Chapter 1

Electronic structure of organic compounds

Introduction:

To understand and interpret an organic chemistry reaction, it is necessary to know the structure of molecules and the forces that bind atoms together. This understanding requires, first and foremost, knowledge of the electronic structure of the elements involved. The following table provides this information for the key atoms involved in organic chemistry.

Table 1.1: Electronic structure of the main atoms used in organic chemistry.

$_{1}$H 1s^{2}							
$_{3}$Li [He]2s^{1}	$_{4}$Be [He]2s^{2}	$_{5}$B [He]2s^{2}2p^{1}	$_{6}$C [He]2s^{2}2p^{2}	$_{7}$N [He]2s^{2}2p^{3}	$_{8}$O [He]2s^{2}2p^{4}	$_{9}$F [He]2s^{2}2p^{5}	$_{10}$Ne [He]2s^{2}2p^{6}
$_{11}$Na [Ne]3s1	$_{12}$Mg [Ne]3s^{2}	$_{13}$Al [Ne]3s^{2}3p^{1}	$_{14}$Si [Ne] 3s^{2}3p^{2}	$_{15}$P [Ne] 3s^{2}3p^{3}	$_{16}$S [Ne] 3s^{2}3p^{4}	$_{17}$Cl [Ne] 3s^{2}3p^{5}	$_{18}$Ar [Ne] 3s^{2}3p^{6}
$_{19}$K [Ar]4s^{1}						$_{35}$Br [Ar]3d^{10}4s^{2}4p^{5}	

In organic chemistry, the number of electrons in the last electron shell (or valence shell) of an atom determines the number of bonds that this atom can exchange with other partners in order to obtain a valence shell of eight electrons (octet rule).

Atom	C	H	O	S	N	F	Cl	Br	I
Number of electrons in the valence shell	4	1	6	6	5	7	7	7	7
Valence	4	1	2	2	3	1	1	1	1

1.1. Physical properties of organic molecules:

1.1.1. Different types of bonds

Atoms can become bonded with each other, and their electronic structure governs the type of bond formed. In organic chemistry, there are two main types of chemical bonds: covalent bonding (nonpolar, polar, and coordination) and ionic bonding.

a. Ionic bond:

Ionic bonding is important between atoms of vastly different electronegativity. The bond results from one atom giving up an electron while another atom accepts the electron. There is no sharing of electrons between the two atoms that form the bond, but rather a transfer of electrons from one atom to another.

Note: Ionic bonds are formed between elements with very low electronegativity that are electron donors (I_A, II_A), and elements with very high electronegativity that are electron acceptors (VI_A, V_{IIA}).

Example 1:

Sodium chloride NaCl

${}_{11}$Na loses an electron → Na^+ : $1s^2\ 2s^2\ 2p^6$

${}_{17}$Cl wins an electron → Cl^- : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

$$Na + Cl \longrightarrow Na^+ + Cl^- \longrightarrow Na^+\ Cl^-$$

Example 2:

In the compound lithium fluoride, the $2s^1$ electron of lithium is transferred to the $2p^5$ orbital of fluorine. The lithium atom gives up an electron to form the positively charged lithium cation with $1s^22s^0$ configuration, and the fluorine atom receives an electron to form a fluoride anion with $1s^22s^2\ 2p^6$ configuration. The ions are held together by the electrostatic attraction of the positive and negative ions.

$$Li \quad + \quad F \xrightarrow{\qquad\qquad} Li^+ \quad + \quad F^-$$

$1s^22s^1$ $\quad$ $1s^22s^22p^5$ $\qquad\qquad$ $1s^22s^0$ $\quad$ $1s^22s^22p^6$

b. Covalent bond:

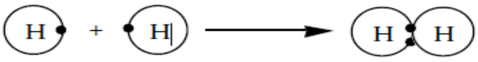
A **covalent bond** is formed by a sharing of two electrons by two atoms.

b.1. Non-polar covalent bond:

Non polar covalent bonding involves an equal sharing of electrons between two identical atoms, each contributing one valence electron.

Examples: H_2, Cl_2, O_2, N_2

A hydrogen atom possessing the $1s^1$ electron joins with another hydrogen atom with its $1s^1$ configuration. The two atoms form a covalent bond with two electrons by sharing their electrons.

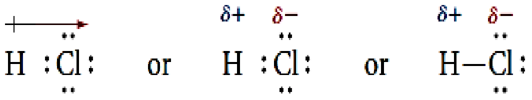


b.2.Polar Covalent Bond :

Covalent bonds can be formed not only between identical atoms (H —H, C — C) but also between different atoms (C—H, C—Cl), provided that the atoms do not differ too greatly in electronegativity. However, if the atoms are different from one another, the electron pair may not be shared equally between them. Such a bond is sometimes called a **polar covalent bond** because the atoms that are linked carry a partial negative and a partial positive charge.

Example:

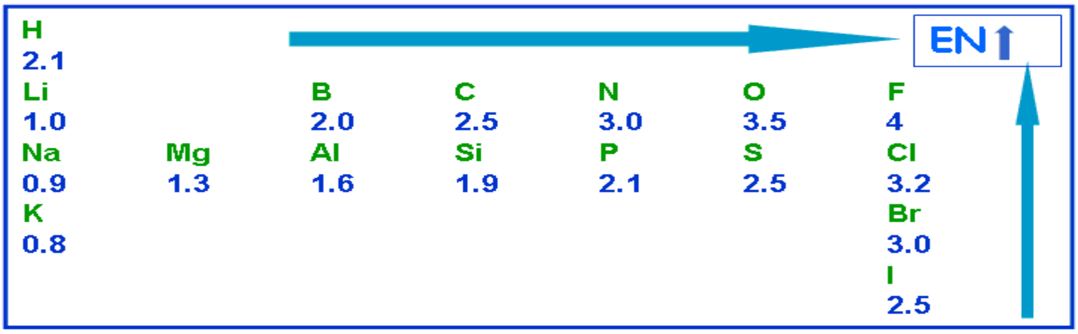
The hydrogen chloride molecule provides an example of a polar covalent bond. Chlorine atoms are more electronegative than hydrogen atoms, but even so, the bond that they form is covalent rather than ionic. However, the shared electron pair is attracted more toward the chlorine, which therefore is slightly negative with respect to the hydrogen. This bond polarization is indicated by an arrow whose head is negative and whose tail is marked with a plus sign. Alternatively, a partial charge, written as δ+ or δ- (read as “delta plus” or “delta minus”), may be shown:



The bonding electron pair, which is shared *unequally*, is displaced toward the chlorine.

The carbon–hydrogen bond, which is so common in organic compounds, requires special mention. Carbon and hydrogen have nearly identical electronegativities, so the C — H bond is almost purely covalent.

Electronegativity is the ability of an atom to attract electrons to itself, and generally increases as one moves from left to the right across the periodic table, and from bottom to top over the same column (see table below):



H 2.1						
Li 1.0		B 2.0	C 2.5	N 3.0	O 3.5	F 4
Na 0.9	Mg 1.3	Al 1.6	Si 1.9	P 2.1	S 2.5	Cl 3.2
K 0.8						Br 3.0
						I 2.5

1.1.2. Bonding in Carbon Compounds:

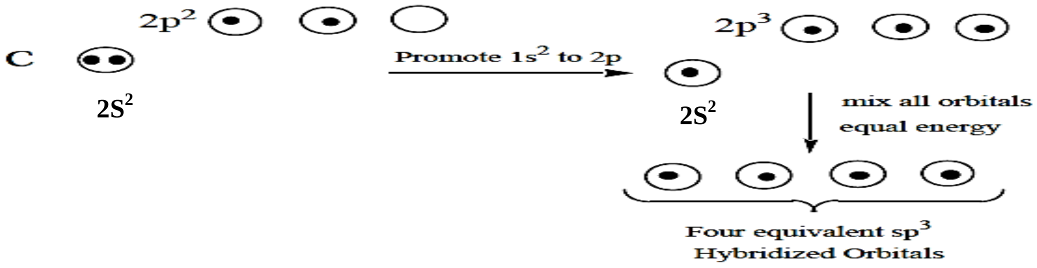
Carbon has four valence electrons ($2s^2\ 2p^2$) and needs four more to reach the neon configuration ($2s^2\ 2p^6$), so it forms four bonds. Carbon has the property of forming single, double and triple bonds with itself and with other atoms (sigma (σ) and pi (π) bonds). This multiple bond ability allows carbon compounds to have a variety of shapes.

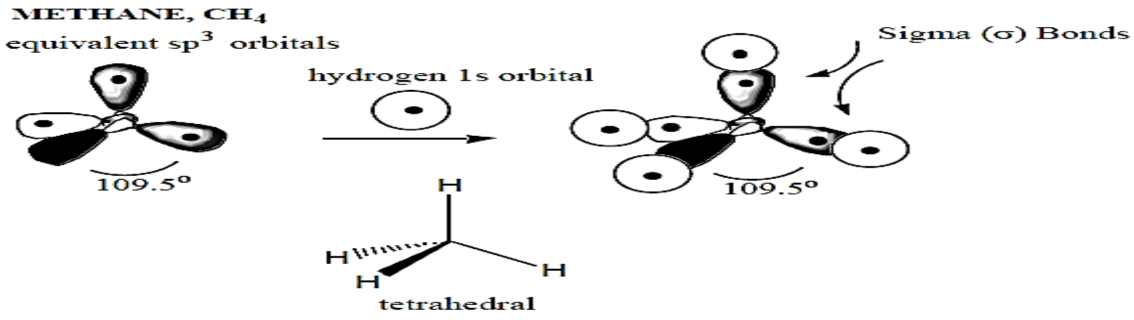
There are three types of carbon hybridization:

a. sp^3 hybridization Tetrahedral (tetragonal) :

In carbon ($1s^22s^22p^2$) one of the electrons of the $2s^2$ orbital is promoted to the third $2p^0$ orbital. The s and three p orbitals hybridize to form four new orbitals of equal energy called sp^3 hybrid orbitals. The electrons in the four sp^3 hybridized orbitals bond by overlap with the $1s^1$ hydrogen orbital. The single covalent bond is called a **sigma (σ)** bond.

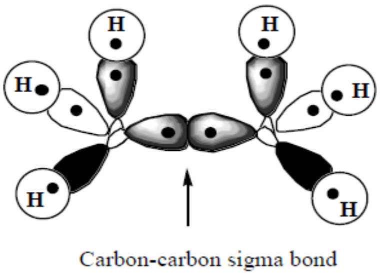
The arrangement is tetrahedral with a bond angle of 109.5°.

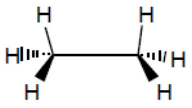




The unique property of carbon that differentiates it from the other elements and allows the formation of so many different organic compounds is the ability of carbon to bond with itself through covalent bonding.

Thus, addition of another carbon atom to methane results in ethane which has covalent sigma bonds to the hydrogen atoms and a covalent sigma bond between the carbon atoms.





Ethane

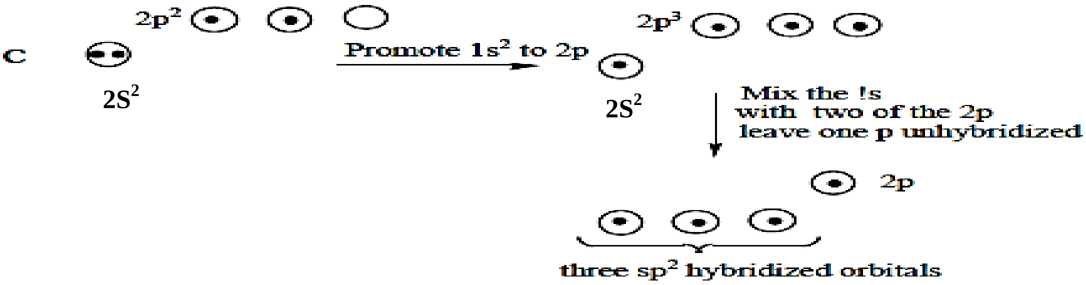
b. sp^2 hybridisation (trigonal):

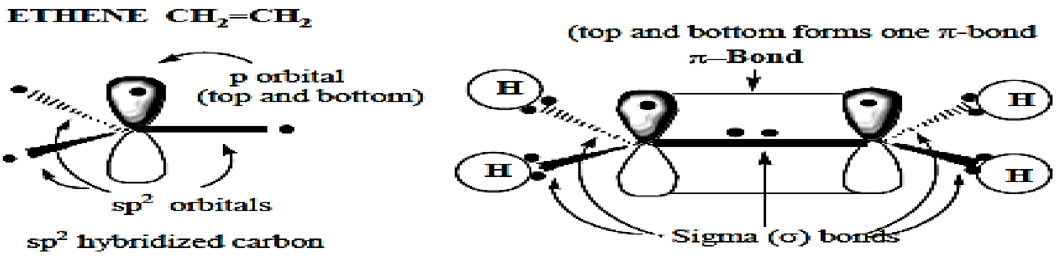
The sp^2 hybridization occurs when the s orbital is mixed with only two p orbitals. So, three orbitals are mixed, and the outcome is three hybrid orbitals which are called sp^2 hybrid orbitals.

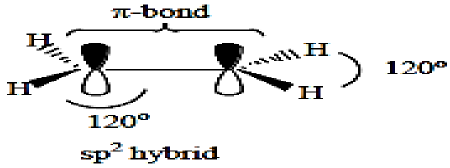
1 s orbital + 2 p orbitals $\longrightarrow$ 3 sp^2 hybrid orbitals + 1 pure p orbital

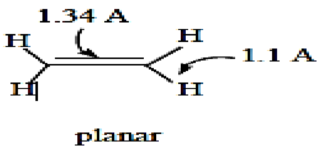
The combination of two of the sp^2 hybridized carbon atom leads to two carbon atoms being joined by overlap of sp^2 orbitals to form a C-C single bond, and the side-to-side overlap of the p orbitals to form another bond known as a pi (π) bond.

The bonding in an ethene, the molecule is planar with bond angles of 120° and a C=C bond length that is longer than the C-H bond length.







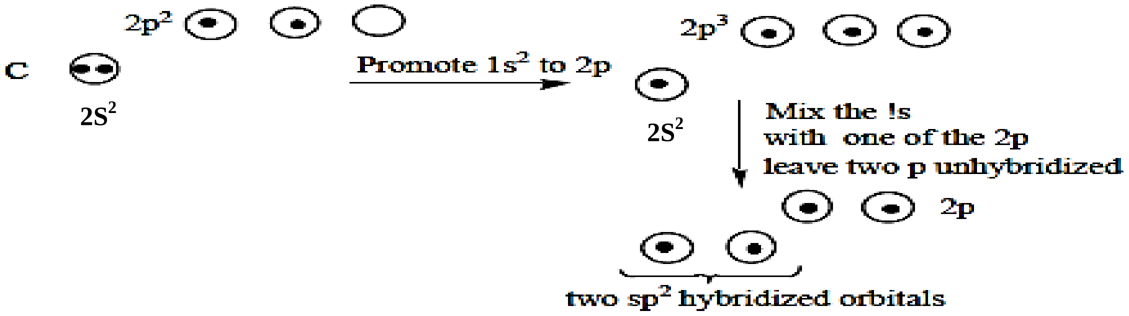


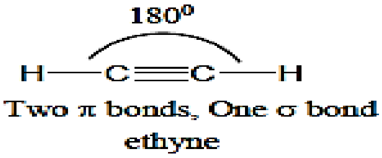
c. sp hybridization or digonal :

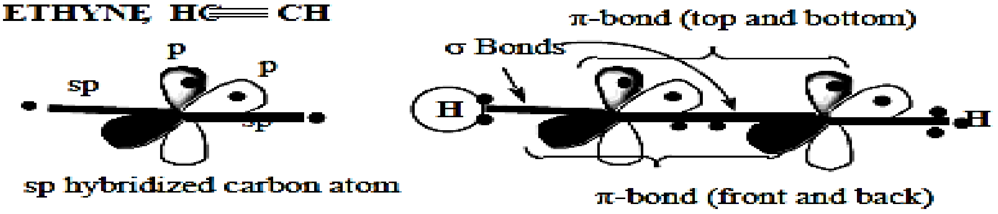
In sp hybridization, the s orbital of the excited state carbon is mixed with only one out of the three 2p orbitals. The new orbitals formed are called **sp hybridized orbitals.** It forms linear molecules with an angle of 180°

1 s orbital + 1 p orbital ⟶ 2 **sp** hybrid orbitals + 2 pure p orbitals

The simplest molecule associating 2 sp hybridized carbons is that of acethylene.







1.2. Polarization and dipole moments:

1.2.1. Polarity and polarization of bonds:

- When a covalent bond unites two identical atoms (X-X), the electron pair is shared between the two atoms. The electron cloud is distributed equally over the two atoms. There is therefore no polarity (μ = 0). **X:X**

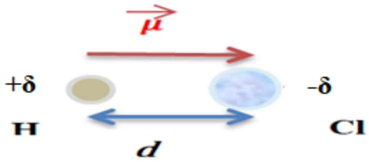
- If the two atoms are different (X-Y), it is the more electronegative atom that attracts the electron pair. The electron cloud is no longer symmetrical: it is moved towards the more electronegative atom: we say that the more electronegative atom polarizes the electron cloud. Partial charges are created on the atoms: **δ+** on the less electronegative atom and **δ-** on the more electronegative atom. $^{\delta+}X\ :Y^{\delta-}$.

The X-Y bond is polarized. It exhibits permanent polarization, characterized by its dipole moment $\overrightarrow{\mu}$.

1.2.2. Dipole moment and partial ionic character of the bond:

a. Dipole moment:

The polarization state of a bond is characterized by the value of the charges δ+ and δ-, but also by the direction and value of its electric moment, or dipole moment μ. It is characterized by a vector and oriented, by convention, from the positive charge to the negative charge.



The dipole moment (μ) is defined by the relation: $\mu = \delta . d$

Where:

δ: the partial electric charge shared between the two atoms (δ<e).

d: the distance separating the two charges (bond length) (m).

In the SI unit system, μ is expressed in Coulomb-meter (C.m), or in Debye (D):

1D = 3,33 .10^{-30} C.m

a. 1. Nonpolar molecules (X_2 molecules)

μ = 0

Example : H_2

a. 2. Polar molecules (XY molecules)

μ ≠ 0

Example : HCl

a. 3. XY_2 molecules

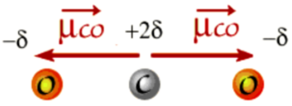
The permanent dipole moment of a polyatomic molecule is the vector sum of the bond dipole moments.

a. 3.1. Linear XY_2 molecules

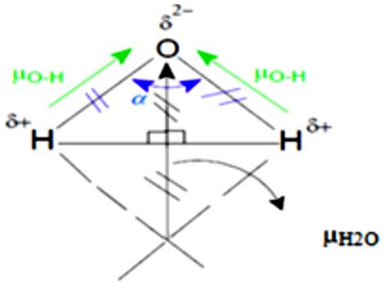
Any molecule with a center of symmetry has a zero dipole moment.

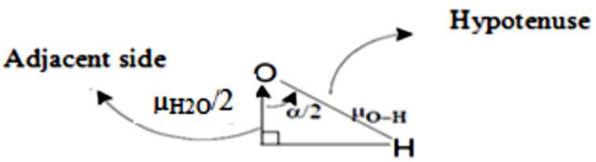
μ = 0

Example : CO_2



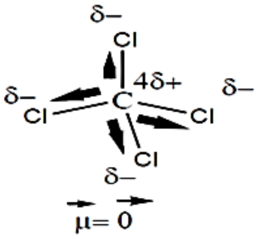
3.2. Angular XY_2 molecules



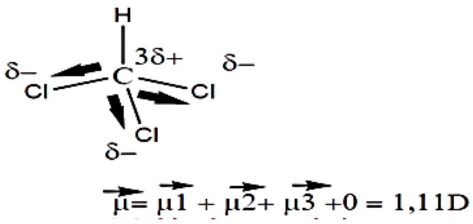


$$\cos(\alpha/2) = (\mu_{H2O}/2) / \mu_{O-H} \Leftrightarrow \mu_{H2O} = 2.\,\mu_{O\text{-}H}\,.\,\cos(\alpha/2)$$

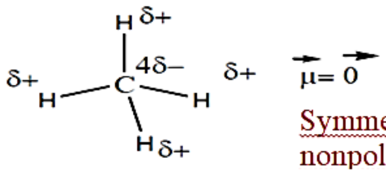
Example:



Symmetric nonpolar molecule



Asymmetric polar molecule

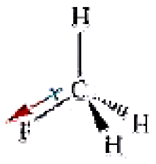


Symmetric nonpolar molecule

Exercise:

Determine whether the molecules CH_3F and CF_4 are polar or nonpolar.

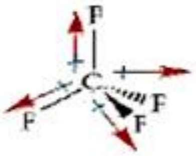
- For the CH_3F molecule, its geometry is that of a tetrahedron. The three C-H bonds are considered to be non-polar covalent bonds, having no significant dipole. On the other hand, the C-F bond is a polar covalent bond in which the dipole points towards the most electronegative element, fluorine. Overall, the molecule is polar, since there is a non-zero dipole (vector).

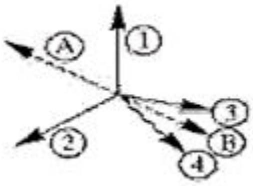


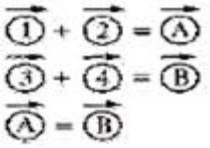
There is only one vector. So the sum of the vectors is not equal to 0. The molecule is polar.

- For the CF_4 molecule, its geometry is also tetrahedral. However, here, the four C-F bonds are polar covalent. The dipole points to the fluorine atom, the most

electronegative, for the four bonds. By summing these vectors (add the vectors two by two), they cancel each other out. The resulting dipole is then zero, and the molecule is globally
non-polar.







b. Partial ionic character of the bond:

The determination of the ionic character of a bond requires knowledge of its dipole moment. It is given by the following relation:

I.C = ($\mu_{experimental}/\mu_{theoretical}$)*100 = ($\delta$.d/e.d)*100 = ($\delta$ /e)*100

If:

I.C = 50% (δ /e = 0.5): the bond is 50% ionic,
I.C = 100% (δ = e): the bond is purely ionic,
I.C = 0% (δ = 0): the bond is purely covalent.

Example: HCl molecule with d = 1.28 Å and μ_{exp} = 1.07 D

I.C = (μ_{exp}/μ_{theo})***100** = $(1,07*3,33.10^{-30})/(1,6.10^{-19}*1,28.10^{-10})$ ***100** = 17%

The bond in the HCl molecule is 17% ionic and (100 – 17) = 83% covalent.

Exercise :

The dipole moment of CO is 0.112D and its intermolecular distance is equal to 1.128A°.
1. Calculate the electric charge carried by each atom and express it in terms of the charge of the electron.
2. Explain why the dipole moment of SCO is not zero, while that of CS_2 is zero.

1.3. Polarizability:

The covalent pair, displaced by the polarity effect, can also be further displaced under the influence of an external electric field created by the approach of a polar reactant, more or less easily depending on the nature of the bonds, which are more or less polarizable. An induced polarity is added to the initial polarity.

σ bonds are relatively poorly polarizable because the electrons are well localized in them. The polarizability varies with the type of σ bond considered. Thus, we observe the following order (> means: more polarizable than).

C-I > C-Br > C-Cl > S-H > O-H > N-H > C-F

The greater the mobility of the electron pair, the more polarizable the bond. Two factors can favor the polarizability of the bond:

- Electron pair less retained by the most electronegative atom;
- Significant bond length.

Indeed, the electron pair is more mobile if it is less hindered in its movement. This is the case when the atoms are large: they are then less electronegative and their internuclear distance is greater. It is said that the electrons are less localized. Thus, the C-F bond is much less polarizable than the C-I bond. In the latter, the electron pair is much more mobile because the iodine atom is less electronegative and the C-I internuclear distance is greater than C-F. The C-F bond, more polarized than the C-I bond, is less polarizable.

Note that very mobile π bonds are highly polarizable.