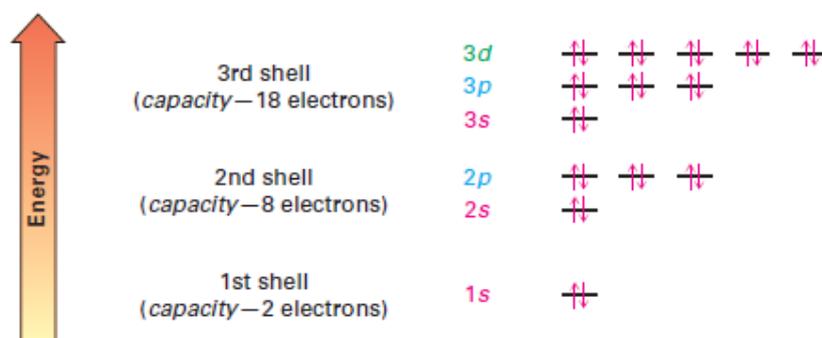


Figure 1-4 The energy levels of electrons in an atom. The first shell holds a maximum of 2 electrons in one $1s$ orbital; the second shell holds a maximum of 8 electrons in one $2s$ and three $2p$ orbitals; the third shell holds a maximum of 18 electrons in one $3s$, three $3p$, and five $3d$ orbitals; and so on. The two electrons in each orbital are represented by up and down arrows, hg. Although not shown, the energy level of the $4s$ orbital falls between $3p$ and $3d$.

The three different *p* orbitals within a given shell are oriented in space along mutually perpendicular directions, denoted p_x , p_y , and p_z . As shown in **Figure 1-5**, the two lobes of each *p* orbital are separated by a region of zero electron density called a **node**. Furthermore, the two orbital regions separated by the node have different algebraic signs, 1 and 2, in the wave function, as represented by the different colors in Figure 1-5. We'll see that these algebraic signs for different orbital lobes have important consequences with respect to chemical bonding and chemical reactivity.

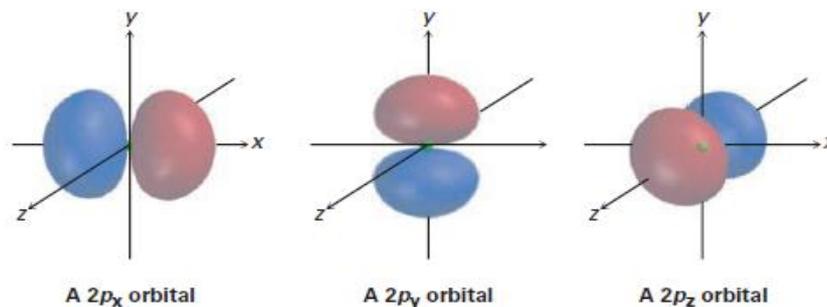


Figure 1-5 Shapes of the $2p$ orbitals. Each of the three mutually perpendicular, dumbbell shaped orbitals has two lobes separated by a node. The two lobes have different algebraic signs in the corresponding wave function, as indicated by the different colors.

Atomic Structure: Electron Configurations

The lowest-energy arrangement, or **ground-state electron configuration**, of an atom is a listing of the orbitals occupied by its electrons. We can predict this arrangement by following three rules.

Rule 1

The lowest-energy orbitals fill up first, according to the order $1s \rightarrow 2s \rightarrow 2p \rightarrow 3s \rightarrow 3p \rightarrow 4s \rightarrow 3d$, a statement called the *Aufbau principle*. Note that the $4s$ orbital lies between the $3p$ and $3d$ orbitals.

Rule 2

Electrons act in some ways as if they were spinning around an axis, somewhat like how the earth spins. This spin can have two orientations, denoted as up (\uparrow) and down (\downarrow). Only two electrons can occupy an orbital, and they must be of opposite spin, a statement called the *Pauli exclusion principle*.

Rule 3

If two or more empty orbitals of equal energy are available, one electron occupies each with spins parallel until all orbitals are half-full, a statement called *Hund's rule*. Some examples of how these rules apply are shown in **Table 1-1**. Hydrogen, for instance, has only one electron, which must occupy the lowest-energy orbital.

Thus, hydrogen has a $1s$ ground-state configuration. Carbon has six electrons and the ground-state configuration $1s^2 2s^2 2p_x^1 2p_y^1$, and so forth. Note that a superscript is used to represent the number of electrons in a particular orbital.

TABLE 1-1 Ground-State Electron Configurations of Some Elements

Element	Atomic number	Configuration	Element	Atomic number	Configuration
Hydrogen	1	1s ↑	Phosphorus	15	3p ↑ ↑ ↑
Carbon	6	2p ↑ ↑ — 2s ↑↑ 1s ↑↑			3s ↑↑ 2p ↑↑ ↑↑ ↑↑ 2s ↑↑ 1s ↑↑

Development of Chemical Bonding Theory

A representation of a tetrahedral carbon atom is shown in **Figure 1-6**. Note the conventions used to show three-dimensionality: solid lines represent bonds in the plane of the page, the heavy wedged line represents a bond coming out of the page toward the viewer, and the dashed line represents a bond receding back behind the page, away from the viewer. These representations will be used throughout the text.

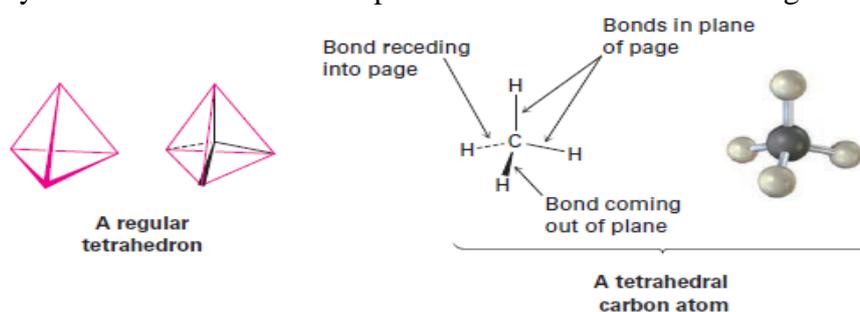


Figure 1-6 A representation of a tetrahedral carbon atom. The solid lines represent bonds in the plane of the paper, the heavy wedged line represents a bond coming out of the plane of the page, and the dashed line represents a bond going back behind the plane of the page.

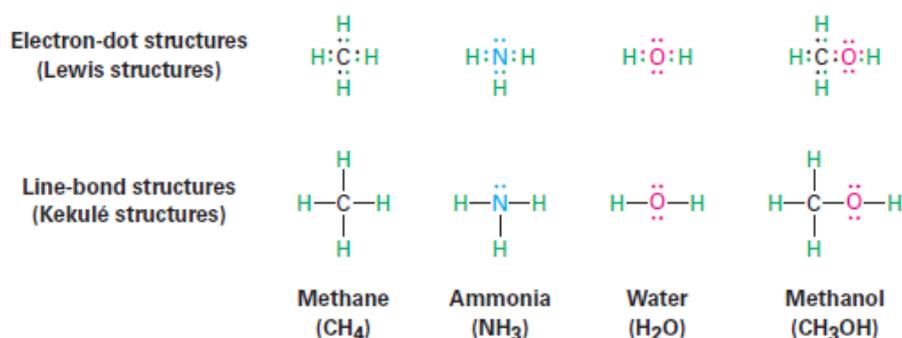
We know through observation that eight electrons (an electron *octet*) in an atom's outermost shell, or **valence shell**, impart special stability to the noble gas elements in group 8A of the periodic table: Ne (2 + 8); Ar (2 + 8 + 8); Kr (2 + 8 + 18 + 8).

We also know that the chemistry of main-group elements is governed by their tendency to take on the electron configuration of the nearest noble gas. The alkali metals in group 1A, for example, achieve a noble-gas configuration by losing the single *s* electron from their valence shell to form a cation, while the halogens in group 7A achieve a noble-gas configuration by gaining a *p* electron to fill their valence shell and form an anion. The resultant ions are held together in compounds like Na^+Cl^- by an electrostatic attraction that we call an **ionic bond**.

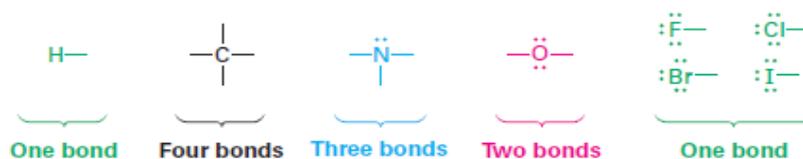
But how do elements closer to the middle of the periodic table form bonds? Look at methane, CH_4 , the main constituent of natural gas, for example. The bonding in methane is not ionic because it would take too much energy for carbon ($1s^2 2s^2 2p^2$) either to gain or lose four electrons to achieve a noble-gas configuration. As a result, carbon bonds to other atoms, not by gaining or losing electrons, but by sharing them. Such a shared-electron bond, first proposed by G. N. Lewis, is called a **covalent**

bond. The neutral collection of atoms held together by covalent bonds is called a **molecule**.

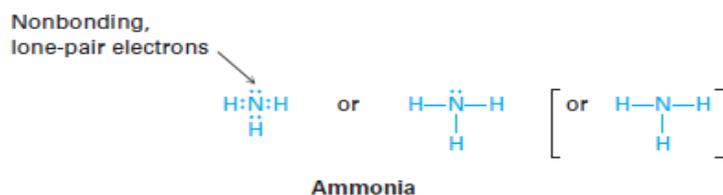
A simple way of indicating the covalent bonds in molecules is to use what are called **Lewis structures**, or **electron-dot structures**, in which the valence shell electrons of an atom are represented as dots. Thus, hydrogen has one dot representing its $1s$ electron, carbon has four dots ($2s^2 2p^2$), oxygen has six dots ($2s^2 2p^4$), and so on. A stable molecule results whenever a noble-gas configuration is achieved for all the atoms eight dots (an octet) for main-group atoms or two dots for hydrogen. Simpler still is the use of **Kekulé structures**, or **line bond structures**, in which a two-electron covalent bond is indicated as a line drawn between atoms.



The number of covalent bonds an atom forms depends on how many additional valence electrons it needs to reach a noble-gas configuration. Hydrogen has one valence electron ($1s$) and needs one more to reach the helium configuration ($1s^2$), so it forms one bond. Carbon has four valence electrons ($2s^2 2p^2$) and needs four more to reach the neon configuration ($2s^2 2p^6$), so it forms four bonds. Nitrogen has five valence electrons ($2s^2 2p^3$), needs three more, and forms three bonds; oxygen has six valence electrons ($2s^2 2p^4$), needs two more, and forms two bonds; and the halogens have seven valence electrons, need one more, and form one bond.



Valence electrons that are not used for bonding are called **lone-pair electrons**, or **nonbonding electrons**. The nitrogen atom in ammonia, NH_3 , for instance, shares six valence electrons in three covalent bonds and has its remaining two valence electrons in a nonbonding lone pair. As time-saving shorthand, nonbonding electrons are often omitted when drawing line-bond structures, but you still have to keep them in mind since they're often crucial in chemical reactions.



sp^3 Hybrid Orbitals and the Structure of Methane

The bonding in the hydrogen molecule is fairly straightforward, but the situation is more complicated in organic molecules with tetravalent carbon atoms. Take methane, CH_4 , for instance. Carbon has four valence electrons ($2s^2 2p^2$) and forms four bonds. Because carbon uses two kinds of orbitals for bonding, $2s$ and $2p$, we might expect methane to have two kinds of C-H bonds. In fact, though, all four C-H bonds in methane are identical and are spatially oriented toward the corners of a regular tetrahedron (Figure 1-6).

Linus Pauling, who showed mathematically how an s orbital and three p orbitals on an atom can combine, or **hybridize**, to form four equivalent atomic orbitals with tetrahedral orientation. Shown in **Figure 1-10**, these tetrahedrally oriented orbitals are called **sp^3 hybrid orbitals**. Note that the superscript 3 in the name sp^3 tells how many of each type of atomic orbital combine to form the hybrid, not how many electrons occupy it.

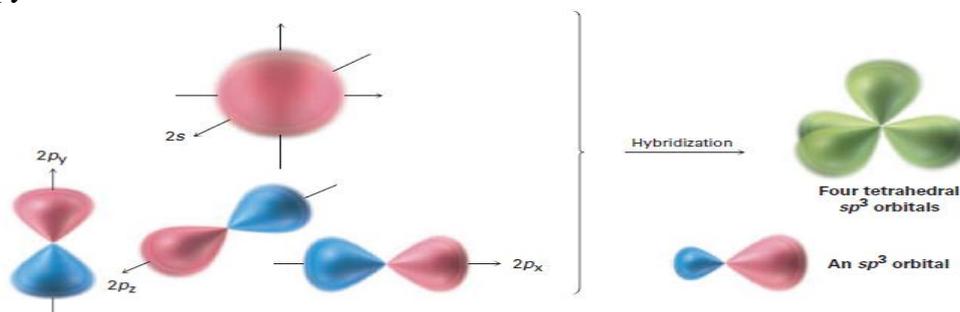


Figure 1-10 Four sp^3 hybrid orbitals, oriented to the corners of a regular tetrahedron, are formed by the combination of an s orbital and three p orbitals (red/blue). The sp^3 hybrids have two lobes and are unsymmetrical about the nucleus, giving them a directionality and allowing them to form strong bonds when they overlap an orbital from another atom.

The concept of hybridization explains how carbon forms four equivalent tetrahedral bonds but not why it does so. The shape of the hybrid orbital suggests the answer. When an s orbital hybridizes with three p orbitals, the resultant sp^3 hybrid orbitals are unsymmetrical about the nucleus. One of the two lobes is larger than the other and can therefore overlap more effectively with an orbital from another atom to form a bond. As a result, sp^3 hybrid orbitals form stronger bonds than do unhybridized s or p orbitals.

The asymmetry of sp^3 orbitals arises because, as noted previously, the two lobes of a p orbital have different algebraic signs, 1 and 2, in the wave function. Thus, when a p orbital hybridizes with an s orbital, the positive p lobe adds to the s orbital but the negative p lobe subtracts from the s orbital. The resultant hybrid orbital is therefore unsymmetrical about the nucleus and is strongly oriented in one direction. When each of the four identical sp^3 hybrid orbitals of a carbon atom overlaps with the $1s$ orbital of a hydrogen atom, four identical C-H bonds are formed and methane results. Each C-H bond in methane has a strength of 439 kJ/mol (105 kcal/mol) and a length of 109 pm. Because the four bonds have a specific geometry, we also can define a property

called the **bond angle**. The angle formed by each H-C-H is 109.5° , the so-called tetrahedral angle. Methane thus has the structure shown in **Figure 1-11**.

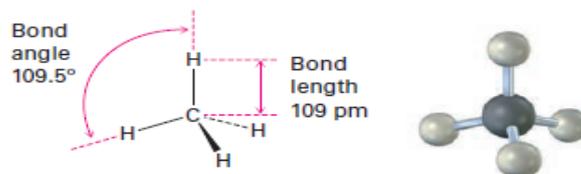
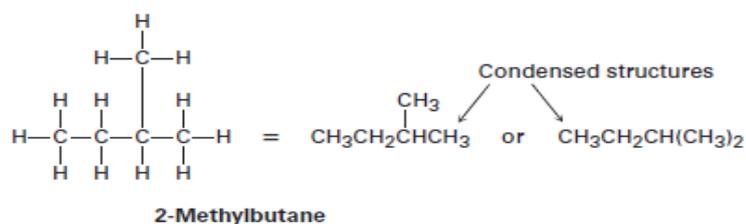


Figure 1-11 The structure of methane, showing its 109.5° bond angles.

Drawing Chemical Structures

In the structures we've been drawing until now, a line between atoms has represented the two electrons in a covalent bond. Drawing every bond and every atom is tedious, however, so chemists have devised several shorthand ways for writing structures. In **condensed structures**, carbon-hydrogen and carbon-carbon single bonds aren't shown; instead, they're understood. If a carbon has three hydrogens bonded to it, we write CH_3 ; if a carbon has two hydrogens bonded to it, we write CH_2 ; and so on. The compound called 2-methylbutane, for example, is written as follows:



Notice that the horizontal bonds between carbons aren't shown in condensed structures the CH_3 , CH_2 , and CH units are simply placed next to each other-but the vertical carbon-carbon bond in the first of the condensed structures drawn above is shown for clarity. Also, notice that in the second of the condensed structures the two CH_3 units attached to the CH carbon are grouped together as $(\text{CH}_3)_2$. Even simpler than condensed structures are **skeletal structures** such as those shown in **Table 1-3**. The rules for drawing skeletal structures are straightforward.

Rule 1

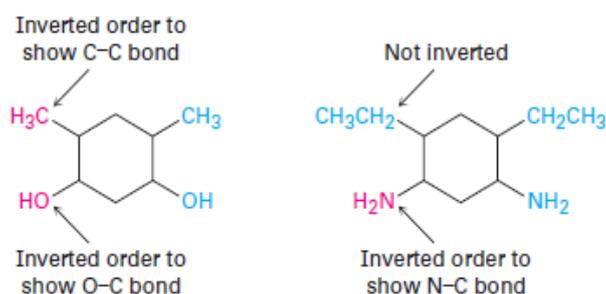
Carbon atoms aren't usually shown. Instead, a carbon atom is assumed to be at each intersection of two lines (bonds) and at the end of each line. Occasionally, a carbon atom might be indicated for emphasis or clarity.

Rule 2

Hydrogen atoms bonded to carbon aren't shown. Because carbon always has a valence of 4, we mentally supply the correct number of hydrogen atoms for each carbon.

Rule 3

Atoms other than carbon and hydrogen *are* shown. One further comment: although such groupings as $-\text{CH}_3$, $-\text{OH}$, and $-\text{NH}_2$ are usually written with the C, O, or N atom first and the H atom second, the order of writing is sometimes inverted to $\text{H}_3\text{C}-$, $\text{HO}-$, and $\text{H}_2\text{N}-$ if needed to make the bonding connections in a molecule clearer. Larger units such as $-\text{CH}_2\text{CH}_3$ are not inverted, though; we don't write $\text{H}_3\text{CH}_2\text{C}-$ because it would be confusing. There are, however, no well-defined rules that cover all cases; it's largely a matter of preference.

**TABLE 1-3** Kekulé and Skeletal Structures for Some Compounds

Compound	Kekulé structure	Skeletal structure
Isoprene, C_5H_8		
Methylcyclohexane, C_7H_{14}		
Phenol, $\text{C}_6\text{H}_6\text{O}$		