BONDING THEORIES

In modem times there have been two major bonding theory:
(1) Valence bond theory (VBT)
(2) Molecular orbital theory (MOT).

(1) VALANCE BOND THEORY

Suppose we have two isolated hydrogen atoms. We may describe them by the wave functions Ψ_A for A and Ψ_B for B, the atoms are sufficiently isolated so that they do not interact, the wave function for the system of these two atoms is -

$\Psi = \Psi_{A(1)}\ \Psi_{B(2)}$……………………………………………………………….(1)

where A and B designate the atoms and the numbers '1' and '2' designate electrons number 1 and 2. Now, we know that when the two atoms are brought together to form a molecule they will affect each other and that the individual wave functions ΨA and ΨB will change, but we may assume that Eq. 1 is a good starting place as a trial function for the hydrogen molecule and then try to improve it. When we solve for energy as function of distance, we find that the energy curve for Eq. 1 does indeed have minimum (**curve a**, Fig. 1) of about -24 kJ/mol at a distance of about 90 pm.

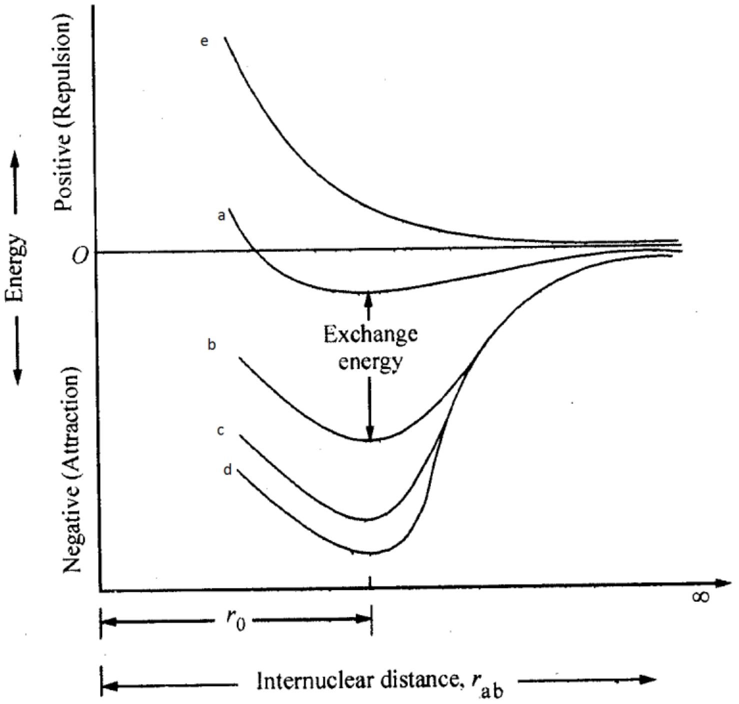


FIG 1: Theoretical energy curves for hydrogen atom
Legends:
Curve a - without any approximation
Curve b - with exchange energy approximation
Curve c – with shielding effect approximation
Curve d – with ionic structure approximation
Curve e - repulsive interactions of two electrons with like spin

The actual observed bond distance is 74 pm, which is not too different from our first approximation, but the experimental bond energy of H_2 is -458 kJ /mol, almost 20 times greater than our first approximation.

Exchange energy approximation

If we examine Eq. 1, we must decide that we have been overly restrictive in using it to describe a hydrogen molecule. we would never be sure that electron ‘1’ will always be on atom A and electron ‘2’on atom B. We must alter Eq. 1 in such a way that the artificial restrictions are removed. We can do this by adding a second term in which the electrons have changed positions:

$$\Psi = \Psi_{A\,(1)}\,\Psi_{B\,(2)} + \Psi_{A\,(2)}\,\Psi_{B\,(1)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

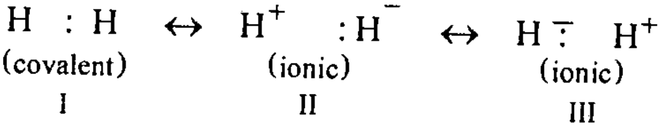
This improvement was suggested by Heitler and London. If we solve for this energy associated with Eq. 2, we obtain **curve b** in Fig. 1. The energy improved greatly (-303 kJ/mol) and also the distance has improved slightly. the improvement is a result of our “allowing” the electrons to exchange places, the increase in bonding energy is often termed the *exchange energy*. The physical explanation is probably best to ascribe the lowering of energy of the molecule to the fact that the electrons now have a larger volume in which to move and hence lowering of its energy (refer to the particle in a box equation i.e., the energy of a particle in a box is inversely related to the size of the box. By providing two nuclei at a short distance from each other, we have ‘enlarged the box’ in which the electrons are enclosed.

Shielding effect approximation

A further improvement can be made if we recall that electrons shield each other and that the effective atomic number Z* will be somewhat less than Z. If we adjust our wave functions Ψ_A and Ψ_B to account for the shielding from the second electron, we obtain energy **curve c** (fig 1) - a further improvement.

‘ Ionic structure’ approximation

Finally, we must again correct our molecular wave function for an over restriction which we have placed upon it. Although we have allowed the electrons to exchange in Eq. 2, we have demanded that they must exchange simultaneously, that is, that only one electron can be associated with a given nucleus at a given time. Obviously this is too restrictive. Although we might suppose that the electrons would tend to avoid each other because of mutual repulsion and thus tend to stay one on each atom, we cannot go so far as to say that they will always be in such an arrangement. It is common to call the arrangement given by Eq.2 the “covalent structure” and to consider the influence of “ionic structures” on the overall wave function:



$$\underset{\text{I}}{\underset{\text{(covalent)}}{\text{H} : \text{H}}} \leftrightarrow \underset{\text{II}}{\underset{\text{(ionic)}}{\text{H}^{+} \ :\text{H}^{-}}} \leftrightarrow \underset{\text{III}}{\underset{\text{(ionic)}}{\text{H}\overset{-}{:}\ \text{H}^{+}}}$$

where the first term (I) represents the covalent structure and the second two terms (II & III) represents ionic structures in which both electrons are on atom A or B. Because the electrons tend to repel each other somewhat, there is a smaller probability of finding them both on the same atom than on different atoms, so the second two terms are weighted somewhat less (A < l). Equation 3 can be expressed more succinctly as:

$$\Psi = \Psi_{A(1)}\Psi_{B(2)} + \Psi_{A(2)}\Psi_{B(1)} + \lambda\Psi_{A(1)}\Psi_{A(2)} + \lambda\Psi_{B(1)}\Psi_{B(2)} \ldots\ldots 3$$

When we investigate the energetics of the wave function in Eq. 3, we find further improvement in energy and distance i.e., 388 Kj/mol at 74.9 pm (**curve d**, Fig.1). This is the first example we have had of the phenomenon of resonance.

(2) MOLECULAR ORBITAL (MO) THEORY

A second approach to bonding in molecules is known as the molecular orbital (MO) theory. The assumption here is that if two nuclei are positioned at equilibrium distance, and electrons are added, they will go into molecular orbitals that are in many ways analogous to the atomic orbitals. In the atom there are s, p, d, f, . . . orbitals determined by various sets of quantum numbers and in the molecule we have σ,π,δ . . . orbitals determined by quantum numbers. Pauli exclusion principle and Hund's principle of maximum multiplicity obeyed in these molecular orbitals just as in the atomic orbitals.

When we attempt to solve the Schrodinger equation to obtain the various molecular orbitals, we run into the same problem found earlier for atoms heavier than hydrogen. We are unable to solve the Schrodinger equation exactly and therefore must make some approximations concerning the form of the wave functions for the molecular orbitals.

Of the various methods of approximating the correct molecular orbitals, linear combination of atomic orbitals (LCAO) method is the most prominent one.

We assume that we can approximate the correct molecular orbitals by combining the atomic orbitals of the atoms that form the molecule. The rationale is that most of the time the electrons will be nearer and hence "controlled" by one or the other of the two nuclei. and when this is so, the molecular orbital should be very nearly the same as the atomic orbital for that atom. The basic process is the same as the one we employed in constructing hybrid atomic orbitals except that now we are combining orbitals on different atoms to form new orbitals that are associated with the entire molecule. Wetherefore combine the atomic orbitals Ψ_A and Ψ_B on atoms A and B to obtain two molecular orbitals:

$\Psi_b = \Psi_A + \Psi_B$……………………………………………………………………..4

$\Psi_a = \Psi_A - \Psi_B$..5

The molecular orbitals thus formed consist of a bonding molecular orbital (Ψ_b) and an antibonding molecular orbital (Ψ_a). Thus, one molecular orbital (bonding molecular orbital or Ψ_b) is obtained by summation of the atomic orbitals, while the other molecular orbital (antibonding molecular orbital or Ψ_a) is obtained by subtraction of the atomic orbitals.

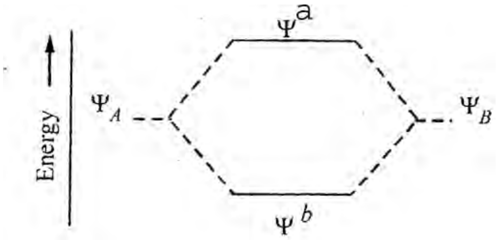


Fig 2: Formation of molecular orbitals from atomic orbitals

The number of molecular orbitals is always equal to the number of atomic orbitals involved in bonding. Effective combination of atomic orbitals to give rise to stable molecular orbitals requires:

(i) Symmetry and relative energies of atomic orbitals Ψ_a and Ψ_b must be close to each other.

(ii) Extent of overlap between the charge clouds of Ψ_a and Ψ_b should be large.

(iii) Atomic orbitals of same sign should overlap.

Bonding and antibonding molecular orbitals

Bonding MO: The-molecular orbital that is obtained by the addition overlap of two atomic orbitals is termed bonding molecular and is represented as Ψ_b.

Some features of bonding molecular orbitals are:

(i) It possesses lower energy than the atomic orbitals from which it is formed.

(ii) It has high electron density in the region between the two nuclei and these accounts for stability of bonding molecular orbitals. The wave functions of the component atoms reinforce each other in the region between the nuclei (Fig 3a).

(iii) It is formed when lobes of the combining atomic orbitals are of same sign. The magnitude of Ψ_b is numerically bigger than Ψ_A or Ψ_B .

(iv) Every electron in a bonding molecular orbital contributes to attraction between two atoms.

Antibonding MO: The other molecular orbital which is obtained by the subtraction overlap two atomic orbitals is termed the antibonding molecular orbital and is represented as Ψ_a.

Some features of antibonding molecular orbitals are:

(i) It possesses higher energy than the atomic orbitals from which it is formed.

(ii) The probability of finding the electron in between the nuclei is negligible. The electron density is concentrated only on one nucleus at any particular moment. The wave functions of the component atoms cancels each other and forms a node between the nuclei (Fig. 3d).

(iii) It is formed when the lobes of combining atomic orbitals have opposite signs.

(iv) Every electron in an antibonding molecular orbital contributes to repulsion between two atoms.

The probability distribution of electron in these two types of molecular orbital is given by Ψ_b^2 (Fig. 3c) and Ψ_a^2(Fig.3e) respectably.

$$\Psi_b^2 = \Psi_A^2 + 2\,\Psi_A\Psi_B + \Psi_B^2$$
$$\Psi_a^2 = \Psi_A^2 - 2\,\Psi_A\Psi_B + \Psi_B^2$$

Evidently, the difference between the probability distribution of electron in these two types of molecular orbitals lies in the term 2 $\Psi_A\Psi_B$, which is referred as overlap integral.

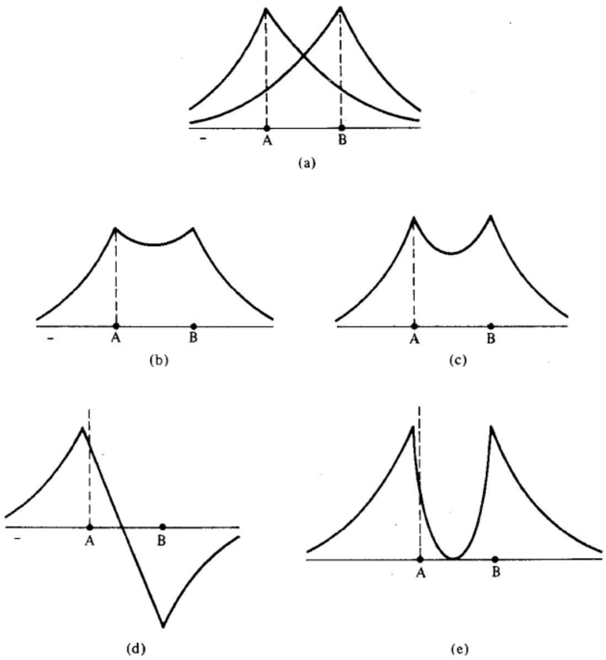


Fig 3: (a) Wave functions of individual hydrogen atoms

(b) Formation of bonding MO or Ψ_b

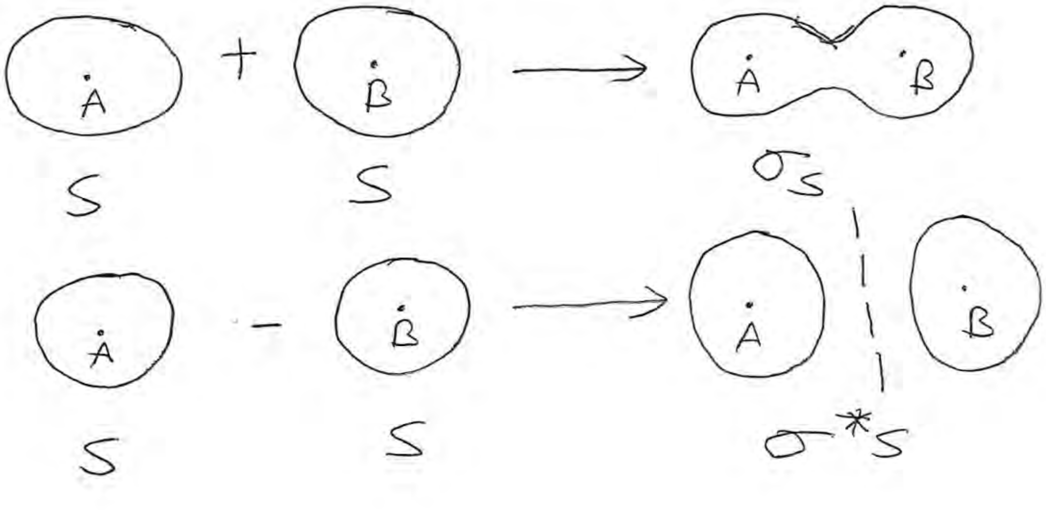
(c) Probability distribution of electron or Ψ_b^2

(d) Formation of anti bonding MO or Ψ_a

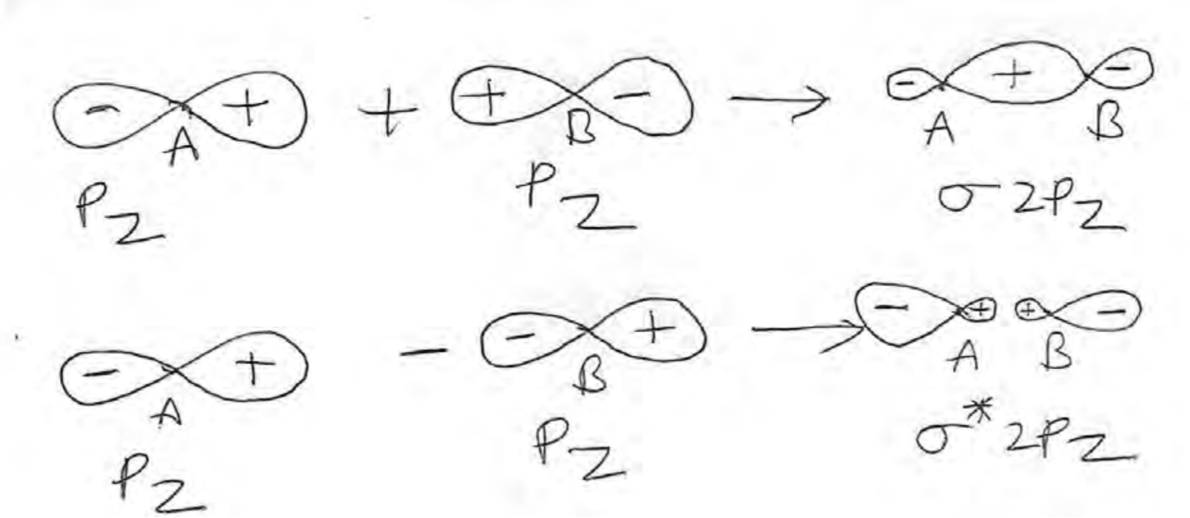
(e) Probability distribution of electron or Ψ_a^2

Overlapping of atomic orbitals to form Bonding and Anti bonding molecular orbitals:

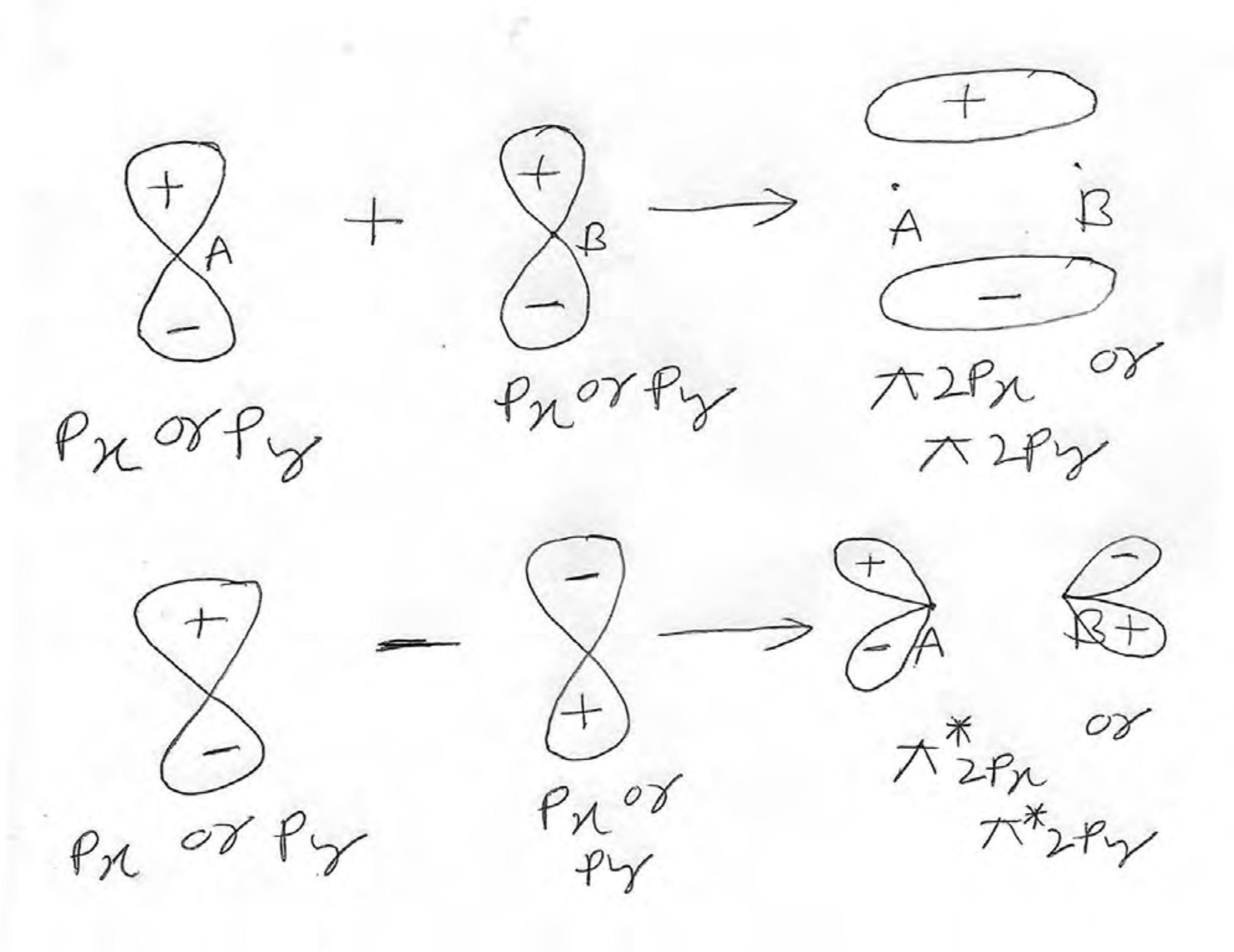
(1) Over lapping of 's' orbitals to form Bonding (σ) and Antibonding (σ*) molecular orbitals.



(2) Axial over lapping of 'Pz' orbitals to form Bonding (σ) and Antibonding (σ*) sigma molecular orbitals.



(3) Sidewise overlapping of 'p' orbitals to form Bonding (π) and antibonding (π*) pi molecular orbitals.



Energy level diagram of molecular orbitals :

In this type of diagram the combining atomic orbitals are shown on two extreme and the resulting molecular orbitals are represented in the middle column. Atomic orbitals of same energy are shown at the same level. The Energy level diagram of various molecular orbitals is shown in Fig.5.

However, for B_2, C_2 & N_2, in addition to interaction of atomic orbitals of participarting atoms, interaction between 2S and 2P orbitals of the same atom also takes place due to similar energy and symmetry. This leads to elevation of energy of σ_{2pz} above that of π_{2px} & π_{2py}.

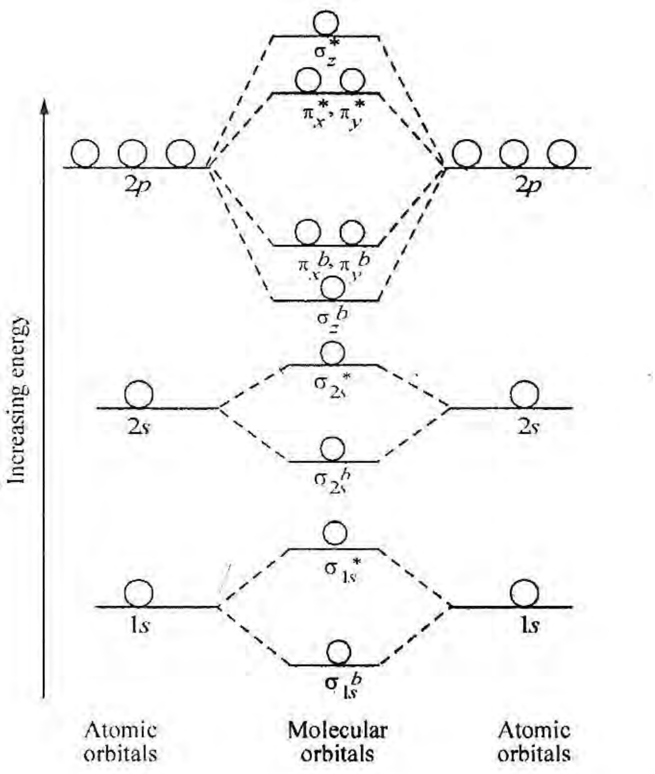


Fig 5: Overlapping of atomic orbitals to form molecular orbitals.

BOND ORDER:

$$\text{Bond Order} = \frac{\text{Number of electrons in bonding MO} - \text{Number of electrons in Antibonding MO}}{2}$$

(1) Bond order shows the nature of bonds between two atoms (whether its single, double or triple).

(2) The dissociation energy of a bond is proportional to its bond order.

(3) Bond order is inversely proportional to bond length.

Molecular energy level diagram for hydrogen molecule (H_2)

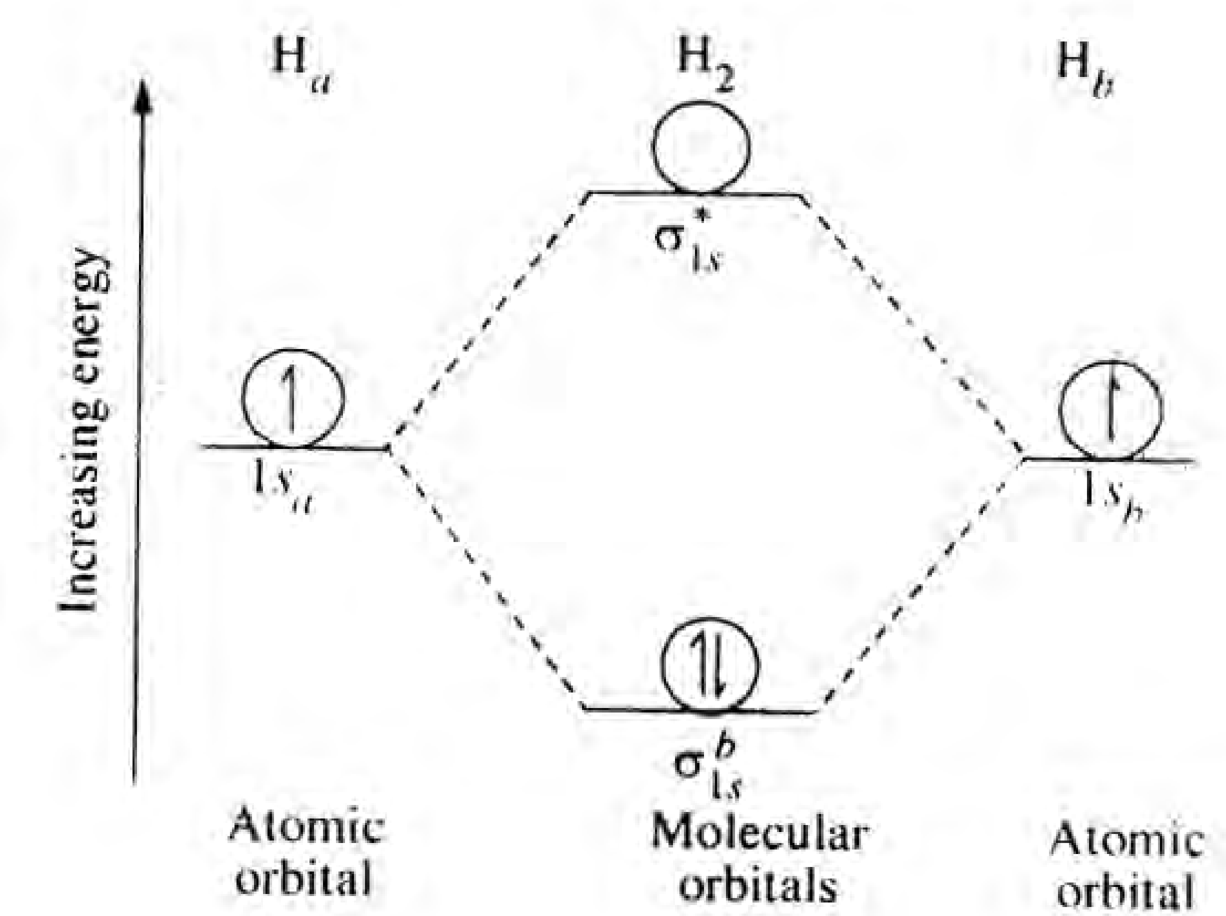


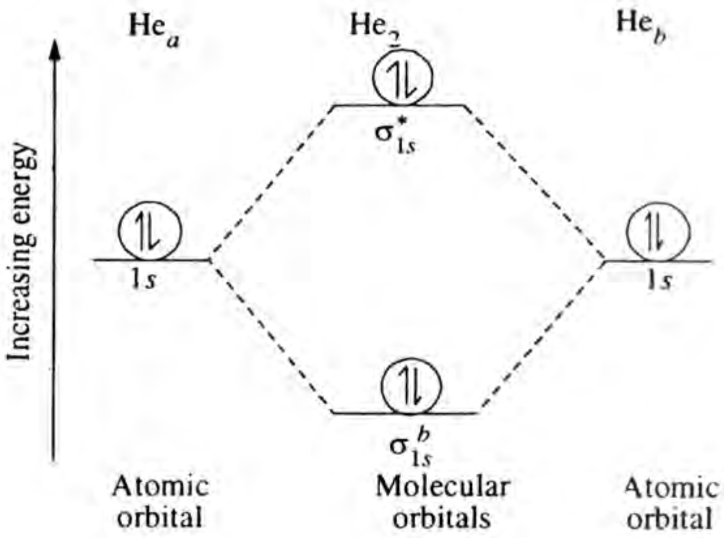
Fig 6: Molecular energy level diagram for hydrogen molecule

The ground state of H_2 is represented as $[(\sigma^b_{1s})^2]$ and the bond order is 1/2 (2 – 0) = 1

Evidently, H_2 molecule has a single sigma bond.

Molecular energy level diagram for Helium molecule (He_2)

Fig 7:



The electronic configuration of He_2 may be written as $[(\sigma^b_{1s})^2 (\sigma^*_{1s})^2]$. The bond order is 1/2 [2 – 2] = 0.

In case of He_2, the bonding and antibonding orbitals cancel each other. Hence, no bond formation is possible i.e, He_2 doesnot exist.

NOTE: : The students can draw in a similar way, the molecular energy level diagram for H_2^+, He_2^+ & Li_2.

Molecular energy level diagram for Oxygen molecule (O_2)

The oxygen has electronic configuration $1s^2$, $2s^2$, $2p^4$. The O_2 molecule is well known and shows paramagnetism (Fig. 3.61), equivalent to that of two unpaired electrons. The molecule has the following configuration:

$$[KK\,(\sigma^b_{2s})^2\,(\sigma^*_{2s})^2\,(\sigma^b_z)^2\,(\pi^b_x)^2\,(\pi^b_y)^2\,(\pi^*_x)^1\,(\pi^*_y)^1]$$

$$[\text{Bond order} = \frac{1}{2}(8-4) = \frac{1}{2} \times 4 = 2$$

The bond order is two. In accordance with Hund's rule the two electrons in the π^* orbitals have parallel spins. The molecular orbital method explains the presence of two unpaired electrons in the molecule which accounts for its paramagnetism (Fig. 3.61). The valence bond theory had failed to predict the presence of unpaired electrons in O_2 molecule.

This is in accordance with the experimental results that O_2 consists of a double bond (one σ and one π bond).

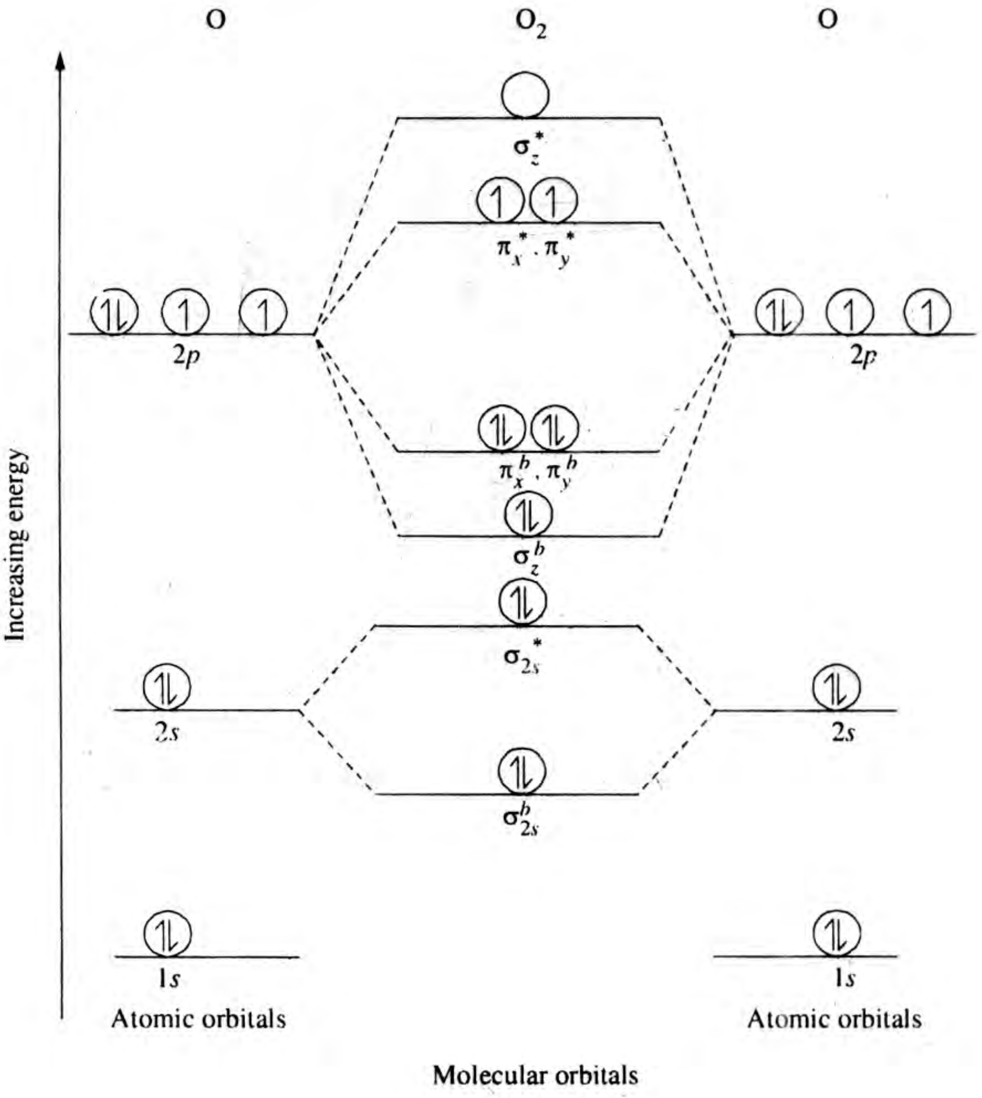


Fig 8: Molecular energy level diagram for Oxygen molecule

NOTE: The students can draw in a similar way, the molecular energy level diagram for O_2^+.

Molecular energy level diagram for Fluorine molecule (F_2)

The molecular orbital configuration of F_2 is:

$$[KK(\sigma^b_{2s})^2\,(\sigma^*_{2s})^2(\sigma^b_z)^2\,(\pi^b_x)^2\,(\pi^b_y)^2(\pi^*_x)^2(\pi^*_y)^2]$$

and its bond order is 1/2 [10 – 8] = 1. It is diamagnetic since it has no unpaired electrons.

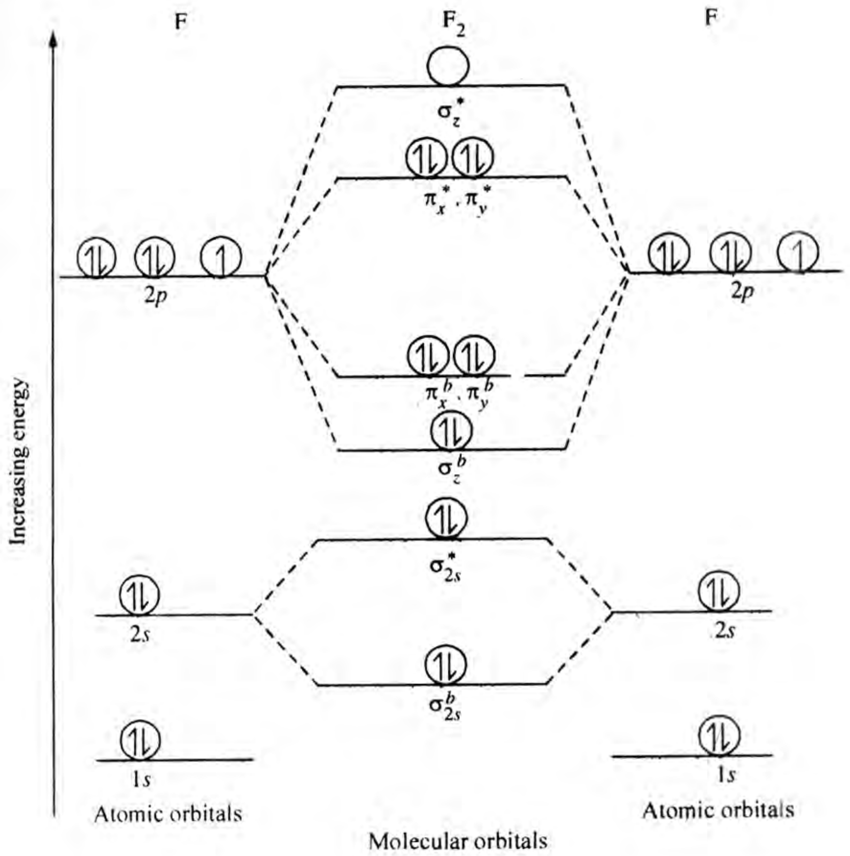
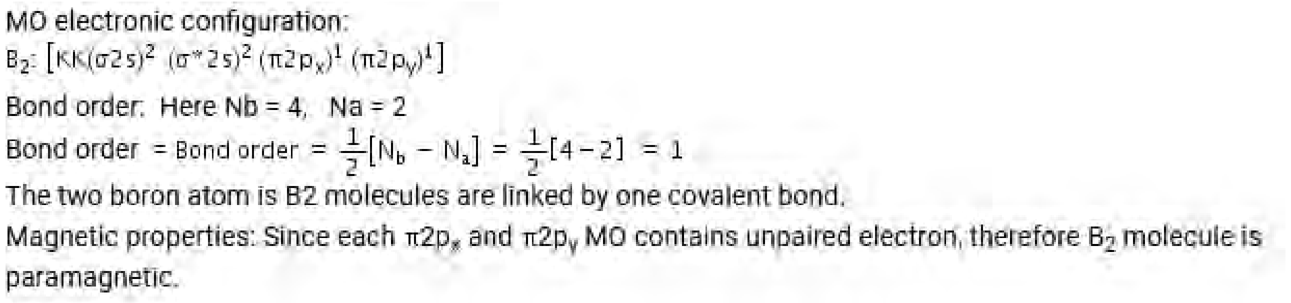


Fig 9: Molecular energy level diagram for Fluorine molecule

Molecular energy level diagram for B_2 molecule (B_2) with mixing of 2S & 2P orbitals.



MO electronic configuration:

B_2: $[KK(\sigma 2s)^2\ (\sigma^* 2s)^2\ (\pi 2p_x)^1\ (\pi 2p_y)^1]$

Bond order: Here Nb = 4, Na = 2

Bond order = Bond order = $\frac{1}{2}[N_b - N_a] = \frac{1}{2}[4-2] = 1$

The two boron atom is B2 molecules are linked by one covalent bond.

Magnetic properties: Since each $\pi 2p_x$ and $\pi 2p_y$ MO contains unpaired electron, therefore B_2 molecule is paramagnetic.

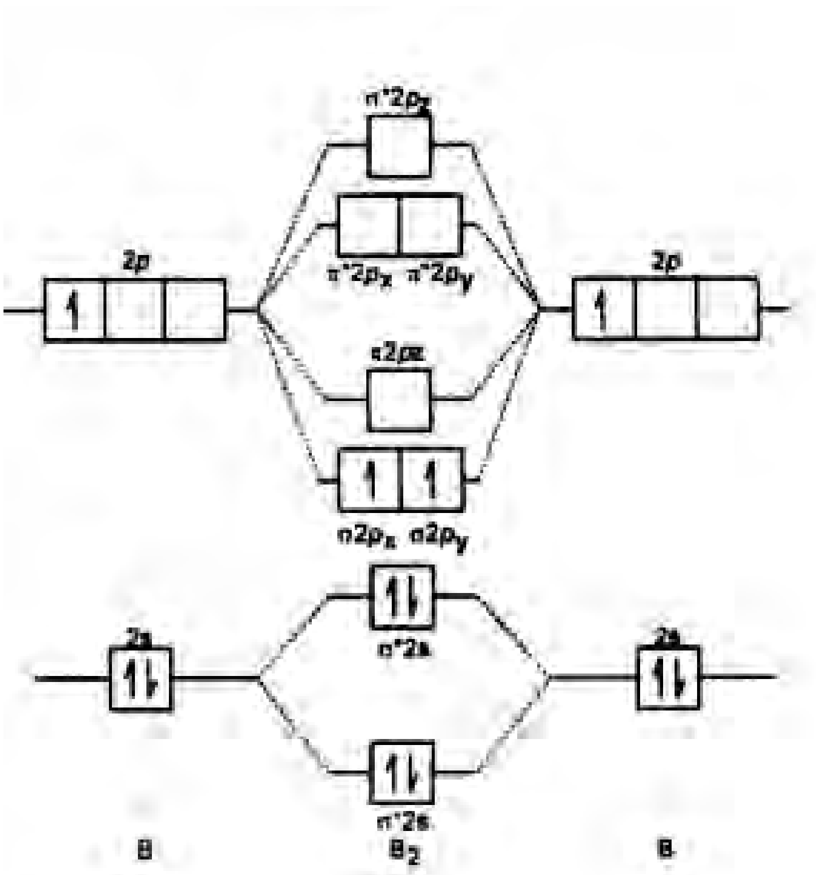


Fig 10: Molecular energy level diagram for B_2 molecule (B_2)

NOTE: The students can draw in a similar way, the molecular energy level diagram for C_2 & N_2.

Molecular energy level diagram for Carbon monoxide (CO)

In CO, the oxygen atomic orbitals are lower in energy than the carbon atomic orbitals. This is because oxygen is more electronegative than carbon. The $2s$ and $2p$ orbitals of oxygen have lower energy than the corresponding orbitals of carbon. Energy levels of different M.O are shown in the figure. Due to this difference, the σ_{2s}^* orbital is higher in energy than the σ_{2px} orbital (Fig. 3.63). Carbon monoxide possesses 10 valence electrons and, therefore, has a valence configuration :

$$(\sigma_{2s}^b)^2(\sigma_{2pz}^b)^2(\pi_x^b \cdot \pi_y^b)^4(\sigma_{2s}^*)^2$$

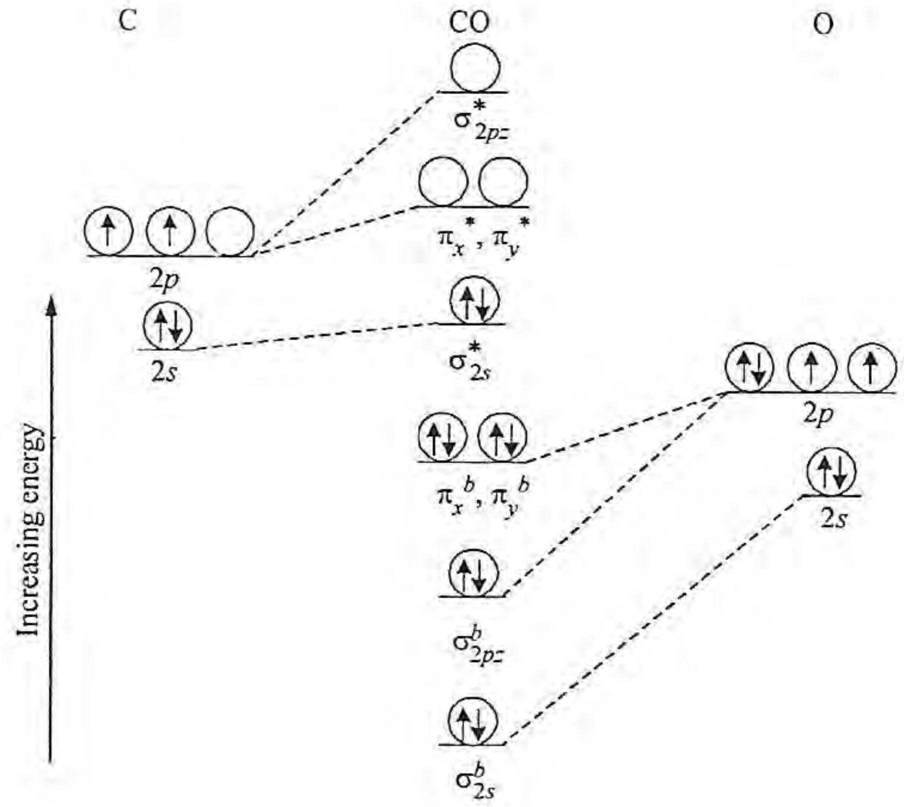


Fig 11: Molecular energy level diagram for Carbon monoxide

Molecular energy level diagram for Hydrogen Fluoride (HF)

The $2s$ atomic orbital of the fluorine atom does not interact with the $1s$ orbital of hydrogen atom because it is of low energy and is retained as atomic orbital. Only the $2p_z$ orbital of fluorine atom has proper symmetry and energy to interact with the $1s$ orbital of the hydrogen atom, giving one sigma bonding molecular orbital and one sigma antibonding molecular orbital (Fig. 3.64). The molecular orbitals formed are named as σ_{sp} (bonding) and σ^*_{sp} (non-bonding) because they result from the combination of 1s orbital of hydgrogen and $2p_z$ orbital of fluorine. The $2p_x$ and $2p_y$ orbitals of fluorine yield non-bonding molecular orbitals at the same energies because of their symmetry because they yield zero overlap with $1s$ orbital.

It is obvious from Fig. 3.64 that the atomic orbitals of electromagnetic fluorine are much lower in energy than the $1s$ atomic orbital of hydrogen. M.O. configuration of HF molecule may the written as:

$$kk\,(2s)^2\,(\sigma_{sp})^2\,(2p_x)^2\,(2p_y)^2$$

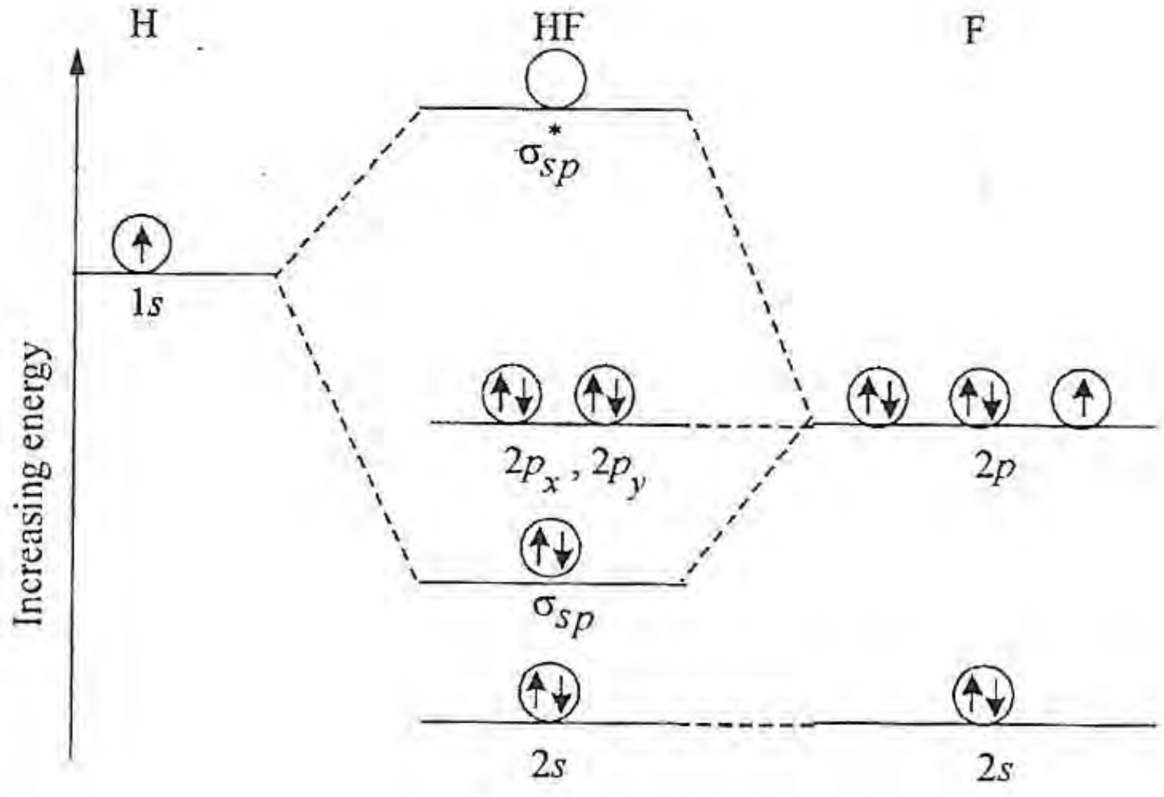


Fig 12: Molecular energy level diagram for Hydrogen Fluoride

HYBRIDIZATION OF ORBITALS

Ground state of configuration of carbon is

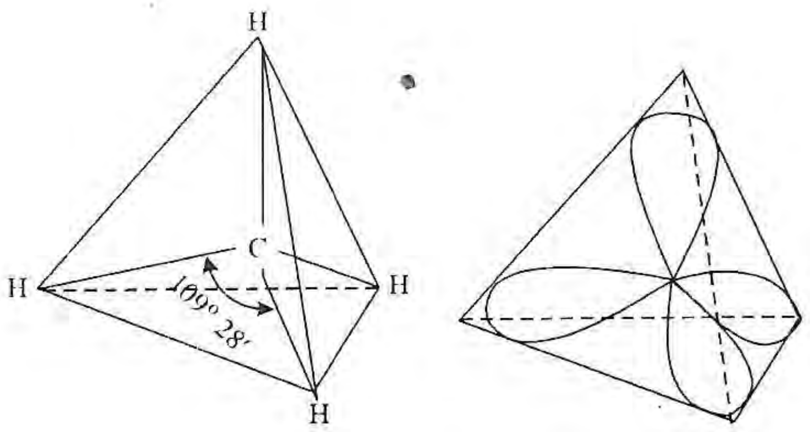
$$1s^2\,2s^2\,2p_x^1 2p_y^1$$

To account for tetravalency of carbon it is assumed that one electron from 2*s* orbital is excited to $2p_z$ orbital so that the configuration in excited state is

$$1s^2\,2s^1\,2p_x^1\,2p_y^1\,2p_z^1$$

The structure of methane consists of four equivalent bonds arranged about the carbon atom at the centre in a manner that all the angles between carbon and hydrogen are equal, its value is 109° 28'. The geometric arrangement which fulfils these requirements is a tetrahedron. In such a structure, carbon atom occupies a position at the centre of the tetrahedron and four hydrogen atoms occupy the corner positions. This arrangement is shown in Fig. 3.6.

The equivalence of four bonds can be explained by assuming that the available orbitals of carbon, the 2*s* and three 2*p* orbitals are intermixed or hybridized in a manner as to result in four equivalent orbitals which are oriented towards the four corners of regular tetrahedron. *This mixing of atomic orbitals to give equal number of symmetrically oriented orbitals of equal energy is referred to as hybridization.*



Structure of methane.

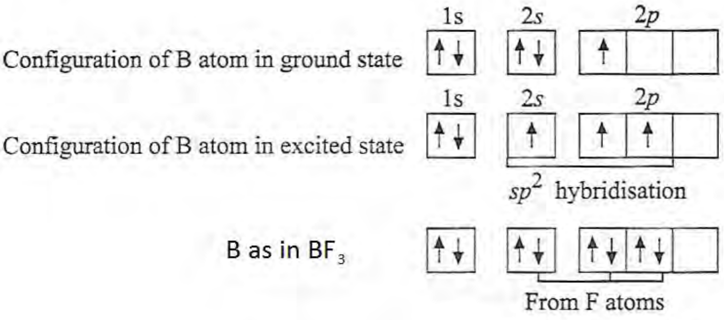
The carbon in this case is said to be sp^3 hybridized and carbon hydrogen bonds are referred to as hybrid bonds.

Different types of hybridization are:

(*i*) sp^3 type
(*ii*) sp^2 type
(*iii*) sp type
(*iv*) sp^3d type
(*v*) sp^3d^2 or d^2sp^3 type
(*vi*) sp^3d^3 type

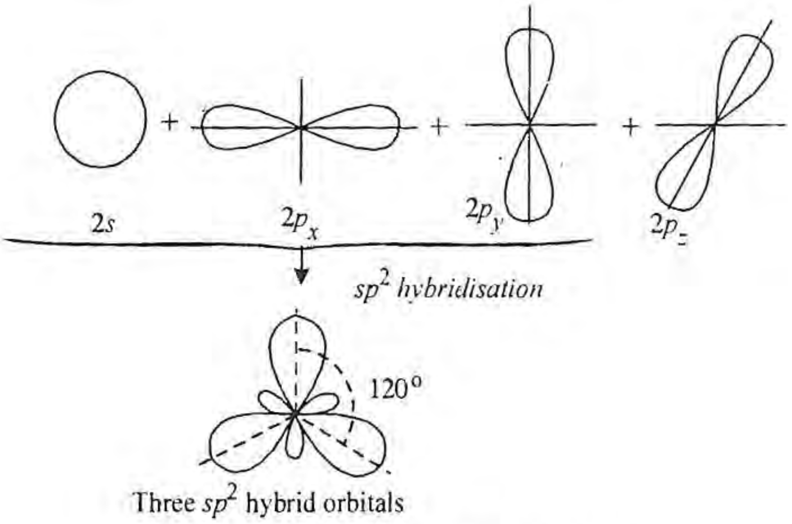
SP ^{2} Hybridization and the shape of BF$_3$ molecule

Electronic configuration of boron in ground state is $1s^2 2s^2 2p_x^1$. One of the two $2s$ electrons gets promoted to next available vacant orbital ($2p_y$). The electronic configuration of boron in the excited state is $1s^2 2s^1 2p_x^1 2p_y^1$.



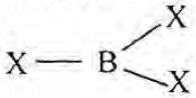
Now there are three half-filled orbitals each having odd unpaired electrons. But they belong to different orbitals. To get equivalent bonds these three orbitals hybridize to form three new equivalent hybridised orbitals. In the above case one *s* and two *p* orbitals are involved to form three hybridised orbitals. This type of hybridization is, therefore, known as *sp^2 hybridization or trigonal hybridization.*

Boron forms sp^2 hybridised orbitals. These three orbitals lie in one plane (*i.e.*, boron atom is planer) and are directed towards the three corners of an equivalent triangle, so that the angle between them is 120°.



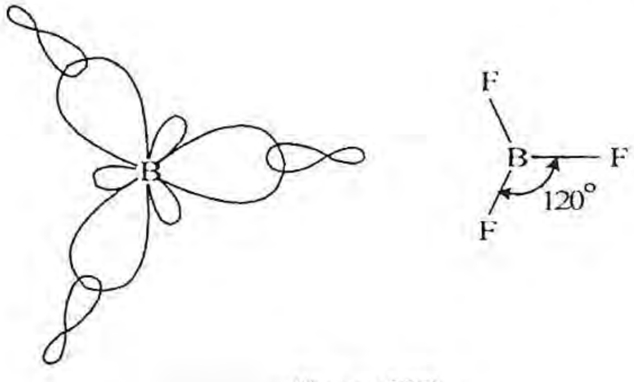
Orientation of sp^2 hybrid orbitals.

Boron atom has now three sp^2 hybridised orbitals each having an odd unpaired electron. They are capable of forming three bonds by overlapping with, three half-filled orbitals of other atoms.

Bonding capacity of boron, therefore, is three. Boron forms compounds of type  where X = H or Cl

Shape of BF_3

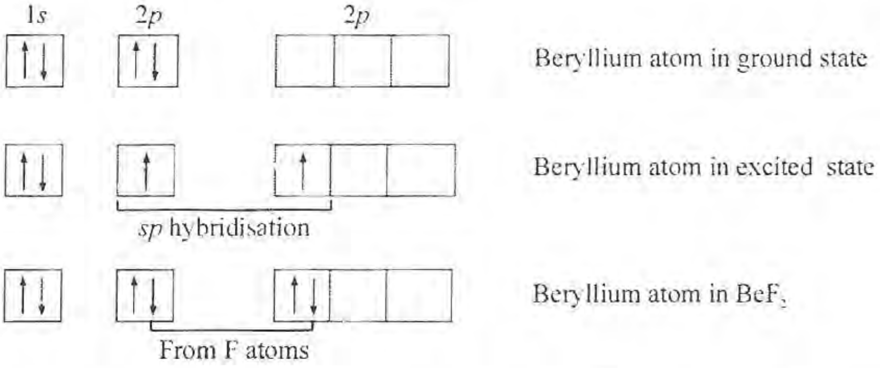
Shape of BF_3 molecule can be represented as shown in Fig. 3.10. There are three bonded electron pairs. The three bonds are equivalent and 120° apart. The molecule is, therefore, triangular and planar in shape.



Shape of BF_3.

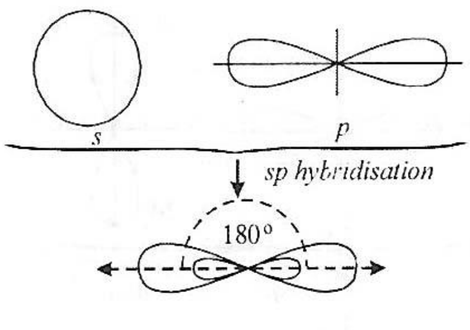
SP Hybridization and the shape of beryllium fluoride

Electronic configuration of beryllium in ground state is $1s^2\ 2s^2$. One of the $2s$ electrons gets promoted to next available empty orbital (*i.e.*, $2p_x$) and therefore electronic configuration of beryllium in excited state is $1s^2$, $2s^1$, $2p_x^1$.



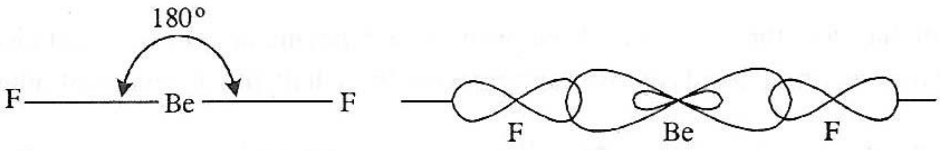
Now there are two half-filled orbitals, each having single unpaired electron. But they belong to two different orbitals. One belongs to *s* and the other two *p*-orbital. Therefore, to get equivalent bonds, these two orbitals hybridise or get mixed up to form two new equivalent orbitals each of which has half *s* and half *p* character.

In the above case one *s* and one *p*-orbitals are involved to form hybridized orbitals. This type of hybridization is therefore known as *sp hybridization* or *diagonal hybridization.* The hybridized orbitals are oriented at an angle of 180° to each other along the same axis



sp hybridisation.

These two hybridized orbitals overlap separately with the *p*-orbitals of fluorine to form two Be-F bonds. Shape of BeF_2 molecule can be represented as shown in Fig. 3.8. There are two bonded



Valance Shell Electron Pair Repulsion (VSEPR) Theory

Nevil Sidgwick

Valence shell electron pair repulsion theory (in short VSEPR theory) is the simplest theory for predicting the geometries of molecules. It is based on the repulsive interactions between the electron pairs in the valence shell. This theory was proposed by Sidgwick and Powell in 1940 and given the final shape by Gillespie and Nyholm (1957). According to this theory, the shapes of molecules can be determined by the number of electron pairs in the valence shell of the central atoms. These electron pairs experience electrostatic repulsions from one another and the bonded atoms in a molecule adopt that particular arrangement in space around the central atom which keeps them on the average as far apart as possible.

Main poins of Valence Shell Electron Pair Repulsion Theory (VSEPR)

The main points of VSEPR theory are as follows:

(*i*) Geometry of a molecule depends upon the total number of valence shell electron pairs (bonded or non-bonded) around the central atom in the molecule.

(*ii*) Repulsion between valence shell electron pairs determines molecular shape. In order to minimise electron-electron repulsion or to acquire a state of minimum energy or maximum stability the valence shell electron pairs keep as far apart as possible.

(*iii*) In case more than one geometrical arrangement is possible for a given number of bonded and non-bonded pairs, then the most stable arrangement is in accordance with the following:

(*a*) Lone pair-lone pair (*lp-lp*) repulsion is greater than lone pair-bond pair (*lp-bp*) repulsion which in turn is greater than bond pair-bond pair (*bp-bp*) repulsion. That is

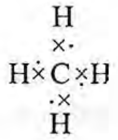
$$lp\text{-}lp > lp\text{-}bp > bp\text{-}bp$$

(*b*) Repulsion between electron pairs at vertices greater than 115° apart can be neglected.

In the formation of a bond, the central atoms shares its valence electrons with the surrounding atoms. However, in certain cases, all the valence shell electrons may not take part in the bond formation. The electrons left in the valence shell without forming bonds exist as lone pairs. For example, in methane, CH_4, carbon uses all the four valence electrons in forming four bond pairs. In water, H_2O, the central oxygen atoms has ($1s^2$, $2s^2\ 2p^4$) six valence electrons. The hydrogen atom shares two of these six valence electrons in bond formation leaving four electrons as two lone pairs.

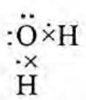
$\cdot\overset{\cdot}{\underset{\cdot}{C}}\cdot$ (Four valence electrons)

$:\overset{\cdot\cdot}{\underset{\cdot}{O}}\cdot$ (Six valence electrons)



$\begin{array}{c} H \\ \times\cdot \\ H\times C \times H \\ \cdot\times \\ H \end{array}$

(Four bond pairs)

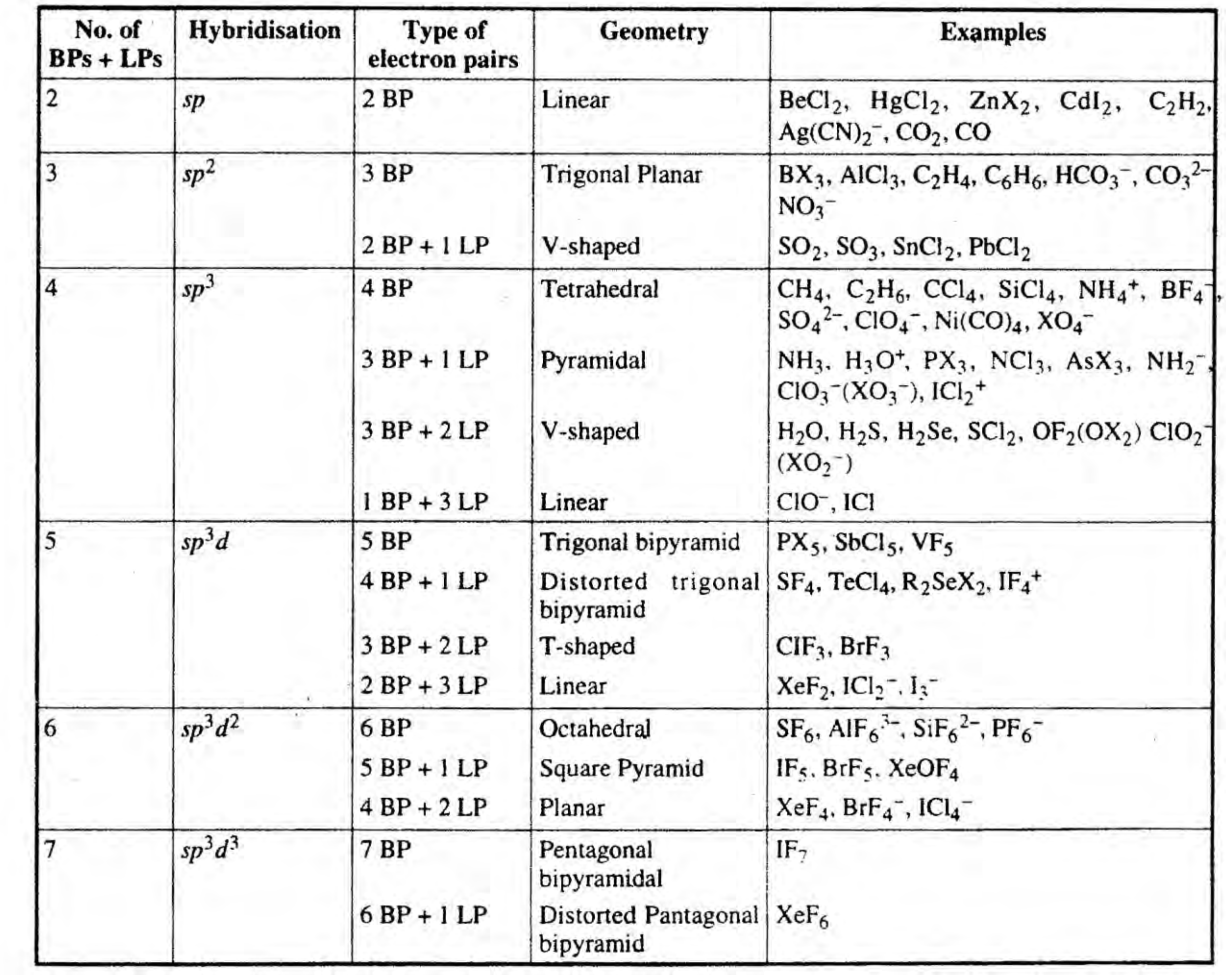


$\begin{array}{c} :\overset{\cdot\cdot}{O}\times H \\ \cdot\times \\ H \end{array}$

(Two bond pairs and two lone pairs)

Thus, in methane, there are four pairs around carbon, while oxygen in water has two bond pairs and two lone pairs around it. According to VSEPR theory, it is the total number of electron pairs (bonded as well as lone pairs) that determines the geometry of molecule.

Applications of VSEPR theory in prediction of structure of molecules:



No. of BPs + LPs	Hybridisation	Type of electron pairs	Geometry	Examples
2	*sp*	2 BP	Linear	$BeCl_2$, $HgCl_2$, ZnX_2, CdI_2, C_2H_2, $Ag(CN)_2^-$, CO_2, CO
3	sp^2	3 BP	Trigonal Planar	BX_3, $AlCl_3$, C_2H_4, C_6H_6, HCO_3^-, CO_3^{2-} NO_3^-
		2 BP + 1 LP	V-shaped	SO_2, SO_3, $SnCl_2$, $PbCl_2$
4	sp^3	4 BP	Tetrahedral	CH_4, C_2H_6, CCl_4, $SiCl_4$, NH_4^+, BF_4^-, SO_4^{2-}, ClO_4^-, $Ni(CO)_4$, XO_4^-
		3 BP + 1 LP	Pyramidal	NH_3, H_3O^+, PX_3, NCl_3, AsX_3, NH_2^-, $ClO_3^-(XO_3^-)$, ICl_2^+
		3 BP + 2 LP	V-shaped	H_2O, H_2S, H_2Se, SCl_2, $OF_2(OX_2)$ ClO_2^- (XO_2^-)
		1 BP + 3 LP	Linear	ClO^-, ICl
5	sp^3d	5 BP	Trigonal bipyramid	PX_5, $SbCl_5$, VF_5
		4 BP + 1 LP	Distorted trigonal bipyramid	SF_4, $TeCl_4$, R_2SeX_2, IF_4^+
		3 BP + 2 LP	T-shaped	ClF_3, BrF_3
		2 BP + 3 LP	Linear	XeF_2, ICl_2^-, I_3^-
6	sp^3d^2	6 BP	Octahedral	SF_6, AlF_6^{3-}, SiF_6^{2-}, PF_6^-
		5 BP + 1 LP	Square Pyramid	IF_5, BrF_5, $XeOF_4$
		4 BP + 2 LP	Planar	XeF_4, BrF_4^-, ICl_4^-
7	sp^3d^3	7 BP	Pentagonal bipyramidal	IF_7
		6 BP + 1 LP	Distorted Pantagonal bipyramid	XeF_6

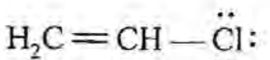
CONJUGATED MOLECULES

Resonance Effect

If two double bonds in a molecule are separated by a single bond, they are said to be in conjugation and the molecule having such bonds are called conjugated molecules e.g., 1, 3-butadiene.

$H_2C=CH-CH=CH_2$

1, 3-Butadiene



$H_2C=CH-\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:$

Vinyl chloride

Another example of conjugation is given by benzene which is a hexagonal ring of carbon atoms with three double bonds in the alternate positions. Alternatively, a double bond or a triple bond may also be in conjugation with a lone electron pair e.g., in vinyl chloride.

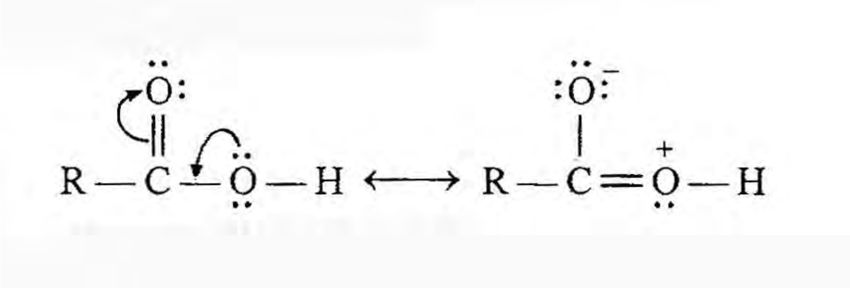
The conjugated molecules do not exhibit the character of pure double bond or triple bond, for example, benzene is expected to be highly reactive since it has three double bonds in the ring but is actually quite stable. In order to explain the difference in the expected and the actual behaviour of the conjugated molecules, Robinson and lngold stated that such compounds exist in two or more forms none of which can explain all the properties of the molecule under investigation. They called this concept as mesomerism or mesomeric effect. Heisenberg studied the same mathematically and named it as resonance or resonance effect. According to the concept, If a compound having a certain molecular formula can be represented by different structural formulae which defer only in the arrangement of the electron pairs and not of the atoms, such like structures are called resonating or contributing or canonical structures and the phenomenon is known as resonance. The compound cannot be represented completely by any of the resonating or contributing structures but by a mixture of all of them which is called resonance hybrid (cannot be actually represented). Resonance is indicated by the sign <—> .

It may be noted that the various resonating or contributing structures do not actually exist i. e., they are all hypothetical structures. They have been given simply to explain certain properties of the compounds which cannot be otherwise explained

Examples of Resonance

A common analogy of a resonance hybrid is that of a mule which is a hybrid of horse and donkey.

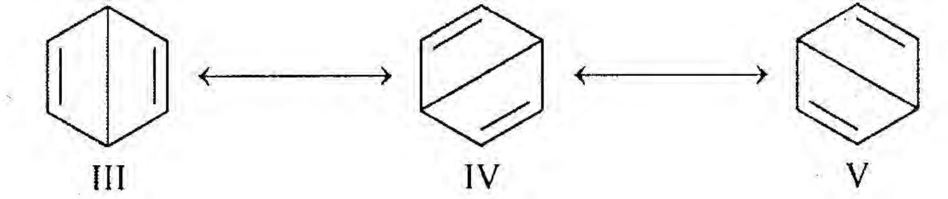
1. **Monocarboxylic acid.** The acidic character of monocarboxylic acid is explained with the help of resonance. The following contributing structures for the monocarboxylic acid are possible which difier in the position of the electron pairs.



As a result of resonance, the oxygen atom of the O — H group acquires a positive charge i. e., it draws the electrons pair towards itself resulting in the release of protons.

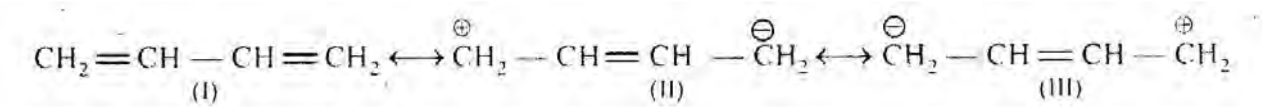
2. **Benzene.** Benzene is a hybrid of two equivalent contributing structures (I and II) which diifer in the position of the pi -electron pairs representing double bonds. These were suggested by Kekule.

Three more contributing structures (III, IV and V) have been proposed by Dewar. Being less symmetrical they have small contribution towards the hybrid.



Benzene exists mainly in the form of Kekule structures (I and II). Benzene is, in fact, quite stable and its stability is explained with the help of resonance. As the 1:-electron charge is distributed over greater area i. e., it gets delocalised.

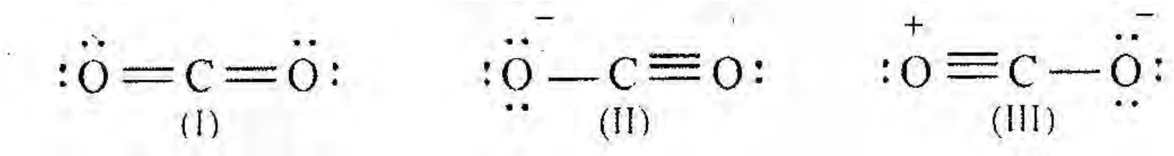
3. 1, 3 - Butadiene. The diene can be regarded as the hybrid of the following contributing structures:



$$CH_2=CH-CH=CH_2 \longleftrightarrow \overset{\oplus}{C}H_2-CH=CH-\overset{\ominus}{C}H_2 \longleftrightarrow \overset{\ominus}{C}H_2-CH=CH-\overset{\oplus}{C}H_2$$

The charged structures II and III make lesser contribution towards the hybrid. However, they do explain the l, 4-addition in the conjugated dienes.

4. Carbon dioxide. The structural formula of carbon dioxide (CO2) molecule is O = C = O. The standard C = O bond length is 122 pm but the bond length which is obtained for the molecule from spectroscopic studies is 115 pm. The difference in the bond length values can be explained by considering the following structures for carbon dioxide which are known as the resonating structures or contributing structures or canonical structures.



The carbon-oxygen bond length is the mean of all the bond length values. Carbon dioxide cannot be represented by any of the contributing structures but by an average of all. Carbon dioxide is said to be a resonance hybrid of these structures.

Conditions of resonance:

Wheland has suggested the following conditions for resonance:
(i) The resonance or the contributing structures must differ only in the position of the electron pairs and not of the atomic nuclei.
(ii) The resonating structures must have the same number of paired and unpaired electrons.
(m) The energies of the various resonating structures must be either same or nearly the same.
(iv) All the contributing or resonating structures do not contribute equally towards the hybrid. The equivalent structures have greater contribution. The contribution of any resonating structure towards the hybrid depends upon the following factors:
  (a) Structures with more covalent bonds are more stable than the structures with less covalent bonds.
  (b) The charged contributing structure is less stable as compared to the structure without any charge.
  (c) Structure with negative charge on more electronegative atom is more stable structure with negative charge on less electronegative atom.

Effects of resonance

Some effects of the resonance are explained as under:

1. Stability. As a result of resonance, the energy of the hybrid decreases and its stability therefore increases. Greater the number of contributing structures; greater will be the stability of the hybrid. The stability also depends upon the equivalence of the contributing structures. Moreover, the charged structures have less contribution than the uncharged structures
Resonance energy: The relative stabilities of two different resonance hybrids may be compared in terms of resonance energy. It may be defined as the difference in the energy content of the hybrid and its most stable contributing structure.

2. Bond length. The resonance causes a change in bond length values. For example, the standard C — C bond length is 154 pm and C == C bond length is 134 pm. But the value as

determined for benzene is 139 pm, which does not coincide with any of the two values and is intermediate between the two values.

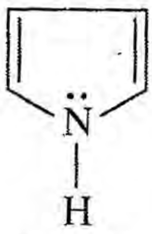
Huckel’s molecular orbital theory of conjugated systems

The German chemist Erich Hückel was the first to recognize that an aromatic compound must have an odd number of pairs of pi electrons. In 1931, he described this requirement by what has come to be known as **Hückel’s rule**, or the **(4n + 2) rule**. According to this rule, monocyclic planar systems of trigonally hybridised atoms which contain (4n + 2) pi electrons possess considerable stability and hence, aromatic character where 'n' may vary from 0, 1, 2, 3, 4...etc. Thus, cyclic compounds having 2, 6, 10, 14, 18 or 22 pi electrons are expected to show aromatic character. But ‘n’ does not denote the number of rings in the cyclic compound.

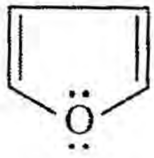
Aromatic character of some cyclic systems:

(1) Monocyclic systems. All the monocyclic compounds shown below have a number of pi electrons in the ring according to the Huckel‘s rule. i.e., all of them have six It-electrons in the ring. They are, therefore, aromatic.

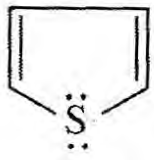

Benzene



Pyrrole

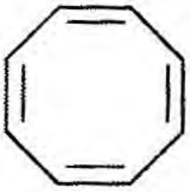


Furan



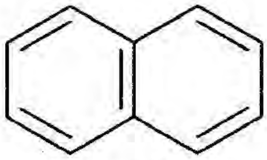
Thiophene

In the heterocyclic compounds pyrrole, furan and thiophene, four pi electrons are contributed by the two double bonds in the ring while two electrons are contributed by the hetero atom.It may be noted that cyclooctatetraene does not show any aromatic character although the ring has four, double bonds in the alternate positions. This is because it does not follow Huckel's rule.

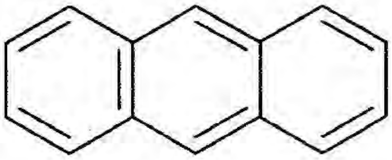

cyclooctatetraene

The number of pi-electrons (8) is not according to Huckel's rule.

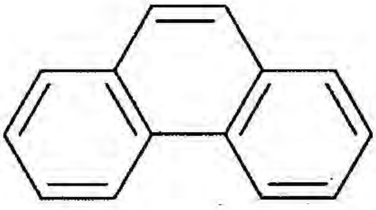
(ii) Fused ring systems. The polynuclear hydrocarbons such as naphthalene, anthracene and phenanthrene are aromatic in nature according to Huckel's rule (6 and 14 pi electrons).



Naphthalene
(10 π-Electrons)

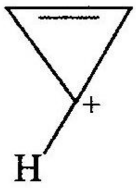


Anthracene
(14 π-Electrons)

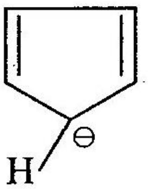


Phenanthrene
(14 π-Electrons)

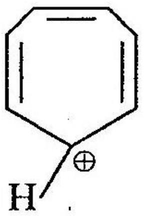
(iii) Aromatic ions system. It may be noted that not only the molecules but even some cyclic ions exhibit aromatic character. A few such ions are listed:



Cyclopropene
cation
(2 π-Electrons)



Cyclopentadiene
anion
(6 π-Electrons)



Cycloheptatriene
cation
(6 π-Electrons)

ISOMERISM

One of the striking features of organic compounds is that they exhibit isomerism. Compounds having the same molecular formula and molecular mass but having different characteristics are called isomers. This phenomenon is called isomerism. The relative position of different atoms or groups in these isomers is different and that causes the difference in properties. Isomerism may be classified into two types:

1. Structural isomerism. In this type of isomerism, the molecules differ in the structural arrangement of the atoms or groups.
2. Stereoisomerism. Here the isomers possess the same structural arrangement but differ with respect to the arrangement of atoms or groups in space.

1. STRUCTURAL ISOMERISM

If two or more compounds differ in the relative arrangement of atoms in the molecule, they are said to be structural isomers and this phenomenon is known as structural isomerism. There are different kinds of structural isomerisms as under:

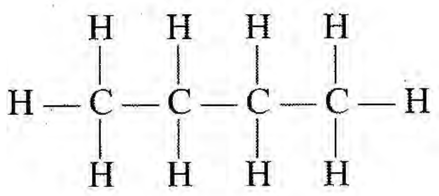
(i) Chain isomerism or Nuclear isomerism.
(ii) Position isomerism.
(iii) Functional isomerism.
(iv) Metamerism.
(v) Tautomerism

Each one of these is discussed as under.

(i) Chain Isomerism or Nuclear Isomerism

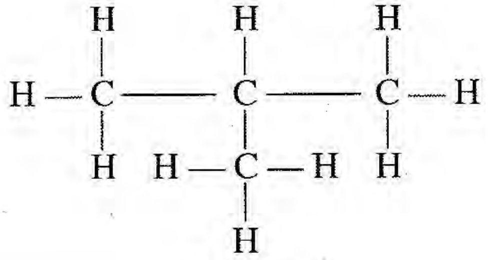
If different compounds of the same class of organic compounds, having the same molecular formula, differ in the structure of carbon chain, they are called chain isomers. Examples of this type of isomerism are:

(a) n-Butane and Isobutane (Mol Formula = C_4H_{10})



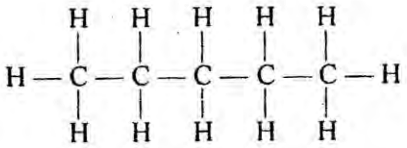
n-Butane

and

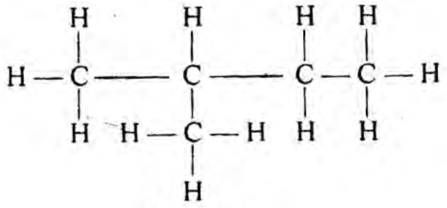


Isobutane

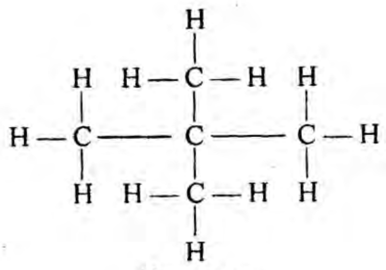
(b) n-Pentane, isopentane and neo pentane (Mol Formula: C_5H_{12})



n-Pentane



Isopentane



Neo-pentane

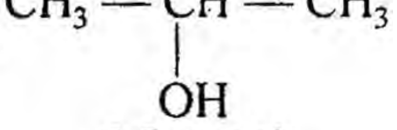
(ii) Position Isomerism

If different compounds, belonging to some homologous series, with same molecular formula have same carbon skeleton but differ in the position of substituent or functional group; these are known as position isomers. Examples of this type of isomers are:

(a) 1-Propanol and 2-propanol (Mol. Formula = C_3H_8O)

$CH_3-CH_2-CH_2OH$ and

1-Propanol



$$CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$$

2-Propanol

(b) 1-Butene and 2-Butene (Mol. Formula = C_4H_8)

$$\underset{\text{1-Butene}}{CH_2=CH_2-CH_2-CH_3} \quad \text{and} \quad \underset{\text{2-Butene}}{CH_3-CH=CH-CH_3}$$

(iii) Functional isomerism

Different compounds, with same molecular formula but different functional groups are known as functional isomers. For example:

(a) Ethyl alcohol and Di methyl ether (Mol. Formula = C_2H_6O)

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \quad \text{and} \quad \underset{\text{Dimethyl ether}}{CH_3-O-CH_3}$$

(b) Propanaldehyde and acetone (Mol. Formula = C_3H_6O)

$$\underset{\text{Propionaldehyde}}{CH_3CH_2CHO} \quad \text{and} \quad \underset{\text{Acetone}}{CH_3-CO-CH_3}$$

(iv) Metamerism:

This is a special kind of structural isomerism in which different compounds, with same molecular formula, belong to same homologous series but difi’er in "the distribution of alkyl groups around a central atom.

Examples are:

(a) Diethyl ether and methyl propyl ether (Mol. Formula = $C_4H_{10}O$)

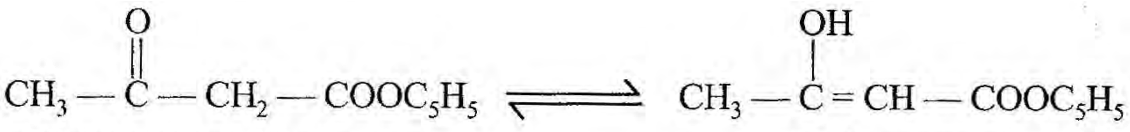
$$\underset{\text{Diethyl ether}}{C_2H_5-O-C_2H_5} \quad \text{and} \quad \underset{\text{Methyl propyl ether}}{CH_3-O-C_3H_7}$$

(b) Diethyl ketone and methyl propyl ketone (Mol. Formula = $C_5H_{10}O$)

$$\underset{\text{Diethyl ketone}}{C_2H_5-CO-C_2H_5} \quad \text{and} \quad \underset{\text{Methyl propyl ketone}}{CH_3-CO-C_3H_7}$$

(v) Tautomerism :

Compounds whose structures differ in the arrangement of atoms but which exist simultaneously in dynamic equilibrium with each other are called tautomers. This phenomenon is called tautomerism. In most of the cases tautomerism is due to shifting of a hydrogen atom from one carbon (or oxygen or nitrogen) to another with the rearrangement of single or double bonds. For example,



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-COOC_5H_5 \rightleftharpoons CH_3-\overset{\overset{\displaystyle OH}{|}}{C}=CH-COOC_5H_5$$

Ethyl acetoacetate (keto form)

Ethyl acetoacetate
(Enolic form)

2. STEREOISOMERISM

Compounds having different three-dimensional relative arrangement of atoms in space are called stereoisomers. This phenomenon is called stereoisomerism. These compounds are said to have different configurations. Stereoisomerism is of the following different kinds:

(i) Geometrical isomerism.
(ii) Optical isomerism
(iii)Conformational isomerism

(i) Geometrical isomerism

Two carbon atoms joined by a single bond (sigma bond) are capable of free rotation around each other, but this rotation is hindered in case of compounds containing carbon-carbon double bond. According to molecular orbital theory, carbon atoms involved in double bond formation are sp^2 hybridised so that each carbon atom has three planar Sp^2 hybridised orbitals and fourth p orbital having its lobes at right angles to the plane of sp^2 orbitals. The formation of pi bond involves the overlapping of p orbitals. With the formation of a pi bond between C — C along with the sigma bond, which is already existing, there remains no possibility of rotation along C — C axis. Neither of the two doubly bonded carbon atoms can be rotated about double bond without destroying the pi bond, which requires large amount of energy. Thus, at ordinary temperature, the rotation about a carbon - carbon double bond is restricted or hindered and gives rise to a kind of stereoisomerism known as 'Geometrical isomerism'.

Geometrical Isomerism, also known as cis-trans isomerism takes place in compounds containing carbon-carbon double bond in which each of the two doubly bonded carbon atoms is attached to two different atoms or groups. All the compound with general formula of the type $C_{AB} = C_{DE}$ or $C_{AB} = C_{AB}$ show geometric isomerism. If either of the two carbon atoms carries two identical/groups as in $C_{AB} = C_{AA}$ or $C_{AB} = C_{DD}$, the isomerism does not exist. This isomerism is due to difference in the relative spatial arrangement of the atoms or groups about the doubly bonded carbon atoms.

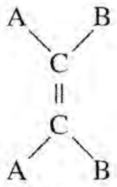
Conditions to be fulfilled by a compound to exhibit geometrical isomerism

For a compound to show geometrical isomerism the following conditions are necessary:

(i) The molecule must contain a carbon-carbon double bond about which there is no free rotation.

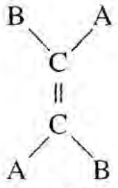
(ii) Each of the double bonded carbon atoms must be attached to two different atoms or groups.

In case of compounds with formula of the type $C_{AB} = C_{AB}$; if two similar groups are on the same side of double bond, the isomer is known a **cis**- and if two similar groups are on the opposite sides of the double bond the isomer is known as **trans** such as:



cis-isomer

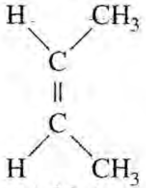
and



trans-isomer

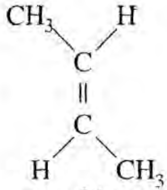
For example,

2-butene exists in two isomeric forms.



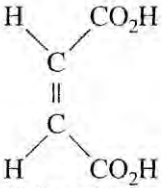
cis-2-butene

and



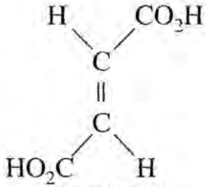
trans-2-butene

Similarly butene-dioic acid exists in two isomeric forms; *cis*- form is called maleic acid and *trans*- form is called fumaric acid



Maleic acid
(*cis*-isomer)

and

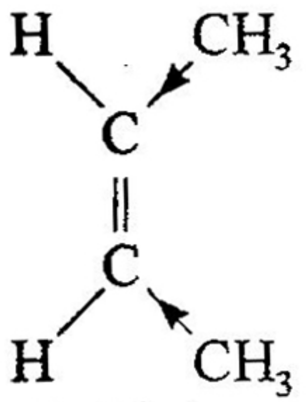


Fumaric acid
(*trans*-isomer)

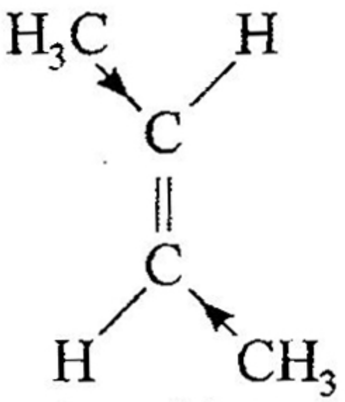
Determination of configuration of a geometrical isomer

Different methods available for determination of configuration of a geometrical isomers are described below;

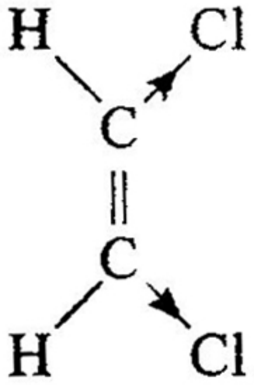
(i) From Dipole moments. Generally cis-isomer has greater dipole moment as compared to trans-isomer. In case of cis- the similar groups being on the same side, the electronic effects are additive; while in case of trans-isomer, the similar groups being on opposite side, the electronic effects cancel each other.



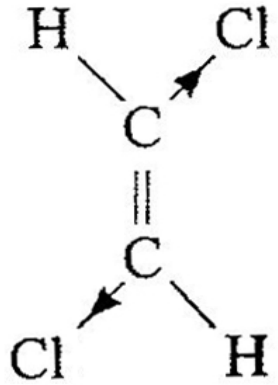
cis-2-butene
$\mu = 0.4$



trans-2-butene
$\mu = 0$

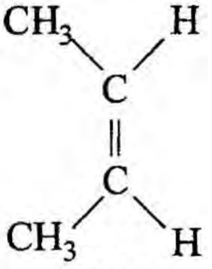


cis-2-Dichlorethene
$\mu = 1.85$

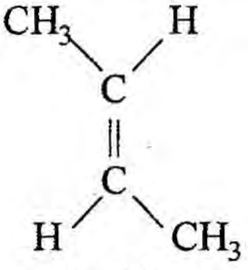


trans-1, 2-dichloroethen
$\mu = 0$

(ii) From boiling point. Generally speaking, a cis isomer has a higher boiling point compared to the trans isomer. This is because of higher dipole moment and higher polarity in the molecule which acts as the binding force and is responsible for higher b.p. of the cis isomer. Boiling point of cis-2- butene is 277 K while the trans-2-butene boils at 274 K.



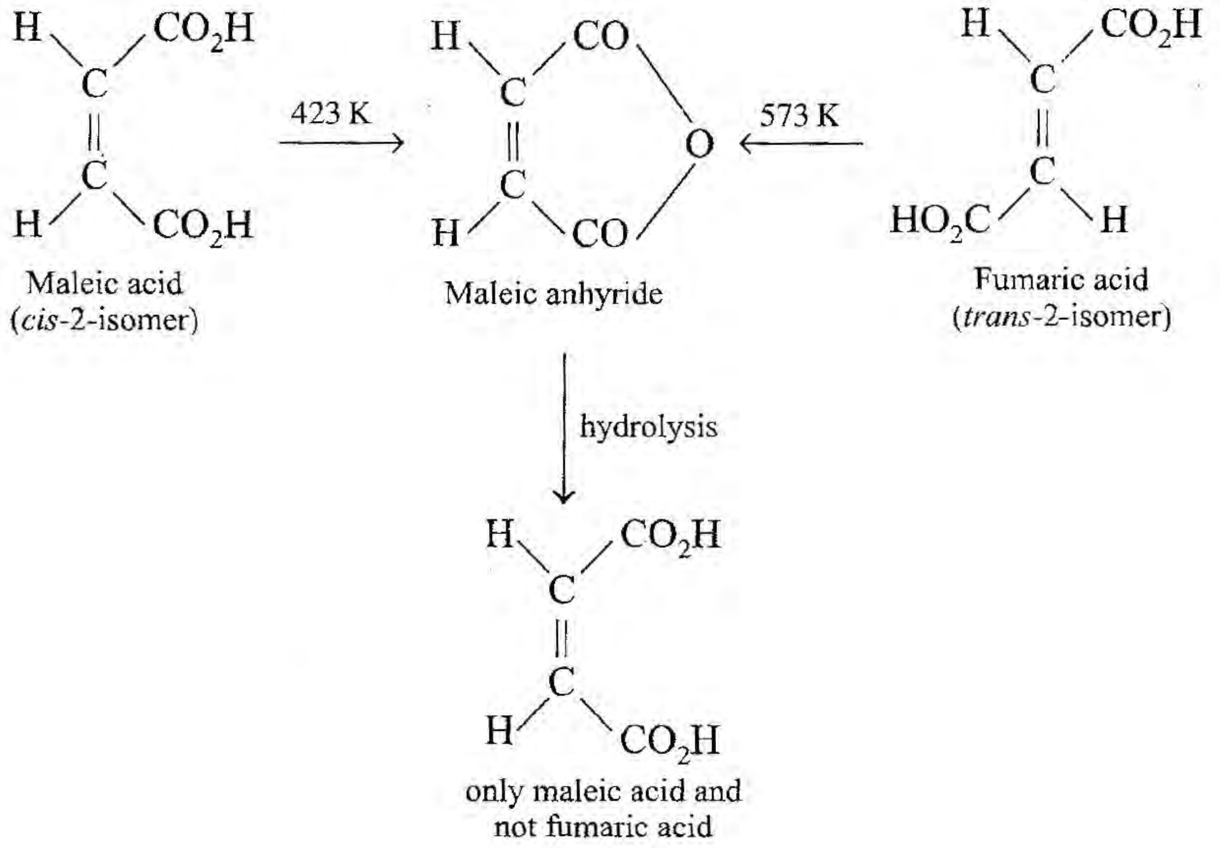
cis-2-butene
b.p. 277 K



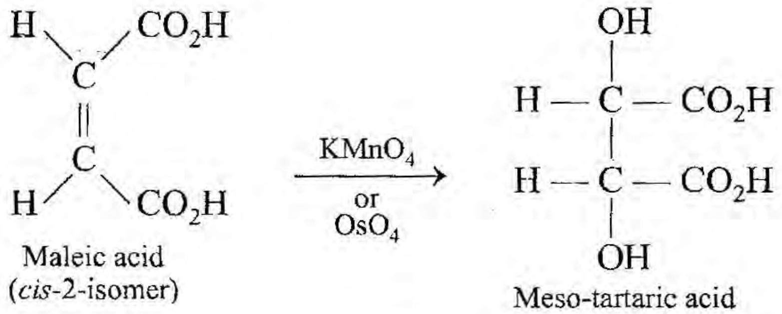
trans-2-butene
b.p. 274 K

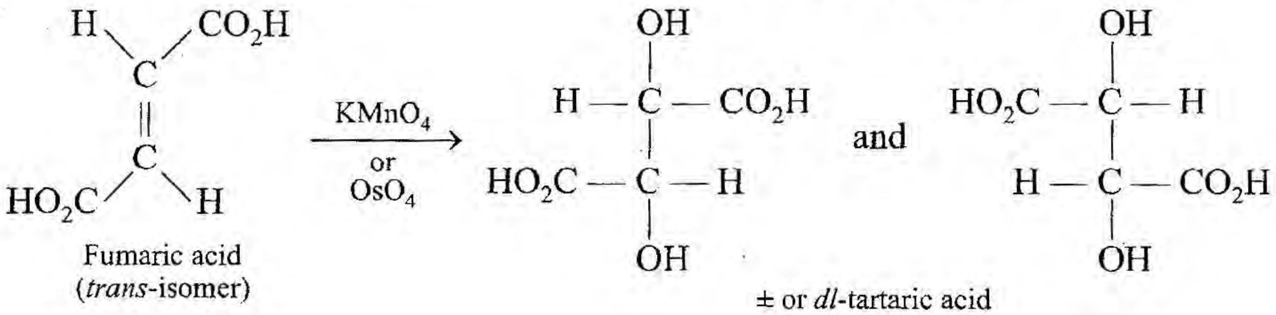
(iii) From melting point. The isomers show a reverse trend here. The 'U' shape of the cis isomer doesn’t pack well compared to the straighter trans isomer. The poorer packing of the cis isomer means that the intermolecular forces are not as effective as they should be and so less energy is required to melt the cis isomers. Thus, maleic acid melts at 403 K whereas fumaric acid melts at 575 K.

(iv) From the formation of cyclic compounds. Two geometric isomers (cis and trans) can be distinguished through reactions that lead to formation of ring. Cis-isomer undergoes ring closure more readily than the trans-isomer. For example maleic acid readily loses water when heated to about 423 K, to give an anhydride; while fumaric acid does not give anhydride at this temperature. Rather it must be heated to 573 K to get the same anhydride. Further, hydrolysis of anhydride yields only maleic acid.

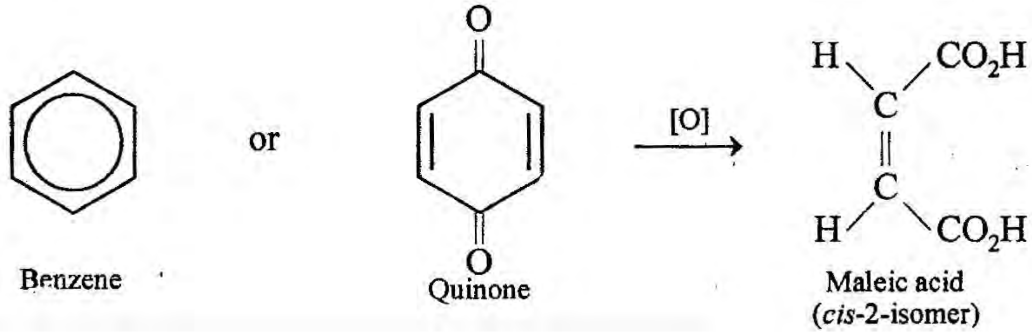


(v) From the formation of the type of optical isomer. Maleic acid and fumaric acid, both on treatment with $KMnO_4$ or OSO_4 yield optically inactive variety of tartaric acid. Maleic acid yields meso tartaric acid, while fumaric acid yields racemic (± or dl) tartaric acid.





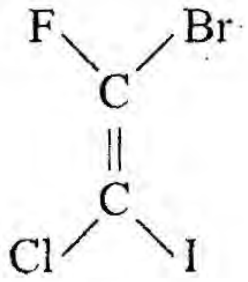
(vi) From the method of preparation. Method of preparation of a compound sometimes leads to its configuration. The isomer obtained by the rapture of a ring must be the cis-isomer, e.g., maleic acid can be prepared by the oxidation of benzene or quinone, so it must be a cis-isomer.



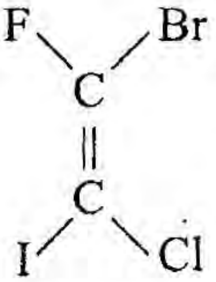
E and Z designations of geometrical isomers

The cis and trans- designated can be used only for the compounds in which two doubly bonded carbon atoms are having similar atoms or groups e. g., of the type $C_{AB} = C_{AB}$. But, when the two doubly bonded carbon atoms are having different atoms or groups attached to them e.g., of the type $C_{AB} = C_{DE}$; it is not possible to assign them *cis* or *trans* configurations. To overcome this difficulty, a more general system for designating the configuration of geometric isomers has been adopted. This system developed by Cahn, Ingold and Prelog originally for the absolute configuration of optical isomers, is known as E and Z system and is based on priority of attached groups. The atoms or groups attached to each carbon of the double bond, are assigned first and second priority. lf the atoms or groups having higher priority attached to two carbons are on the same side of double bond the configuration is designated as Z (derived from German word Zusammen meaning together)
and if the atoms or groups of higher priority are on the opposite side of the double bond, the configuration is designated as E (derived from German word -entgegen meaning across or opposite). Priorities of atoms or groups are determined in the same way as for R & S configurations of optical isomers. At. weights or atomic numbers of atoms directly linked with ethylenic carbon atoms are taken into consideration.

Let us consider an example in which two doubly bonded atoms are attached to four different halogens such as $C_{BrF} = C_{ICl}$. Since Br is having higher priority over F and I is having priority over Cl (due to their higher atomic numbers). The isomer in which Br and I are on the same side of double bond will be called Z and the isomer in which Br and I are on the opposite sides of double bond will be called E.

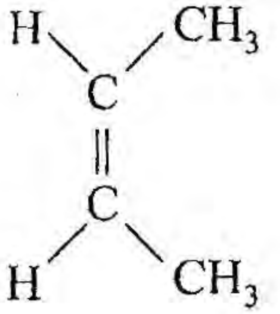


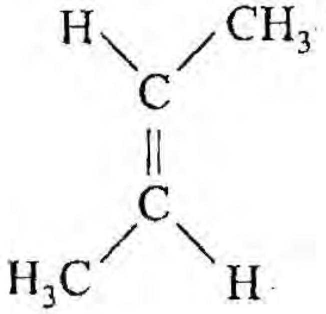
Z-isomer



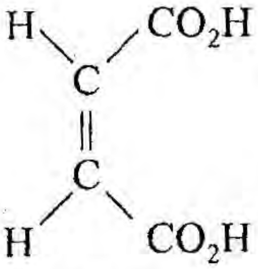
E-isomer

In the same way cis and trans isomers of 2-butene can be called Z and E-2-butenes respectively.

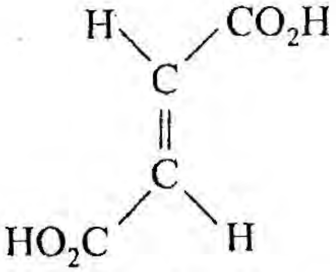




Similarly maleic acid can be specified as Z-isomer and fumaric acid as E-isomer.



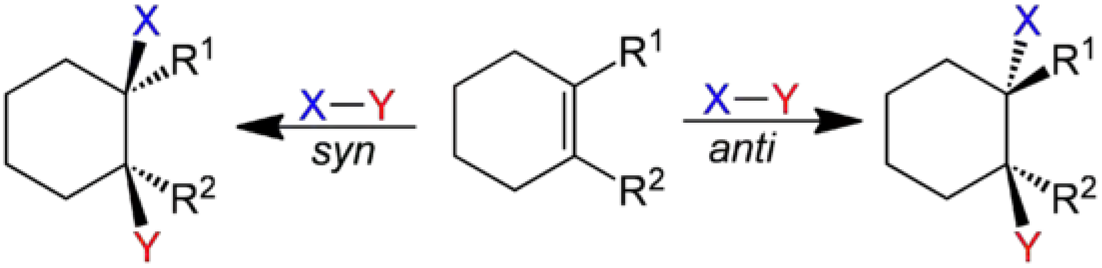
Maleic acid
(*Z*-isomer)



Fumaric acid
(*E*-isomer)

ln determining the configuration, we have to select the group of higher priority on one carbon. Similarly we select the group of higher priority on the other carbon 'atom. Alf these two groups are on the, same side of double bond, the configuration is Z, otherwise it is E.

Syn anti Isomerism



Syn addition is the addition of two substituents to the same side (or *face*) of a double bond or triple bond, resulting in a decrease in bond order but an increase in number of substituents. Generally, the substrate will be an alkene or alkyne. An example of syn addition would be the oxidation of an alkene to a diol via a suitable oxidizing agent such as Osmium tetroxide OsO_4 or Potassium permanganate $KMnO_4$.

Anti addition is in direct contrast to syn addition. In anti addition, two substituents are added to opposite sides (or faces) of a double bond or triple bond, once again resulting in a decrease in bond order and increase in number of substituents. The classical example of this is bromination (any halogenation) of alkenes.

Depending on the substrate double bond, addition can have different effects on the molecule. After addition to a straight-chain alkene such as C_2H_4, the resulting alkane will rapidly and freely rotate around its single sigma bond under normal conditions (i.e. room temperature). Thus whether substituents are added to the same side (syn) or opposite sides (anti) of a double can usually be ignored due to free rotation. However, if chirality or the specific absolute orientation of the substituents needs to be taken into account, knowing the type of addition is significant. Unlike straight-chain alkenes, cycloalkene syn addition allows stable addition of substituents to the same side of the ring, where they remain together. The cyclic locked ring structure prevents free rotation.

(ii) Optical isomerism or enantiomerism

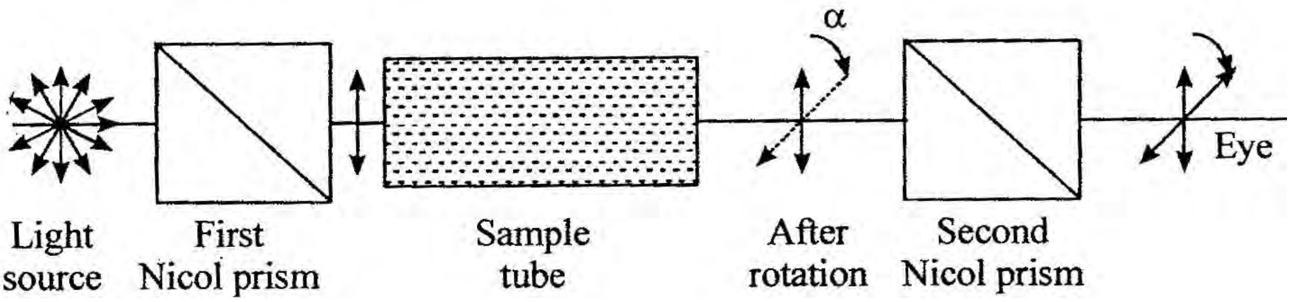
Before taking up optical isomerism, let us understand the terms: plane polarised light, optical activity and specific rotation.

Plane polarised light:

Ordinary light has vibrations taking place at right angles to the direction of propagation of light spread in all the possible planes. If we pass ordinary light through nicol prism, vibrations in all planes except one are cut off. Thus light coming out of nicol prism has vibrations only in one plane. Such a light is called plane polarised light.

Optical activity

Behaviour of certain substances is strange. When a plane polarised light is passed through the solution of such substances, the light coming out of the solution is found to be in a different plane. The plane of polarised light is rotated. Such substances, which rotate the plane of plane polarised light when placed in its path are known as optically active substances and the phenomenon is known as optical activity. The angle of rotation (α) of plane polarised light is known as Optical rotation. The substances which rotate the plane of polarised light to the clockwise or right direction are known as dextrorotatoxy or having positive (+) rotation and those which rotate the plane polarised light to the anticlockwise or left direction are known as laevorotatory or having negative (-) rotation. Substances which do not rotate the plane of polarised light are said to be optically inactive. The instrument used for measuring optical rotation is called polarimeter. It consists of a light source, two nicol prisms and in between a tube to hold the solution of organic substance. The schematic representation of a polarimeter is given below:



Specific rotation. The angle of rotation of plane-polarised light or optical rotation (om) of /an organic substance depends not only on the kind of molecules but also varies considerably with the number of molecules that light encounters in its path which in turn depends on the concentration of the solution used and the length of polarimeter tube containing it. Besides this, it depends on temperature, wavelength of light and nature of solvent used.

The optical activity of a substance is expressed in terms of *specific rotation.* $[\alpha]^t_\lambda$ which is a constant quantity, characteristic of a particular substance,

$$[\alpha]^t_\lambda = \frac{\alpha}{l \times c}$$

where, α = observed rotation in degrees
λ = length of polarimeter tube in decimeter
c = concentration of substance in gm per ml of solution
t and λ signify the temperature and wavelength of light used.

When $l = 1$ and $c = 1$, $[\alpha]^t_\lambda = \alpha$

Specific rotation is thus defined as the optical rotation produced by a compound when plane polarised light passes through one decimeter length of the solution having concentration one gram per millilitre. Usually the monochromatic light used is D line of sodium (λ = 589 nm). Thus specific rotation of cane sugar can be expressed as

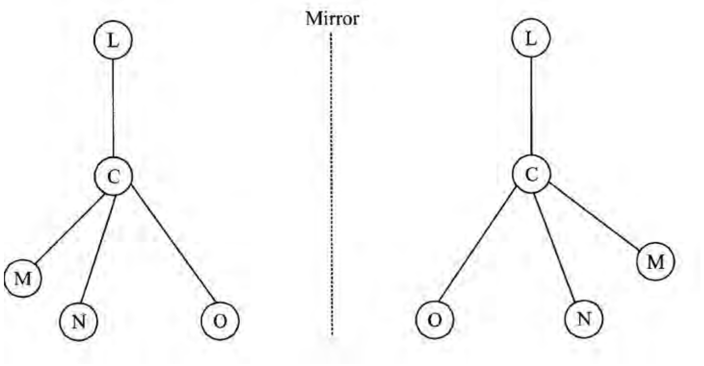
$$[\alpha]^{20°C}_{D} = +66.5° \text{ (water)}$$

In this expression D stands for D line of sodium, 20°C is temperature of measurement, + sign shows the dextrorotation and water is the solvent used.

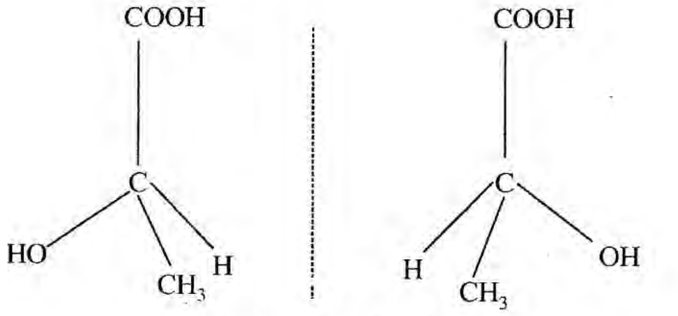
Louis Pasteur, while studying the crystallography of salts of tartaric acid made a peculiar observation. He observed that optically inactive sodium ammonium tartarate existed as a mixture of two different types of crystals which were mirror images of each other. With the help of 'a' hand lens and a pair of forceps, he carefully separated the mixture into two different types of crystals. These crystals were mirror images of each other and were called enantiomorphs and the phenomenon as enantiomorphism. Although the original mixture was optically inactive;

each type of crystals when dissolved in water, were found to be optically active. Moreover the specific rotations of the two solutions were exactly equal but of opposite sign i.e. one solution rotated the plane polarised light to the right or clockwise while the other to the left or anticlockwise and to the same extent. Two types of crystals or solutions were identical in all other physical and chemical properties. Isomers which are non superimposable mirror images of each other are called enantiomers.

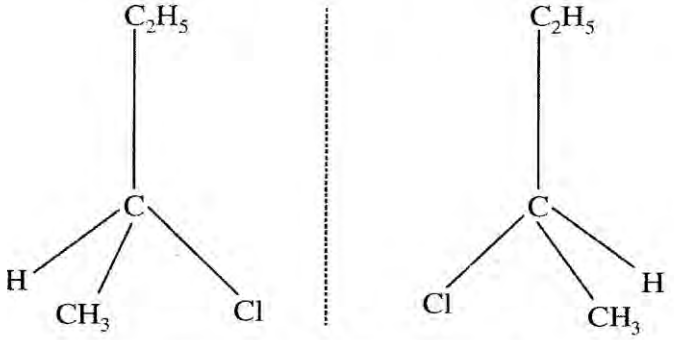
According to La Bell and Van't Hoff the four valencies of a carbon atom are directed towards the four corners of a regular tetrahedron at the centre of which lies the carbon atom. Consider a compound of formula $CLMNO$ having four different groups L, M, N and O - attached to a carbon atom. This compound can be represented by two models which look like mirror images of each other.



It is important to note here that these two molecules cannot be superimposed on each other i.e. they will not coincide in all their parts. We may turn them in as many ways as we like but we find that though two groups of each may coincide, the other two do not. Hence these must represent two isomers of formula $CLMNO$. Lactic acid $CH_3CHOHCOOH$ and sec-Butyl chloride $C_2H_5CHClCH_3$ exist as two optically active isomers which are enantiomers i.e. mirror images of each other.



Enantiomers of Lactic Acid



Enantiomers of Sec. Butyl Chloride

Mirror images of the two compounds are represented as above. The carbon atom to which four different groups are attached, is known as asymmetric or chiral carbon atom or stereogenic centre. If two of the groups attached to carbon are same, we shall observe that it is possible to superimpose the mirror images on each other. Such a compound will not show optical isomerism or enantiomerism.

Hence non-superimposability of the mirror images is responsible and essential for the type of stereoisomerism known as enantiomerism.

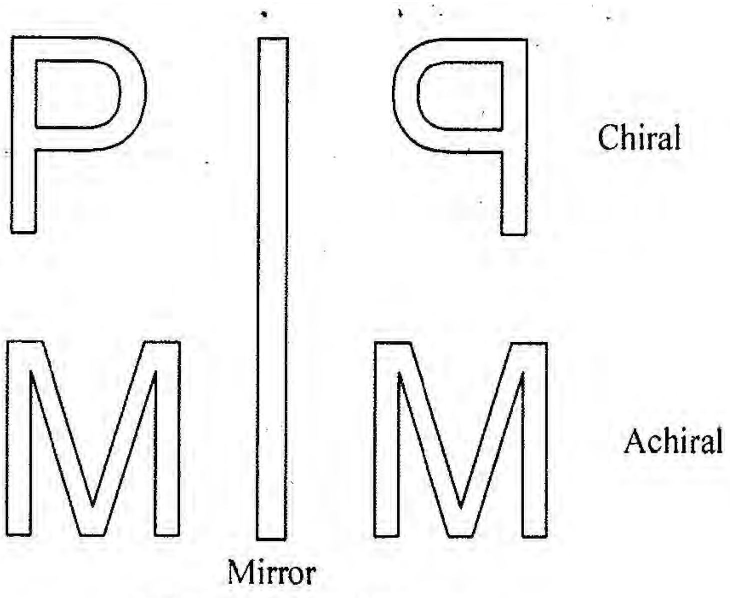
The term optical isomerism is used for the existence of stereoisomers which differ in their behaviour towards the plane polarised light. Thus enantiomeric molecules are always non-superimposable mirror images of each other. The non—superimposability of mirror images arises due to chiral or asymmetric nature of molecule. A molecule is said to be chiral if it has no plane of symmetry and is therefore non-superimposable on its mirror image.

It may be concluded with the remarks that chirality is the fundamental condition of enantiomerism or optical isomerism.

Chirality and dissymetry

An object which is non-superimposable on its mirror image is called chiral object. And an object which is superimposable on its mirror image is called achiral object. Examples of chiral objects including letters from English alphabets are: A pair of hands, shoes, gloves, letters P, F, J etc.

Examples of achiral objects and letters are: Ball, sphere, letters A, O, M, etc.

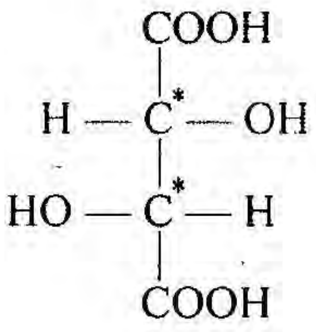


Chiral and achiral Objects

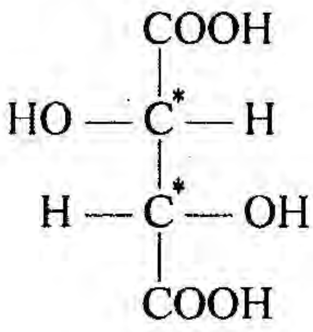
Achiral objects or molecules possess a plane of symmetry that can divide the molecule into two identical halves. Chiral objects or molecules do not possess a plane of symmetry that can divide the molecule into two identical halves. The chirality is also known as dissymetry while achirality is also known as symmetry.

Thus chirality or dissymmetry is the property associated with certain compounds which do not have a planes of symmetry andare thus non-superimposable on their mirror images. Dissymmetry is an essential condition for optical activity. In the study of enantiomers containing one chiral carbon atom, we find that they do not have a plane of symmetry and hence are dissymmetric in nature, for example, lactic acid, sec-butyl chloride etc. We can thus say that compounds with a chiral carbon atom are optically active in nature.

This is not true, however, for compounds with two or more chiral carbon atoms. Here, one or more isomers may be optically inactive in spite of the presence of chiral carbon atoms. Consider for example, the case of tartaric acid, CH(OH) COOHCH (OH) COOH. It has two chiral carbons (stereogenic centres) marked * and thus has four isomers as shown below:

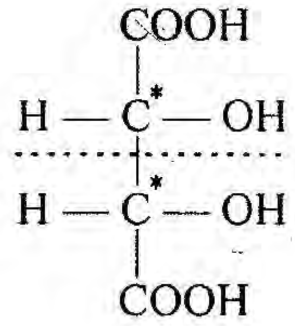


I

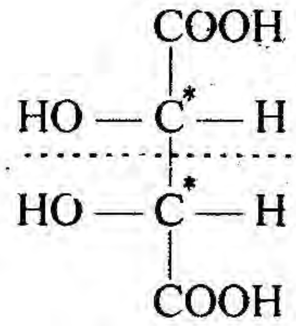


II

I and II are optically active due to the absence of plane of symmetry



III



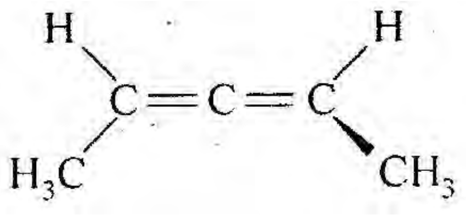
IV

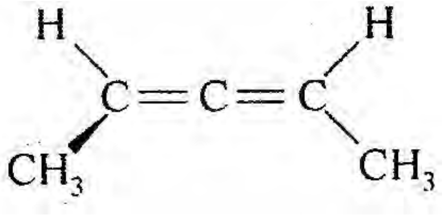
III and IV are optically inactive due to the presence of plane of symmetry (shown by dotted line)

Isomers I and II are non-superimposable mirror images of each other, they are dissymetric and optically active. But lll and IV have a plane of symmetry. Therefore, they are symmetric and optically inactive in nature. In other words, optical activity in organic compounds is due to the presence of dissymetry and not due to chiral carbon atoms alone.

No. of optical isomers for a compound is given by 2^n where n is the number of chiral carbon atoms.

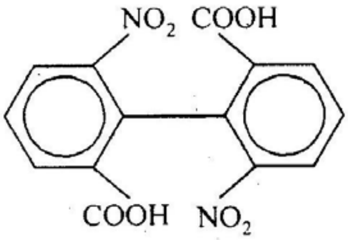
It may be noted that some organic compounds are optically active even though they do not contain chiral atom. For example, **Substituted allenes**. Dienes with double bonds in adjacent positions are called allenes. Substituted allenes may be represented as RCH = C = CHR. Pentane —2, 3-diene exists in two optically active forms. This is because the groups linked to one end carbon are in different plane than those linked to the other end carbon.





ln allenes, the central carbon is sp hybridized, and the terminal carbons are Sp^2 hybridized. The central carbon forms two $Sp\text{-}Sp^2$ sigma bonds. The central carbon also has two p orbitals which are mutually perpendicular. These forms pi bonds with the p orbitals on the other carbon atoms. As a result, the substituent at one end of the molecule are in a plane which is perpendicular to that of the substituents at the other end, so that the compound exists in two forms which are non-superimposable mirror images and are optically active.

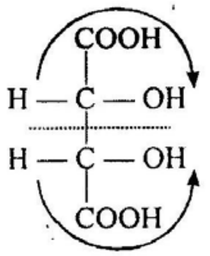
Substituted biphenyl. Benzene rings in substituted biphenyl lie in different planes; flence the compound exhibits optical activity.



We can conclude from the above discussion that the most essential condition for a compound to show optical activity is the presence of dissymmetry and not chirality. However, compounds containing only one chiral carbon are always dissymmetric since they do not have a plane of symmetry.

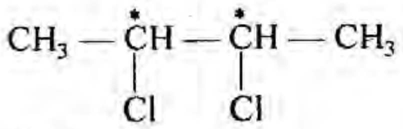
The compounds, with two or more similar chiral carbon atoms which are optically inactive due to the presence of plane of symmetry, are called **meso** compounds.

Consider the following isomer of tartaric acid



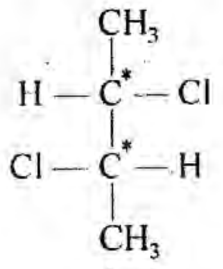
It has a plane of symmetry denoted by the denoted line. The optical rotation of upper half of the molecule is neutralized by that of the lower half as the two rotations are in opposite directions. The net result is that the molecule is optically inactive. Such compounds are known as meso compounds.

Similarly, we come across meso structures in 2, 3-Dichlorobutane. This compound also possesses two asymmetric carbon atoms (stereogenic centres) marked with *.

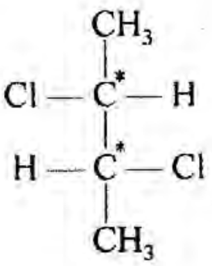


$$CH_3-\underset{\displaystyle Cl}{\overset{*}{C}H}-\underset{\displaystyle Cl}{\overset{*}{C}H}-CH_3$$

The different isomers can be written as

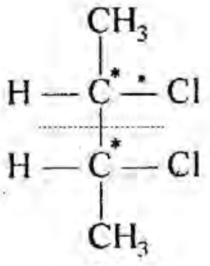


I

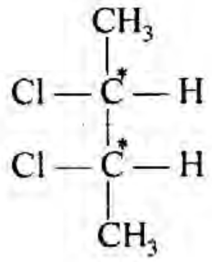


II

I and II show optical activity due to absence of plane of symmetry (Dissymmetry)



III



IV

III and IV are optically inactive because of the presence of plane of symmetry

Structures III and IV are meso compounds because the optical activity of the upper half of the molecule is neutralised by that of the lower half.

Properties of enantiomers

(i) They have identical physical properties but differ in direction of rotation of plane polarised light. Though the two enantiomers rotate the plane polarised light in opposite direction, the extent of rotation is the same.

(ii) They have identical chemical properties except towards optically active reagents. The rates of reaction of optically active reagents with two enantiomers differ and sometimes one of the enantiomers does not react at all.

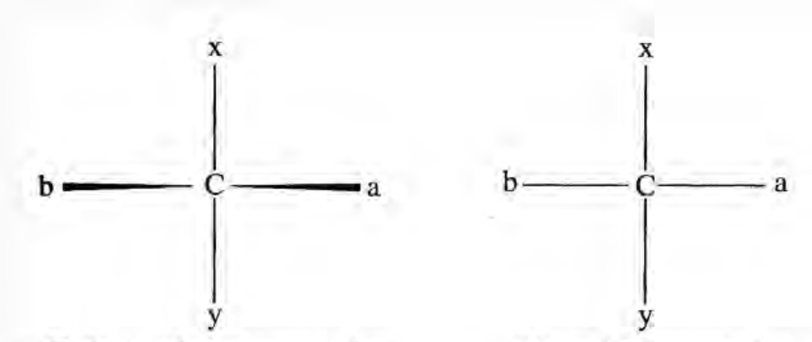
Example: ln biological system (-) or I-glucose is neither metabolised by animals nor fermented by yeast whereas (+) or d-glucose undergoes both these processes and plays an important role in animal metabolism and fermentation. Similarly mould penicillium glaucum consumes only d-tartaric acid when fed with a mixture of equal quantities of d- and I-tartaric acid.

(iii) When equal amounts of enantiomers are mixed together an optically inactive racemic modification denoted by (±) or dl is obtained.

Fischer's projection formula for planar representation of three dimensional molecules.

Emil Fischer in 1891 introduced a simple method for representing three dimensional molecules in one plane. It is known as Fischer projection formula. Following points' are to be observed for this purpose:

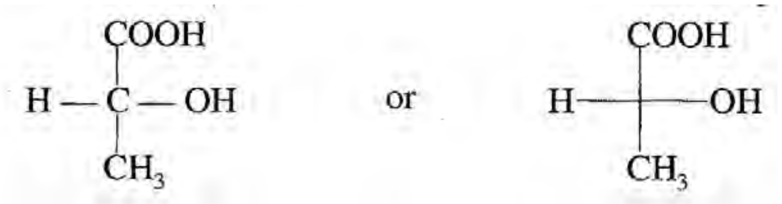
(i) The chiral molecule is imagined in such a way that two groups point towards the observer and two away from the observer. The groups pointing towards the observer are written along the horizontal line (shown by thick wedge-like bonds) and those pointing away are written along the vertical line. The central carbon is present at the crossing of the horizontal and vertical lines.



Flying wedge representation   Normal representation

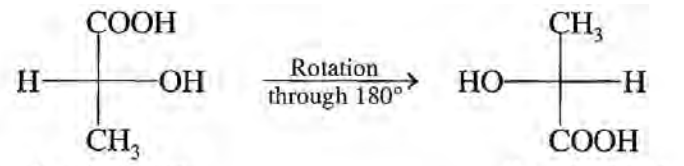
Thus if a, b, x and y are four groups attached to a carbon, the molecule will be represented by the projection formula as above. Here a and b groups point towards the observer (or above the plane) and groups x and y are away from the observer (or below the plane).

(ii) The longest chain of carbon atoms in the molecule should be represented along the-vertical line. Lactic acid, therefore, according to the above conventions will be represented as



(iii) We can avoid writing carbon at the crossing of the vertical and horizontal lines. A crossing automatically means the presence of a carbon.

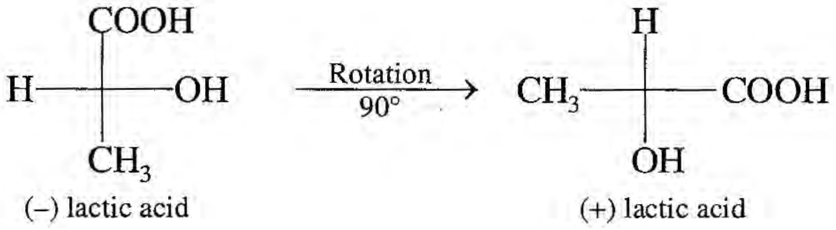
(iv) If necessary, planar formula may be imagined to be rotated from end to end without lifting it from the plane of the paper. Rotation by 180° in the plane of the paper does not create any change in the configuration of the molecule.



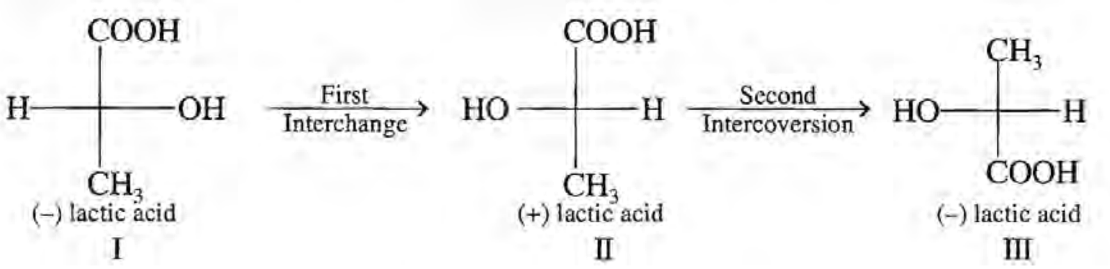
I (–) lactic acid   II (–) lactic acid

In the above rotation by 180°, II has been obtained from I. There has been no change in configuration of the molecule. I and II are in fact the same thing.

(v) Rotation by 90° or 270° brings about a change in configuration of the molecule. Consider the following rotation.



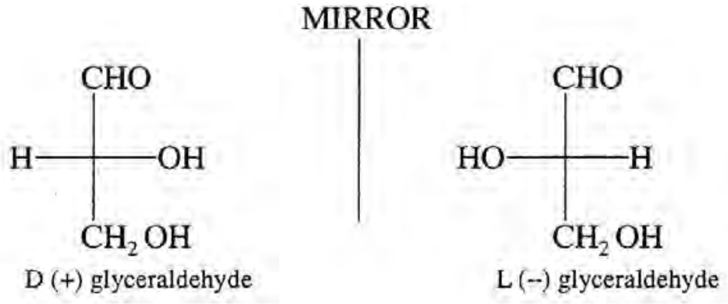
(vi) If the positions of two groups across the chiral atom are interchanged, it leads to inversion of configuration. Two consecutive such changes neutralise the effect.



Structure III and I are the same because as per rule (iv) above, III on rotation through 180° will give I.

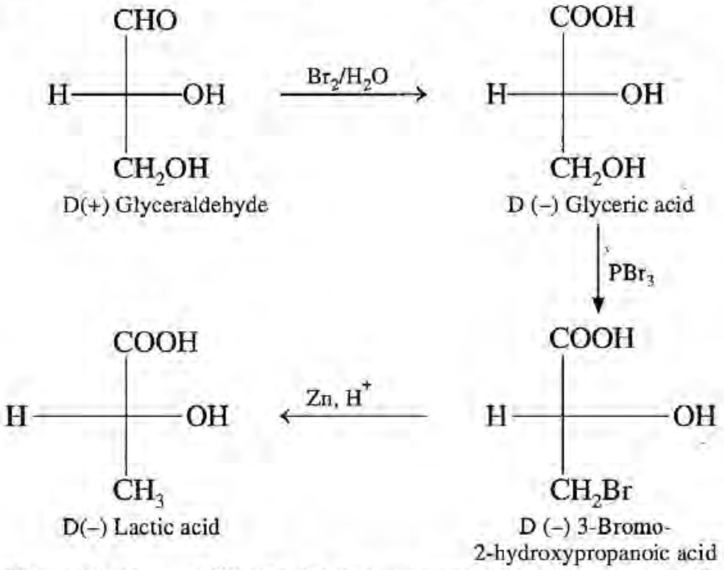
Absolute configuration of optical isomers

In the earlier days, as the modern techniques of finding out configuration were not available, Fischer assigned the following configurations to the (+) and (-) enantioniers of glyceraldehyde arbitrarily and denoted them by capital letters D and I. respectively. Small letters d and l represent sign of rotation, While capital letters D and L represent configuration.



The relative configurations of a number of other optically active compounds have been established by correlating them with D(+) or L(–) glyceraldehyde. All those optically active compounds, which are obtained from D(+) glyceraldehyde through a sequence of reactions *without breaking the bonds of asymmetric carbon atom*, are designated as D configuration irrespective of their sign of rotation and the other enantiomer as L configuration.

For example,



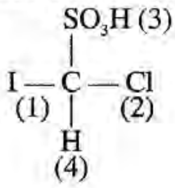
In all the D configurations, — OH attached to asymmetric carbon atom is written on the right hand side of Fischer projection formula. Similarly, in all the L-configurations, –OH attached to the lowest asymmetric carbon atom is written on the left hand side in the Fisher's projection formula.

R and S specification for the configuration of an optically active compound

Cahn, Ingold and Prelog developed a method which can be used to designate the configuration of all the molecules containing asymmetric carbon atom (chiral centre). This system is known as *Cahn-Ingold-Prelog system* or R and S system and involves two steps.

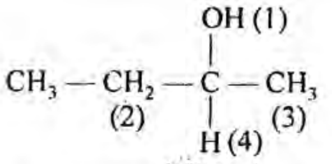
Step I. The four different atoms or groups of atoms attached to chiral carbon atom are assigned a sequence of priority according to the following set of sequence rules.

Sequence Rule 1. *If the four atoms, directly attached to asymmetric carbon atom, are all different, the priority depends on their atomic number. The atom of higher atomic number gets higher priority.* For example, in chloroiodomethane sulphonic acid the priority sequence is I, Cl, SO_3H, H



We consider the atom of the group which is directly linked to the central carbon.

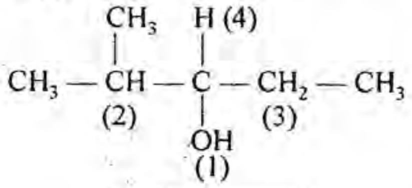
Sequence Rule 2. *If Rule 1 fails to decide the relative priority of two groups it is determined by similar comparison of next atoms in the group and so on.* In other words, if two atoms directly attached to chiral centre are same, the next atoms attached to each of these atoms, are compared. For example in 2-butanol two of the atoms directly attached to chiral centre are carbon themselves. To decide the priority between the two groups —CH_3 and —CH_2CH_3, we proceed like this. Methyl carbon is further linked to H, H and H. The sum of atomic numbers of three H is 3. The methylene carbon of the ethyl group is linked to two hydrogens and one carbon directly. The sum of at. no. of two H and one C is 8. Thus ethyl group gets the priority over methyl. Hence the priority sequence is OH, C_2H_5, CH_3, H.



$$CH_3-\underset{(2)}{CH_2}-\underset{H\,(4)}{\overset{OH\,(1)}{C}}-\underset{(3)}{CH_3}$$

2-Butanol

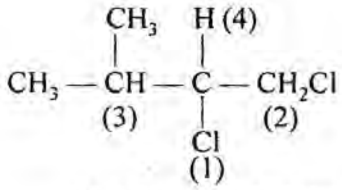
In 2-methyl - 3-pentanol, the C, C, H of isopropyl gets priority over the C, H, H of ethyl, so the priority sequence is OH, isopropyl, ethyl, H.



$$CH_3-\underset{(2)}{\overset{CH_3}{CH}}-\underset{\underset{(1)}{OH}}{\overset{H\,(4)}{C}}-\underset{(3)}{CH_2}-CH_3$$

2-Methyl-3-pentanol

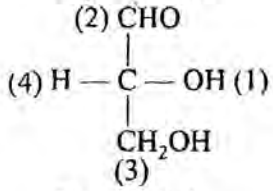
In 1, 2-dichloro-3-methylbutane the Cl, H, H of CH_2 Cl gets priority over the C, C, H of isopropyl due to atomic number of Cl being higher than that of C. So the priority sequence is Cl, CH_2Cl, isopropyl, H.



$$CH_3-\underset{(3)}{\overset{CH_3}{CH}}-\underset{\underset{(1)}{Cl}}{\overset{H\,(4)}{C}}-\underset{(2)}{CH_2Cl}$$

1, 2-dichloro-3-methylbutane

Sequence Rule 3. *A doubly or triply bonded atom is considered equivalent to two or three such atoms; but two or three atoms, if attached actually, get priority over doubly or triply bonded atom.* In glyceraldehyde, O, O, H of — CHO gets priority over the O, H, H of — CH_2OH; so the priority sequence is — OH, — CHO — CH_2OH — H.

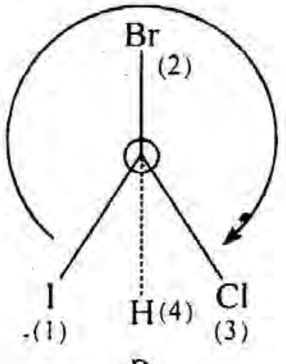


$$(4)\,H-\underset{\underset{(3)}{CH_2OH}}{\overset{(2)\,CHO}{C}}-OH\,(1)$$

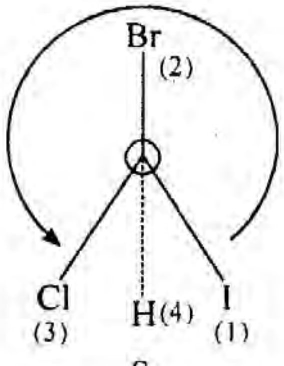
Glyceraldehyde

Step II. After deciding the sequence of priority for four atoms or groups attached to asymmetric carbon atom; the molecule is visualised in such a way that the atom or group of lowest or last (*i.e.* fourth) priority is directed away from us, while the remaining three atoms or groups are pointing towards us. Now if on looking at these three groups (pointing towards us) in the order of their decreasing priority, our eye moves in clockwise direction, the configuration is specified as R (from Latin word *rectus* meaning right) and on the other hand if our eye moves in anticlockwise direction the configuration is specified as S (from Latin word *sinister* meaning left).

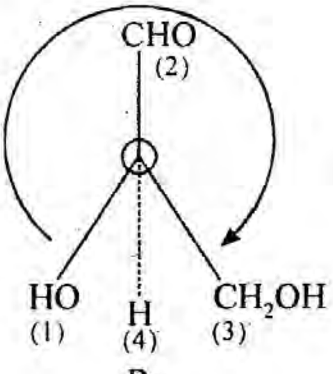
The following examples illustrate the above method for specification of configurations of R and S to molecules of compounds containing an asymmetric or chiral carbon atom.



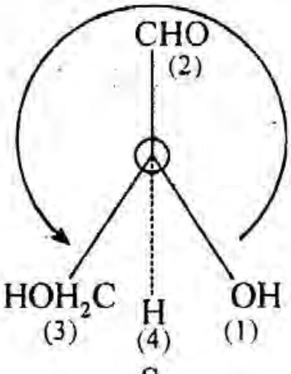
R



S



R



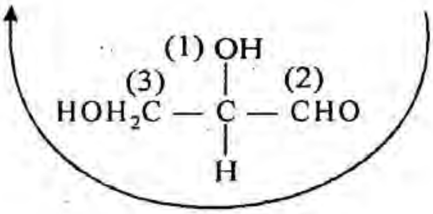
S

Configuration on the basis of projection formula

When a compound is represented by the Fischer projection formula, the configuration can be easily determined without constructing the model. To determine whether the eye travels clockwise or anticlockwise, we have to place the group or atom of the lowest priority at the bottom of the Fischer projection formula. The following four situations arise:

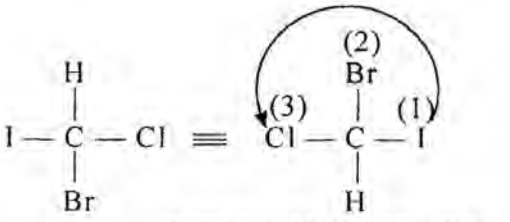
(i) The atom/group of lowest priority is at the bottom. In such a case, simply rotate the eye in the order of decreasing priorities. The configuration is R if the eye travels in clockwise direction and S if the eye travels in anticlockwise direction.

For example, Glyceraldehyde, represented by the following projection formula has R configuration:



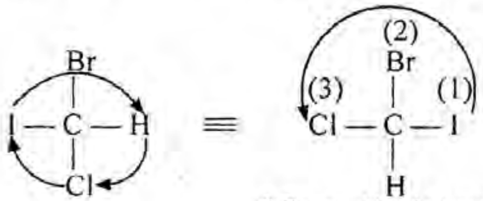
R—Glyceraldehyde

(ii) The atom/group of lowest priority is at the top. In such case, rotate the molecule by 180° so as to bring atom/group of lowest priority at the bottom. This can be done by reversing the position of all the atoms or groups. Then find the direction in the order of decreasing priorities. For example, the compound CHBrCII, represented by following projection fonnula, has S configuration:



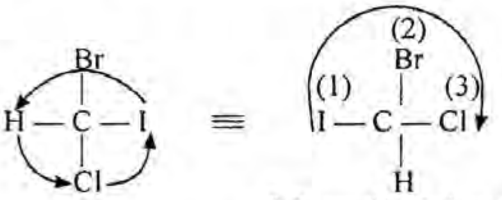
S-Bromochloroiodomethane

(*iii*) *The atom/group of lowest priority is at the right hand side of the horizontal line.* In such case, change the position of atoms or groups in clockwise direction so that atom/group of the lowest priority comes at the bottom but do not change the position of the atom/group at the top of the vertical end. Then find the direction in the order of decreasing priorities. For example, CHBrClI, represented by following projection formula, has S configuration.



S-Bromochloroiodomethane

(*iv*) *The atom/group of lowest priority is at the left hand side of the horizontal line.* In such case, without changing the position of atom/group at the top of the vertical end, change the position of other atoms/groups in the anticlockwise direction so that atom/group of lowest priority comes at the bottom. Then find the direction in the order of decreasing priorities. For example, CHBrClI, represented by following projection formula, has R configuration.



R-Bromochloroiodomethane

Racemic modifications

Racemic modification is the term used for a mixture of equal amounts of enantiomers. A racemic mixture is optically inactive because of external compensation. The optical activity caused by one enantiomer is neutralised by the activity of the other enantiomer. The notation for a racemic modification or mixture is ± or dl. A racemic mixture may also be denoted by the letters R and S. For examples RS-sec. butyl chloride.

Methods for the resolution of racemic mixtures

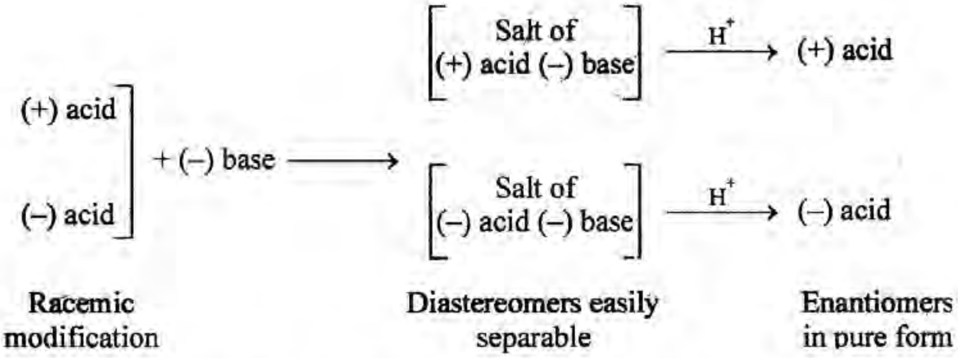
The separation of racemic modification into enantiomers is called resolution. Since the two enantiomers in a racemic mixture have identical physical and chemical properties, These cannot be separated by usual methods of fractional distillation or fractional crystallisation. Special methods are adopted for their separation as given below:

(i) Mechanical separation. This method was first adopted by Pasteur for separating the enantiomers of ammonium tartarate. When racemic modification is crystallized from a solution, two types of crystals are obtained. These are mirror images of each other consisting of (+)/and (-) foms which can be separated by hand picking with the help of a pair of tweezers and a powerful lens. This is a very laborious method and can be applied only to those compounds which give well defined distinguishable crystals of enantiomers.

(ii) Biochemical method. Certain micro-organisms grow in a racemic mixture, consuming only one of the enantiomers while leaving the other unaffected. Thus penicillium glaucum when placed in (i) tartaric acid, consumes only (+) tartaric acid and leaves (-) tartaric acid unused. The major disadvantage of this method is that one of the enantiomers get destroyed.

(iii) Chemical method. This method is mostly used for the resolution of racemic modification. In this method the racemic modification is treated with an optically active reagent to get a pair of diastereomers. Since diastereomers differ in their physical properties, it is possible to separate them by physical methods such as fractional crystallisation, fractional distillation etc. The pure diastereomers are then decomposed, into a mixture of optically active reagent and corresponding enantiomer, which can be separated.

Suppose the racemic modification is an (±) acid. When it is treated with an optically acitve, say (—) base, it gives a mixture of two salts, one of (+) acid (-) base, the other of (-) acid (-) base. These salts are neither superimposable nor mirror images; so these are diastereomers having different physical properties and can be separated by fractional crystallisation. After separation the optically active acids can be recovered in pure forms by adding a mineral acid.



The commonly used optically active bases for the purpose are naturally occurring alkaloids such as (–) brucine, (–) quinine, (–) strychnine and (+) cinchonine.

Similarly, the resolution of racemic bases can be carried out using a naturally occurring optically active acid such as (–) malic acid. Alcohols can be resolved in a similar way by ester formation using an optically active acid.

CONFORMATIONAL ISOMERISM

Carbon-carbon single bond in alkanes is a sigma bond formed by the overlapping of sp^3 hybrid atomic orbitals along the inter-nuclear axis. The electron distribution in such a bond is symmetrical around internuclear axis; so that free rotation of one carbon against the other is possible without breaking sigma or single covalent bond. Consequently such compound can have different arrangements of atoms in space, which can be converted into one another simply by rotation around single bond, without breaking it. These different arrangements are known as *Conformational Isomers or Rotational Isomers or Conformers.* Since the potential energy barrier for their inter-coversion is very low, it is not possible to isolate them at room temperature. At least 60-85 kJ/mole must be the energy difference between two conformers to make them isolatable at room temperature.

Hence, conformations can be defined as different arrangements of the atoms which can be converted into one another by rotation around single bonds.

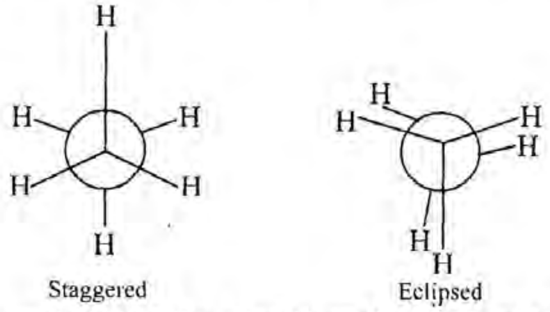
Newman and Sawhorse representations for the conformations of ethane

Alkanes can have an infinite number of conformations by rotation around carbon-carbon single bonds. In ethane two carbon atoms are linked by a single bond and each carbon atom is further linked with three hydrogen atoms. If one of the carbon atoms is allowed to rotate about carbon-carbon single bond keeping the other carbon stationary, an infinite number of arrangements of the hydrogens of one carbon, with respect to those of the other, are obtained. All these arrangements are called conformations (Bond angles and bond lengths remain the same).

Newman reppresentation

This can be easily understood with the help of Newman Projection formulae. The molecule is viewed from front to back in the direction of carbon-carbon single bond. The carbon nearer to the eye is represented by a point and three hydrogen attached to it are shown by three lines at an angle of 120° to one another. The carbon atom away from the eye is represented by a circle and three hydrogens attached to it are shown by shorter lines at an angle of 120° to each other.

Out of infinite number of conformations, Newman Projection formulae for two extreme cases are as shown below:

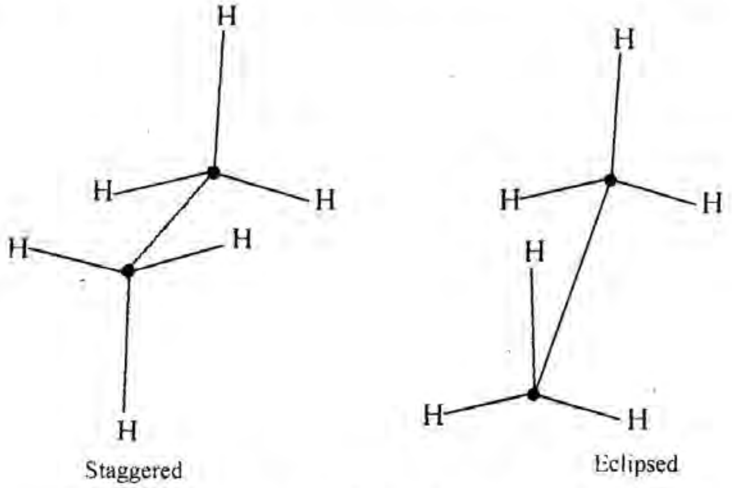


Newman Projection Formulae for conformations of ethane.

The conformation in which the H atoms of two carbons are as far apart as possible, is known as *Staggered conformation* and the conformation in which the H atoms of back carbon are just behind those of the front carbon is known a *Eclipsed conformation.* These are converted into one another by rotation of one carbon against the other through 60°. The other conformations, in between these two, are known as *skew conformations.*

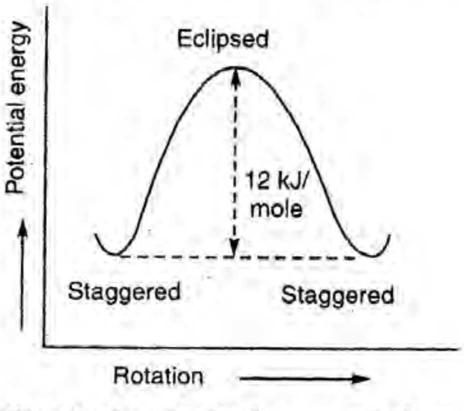
Sawhorse representation

In this representation, the molecule is visualised slightly from above and from the right and then projected on the paper. The bond between two carbons is drawn diagonally and is a bit longer for the sake of clarity. The lower left hand carbon is taken as front carbon and the upper right hand carbon is taken as back carbon. The Sawhorse representation of staggered and eclipsed conformations of ethane are given below :



Sawhorse representation for conformations of ehtene

Pitzer in 1936 found that the rotation is not completely free. Rather there exists a potential energy barrier which restricts the free rotations. It means that the molecule spends most of its time in the most stable staggered conformation and it spends least time in the least stable eclipsed conformation; the energy difference being 12 kL/mole in the case of ethane.



Rotational or torsional energy of ethane

The energy required to rotate the molecule about carbon-carbon bond is called rotational or torsional energy.

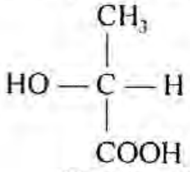
Difference between conformation and configuration

Conformation

Structures containing different arrangement of atoms of a molecule in space which can arise by rotation about a single bond are called *conformers*. For example ethane exists in different conformations called staggered, eclipsed and skew conformations. The energy difference between different conformers is rather small. This phenomenon is called conformation. The property of conformation is also exhibited by *n*-butane, cyclohexane, stilbene dichloride etc.

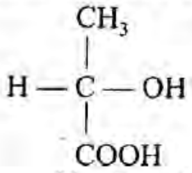
Configuration

Structures of a compound differencing in the arrangement of atoms or groups around a particular atom in space are called *configurations*. Enantiomers, distereomers and geometrical isomers come under this category. For example *d*-and *l*-lactic acids are configurations of lactic acid.



$$\begin{array}{c} CH_3 \\ | \\ HO-C-H \\ | \\ COOH \end{array}$$

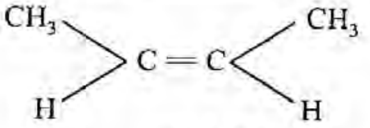
d-lactic acid



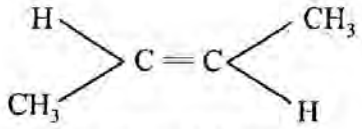
$$\begin{array}{c} CH_3 \\ | \\ H-C-OH \\ | \\ COOH \end{array}$$

l-lactic acid

cis and *trans* butenes are configuration of butene



cis-2-butene



trans-2-butene

Factors affecting relative stability of conformations

The following factors play a vital role in the stability of conformations.

1. Angle strain. Every atom has the tendency to have the bond angles that match those of its bonding orbitals. If there is any deviation from this normal bond angle, the molecule suffers from *angle strain*. Conformations suffering from angle strain are found to be less stable.

2. Torsional strain. There is a tendency on the part of two carbons linked to each other to have their bonds staggered. That is why the staggered form of any molecule like ethane, *n*-butane is most stable. As the bonds of two connected carbons move towards eclipsed state, a *torsional strain* is set up in the molecule thus raising its energy. Thus the staggered conformations have the least and eclipsed the highest torsional strain. The energy required to rotate the molecule around the carbon-carbon bond is called *torsional energy*.

3. Steric strain (van der Waals' Strain). Groups attached to two linked carbons can interact in different ways depending upon their size and polarity. These interactions can be attractive or repulsive. If the distance between the groups or atoms is just equal to the sum of their van der Waals' radii, there will be attractive interactions between them. And if these atom or groups are brought closer than this distance, there will be repulsions leading to *van der Waals' strain or steric strain* in the molecule.

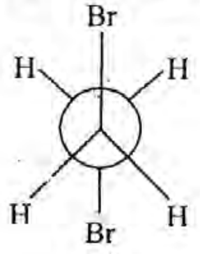
4. Dipole-dipole Interactions. Atoms or groups attached to bonded carbons orient or position themselves to have favourable dipole-dipole interactions. It will be their tendency to have maximum dipole-dipole attractions. Hydrogen bond is a particular case of powerful dipole-dipole attractions.

The stability of a conformer is determined by the net effect of all the above factors.

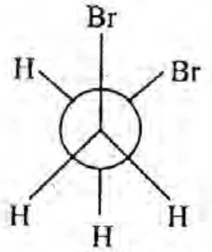
Conformations and change in dipole-moment of 1, 2-dibromoethane with temperature

The conformations of 1, 2 dibromoethane have been extensively studied by dipole-moment measurement. The conformations are depicted as under :

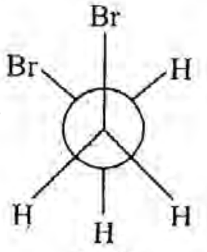
In the liquid state, the percentage of anti forms is 65 corresponding to conformational free energy of 3.5 kJ mol^{-1} in favour of *anti*.



anti



gauche

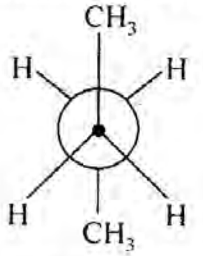


gauche

stability of *anti*-form is due to combined effects of steric factor and dipole-dipole interactions. It goes in favour of formation of *anti*- conformer. Dipole movement increases with increase of temperature.

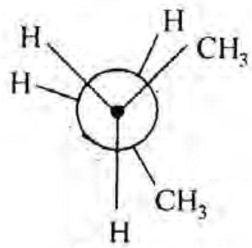
Conformations of butane

n-butane is an alkane with four carbon atoms, which can be considered to be derived from ethane by replacing one hydrogen on each carbon with a methyl group. If we consider the rotation about the central carbon-carbon bond ($C_2 — C_2$), the situation is somewhat similar to ethane; but *n*-butane has more than one staggered and eclipsed conformations (unlike ethane which has only one staggered and one eclipsed conformation). Newman Projection formulae for various staggered and eclipsed conformations of *n*-butane are as given below :



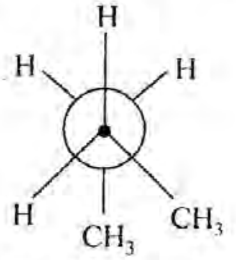
Completely
staggered or anti form

I



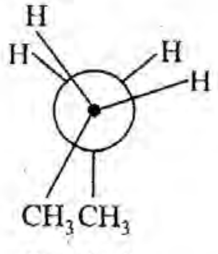
Partially
eclipsed form

II



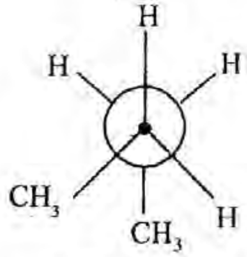
Partially staggered or
gauche form or skew form

III



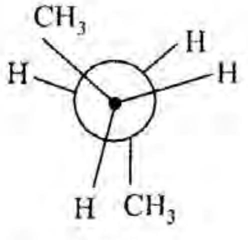
Completely
eclipsed form

IV



Partially staggered
or gauche

V

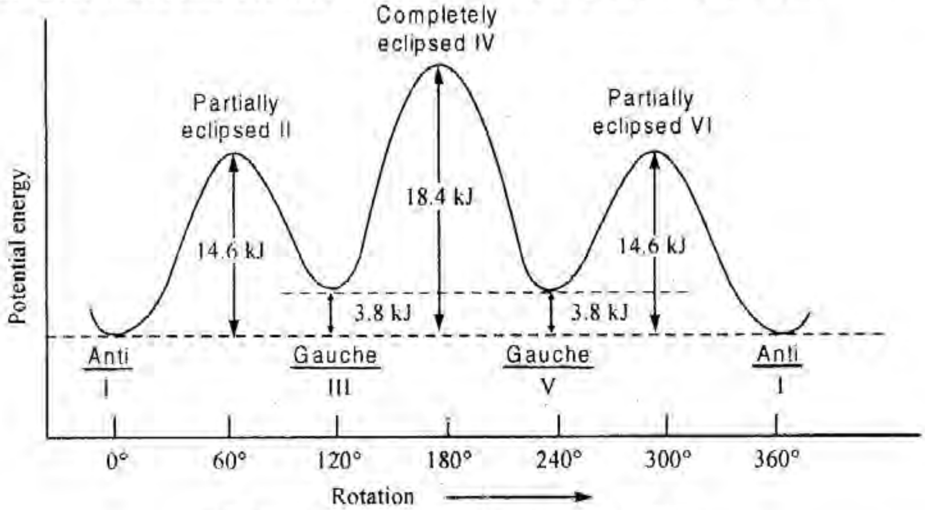


Partially
eclipsed form

VI

The *completely staggered* conformation, (I) also known as *anti* form, is having the methyl goups as far apart at possible. Let us see how these forms have been obtained. Let us start from structure I. Holding the back carbon (represented by circle) fixed along with its groups, — H, — H and — CH_3, rotate the front carbon (shown by a dot) in clockwise direction by an angle of 60°. Groups attached to it will also move. *Partially eclipsed* form (II) is obtained. In this conformation (II), methyl group of one carbon is at the back of hydrogen of the other carbon. Further rotation of 60° leads of a *partially staggered* conformation (III), also known as *gauche* form, in which the two methyl groups are at an angle of 60°. Rotation by another 60° gives rise to a *fully eclipsed* form (IV) having two methyl groups at the back of each other. Further rotation of 60°, again leads to *partially staggered or gauche* form (V) having methyl groups at an angle of 60° (as in III). Still further rotation of 60° leads to *partially eclipsed* form (VI), having methyl group of one carbon at the back of hydrogen of the other (as in II). If a further rotation of 60° is operated (completing the rotation of 360°), again form I is obtained. Of course, there will be an infinite number of other conformations in between these six conformations (I to VI). (*Gauche* form is also known as skew form).

Out of these six conformations, the *completely staggered* or *anti conformation* (I) is most stable and *partially staggered* or *gauche* conformation (III or V) is slightly less stable: the energy difference being only 3.8 kJ/mole. On the other hand the *completely eclipsed* conformation (IV) is least stable and *partially eclipsed* conformation (II or VI) is slightly more stable, again the energy difference being 3.8 kJ/mole. (This is due to presence of steric strain between two methyl groups). The energy difference between most stable conformation (I) and least stable conformation (IV) is about 18.4 kJ/mole while that between I and II (or VI) is about 14.6 kJ/mole.

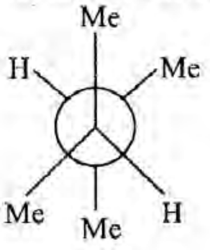


Rotational or torsional energy of *n*-butane.

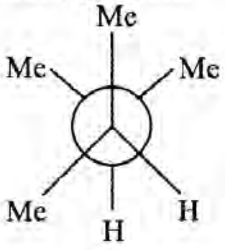
Thus at ordinary temperature, *n*-butane molecule exists predominently in *anti* form with some *gauche* forms.

Conformational enantiomers of 2, 3-Dimethylbutane and 2, 2, 3-Trimethylbutane

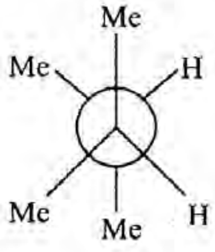
Conformational isomers of 2,3-Dimethylbutane



I



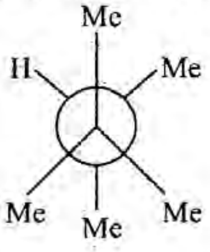
II



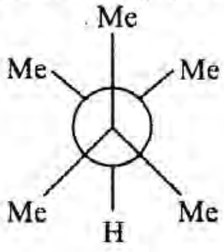
III

Structure I is supposed to have maximum stability out of these three isomers, II and III are conformational enantiomers (mirror-images) also. This can be visualized after rotation of III as a whole.

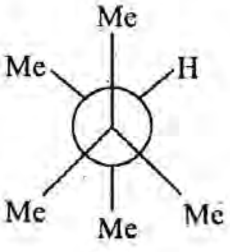
Conformational isomers of 2, 2, 3-Trimethylbutane



I



II



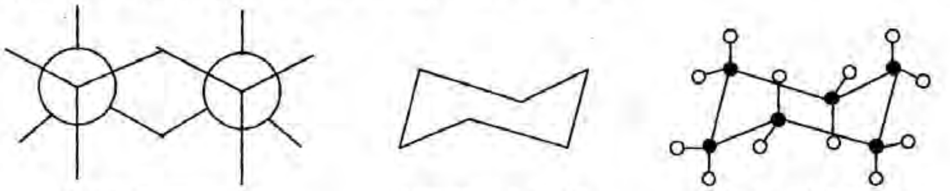
III

All these structures have the same stability and the compound may be assumed to occur in one conformation only.

Conformations of cyclohexane

Chair conformation

Chair conformation of cyclohexane is represented below :



Newman projectioin formula

Usual representation

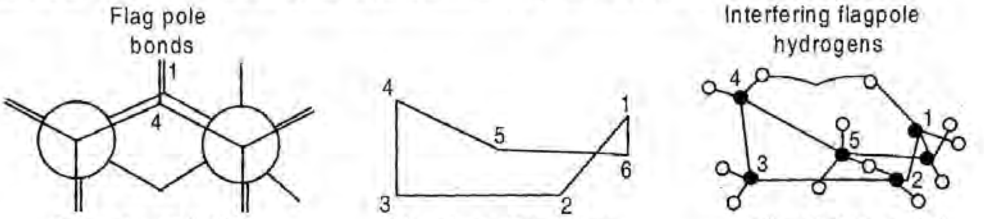
Ball and stick model

Chair conformation of *n*-butane.

This is the most stable conformation of cyclohexane. In this conformation, all the bond angles are tetrahedral and the C — H bonds on adjacent carbons are in a staggered position. This conformation has no strain and has minimum energy.

Boat Conformation

There is no angle strain in the molecule as all the angles are tetrahedral. But hydrogens on four carbon atoms (C_2 and C_3, C_5 and C_6) are eclipsed. As a result, there is considerable torsional strain. Also, two hydrogens pointing towards each other at C_1 and C_4 (called flagpole hydrogens) are very close to each other. This brings in van der Waals strain in the molecule. Due to these reasons boat conformation is less stable than chair conformation by an amount 28.8 kJ/mole.

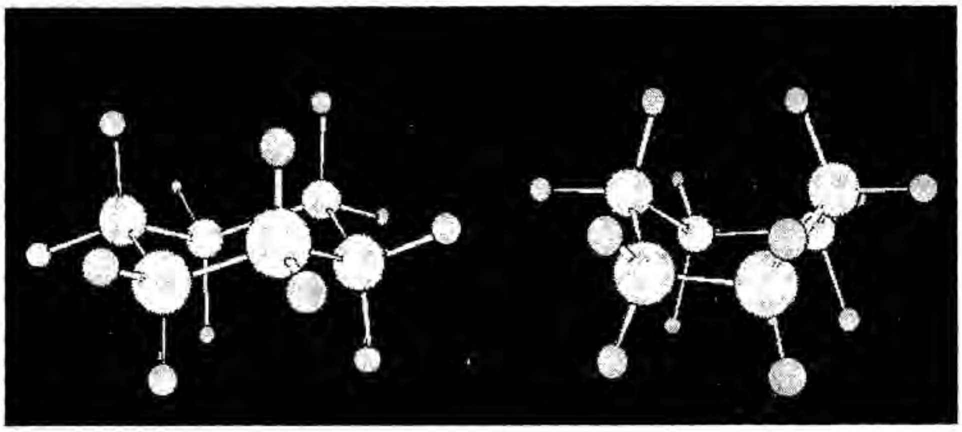


Newman projectioin formula

Usual representation

Ball and stick model

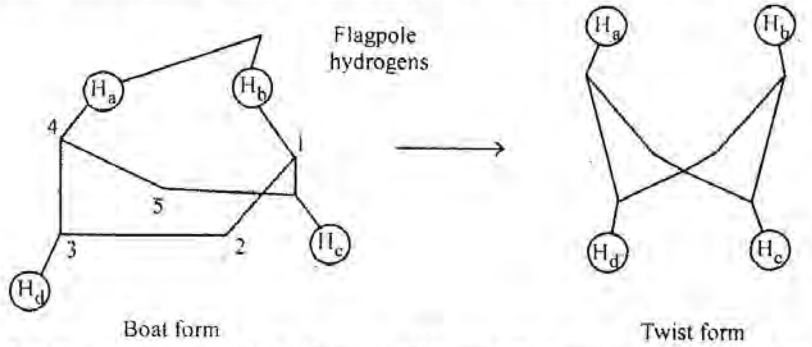
Boat conformation of cyclohexane



Conformations of cycloalkanes

Twist conformation of cyclohexane. Sequence of changes in going from chair form to boat form

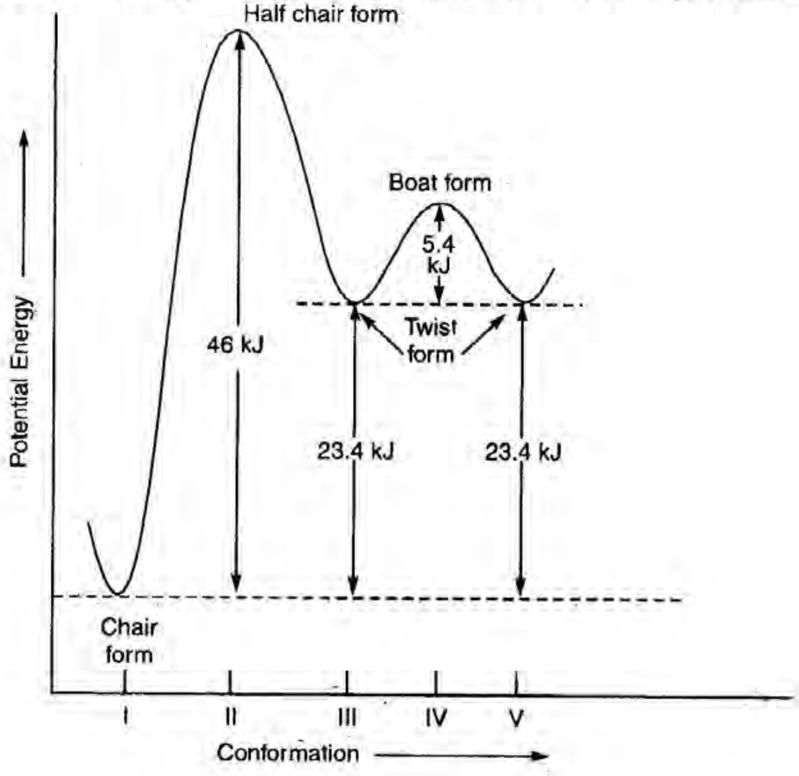
Besides chair and boat conformation, cyclohexane can have several other possible conformations. Consider model of boat conformation of cyclohexane. Hold C_2 — C_3 bond in one hand and C_5 — C_6 in the other and twist the model so that C_2 and C_5 come upwards and C_3 and C_6 go downwards. We will get another conformation known as *twist form* or *skew boat* form.



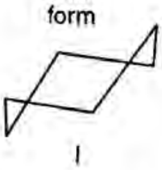
During this twisting, the flagpole hydrogens (H_a and H_b) move apart while the hydrogens H_c and H_d move closer. If this motion is continued another boat form will be obtained in which H_c and H_d become the flagpole hydrogens.

In twist forms the distance between H_a and H_b is equal to that of H_c and H_d and the steric strain is minimum; also the torsional strain of C_2 — C_3 and C_2 — C_6 (due to their being eclipsed) is partly relieved. Thus the twist form is more stable than boat form by about 5.4 kJ/mole, but it is much less stable than chair form by 23.4 kJ/mole.

If we want to convert the chair form into boat form it will have to pass through a half chair form having considerable angle strain and torsional strain. The energy difference between chair form and half chair form being about 11 kcal/mole, half chair form is quite unstable.

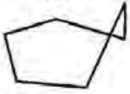


Chair form



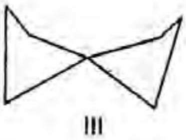
I

Half chair form



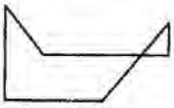
II

Twist form



III

Boat form



IV

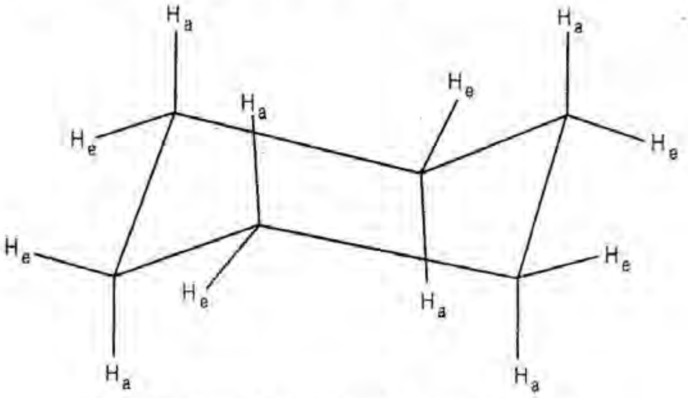
Twist form

V

Equatorial and axial bonds in cyclohexane

Consider the structure of chair form of cyclohexane as given below :

Although, the cyclohexane ring is not planar completely, but for approximation, we can take i. as planar. Consider the position of various hydrogens in the chair conformation. There are two distinct kinds of hydrogens, Six of the hydrogens which are marked H_e are almost oriented within the plane of cyclohexane ring. These are called **Equatorial hydrogen atoms.** The bonds by which these are held to the ring are called **Equatorial bonds.**



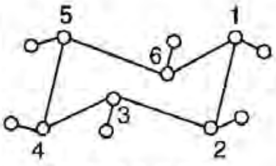
Equatorial and axial bonds in cyclohexane.

We again observe that six hydrogen atoms which are shown as H_a in the figure above are oriented perpendicular to the cyclohexane ring. These are called **Axial hydrogen atoms** and the bonds by which they are held to the ring are called **Axial bonds.**

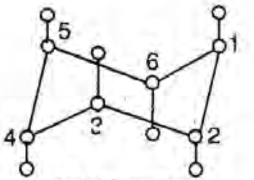
It may be noted that there is one axial and one equatorial hydrogen on each carbon in the chair conformation of cyclohexane.

1, 3-diaxial interaction

Consider the chair model of cyclohexane. Looking at the molecule, we find that six hydrogens lie in the plane while six lie above or below the plane. Six bonds holding hydrogens in the plane are called *equatorial bonds* and six bonds holding hydrogens above or below the plane are called axial bonds. By and large, there is no stress in the molecule and it is as stable as staggered ethane.

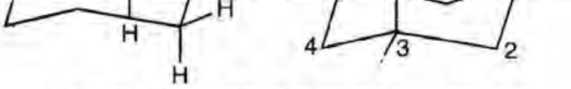


Equatorial bonds



Axial bonds

If a hydrogen is replaced by a larger group or atom, than crowding occurs. Atoms linked by axial bonds on the same side face severe crowding. This interaction is called 1, 3-diaxial interaction. Generally speaking, atoms or groups have more free space in equatorial position than in axial position.



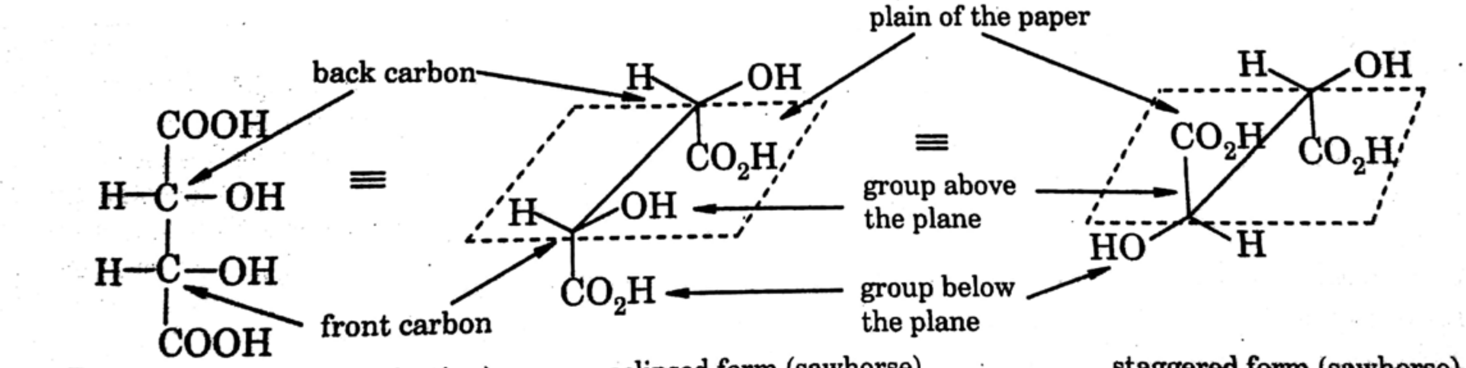
1, 3-diaxial interactions in methyl cyclohexane

There are two possible chair conformations of methyl cyclohexane one with – CH_3 in equatorial position and the other with – CH_3 in axial position.

It is observed that –CH_3 in equatorial position faces less crowding by hydrogens compared to –CH_3 in the axial position. Methyl group in the axial position is approached more closely by axial hydrogens on C – 3 and C – 5. This is called *1, 3-diaxial interaction*.

Wedge, Fischer, Newmann and Sawhorse Projection interconversions

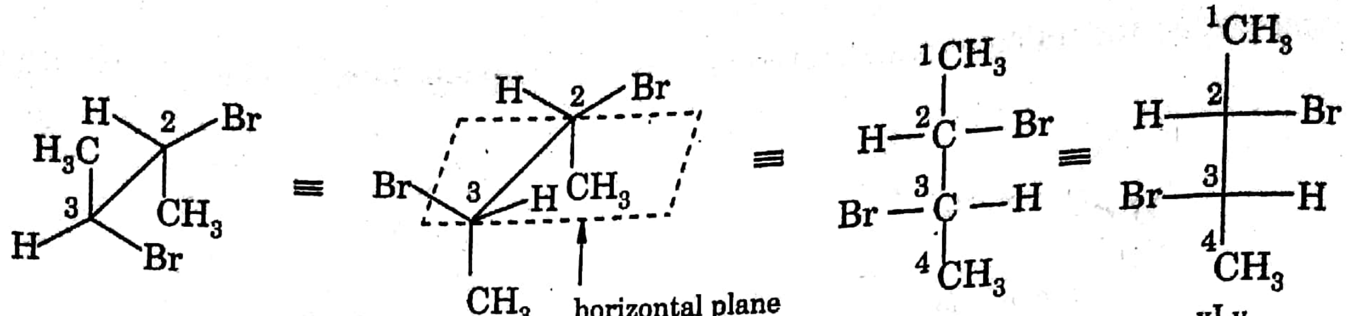
- ***Fischer projection to Sawhorse and vice -versa*:**



meso-Tartaric acid (Fisher projection)

eclipsed form (sawhorse)

staggered form (sawhorse)



2,3 - Dibromobutane
(*threo*- enantiomer)
sawhorse of staggered form

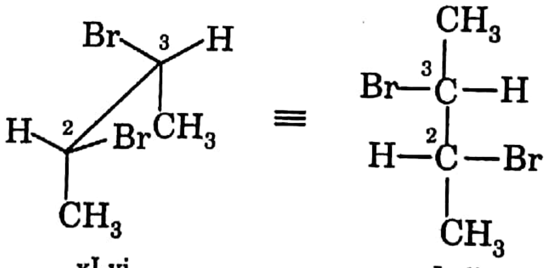
sawhorse projection
eclipsed form

xLv
Fischer projection

Fig. 2. 66

It is evident from the above examples that conversions of Fischer to sawhorse and *vice-versa* can be easily carried out through eclipsed form of sawhorse with proper numbering of carbon atoms, otherwise transformation may lead to a mirror image (other enantiomer). In conversions, the last chiral centre in Fischer projection (counting from the top) may be considered as the front carbon in sawhorse formula. In transposing chiral centres of eclipsed sawhorse to Fischer, if we write the front carbon as back and *vice-versa* then we will actually get the mirror image of the original configuration.

For example, in case of 2,3-dibromobutane (as shown in the above example,xLv) if the sawhorse form is written as C-2 in front and C-3 as back carbon, then the eclipsed form becomes (xLvi) and its Fischer projection will be as shown by structure (xLvii). (xLvii) is in fact the mirror image of (xLv). Therefore, we are getting the mirror image configuration of the original stereoisomer (xLv).

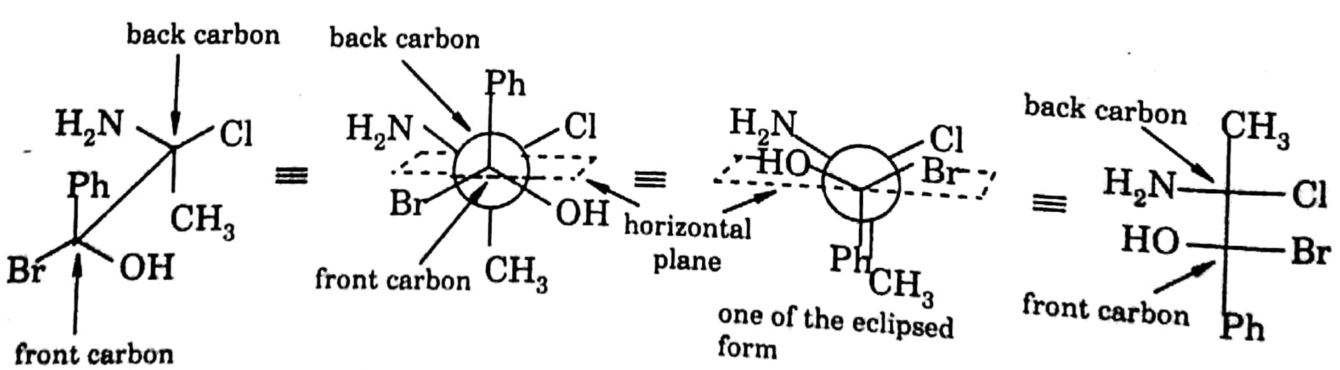


xLvi

xLvii

Fig. 2. 67

• ***Sawhorse to Newman to Fischer and vice-versa*:**



sawhorse Projection
(staggered)

Newman Projection
(staggered)

Newman Projection
(eclipsed)

Fischer
Projection

Fig. 2. 68

It should be remembered that in eclipsed form of Newman projection, the vertical bonds may be arranged in such a way that they remain below the horizontal plane, as shown above shown by dotted line, and transformation to Fischer projection is then carried out keeping front chiral atom as the lowest chiral centre in the Fischer projection (counting from the top).

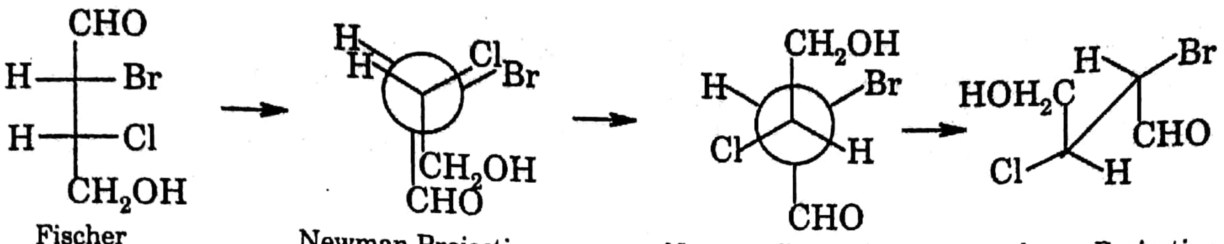
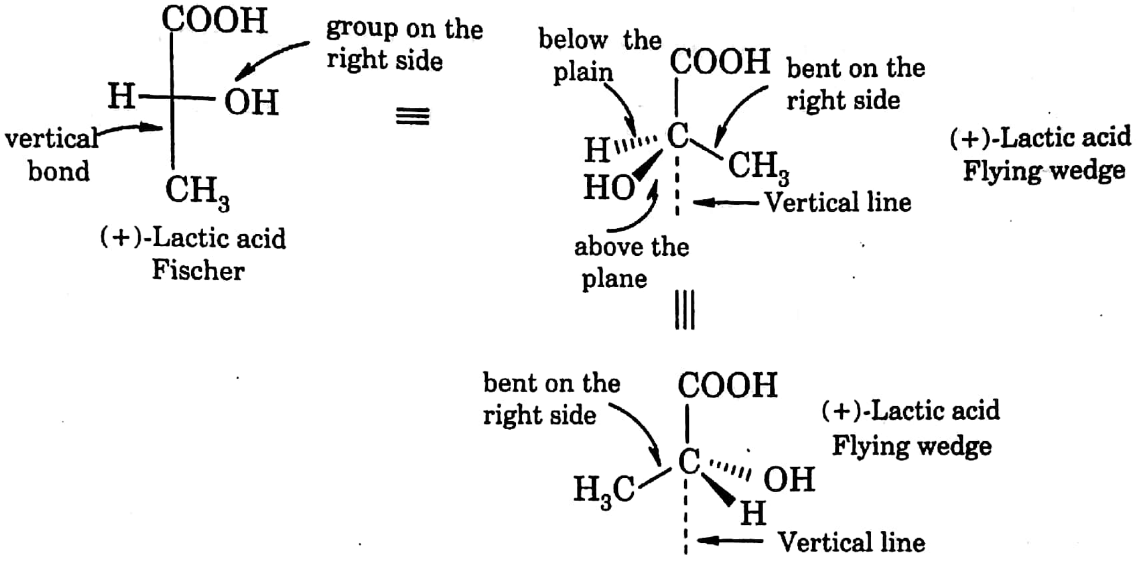

Fischer Projection
Newman Projection eclipsed
Newman Projection staggered
sawhorse Projection staggered

Fig. 2. 69

• *Fischer Projection to Flying wedge and vice-versa:*

Conversion of Fischer projections to flying wedge and *vice-versa* may be carried out as follows.



xLviii

xLix

Lactic acid Fischer projection

Flying wedge

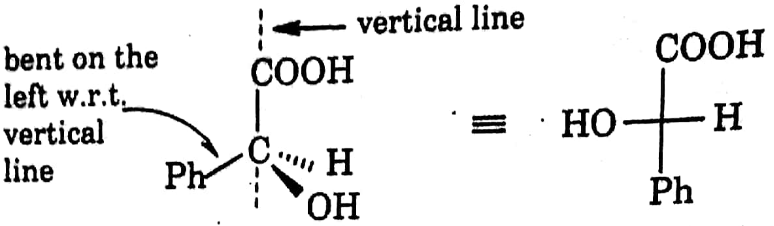
Flying wedge

Fig. 2. 70

In the above example (Fig. 2.70) Fischer projection of one of the stereoisomers of lactic acid is converted into flying wedge (xLviii, xLix) forms. In doing so, vertical bonds in Fischer projection are considered to be in the plane of the paper and horizontal bonds are to be above and below the plane.

Note that when lower vertical bond linked to -CH_3 group in Fischer projection is bent on the right side in xLviii, the group (–OH) on the right side in the horizontal bond in Fischer projection should be written above the plane of the paper (represented by solid wedge, (▬), the H atom, therefore, should be placed below the plane (represented by hashed wedge, ⋯⋯), If the lower bond linked to CH_3 group in Fischer projection is bent on the left side (as in xLix), the group on the left side in the horizontal bond in Fischer projection is to be placed above (▬) the plane of the paper and group on the right side (H) should be placed below (⋯⋯) the plane. Thus, both xLviii and xLix represent the flying wedge forms of Fischer projection of same isomer of lactic acid, shown above.

The reverse method may be followed to convert a flying wedge representation to Fischer projection. An example is given below (Fig. 2.71).



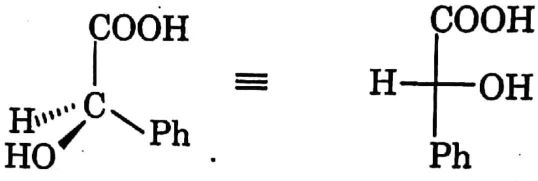
flying wedge Projection
(Mandelic acid)

Fischer projection

Fig. 2. 71

In the above example, CO_2H and Ph groups are in the plane of the paper in flying wedge representation. In transforming into Fischer projection, the OH group, which is above the plane in flying wedge structure, is put on the left in horizontal bond in Fischer projection, because Ph group in flying wedge projection is bent on the left side with respect to the vertical lines in Fischer projection.

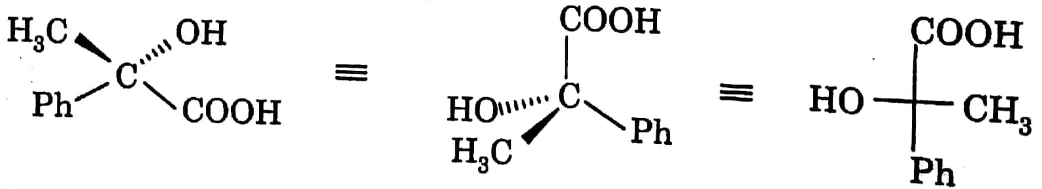
A few more conversions of different flying wedge forms to Fischer projections are given below (Fig. 2.72- 75)



(a) Mandelic acid
Flying wedge projection

Fischer projection

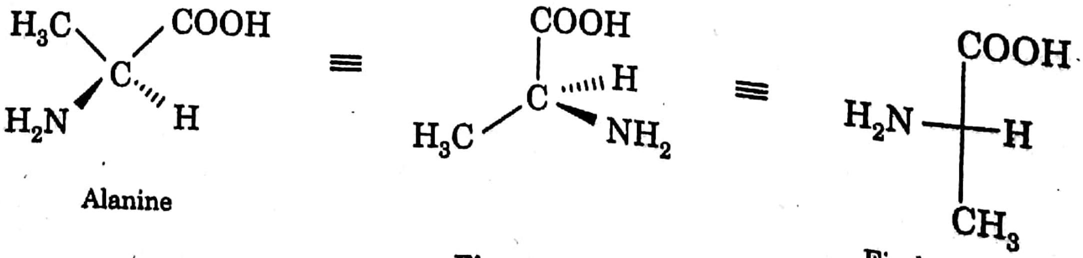
Fig. 2. 72



(b) Atrolactic acid

Fischer projection

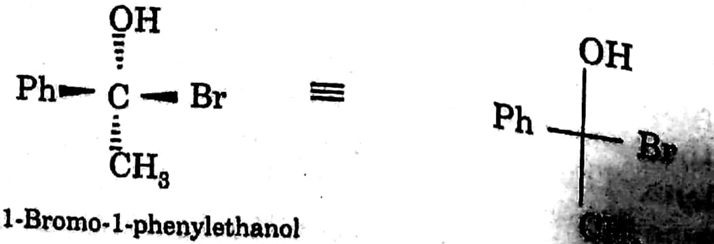
Fig. 2. 73



(c) Alanine

Fischer projection

Fig. 2. 74



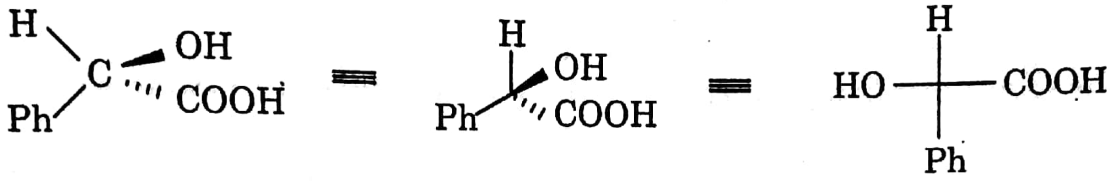
(d) 1-Bromo-1-phenylethanol

Fischer projection

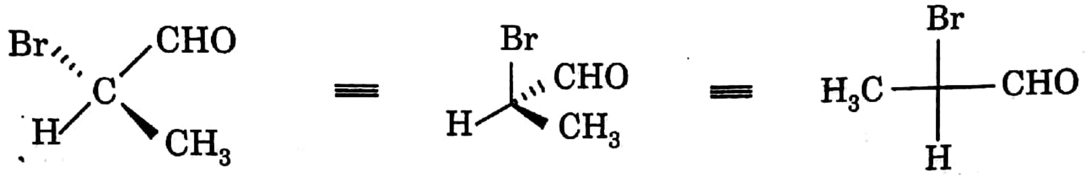
Fig. 2. 75

In the above example (d), horizontal bonds are shown above the plain and vertical bonds below the plain and these are in accordance with the Fischer convention. Therefore, in Fischer projection, the positions of atoms and groups are retained as they were in the form showing by solid and broken bonds.

(e)



(f)



(g)

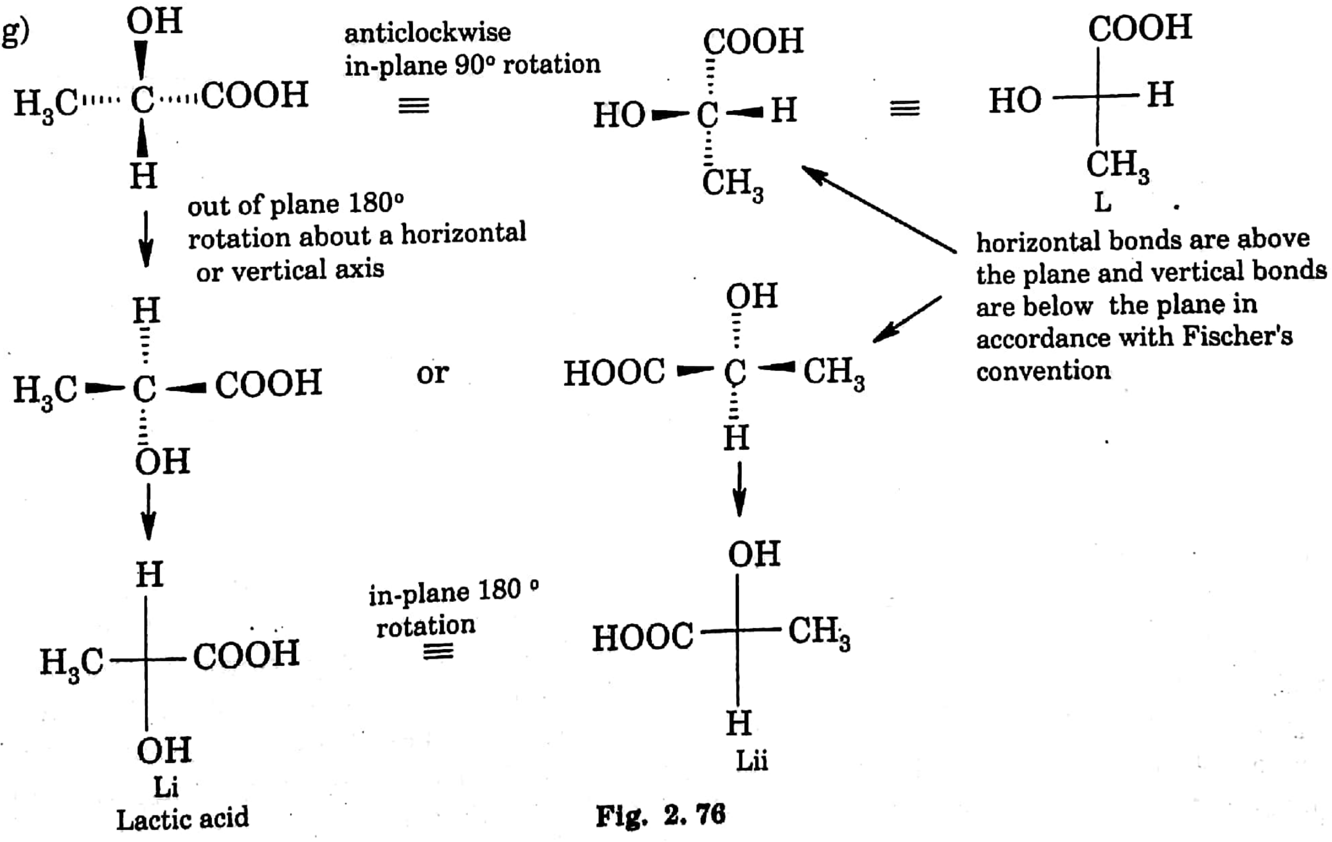


Fig. 2. 76

In example (g), the given structure is not the correct representation in accordance with the Fisher projection , because vertical substituent are shown above the plain and horizontal substituent are shown below. This is in contrary to Fisher's convention. Therefore, the given structure is rotated in- plain by 90⁰ or out of- plane by 180⁰. These operations give the correct representation of the lactic acid according to the Fisher's convention. The structures (L), (Li) and (Lii) are identical configurations and represent the same isomer of the lactic acid.

The structure (f) is another way of representing three-dimensional form of a stereoisomer. It can also be easily transformed into Fischer projection in the way shown below.

(h)

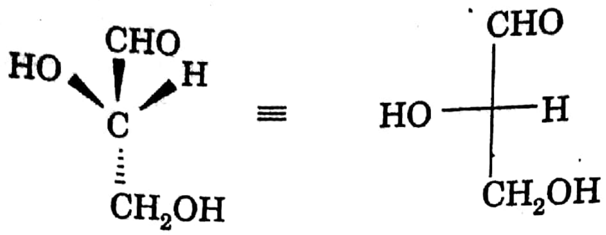
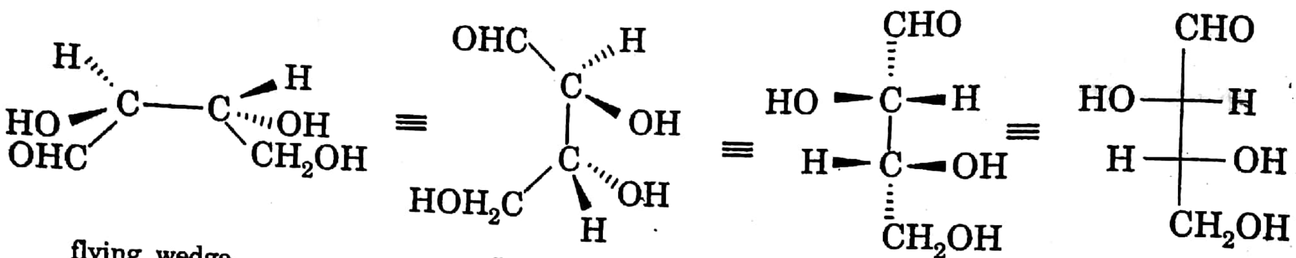


Fig. 2.77

- ***Flying wedge containing more than one chiral centre to Fisher projection and vice versa:***

Flying wedge structures of stereoisomers containing two stereocentres can similarly be converted into Fischer projection and *vice-versa*. A few examples are given below in Fig. 2.78 and 2.79.



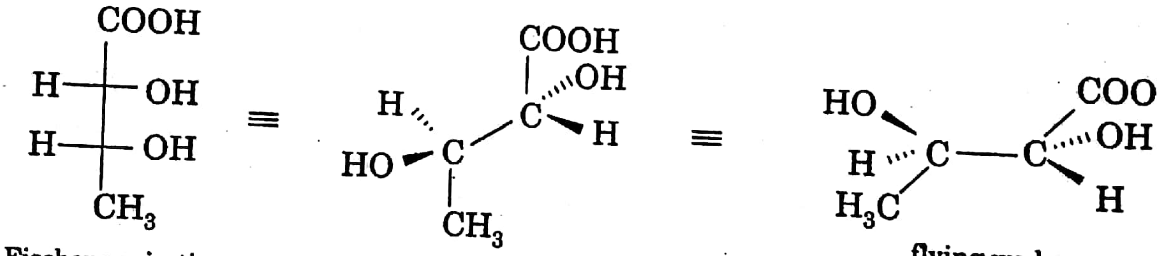
flying wedge

flying wedge

Fischer projection

Fischer projection

Fig. 2. 78

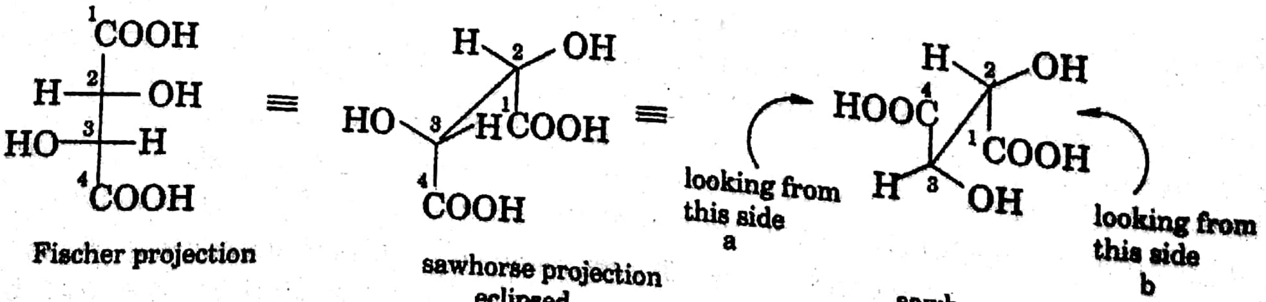


Fischer projection

flying wedge

Fig. 2. 79

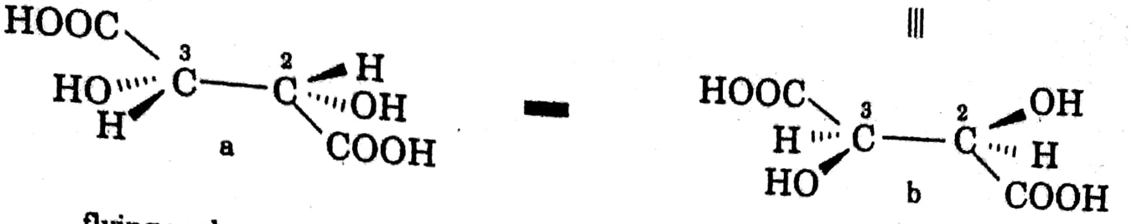
Fischer projection can be transformed into sawhorse form and then to flying wedge structure. An example is shown below (Fig. 2.80). It must be remembered that the same stereoisomer can be represented by eighteen different Fischer projections. In the example below, one Fischer projection of *threo*-tartaric acid (active) is first transformed into sawhorse in eclipsed conformation and then converted into desired staggered form. The same structure can be written in other eclipsed and staggered forms also. Then the staggered form is transferred into flying wedge looking from two directions (a) and (b).



Fischer projection

sawhorse projection eclipsed

sawhorse projection staggered

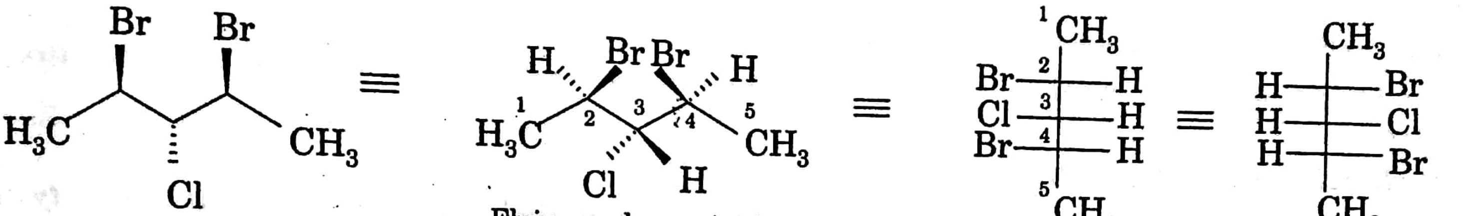


flying wedge (staggered) projection

flying wedge (staggered) projection

Fig. 2.80

• *Zigzag form to Fischer Projection:*



zigzag form

Flying wedge projection

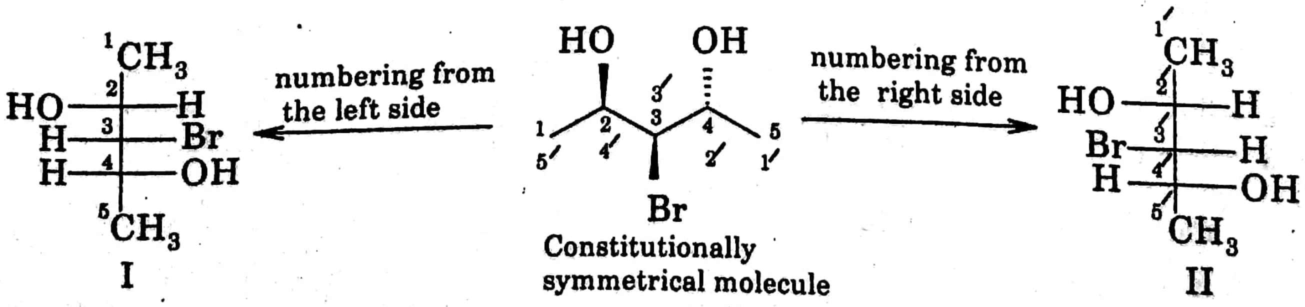
Fisher projection (*meso*-compound)

Fisher projection (*meso*-compound)

Fig. 2.81

In the above zigzag structure, H atoms, according to convention, are not drawn. Therefore, zigzag form is first converted in to flying wedge projection by inserting H atoms above and below the plain of the carbon-backbone as the structure demands. It is then converted into Fisher projection by applying the technique discussed earlier

It is to be noted that in the above example, carbon-backbone is numbered from the left side and C-1 is placed at the top in the Fisher projection. Since the compound is symmetrical, the structure can also be numbered from the right side, when we can get the mirror- image Fisher projection of the previous Fisher projection of the same compound. However, in this particular case both are same *meso*-compound (superimposable). In case of a symmetrical molecule, numbering can be done from either end of the carbon chain leading to two apparently different Fischer projections but they are homomers. In unambiguous case numbering should follow IUPAC rules. Two more examples are given below for more illustrations.



I and II are homomers because one can be superimposed on the other by 180° in-plane rotation.