Molecular Structure and Bonding- 2

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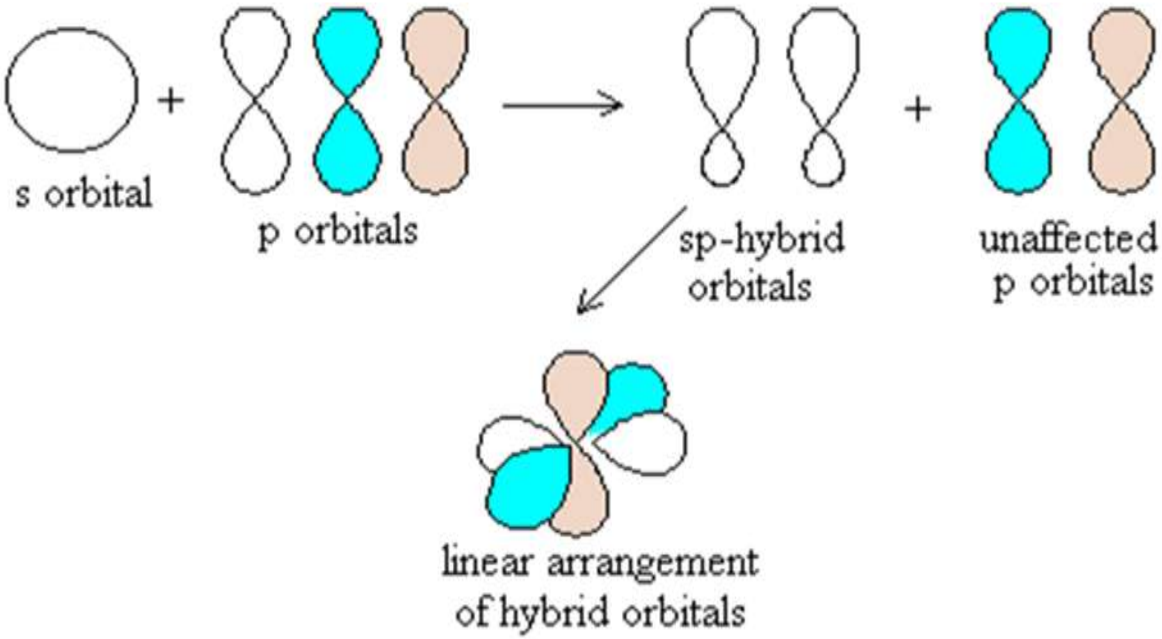
Lecture 3

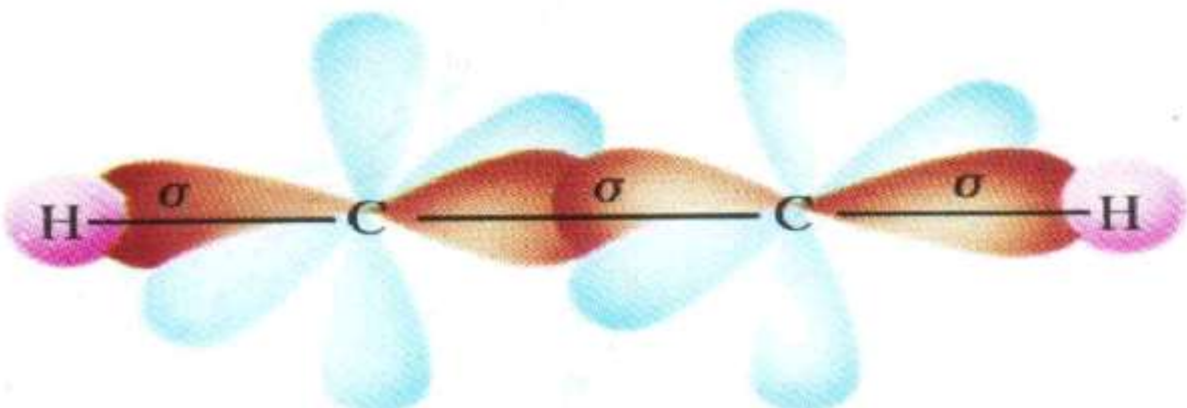
Hybridization of atomic orbitals

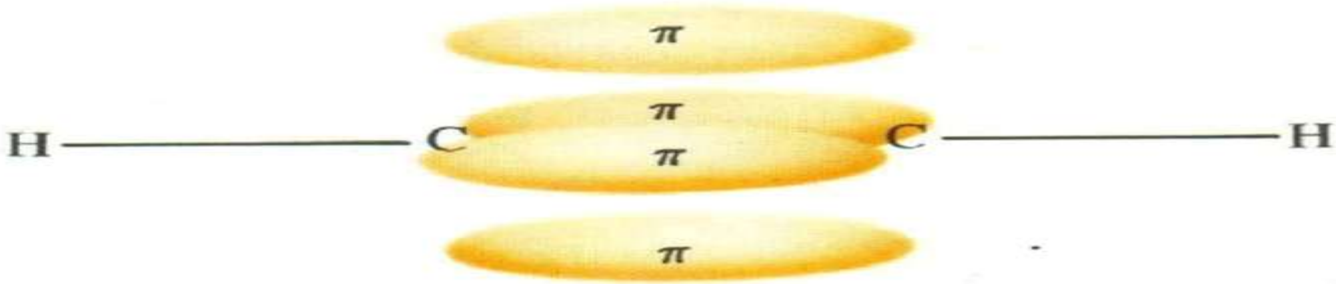
Orbital hybridization was proposed to explain the geometry of polyatomic molecules. Covalent bonding was presumed to arise due to the overlap of atomic orbitals and the sharing of electron pairs.

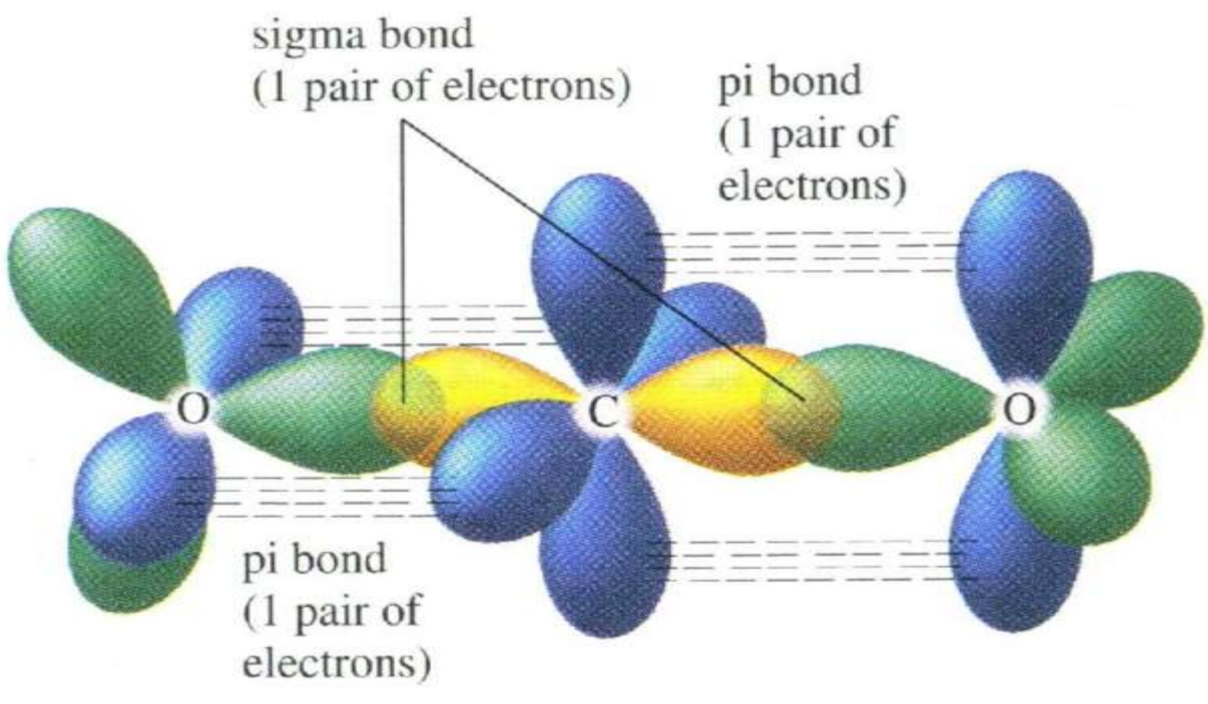
Linear *sp* hybrids. These are composed of the valence shell s-orbital and one of the three p-orbitals. The other two p-orbitals remain unhybridized and may hold lone pairs or participate in p-bonding. The two equivalent sp hybrid orbitals pointat 180^o to each other and their formation is depicted graphically and mathematically below:

Acetylene or ethyne C_2H_2

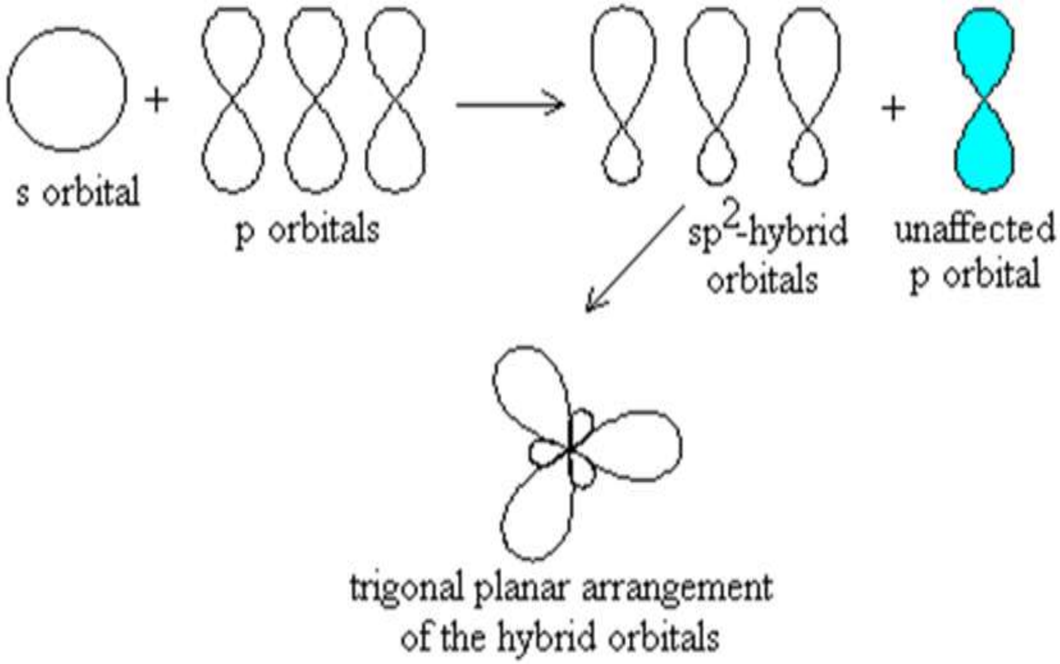




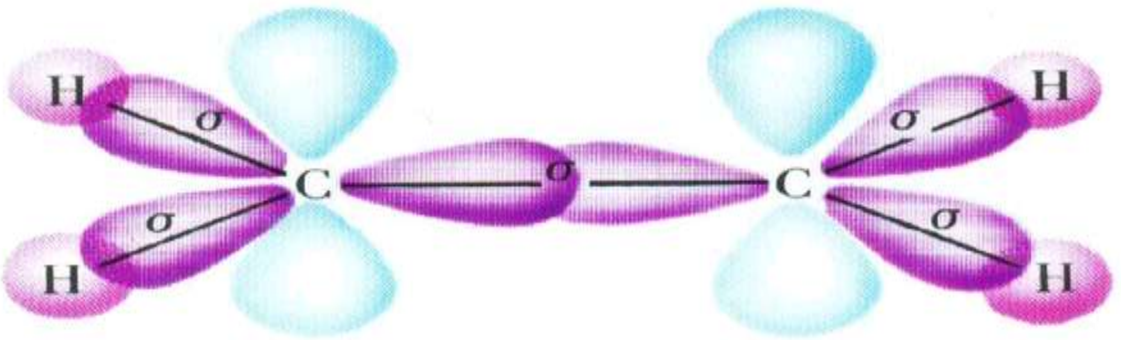

π
π
π
π
H
C
C
H

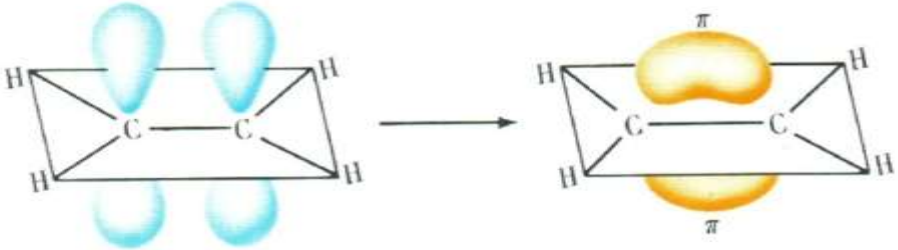

sigma bond
(1 pair of electrons)
pi bond
(1 pair of
electrons)
O
C
O
pi bond
(1 pair of
electrons)

Trigonal sp^2 hybrids. These are composed of the valence shell s-orbital and two of the p-orbitals, say the p_x and p_y to produce a set of hybrids directed in the xy plane at 120° to each other. The p_z orbital will be left to hold a lone pair or participate in p-bonding. The diagram below shows the 2s, $2p_x$ and $2p_y$ orbitals superimposed in the same space before hybridization.

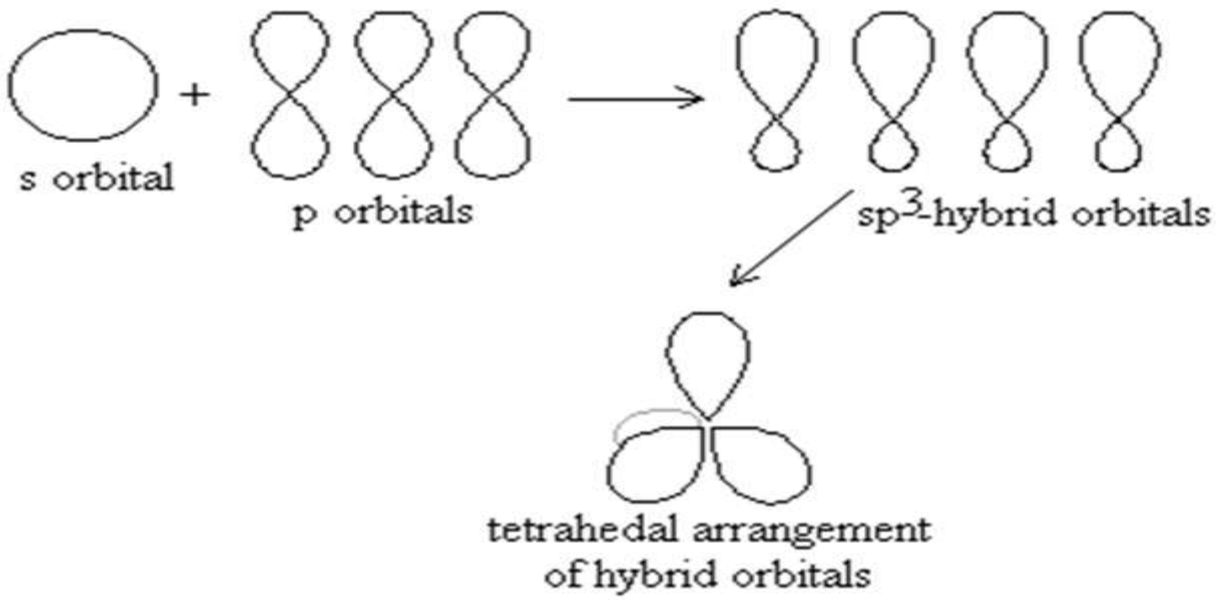


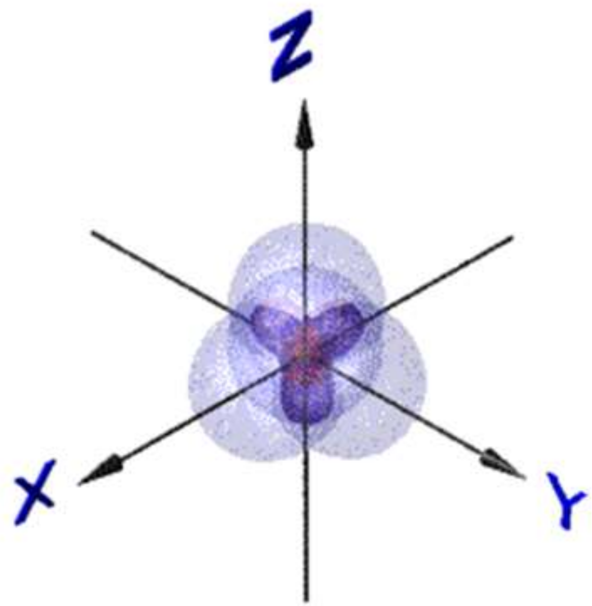
Ethylene or ethyene C_2H_4

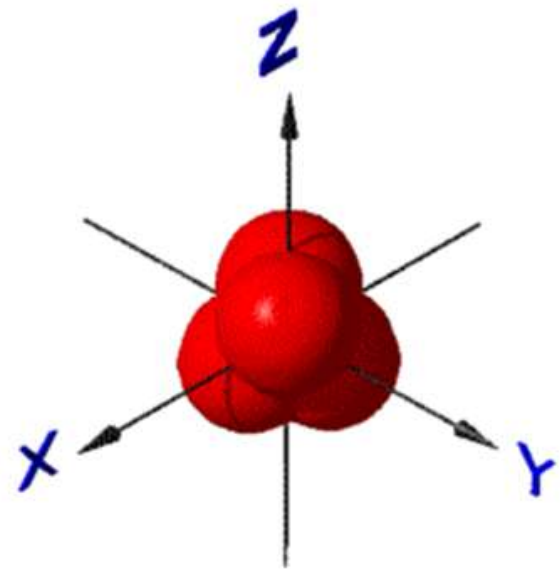




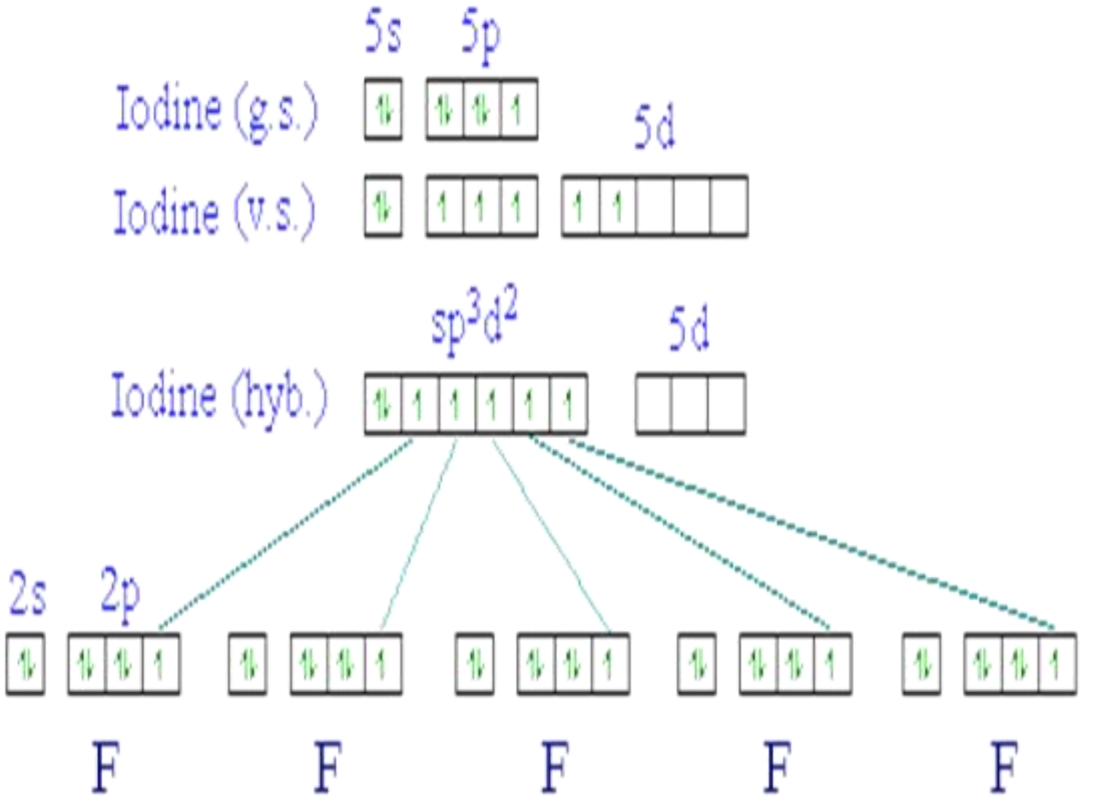
Tetrahedral sp³ hybrids. These are composed of the valence shell s-orbital and all three p-orbitals. The diagram below shows these superimposed in the same space before hybridization.

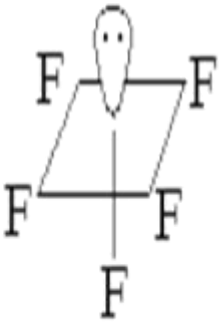



Z
X
Y

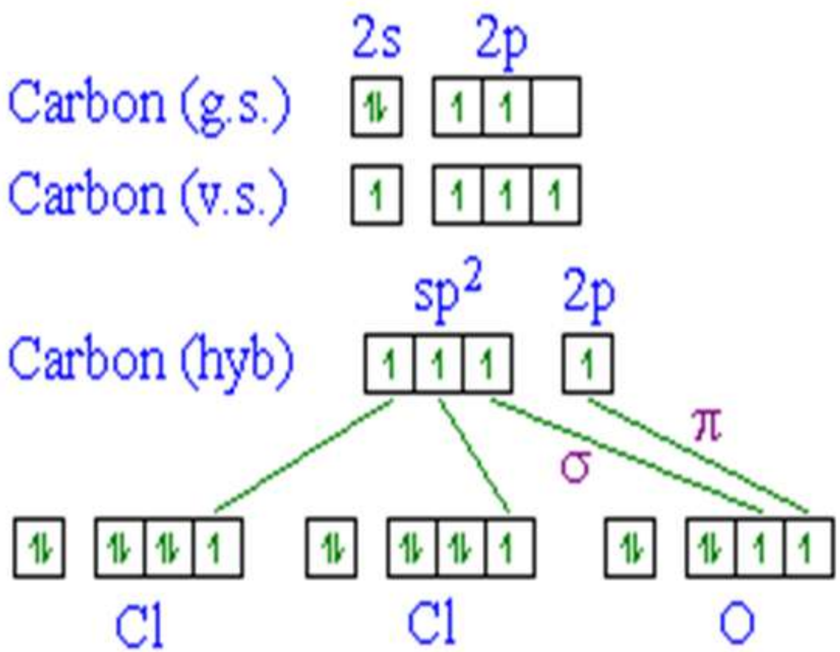

Z
X
Y

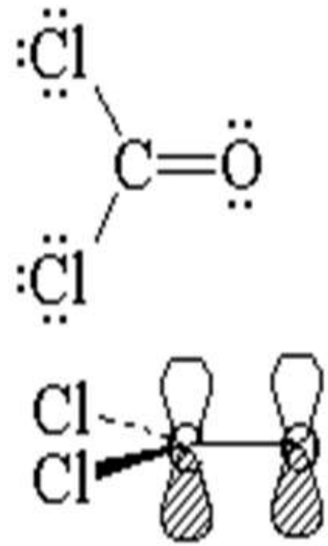
Iodine pentafluoride - IF_5 atm. No. I=53. F=9



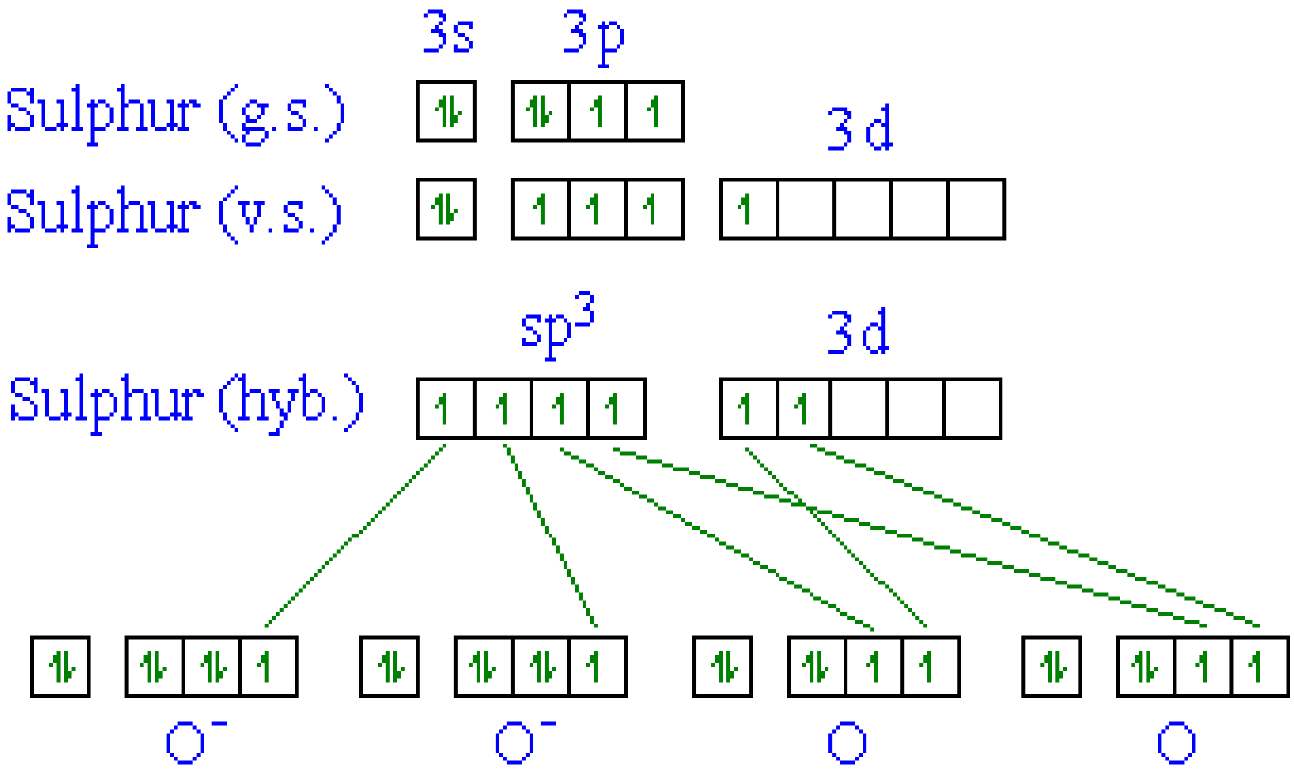


Carbonyl Chloride (Phosgene) - $COCl_2$





Sulphate - SO_4^{2-} S=16)



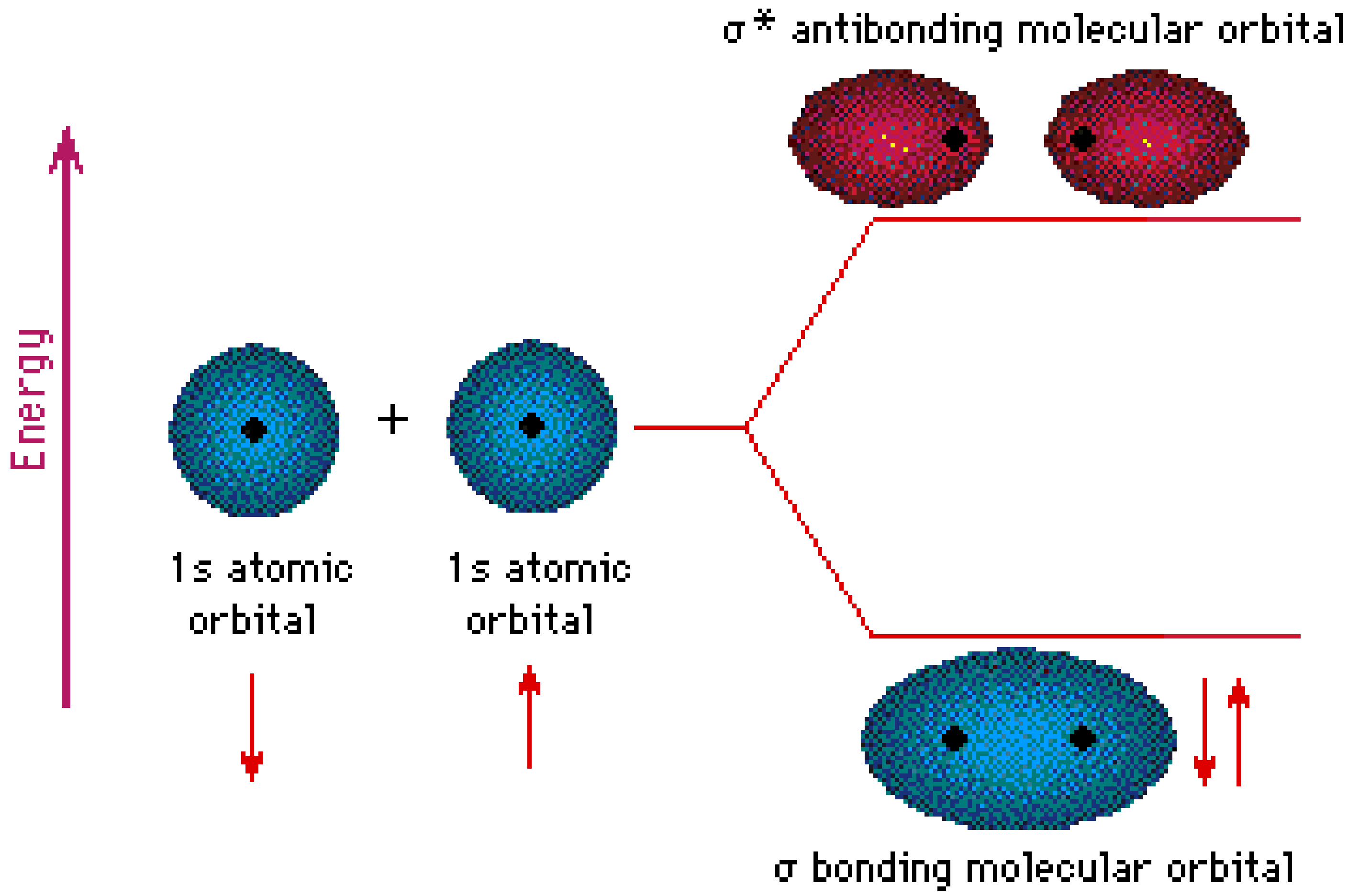
Molecular Orbitals

Just as the valence electrons of atoms occupy atomic orbitals (AO), the shared electron pairs of covalently bonded atoms may be thought of as occupying molecular orbitals (MO).

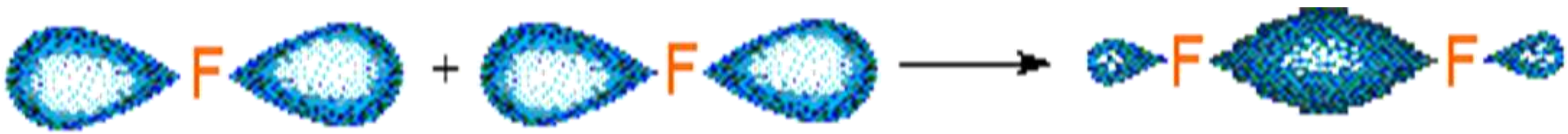
It is convenient to approximate molecular orbitals by combining or mixing two or more atomic orbitals.

In general, this mixing of **n** atomic orbitals always generates **n** molecular orbitals. The hydrogen molecule provides a simple example of MO formation.

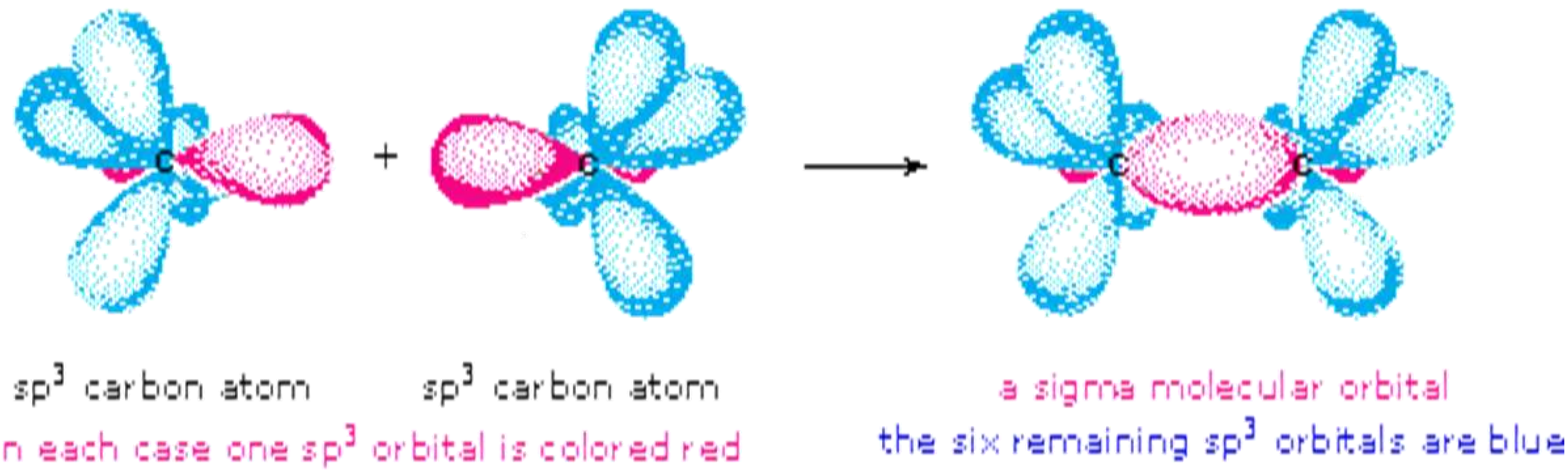
In the following diagram, two 1s atomic orbitals combine to give a sigma (σ) bonding (low energy) molecular orbital and a second higher energy MO referred to as an antibonding orbital. The bonding MO is occupied by two electrons of opposite spin, the result being a covalent bond.



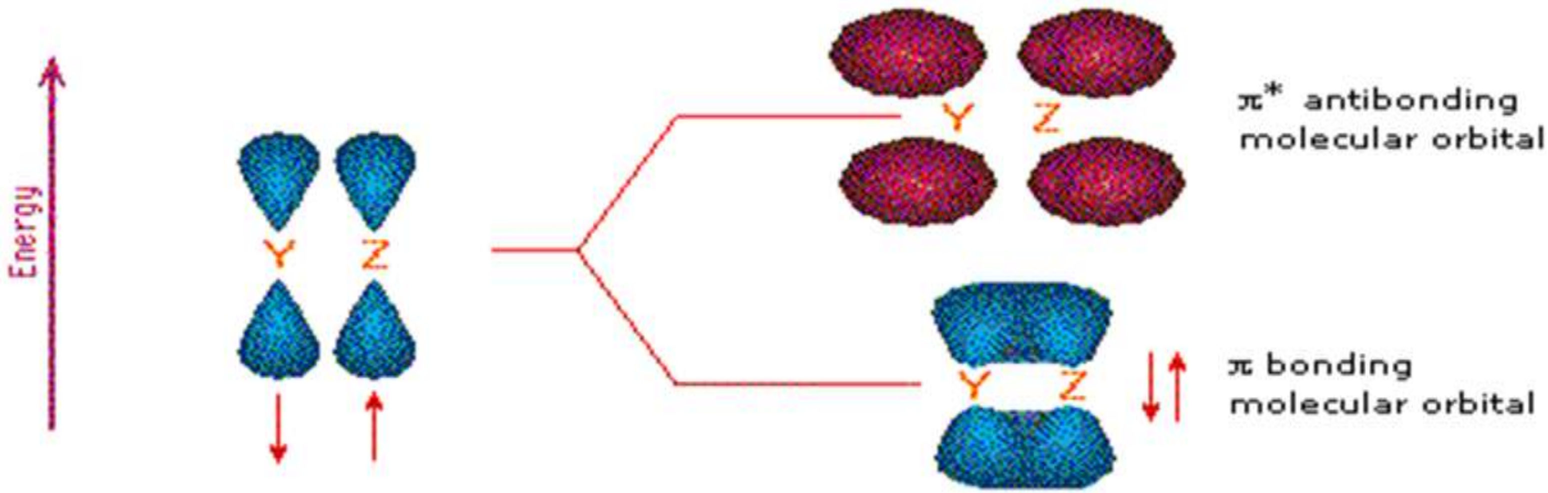
σ* antibonding molecular orbital
Energy
1s atomic orbital
1s atomic orbital
σ bonding molecular orbital



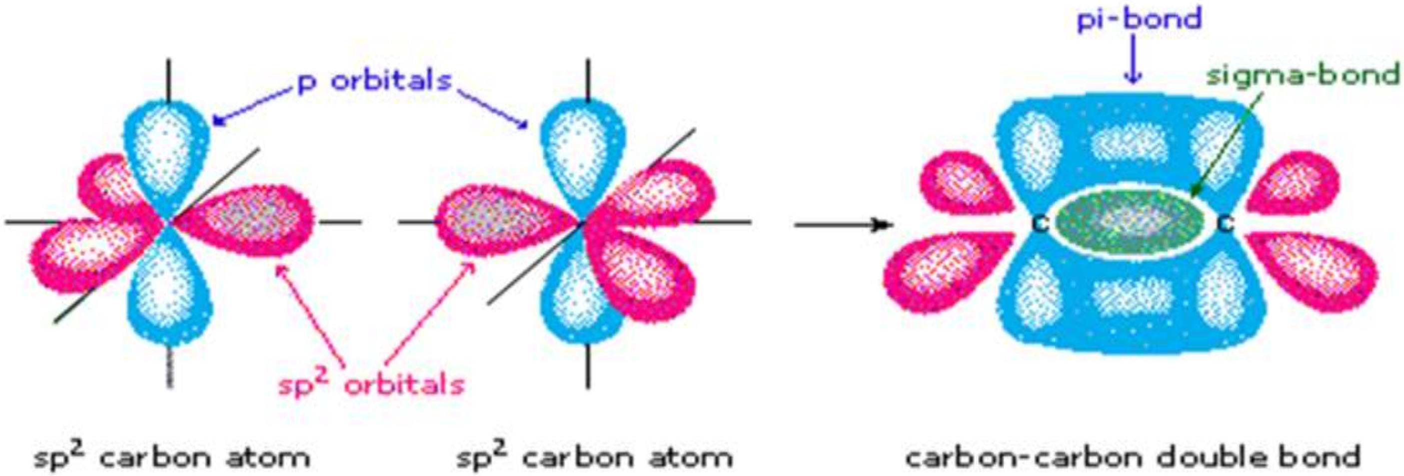
A σ-orbital formation from two p-orbitals



B σ-orbital formation from two sp^3 orbitals

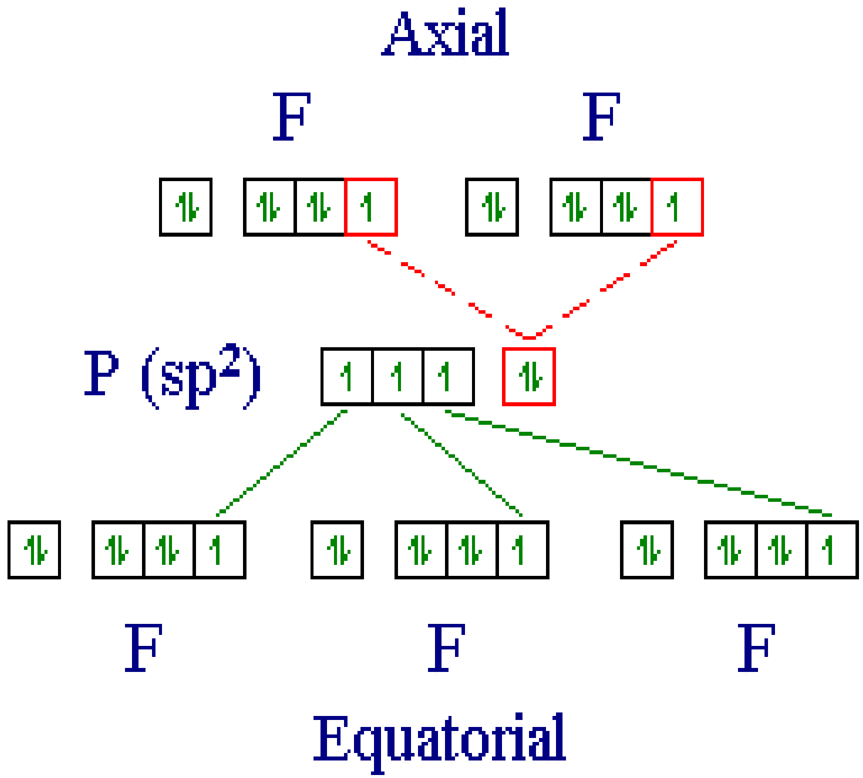


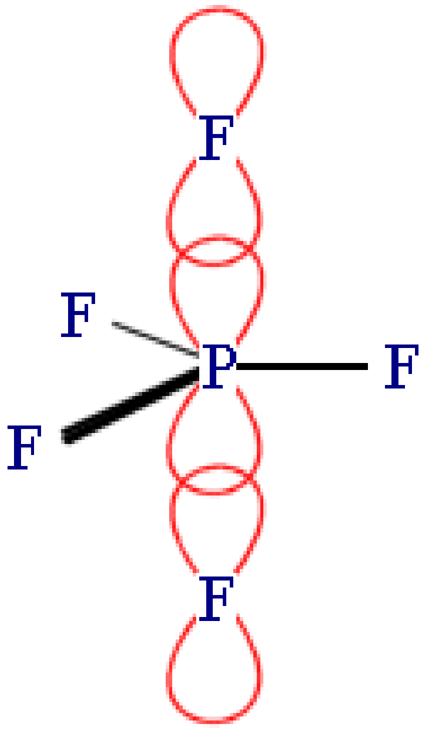
A π-orbital formation from two p-orbitals



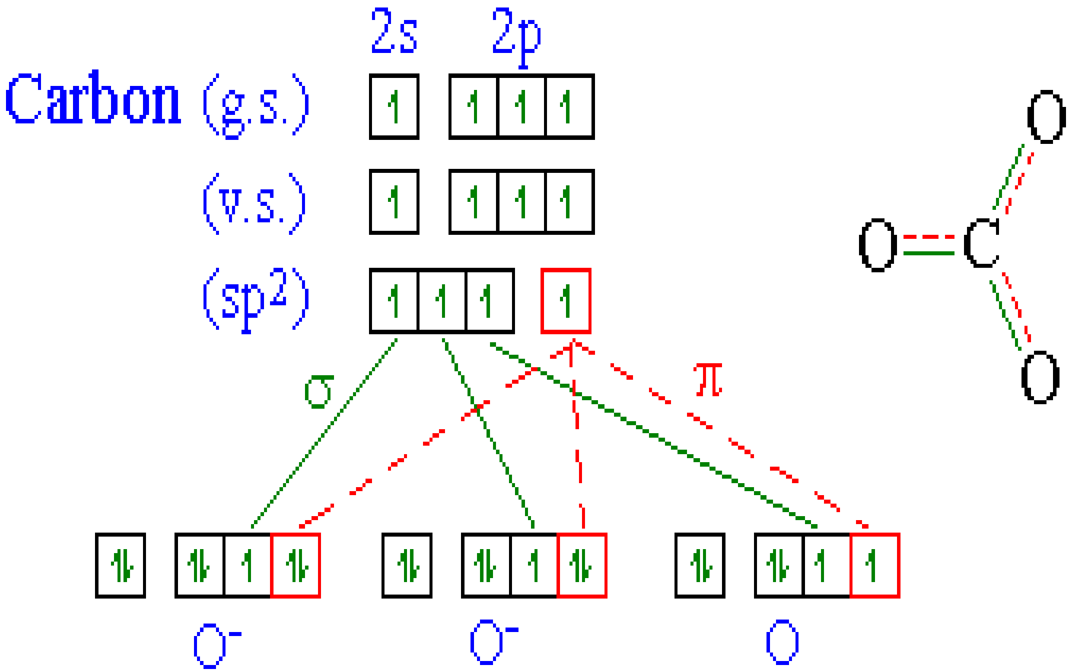
B Formation of σ- and π- molecular orbitals from two sp^2 hybridized carbon atoms

Phosphorus Pentachloride





Molecules and Ions with double bonds



IONIC OR ELECTROVALENT BOND

From the Kössel and Lewis treatment of the formation of an ionic bond, it follows that the formation of ionic compounds would primarily depend upon:

- The ease of formation of the positive and negative ions from the respective neutral atoms;
- The arrangement of the positive and negative ions in the solid, that is, the lattice of the crystalline compound. The formation of a positive ion involves ionization, i.e., removal of electron(s) from the neutral atom and that of the negative ion involves the addition of electron(s) to the neutral atom.

Most ionic compounds have cations derived from metallic elements and anions from non-metallic elements. The ammonium ion, NH_4^+ (made up of two nonmetallic elements) is an exception. It forms the cation of a number of ionic compounds.

Polarity of Molecules

The "charge distribution" of a molecule is determined by
The ***shape*** of the molecule
The ***polarity*** of its bonds

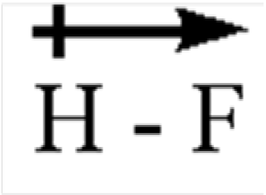
A ***Polar*** Molecule:

The center of the overall negative charge on the molecule does not coincide with the center of overall positive charge on the molecule
The molecule can be oriented such that one end has a net negative charge and the other a net positive charge, i.e. the molecule is a ***dipole***

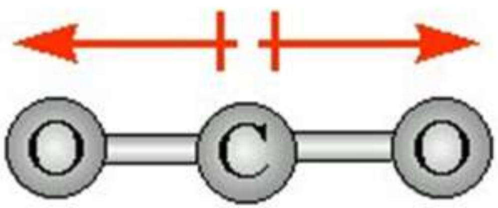
A ***Nonpolar*** molecule

Has no charges on the opposite ends of the molecule
Or, has charges of the ***same sign*** on the opposite ends of the molecule
Molecule is ***not*** a dipole

Any diatomic molecule with a polar bond is a polar molecule (dipole)

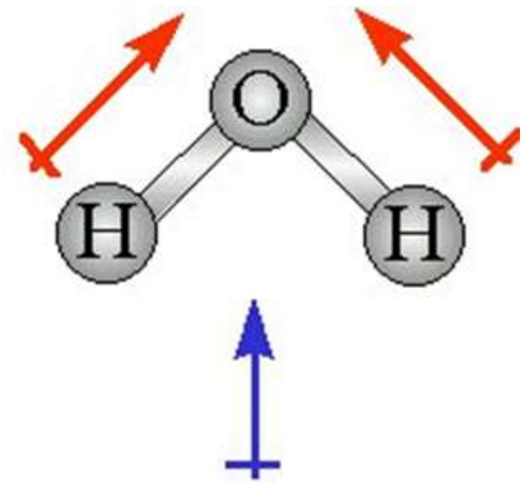


Dipoles



Overall Dipole:

(none)



HYDROGEN BONDING

Nitrogen, oxygen and fluorine are the higly electronegative elements. When they are attached to a hydrogen atom to form covalent bond, the electrons of the covalent bond are shifted towards the more electronegative atom.

This partially positively charged hydrogen atom forms a bond with the other more electronegative atom. This bond is known as hydrogen bond and is weaker than the covalent bond. For example, in HF molecule, the hydrogen bond exists between hydrogen atom of one molecule and fluorine atom of another molecule as depicted below :

$$- - -H^{\delta+} - F^{\delta-} - - -H^{\delta+} - F^{\delta-} - - -H^{\delta+} - F^{\delta-}$$

Types of H-Bonds

(1) Intermolecular hydrogen bond : It is formed between two different molecules of the same or different compounds. For example, H-bond in case of HF molecule, alcohol or water molecules, etc.

(2) Intramolecular hydrogen bond : It is formed when hydrogen atom is in between the two highly electronegative (F, O, N) atoms present within the same molecule. For example, in o-nitrophenol the hydrogen is in between the two oxygen atoms.

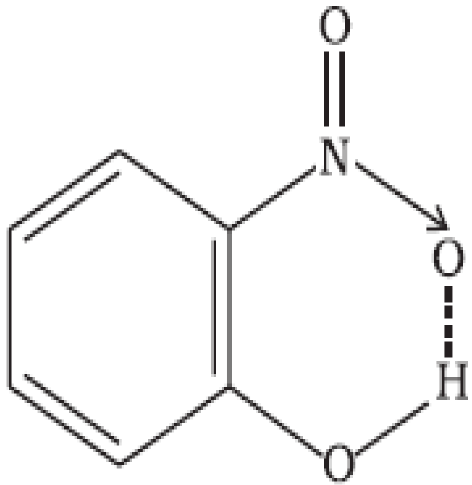


Fig. 4.22 *Intramolecular hydrogen bonding in o-nitrophenol molecule*

van der Waals force

Relatively weak electrical forces that attract neutral (uncharged) molecules to each other in gases, liquefied and solidified gases, and almost all organic liquids and solids. Solids held together by van der Waals forces typically have lower melting points and are softer than those held together by ionic, covalent, or metallic bonds (bonding).

The forces arise because neutral molecules, though uncharged, are usually electric dipoles, which have a tendency to align with each other and to induce further polarization in neighbouring molecules, resulting in a net attractive force. They are somewhat weaker than the forces involved in hydrogen bonding.

EXERCISES

1-Write Lewis dot symbols for atoms of the following elements : Mg, Na, B, O, N, Br.

2-Write Lewis symbols for the following atoms and ions:

S and S^{2-}; Al and Al^{3+}; H and H^{-}

3-Draw the Lewis structures for the following molecules and ions :

H_2S, $SiCl_4$, BeF_2, CO_3^{2-} , HCOOH

4-Write the favourable factors for the formation of ionic bond

5-Explain the important aspects of resonance with reference to the CO_3^{2-}

6-Explain with the help of suitable example polar covalent bond.

7-Which out of NH_3 and NF_3 has higher dipole moment and why .

8-What is meant by hybridisation of atomic orbitals? Describe the shapes of sp, sp^2, sp^3 hybrid orbitals.

9-Describe the change in hybridisation (if any) of the Al atom in the following reaction.

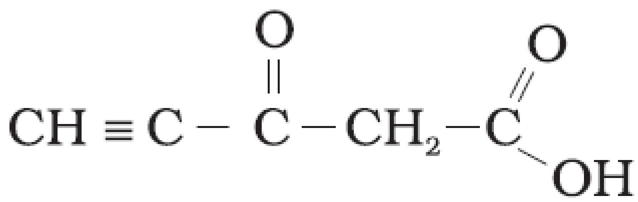
$AlCl_3 + Cl^- \rightarrow AlCl_4^-$

10-Draw diagrams showing the formation of a double bond and a triple bond between carbon atoms in C_2H_4 and C_2H_2 molecules.

11-What is the total number of sigma and pi bonds in the following molecules ?

(a) C_2H_2 (b) C_2H_4

12-Which hybrid orbitals are used by carbon atoms in the following molecules ?
CH_3-CH_3; (b) CH_3-CH=CH_2; (c) CH_3-CH_2-OH; (d) CH_3-CHO (e) CH_3COOH.
13-What do you understand by bond pairs and lone pairs of electrons ? Illustrate by giving one exmaple of each type.
14-Describe the hybridisation in case of PCl5. Why are the axial bonds longer as compared to equatorial bonds ?
15-Define hydrogen bond. Is it weaker or stronger than the van der Waals forces?
16-What is an ionic bond? With two suitable examples explain the difference between an ionic and a covalent bond?
17-Predict the hybridisation of each carbon in the molecule of organic compound given below. Also indicate the total number of sigma and pi bonds in this molecule.



18-Group the following as linear and non-linear molecules :
H_2O, HOCl, $BeCl_2$, Cl_2O.

19-Predict the shapes of the following molecules on the basis of hybridisation.
BCl_3, CH_4, CO_2, NH_3.