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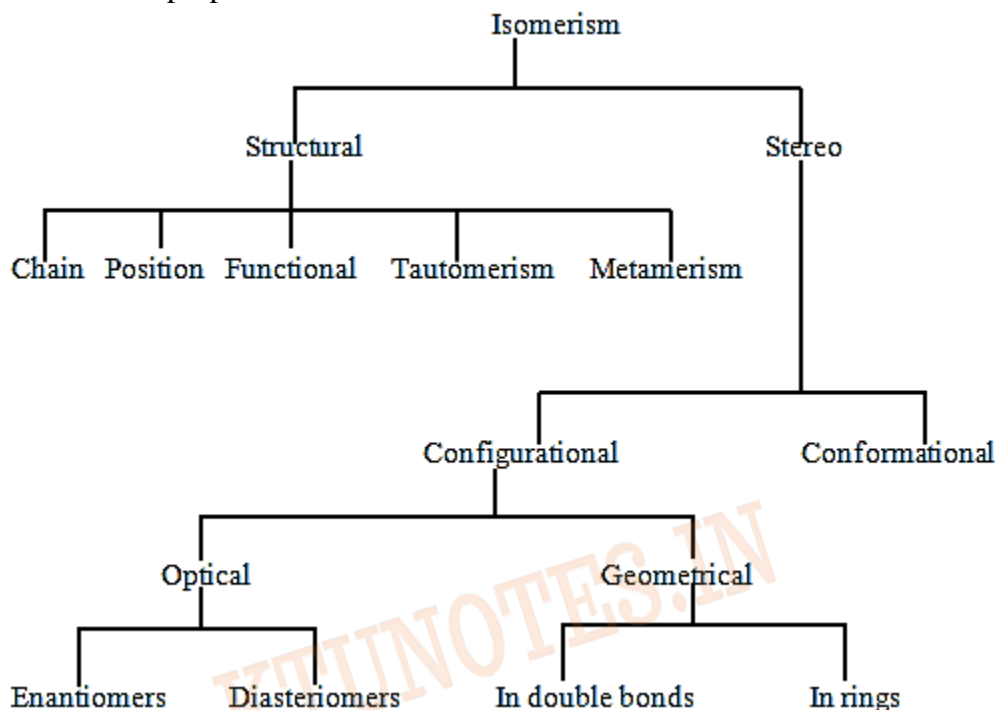
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## MODULE IV

### Stereochemistry and Polymer Chemistry

#### Stereochemistry:

Stereochemistry is the branch of chemistry which deals with the spatial arrangement of atoms or groups in a molecule. Organic compounds with same molecular formula but different structures are called isomers. This phenomenon is called isomerism. Isomers differ in their physical and chemical properties.

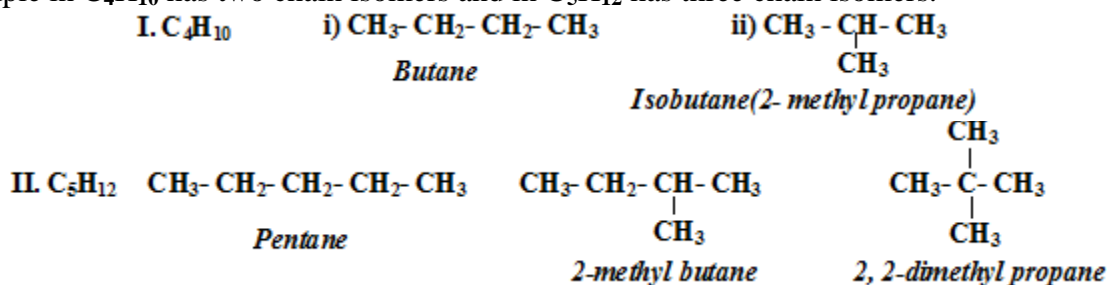


#### Structural isomerism

Isomerism arises due to the difference in the arrangement of atoms within the molecule and is independent of the position of atoms in the space around the molecule. Structural isomerism is of different types.

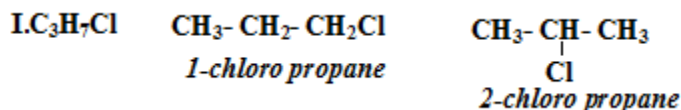
##### 1. Chain (nuclear) isomerism:

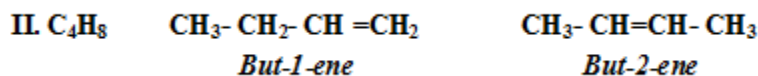
It arises due to the different arrangement of carbon atoms in a carbon chain or skeleton, for example in  $C_4H_{10}$  has two chain isomers and in  $C_5H_{12}$  has three chain isomers.



##### 2. Position isomerism

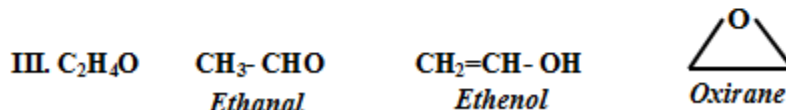
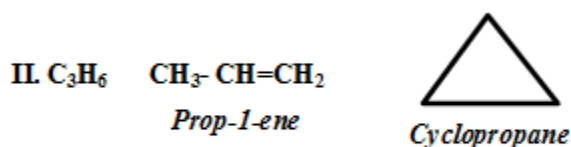
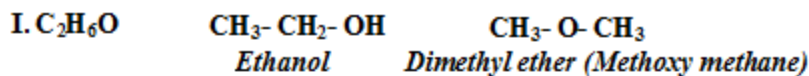
It arises due to the different position of atoms or groups in a carbon chain.





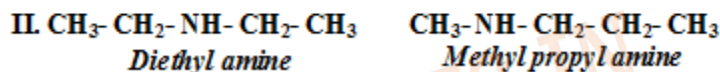
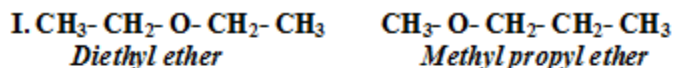
### 3. Functional isomerism

It arises due to the difference in the functional groups attached to the carbon chain.



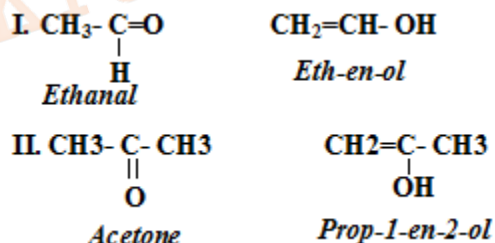
### 4. Metamerism

It arises due to the unequal distribution of carbon atoms on either side of the functional group.



### 5. Tautomerism

It is a type of functional isomerism. When two isomers are mutually interconvertible and exist in dynamic equilibrium, they are called tautomers and this phenomenon is called tautomerism.



### II. Stereo isomerism:

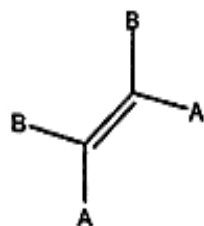
Isomerism arises due to the difference in the spatial arrangement of atoms is called stereo isomerism. This can be divided into conformational isomerism and configurational isomerism. In conformational isomerism, the isomers go on changing into another rapidly due to the rotation about single covalent bonds and cannot be separated. In configurational isomerism, the isomers do not change into one another automatically. These isomers can be interconverted only by breaking and remaking of covalent bonds. Configurational isomerism can be divided into geometrical isomerism and optical isomerism.

#### 1. Geometrical isomerism:

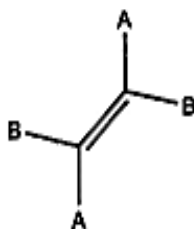
Isomerism arises due to the different spatial arrangement of atoms or groups around a double bond or ring structure is called geometrical isomerism.

##### a) Geometrical isomerism in double bonds:

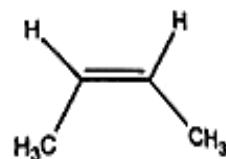
When carbon atoms are joined by a double bond, free rotation about the bond is restricted and the two substituents on each carbon atom are different, geometrical isomerism arises.



Cis- form



Trans-form



(cis)-but-2-ene

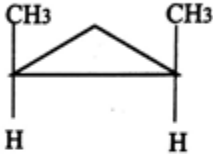
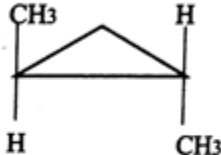
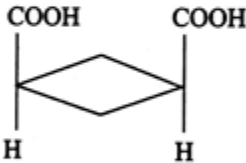
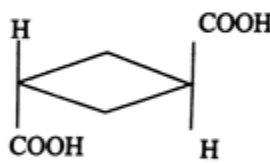
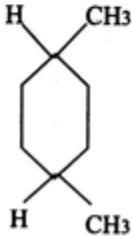
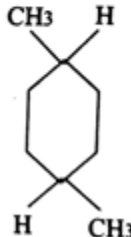
### Examples

No	Compound	Cis-Isomer	Trans-Isomer
1	1,2 -Dichloroethane		
2	Maleic & Fumaric Acids	<p>Maleic Acid</p>	<p>Fumaric Acid</p>
3	2-Butene		
4	Crotonic & Isocrotonic acid	<p>Crotonic acid</p>	<p>Isocrotonic acid</p>

b) Geometrical isomerism in cyclic structures:

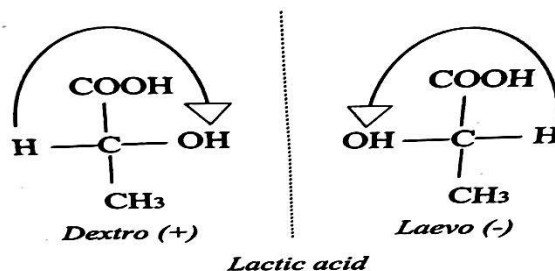
Geometrical isomerism arises in cyclic structures or ring compounds due to the restricted free rotation of carbon atoms about their axis.

### Examples

No	Compound	Cis-Isomer	Trans-Isomer
1	1,2-Dimethyl cyclopropane		
2	Cyclobutane dicarboxylic acid		
3	1,4-Dimethyl cyclohexane		

### Optical isomerism (Enantiomerism)

Substances which have the ability to rotate the plane polarized light towards right or left are called optically active substances. This phenomenon of rotating plane polarized light is called optical activity. Substances which rotate the plane polarized light clockwise is called dextrorotatory and is indicated as d or + whereas substances which rotate the plane polarized light anticlockwise is called laevorotatory and is indicated as l or -. The d and l isomers have same degree of rotation but opposite sign. Optically active isomers of a compound forms non-super imposable mirror images are called **enantiomers or enantiomorphs**. Example, Lactic acid



Conditions for optical isomerism

- ❖ Molecule should possess chiral carbon atom.
- ❖ Molecule should not super impose on its mirror image.
- ❖ Molecule should not have plane of symmetry.

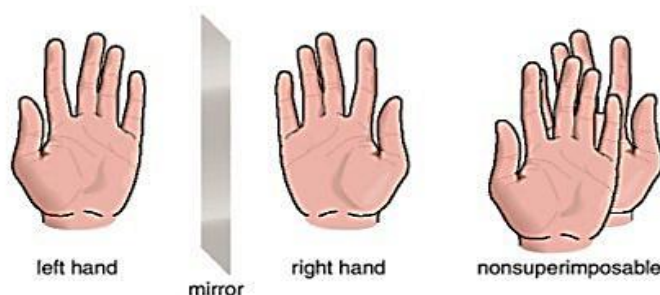
If a molecule possess plane of symmetry its mirror image will be superimposable and optically active. All planar molecules are optically inactive since they possess plane of symmetry. For example, a man standing in front of a mirror with his both hands down has a plane of symmetry and the mirror image is superimposable. If he raises right hand while keeping left hand down, he

does not possess plane of symmetry. The mirror image has left hand up and right hand down, the mirror image will not be superimposable.

## Stereoisomers

### Chiral and Achiral Molecules:

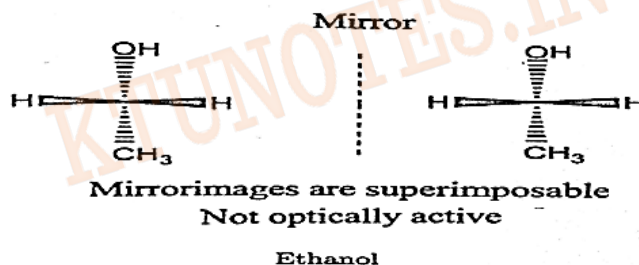
- Some molecules are like hands. Left and right hands are mirror images, but they are not identical, or superimposable.



- A molecule (or object) that is *not* superimposable on its mirror image is said to be *chiral*.

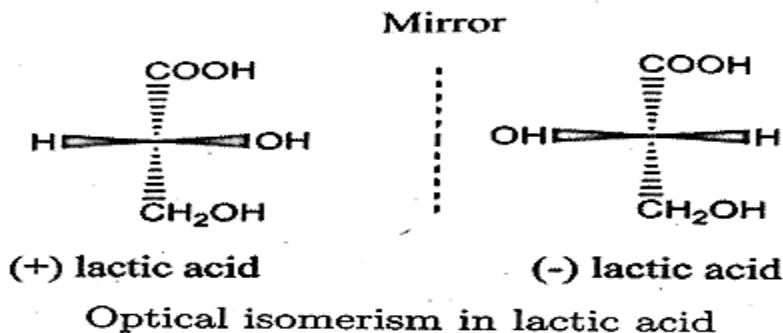
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If two groups around a carbon atom are the same, the mirror image is superimposable and the molecule is not optically active example ethanol.



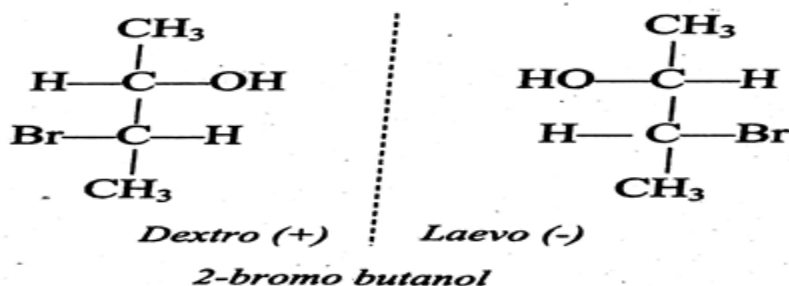
Ethanol

If a molecule possesses one chiral carbon atom it has  $2^1 = 2$  optical isomers. They are related to each other as mirror images. Example lactic acid. (+) lactic acid is having specific rotation  $+2.67^\circ$  whereas its mirror image (–) lactic acid is having specific rotation  $-2.67^\circ$ . Lactic acid present in sour milk is (+) lactic acid. Equimolar mixture of + and – forms of an optically active substance is called racemic mixture. It is having net optical rotation zero and is optically inactive due to external compensation. It is represented as dl or  $\pm$ .



### Properties of enantiomers:

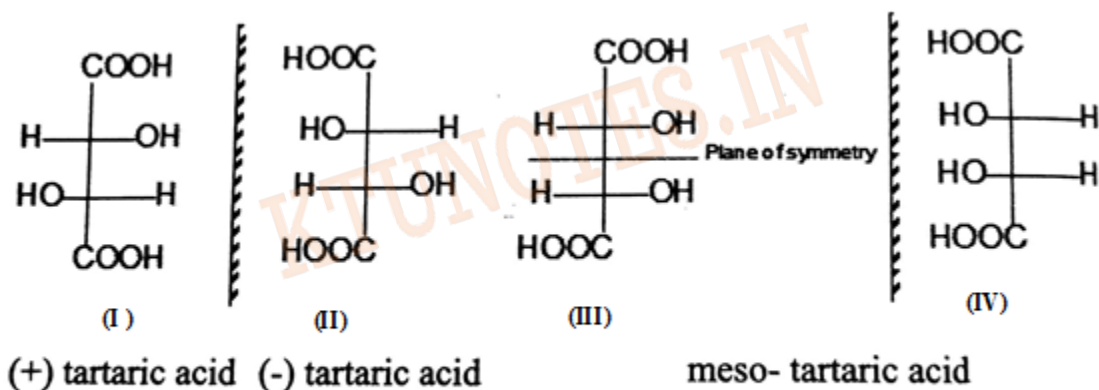
Optically active non-super imposable mirror images of a compound are called enantiomers.



- They have identical properties in all respects except in their interaction with plane polarized light.
- They have identical chemical properties, but differ in their reactivity with optically active reagents.
- They have different biological properties.

### Diastereomers:

The stereoisomers which are non-superimposable and are not related as object and mirror images are called diastereoisomers. Due to the difference in the free energy they have different physical and chemical reactivity. Since they differ in physical and chemical properties, they can be separated by crystallization or chromatography.



(I) & (II) are being mirror images of each other, are enantiomers. But (III) & (IV) are not mirror images of each other are termed as diastereoisomers.

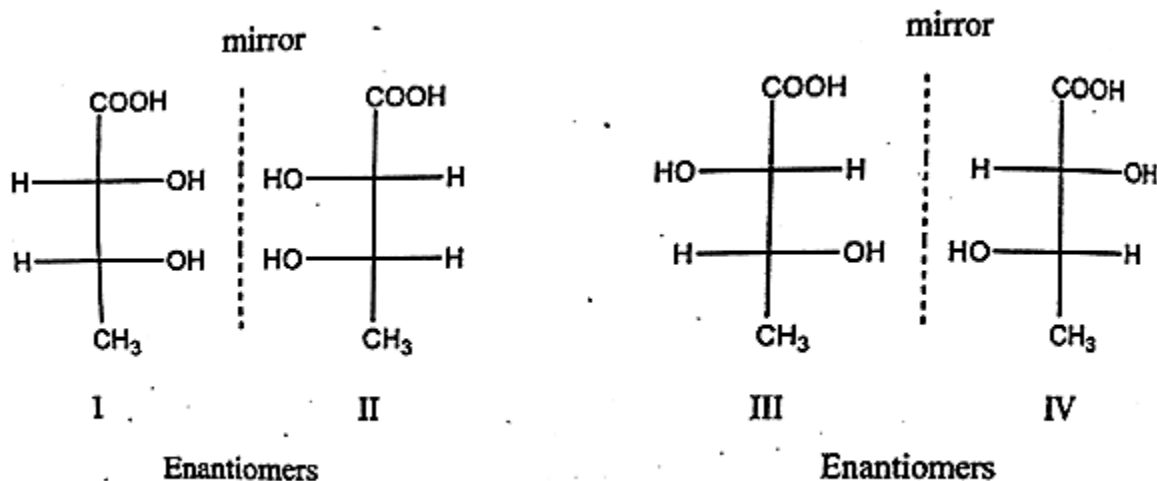
### Comparison of enantiomers & diastereomers

Enantiomers	Diastereomers
Have identical physical properties	Have different physical properties
Have identical chemical properties	Have similar but not identical chemical properties
Cannot be separated by physical methods	Can be easily separated by physical methods such as chromatography, fractional distillation etc.
Originates from chirality.	May result from chirality or from cis-trans isomerism.
Cis-trans isomers are not enantiomers	Cis-trans isomers are always diastereomers.

### Molecules having two asymmetric carbon atoms with different terminal groups:

Example, 2, 3-dihydroxy butanoic acid,  $\text{CH}_3\text{--}^*\text{CH}(\text{OH})\text{--}^*\text{CH}(\text{OH})\text{--COOH}$ , here carbon atoms marked with \* are asymmetric. If there are two asymmetric carbon atoms,  $2^2 = 4$  optical isomers are possible. They are

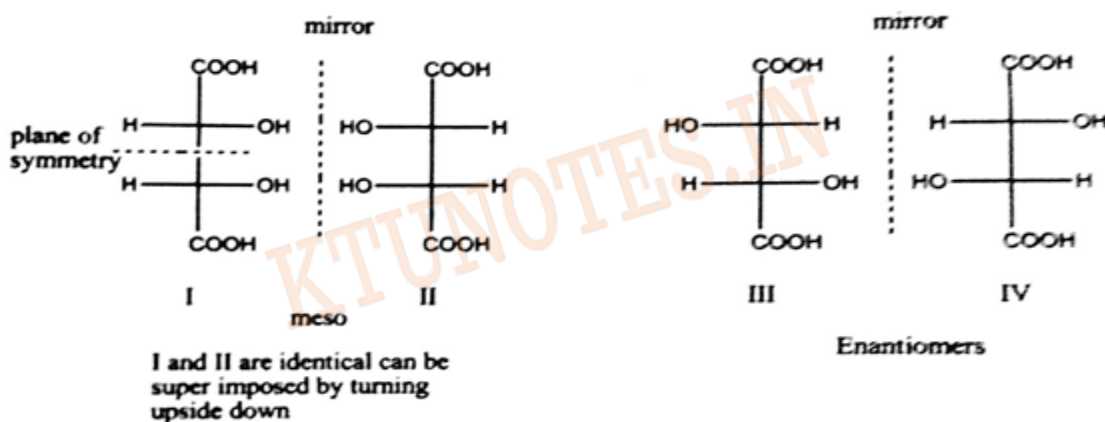




### Optical isomerism in 2,3-dihydroxy butanoic acid

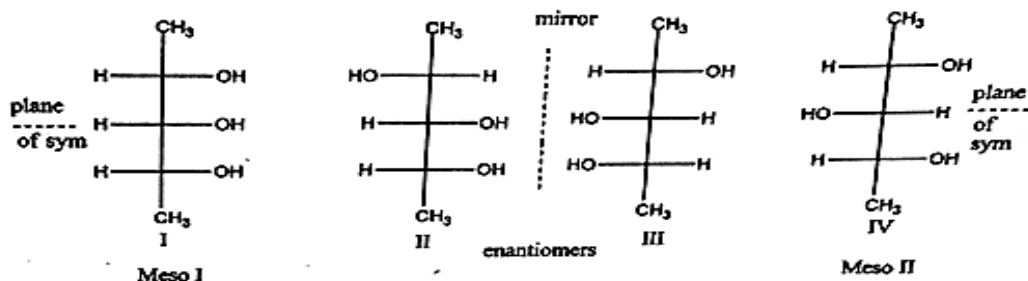
#### Molecules having two asymmetric carbon atoms with same terminal groups:

Example, tartaric acid,  $\text{COOH}-\text{*CH}(\text{OH})-\text{*CH}(\text{OH})-\text{COOH}$ , here there are two asymmetric carbon atoms,  $2^2 = 4$  optical isomers are expected but since terminal groups are identical, only one enantiomeric pair and an optically inactive form called meso exists (total 3 forms).



### Optical isomerism in tartaric acid

1. How many optical isomers are possible for  $\text{CH}_3-(\text{CHOH})_3-\text{CH}_3$



### Optical isomerism in $\text{CH}_3 - (\text{CHOH})_3 - \text{CH}_3$

Four optical isomers, two enantiomer and two meso forms (meso-I & meso-II)

2. Which of the following molecules are optically active?

(a)  $\text{CH}_3-\text{CH}_2-\text{OH}$  (b)  $\text{CH}_3-\text{CH}(\text{NH}_2)-\text{CHO}$  (c) 2-butanol (d) trans-but-2-ene.

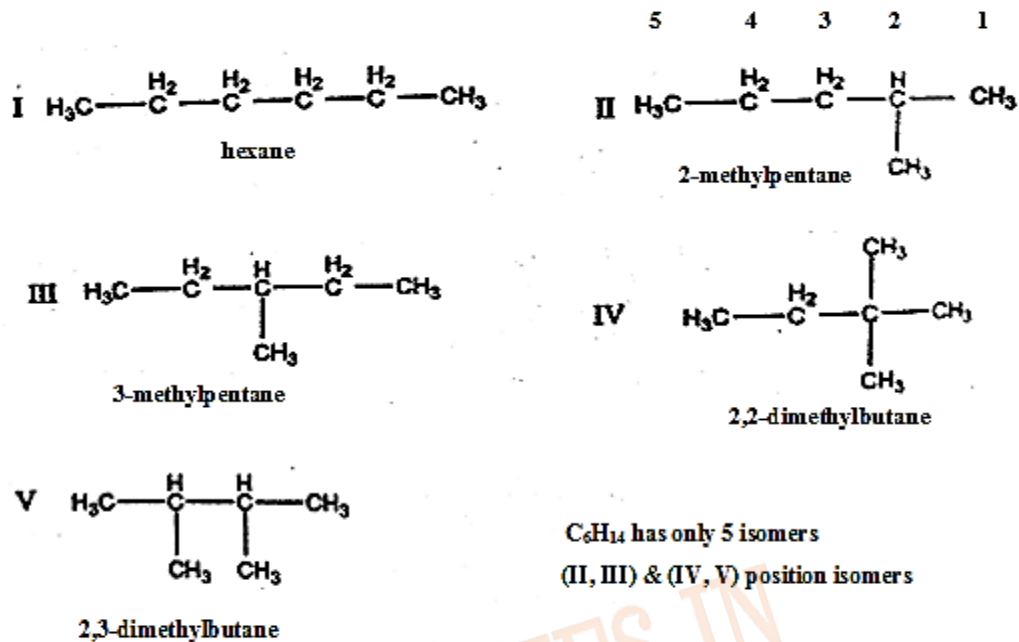


In  $\text{CH}_3-\text{*CH}(\text{NH}_2)-\text{CHO}$ , here all the four groups around the marked carbon atoms are different.

In butanol,  $\text{CH}_3-\text{CH}_2-\text{*CH}(\text{OH})-\text{CH}_3$ , here also all the four groups around the marked carbon atoms are different.

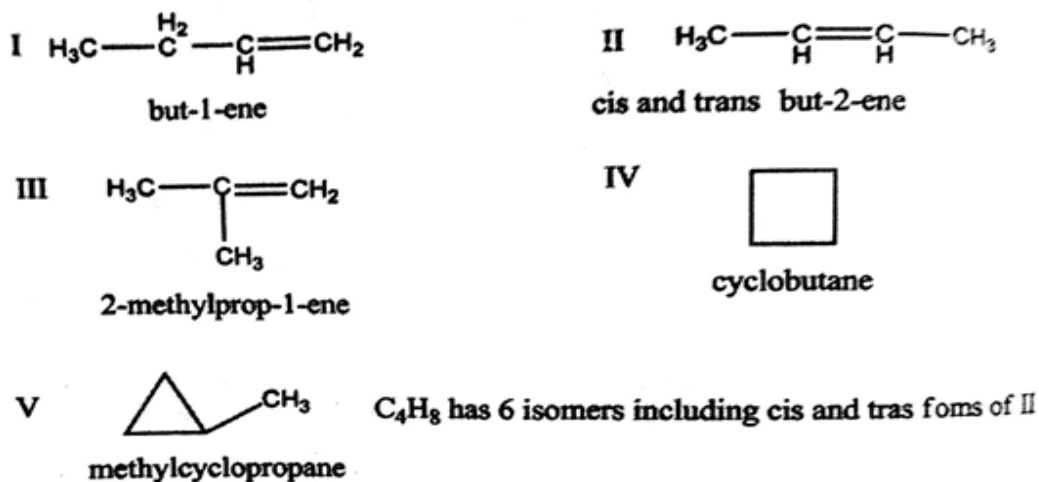
So (b) & (c) are optically active.

3. How many isomers are possible for  $\text{C}_6\text{H}_{14}$ ?



Isomers of  $\text{C}_6\text{H}_{14}$

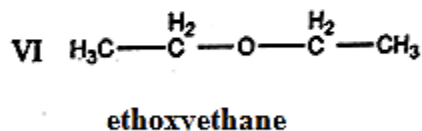
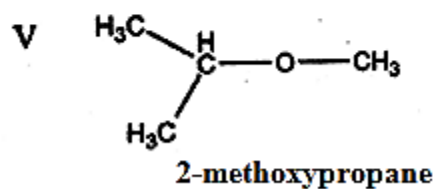
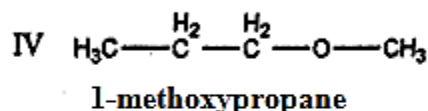
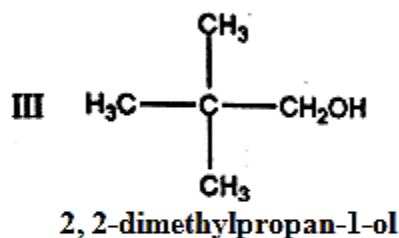
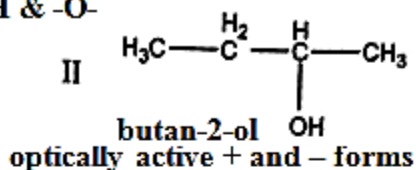
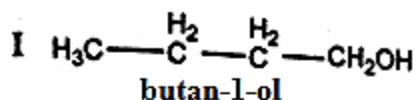
4. How many isomers are possible for  $\text{C}_4\text{H}_8$ ?



Isomers of  $\text{C}_4\text{H}_8$

5. How many isomers are possible for  $\text{C}_4\text{H}_{10}\text{O}$ ?

The possible functional groups are  $\text{-OH}$  &  $\text{-O-}$



$\text{C}_4\text{H}_{10}\text{O}$  has seven isomers including optically active forms

6. Which of the following compounds are optically active?

(Cis) 1, 2-dimethyl cyclopropane, (Trans) 1, 2-dimethyl cyclopropane, (Cis) 1, 3-dimethyl butane, (Trans) 1, 2-dimethyl butane, (Cis) 1, 2-dimethyl cyclohexane, (Trans) 1, 2-dimethyl cyclohexane

(Trans) 1, 2-dimethyl cyclopropane & (Trans) 1, 2-dimethyl cyclohexane are optically active.

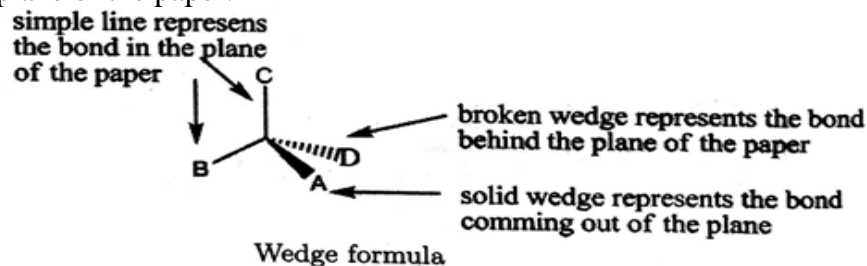
### Three dimensional representations of organic molecules

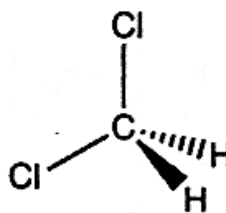
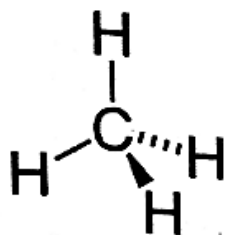
Three dimensional representations of structures are important in stereochemistry. The  $\text{SP}^3$  hybridized C-atom has tetrahedral structure with a bond angle of  $109.5^\circ$ . Wedge formula, Fischer projection formula, Saw-Horse formula, Newman projection formula etc are used to represent 3D structures.

#### Wedge formula

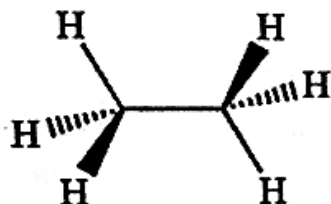
Wedge formulas are the most popular representations used to represent 3D shape and are suitable showing the structures of  $\text{SP}^3$  hybridized (tetrahedral) atoms. A Wedge formula represents a molecule in which three types of lines are used to represent 3D structure.

- Solid lines to represent bonds which are in the plane of the paper.
- Dashed lines to represent bonds that extend away from the viewer or the bonds behind the plane of the paper.
- Wedge (dark thick) lines to represent bonds oriented facing the viewer (bonds coming out of the plane of the paper).

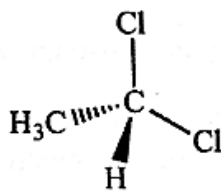




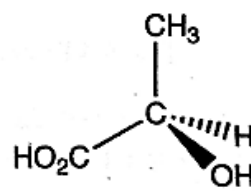
Wedge Projection of Methane and dichloromethane molecules



Ethane



1,1 Dichloro ethane



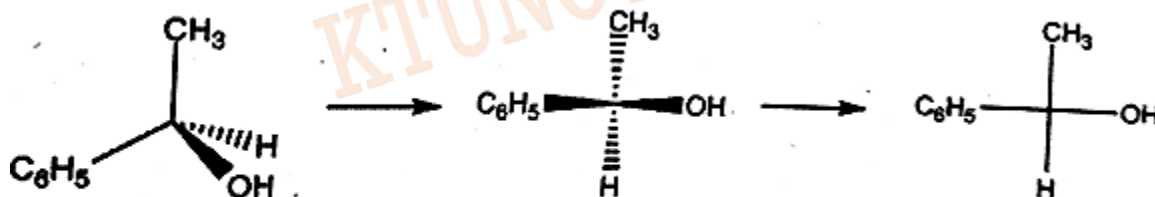
Lactic acid

### Fischer projection

In Fischer projection the asymmetric carbon atom is taken at the center with bonds attached to this are represented by crossed horizontal and vertical lines. The horizontal bonds represent the groups which are oriented towards us. The vertical bonds represent the groups which are oriented away from us. Carbon -1( $C_1$ ) of the compound can be written vertically at the top. Molecules with multiple chiral centers are written in an eclipsed conformation. Fischer projections are 2D representations of a 3D molecule.

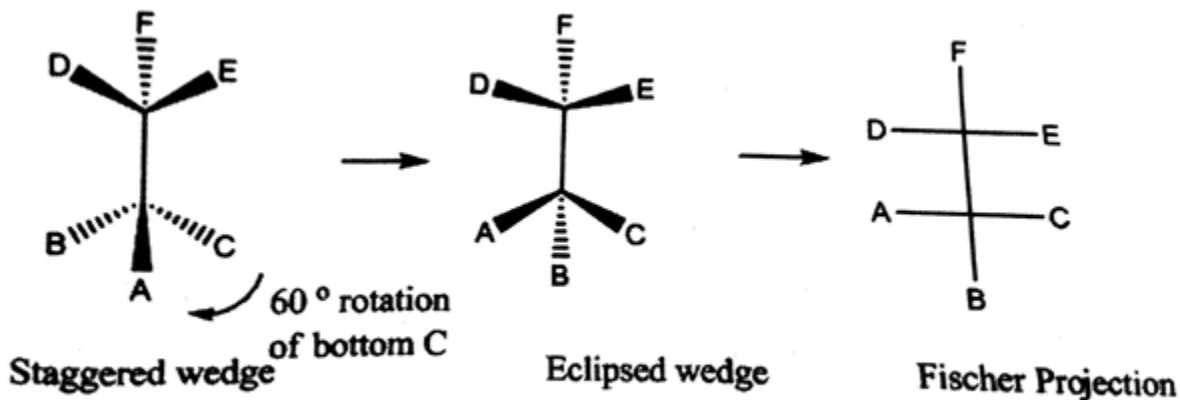
### Conversion of wedge formula into Fischer projection formula

In Fischer projection formula thick bond and any of the bonds in the plane are brought to horizontal direction.



Conversion of wedge formula into Fischer projection formula

### Conversion of wedge formula of substituted ethane to Fischer projection



Conversion of wedge formula into Fischer projection formula

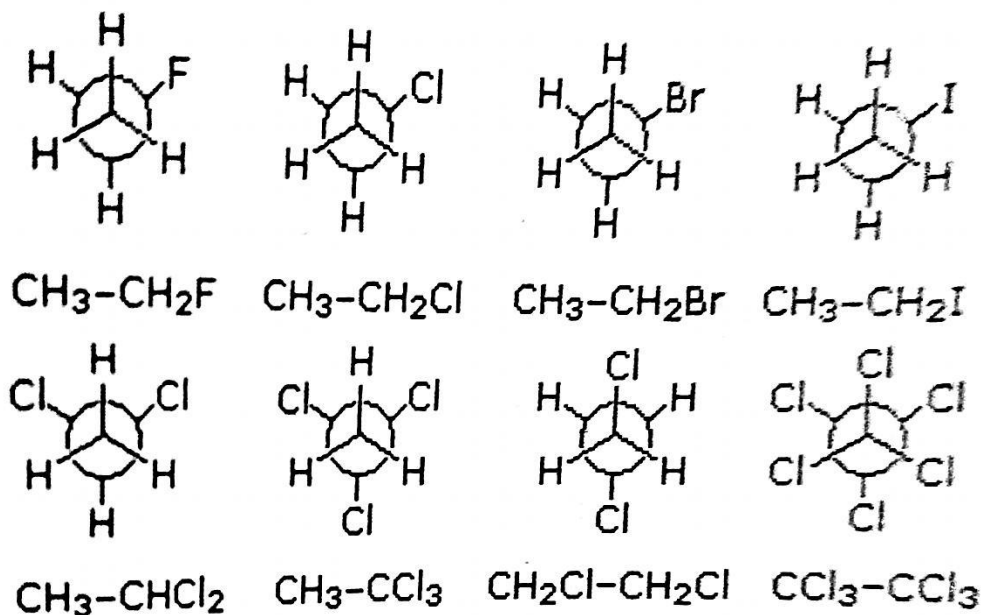
Wedge formula for substituted ethane can be drawn either in staggered conformation or eclipsed conformation. But Fischer projection formula can represent only eclipsed conformation of ethane. Thus in order to convert staggered wedge formula to Fischer projection formula, first transform staggered wedge formula to eclipsed wedge formula and then to Fischer projection formula. The same is shown above.

### Newman projection formula

Newman projection formula is used only for substituted ethane and not for substituted methane. Both eclipsed and staggered conformations of ethane can be represented by using this formula. In this formula, the bonds originating from the center of a circle represent the front carbon atom (orienting towards us) and the bonds originating from the circumference of a circle represent the back carbon atom.

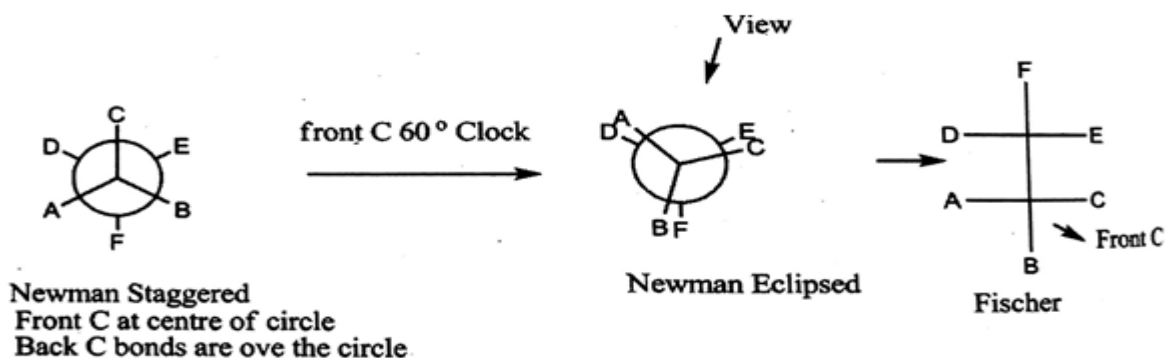
<i>Molecule</i>	<i>Staggered form</i>	<i>Eclipsed form</i>
<i>Ethane</i>		
<i>Butane</i>		

### New man projection formulas of some compounds



### Conversion of Newman formula of substituted ethane to Fischer projection

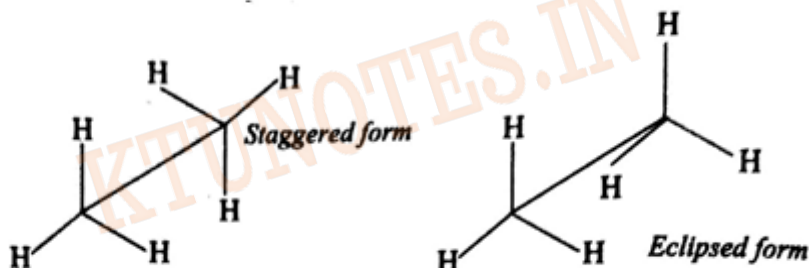
Newman formula of substituted ethane can be drawn either in staggered conformation or eclipsed conformation. But Fischer projection formula can represent only eclipsed conformation of ethane. Thus in order to convert staggered Newman formula into Fischer projection formula, first transform staggered Newman formula to eclipsed Newman formula and then to Fischer projection formula.



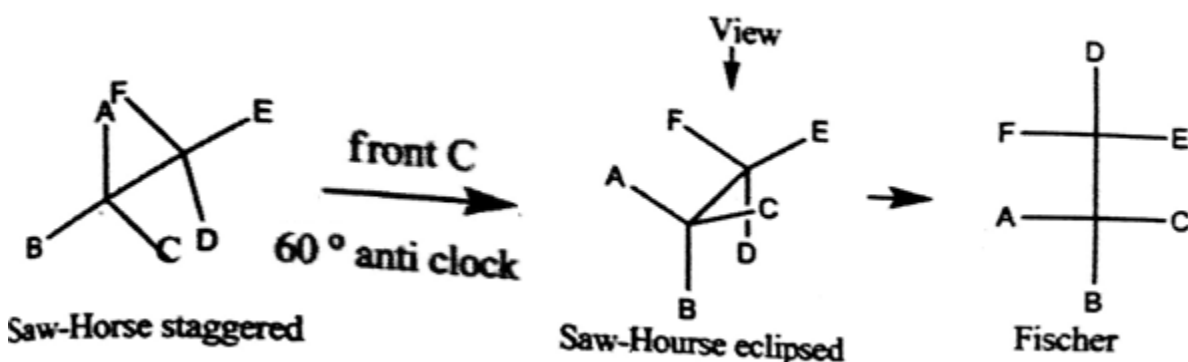
Conversion of Newman formula into Fischer projection formula

### Saw horse formula

Saw horse formula represent either eclipsed or staggered conformations of ethane. In this formula, the Carbon atom oriented downwards represent front C- atom.

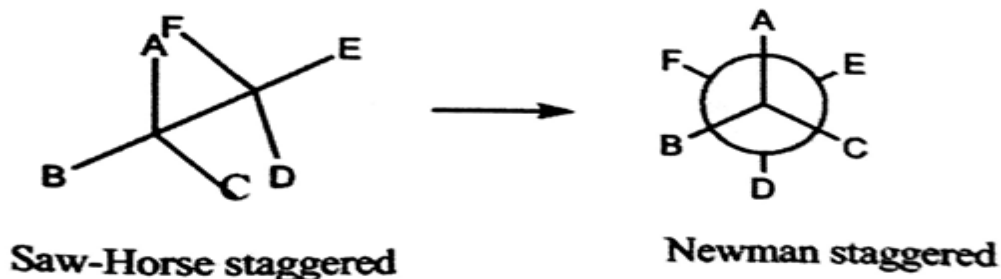


### Conversion of Sawhorse formula of substituted ethane to Fischer projection formula



Saw Horse formula of substituted ethane can be drawn either in staggered conformation or in eclipsed conformation. But Fischer projection formula can represent only eclipsed conformation of ethane. Thus in order to convert staggered Saw-Horse formula into Fischer projection formula, first transform staggered Saw-Horse formula into eclipsed Saw-Horse formula and then to Fischer projection formula and the scheme is given above.

### Conversion of Sawhorse formula of substituted ethane to Newman formula



### E and Z notation of geometrical isomers

The term cis-trans are being widely used to describe geometrical isomers. But, in compounds where all the four atoms or groups attached to C-atoms of double bond are different, then cis-trans cannot be effective. Such geometrical isomers are designated by E & Z nomenclature. The terms E & Z have been derived from the German words entgegen (meaning opposite) and zusammen (meaning follow together)

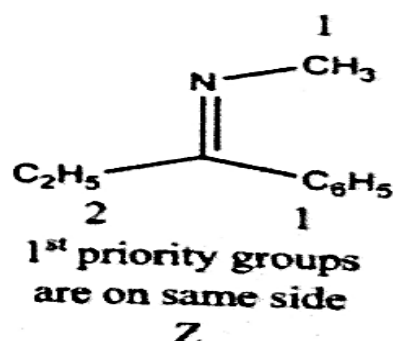
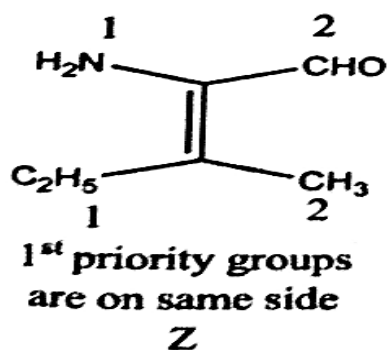
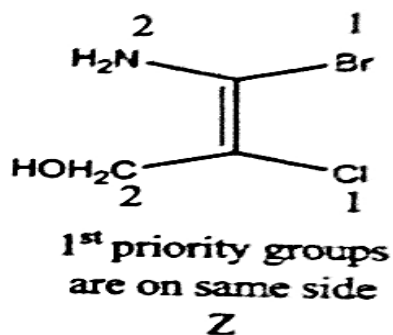
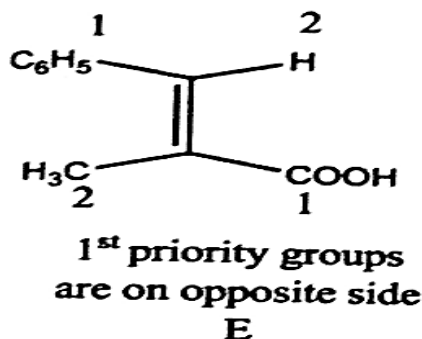
#### A set of rules are used for assigning E & Z nomenclature

1. Assign priority number 1 or 2 to groups on each Carbon atoms of the double bond.
2. Compare the priority of the group or atom at one Carbon relative to the other.
3. The configuration is represented as Z, if both the first priority groups are on opposite sides of the double bond. If the high priority groups are on the opposite sides of the double bond, then the configuration is E.

Atoms or groups are assigned priority by the following rules,

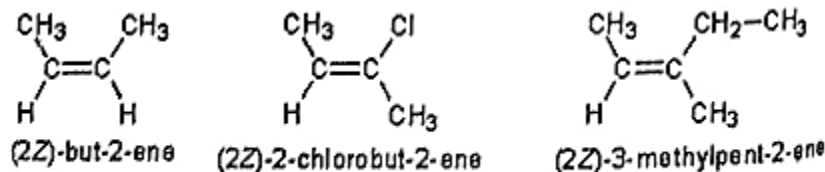
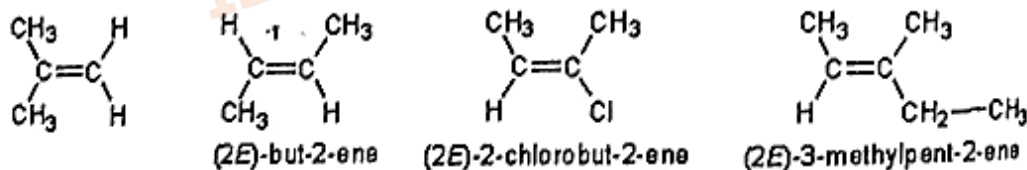
- a. A group gets first priority or high priority, if its atomic number is high.
- b. When the first atoms attached to the double bond have the same atomic number (i.e., have the same priority), the second atoms are considered. Then priority is given to the group with second atom of higher atomic number.





#### E-Z notations

#### Some examples of E & Z notation in Geometrical isomers



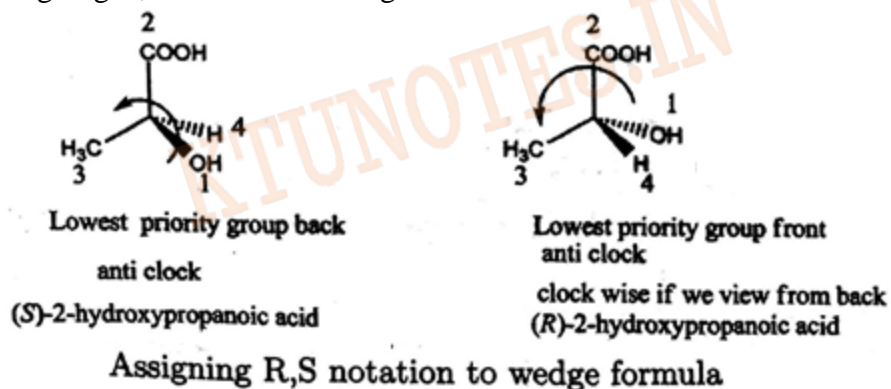
#### R & S configuration (absolute)(Cahn, Ingold and Prelog system) for optical isomers

R, S notation is the 3D arrangement of group or atoms in an asymmetric molecule. This system was suggested by Cahn, Ingold and Prelog. This system is based upon the nature of group attached to the asymmetric center and the priority is assigned to them. Here the absolute configuration is given by a prefix R (from Greek word rectus, meaning right handed) or prefix S (from the Greek word sinister, meaning left handed depending upon the sequence of groups. The following rules are used for assigning R, S nomenclature.

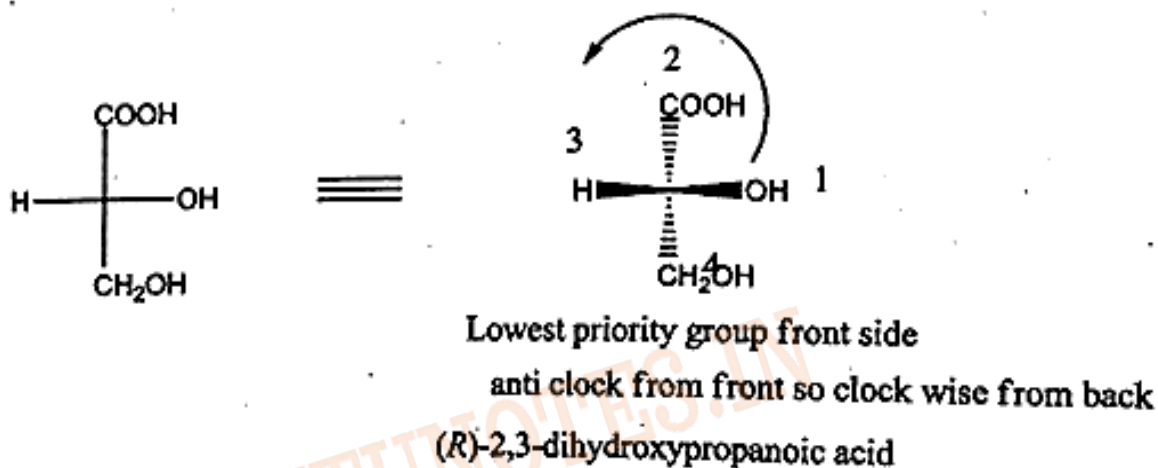
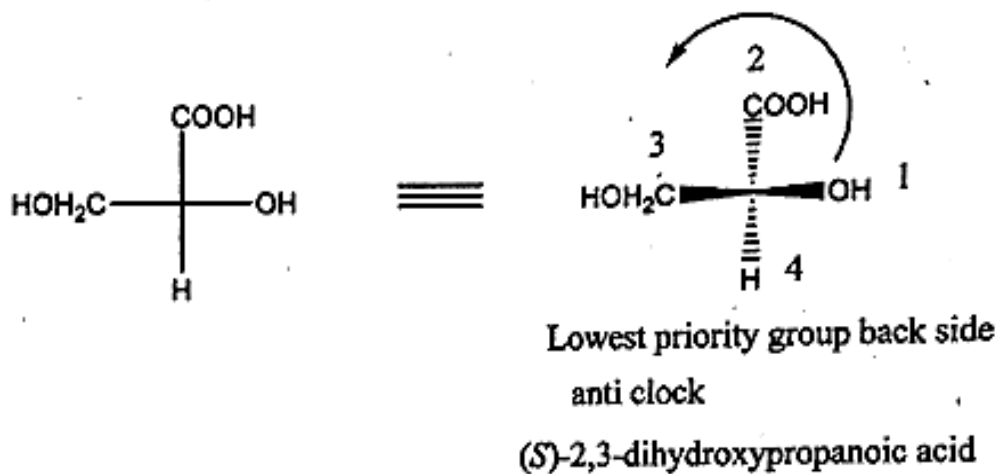


- The order of priority is determined on the basis of atomic numbers of atoms attached directly to the chiral Carbon. The greater the atomic number, the higher is the priority. For example if  $\text{-H}$ ,  $\text{-OH}$ ,  $\text{-CH}_3$  and  $\text{-Br}$  are the groups attached to the chiral Carbon, then Br (At. No. 35) will have highest priority, followed by  $\text{-OH}$  group (At. No. of O is 16) then  $\text{-CH}_3$  (At. No. of C is 6) and finally hydrogen (At. No. of H is 1). So the order of priority will be  $\text{Br} > \text{O} > \text{C} > \text{H}$ .
- If two isotopes of same element are present, then heavier isotope has higher priority, that is  $\text{D} > \text{H}$  and  $^{13}\text{C} > ^{12}\text{C}$ .
- If the two atoms directly linked to the chiral C are identical, then atomic numbers of the next atoms are used for assigning priority. For example when  $\text{-COOH}$  &  $\text{-CHO}$  are present, then  $\text{-COOH}$  has higher priority.
- A doubly or triply bonded atom present in a group attached to the chiral carbon is considered equivalent to two or three singly bonded atoms in determining the priority. For example bonds like  $\text{-C=O}$ ,  $>\text{C}=\text{C}<$ , are treated as two oxygen attachment and two carbon attachment.
- A molecule is viewed in such a way that the lowest priority group is away from us and if we look for the priority order, the sequence is clockwise or right handed direction, then the notation R is given and the sequence is anticlockwise or left handed direction, then the notation S is given.
- If the lowest priority group given in the structure is towards us, then take the opposite rotation of what we obtained from front side, so that the lowest priority group is made away from us.

Problem 1: Assigning R, S notation to wedge formula

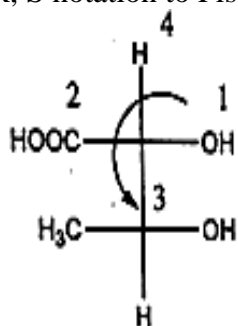


Problem 2: Assigning R, S notation to Fischer formula

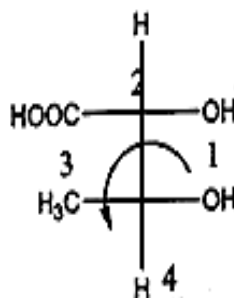


### Assigning R,S notation to Fischer formula

Problem 3: Assigning R, S notation to Fischer projection formula for two chiral carbon molecule



Carbon -2  
H-atoms is on vertical line  
Lowest priority group is away  
anticlock -notation -S

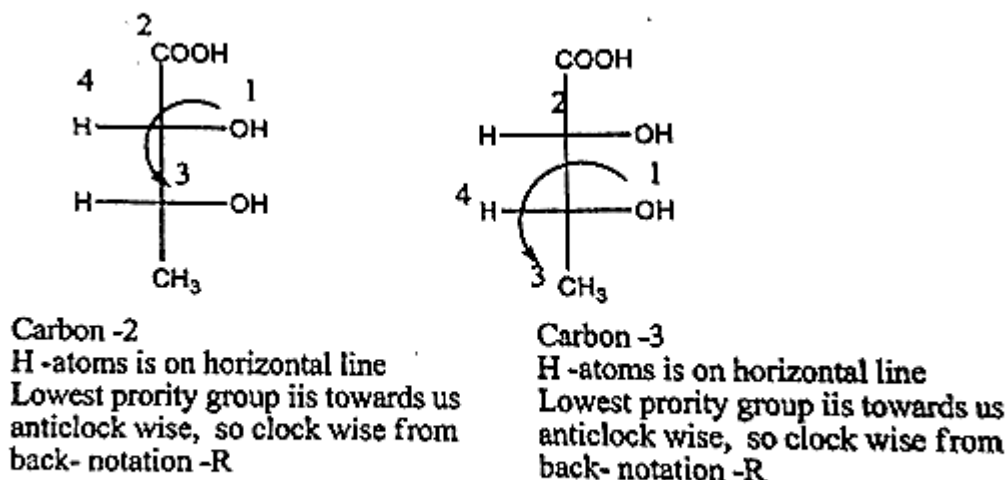


Carbon -3  
H-atoms is on vertical line  
Lowest priority group is away  
anticlock -notation -S

2(*S*),3(*S*)-dihydroxybutanoic acid

Assigning R,S notation to Fischer projection formula for two chiral Carbon

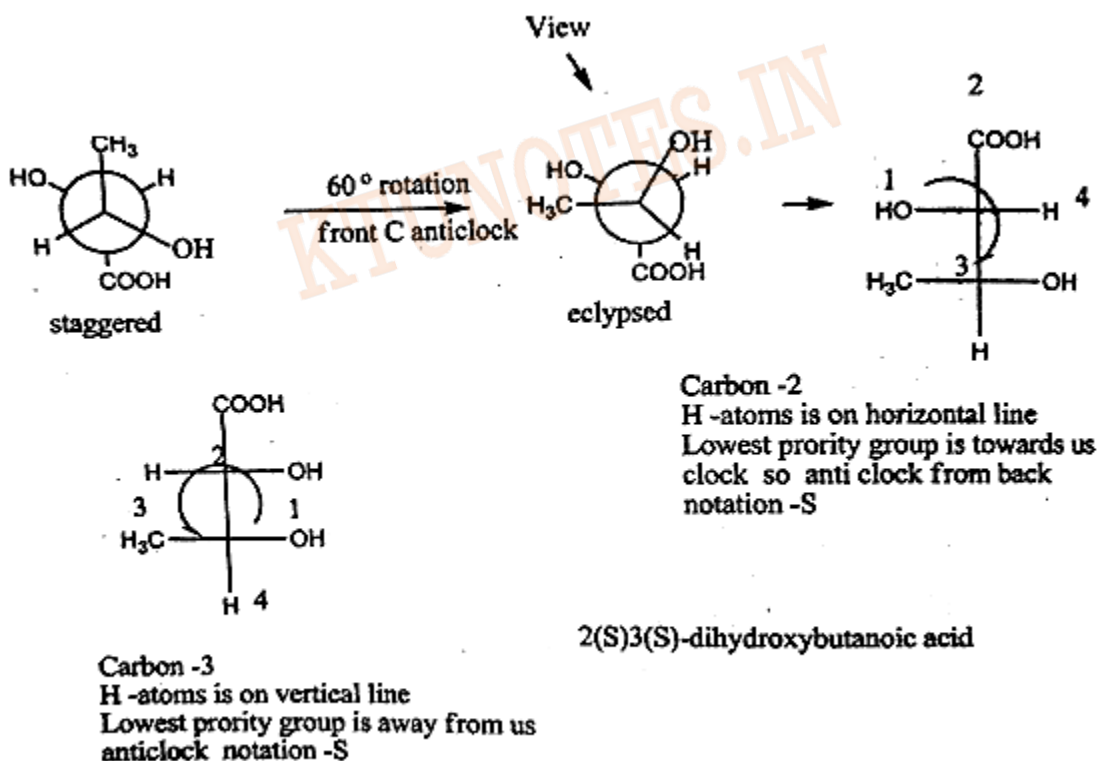
Problem 4: Assigning R, S notation to Fischer projection formula for two chiral carbon molecule



### 2(R),3(R)-dihydroxybutanoic acid

Assigning R,S notation to Fischer projection formula for two chiral Carbon molecule

Problem 5: Assigning R, S notation to Newman projection formula for two chiral carbon molecule



### 2(S)3(S)-dihydroxybutanoic acid

Assigning R,S notation to Newman projection formula

### Conformational analysis

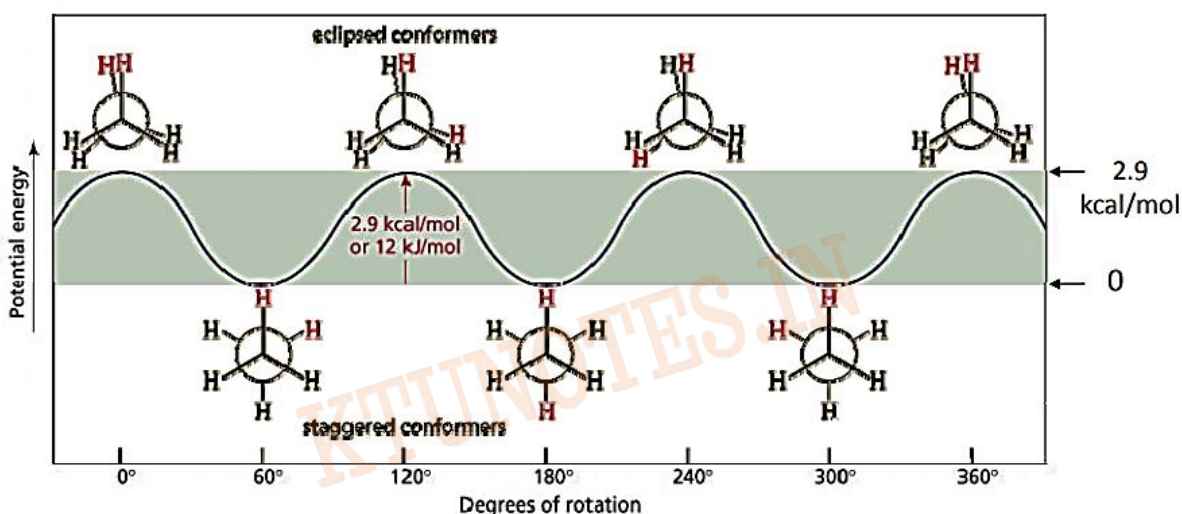
The different spacial arrangement of atoms due to the rotation of groups about a C- C  $\sigma$  bond is called conformational isomers or rotational isomers. The energy difference between two extreme conformations is very small, thus rapid inter conversions takes place at room temperature. It is

not possible to separate one conformer from other, low energy conformer is more populated than high energy conformer at room temperature.

### Conformations of ethane

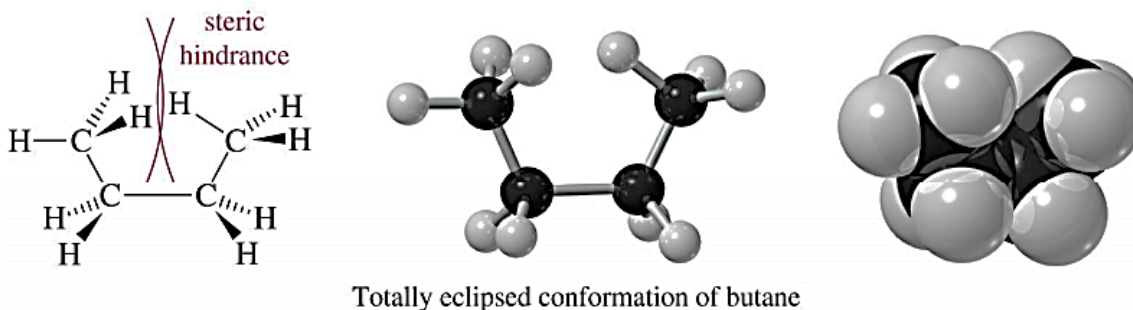
For ethane, we get various conformations due to the number of rotations of  $-\text{CH}_3$  group about the C-C  $\sigma$  bond. The staggered conformation is the most stable conformation. Since it has the lowest PE. This conformation allows the maximum possible separation of electron pairs of the six carbon-hydrogen bonds and therefore it has the lowest energy. The least stable conformation of ethane is the eclipsed conformation. In this conformation, hydrogen atoms attached to each carbon atom are directly opposite to each other. This conformation requires the maximum repulsive interaction between electron pairs of the six carbon-hydrogen bonds and therefore it has the highest PE. We can represent the conformational analysis graphically by plotting PE as a function of rotation about the C-C bond. In ethane, the difference in energy between the staggered and eclipsed conformation is 12KJ/mol.

### Conformations of Ethane



### Conformations of butane

Butane has steric and torsional strain in its eclipsed conformation



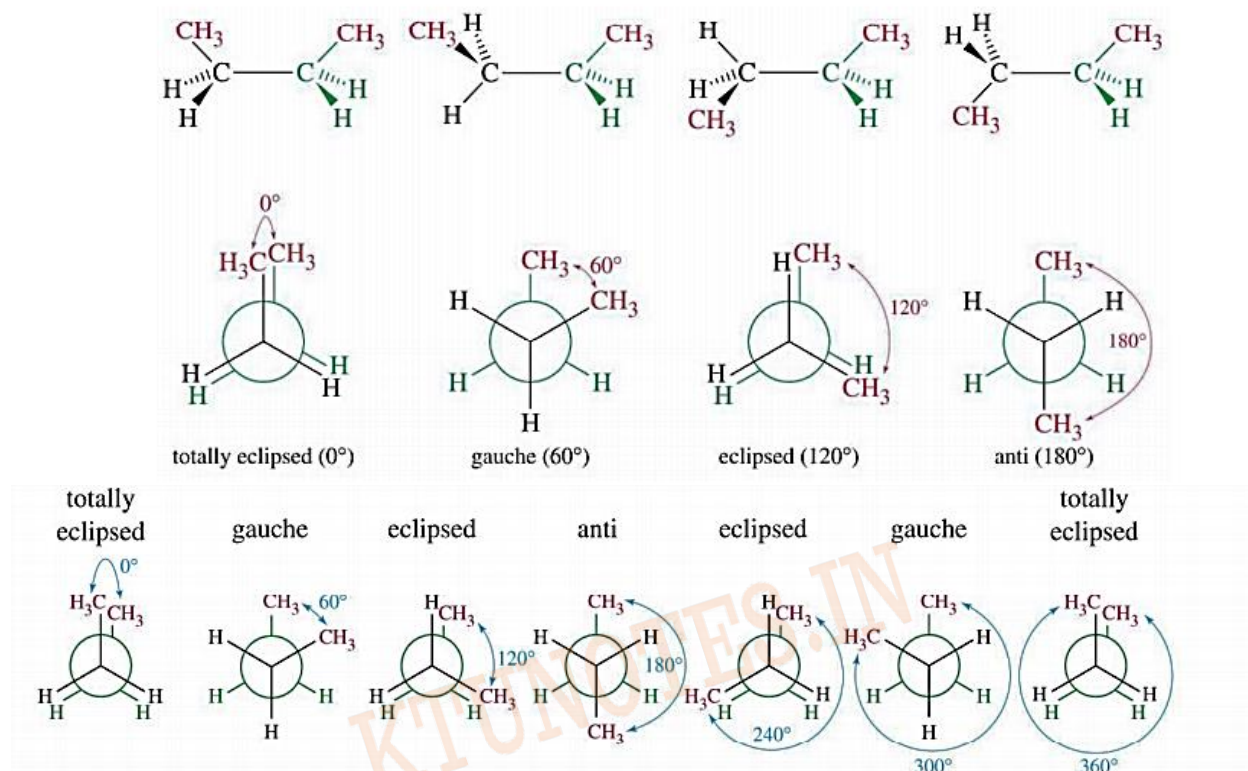
If one  $\text{CH}_3\text{-CH}_2\text{-}$  group is kept stationary, and the other  $\text{CH}_3\text{-CH}_2\text{-}$  group is allowed to rotate through  $360^\circ$  in six steps ( $60^\circ$  each time), then the following conformations are obtained. In the conformational isomerism of butane, it is observed that,

- The fully staggered form in which the methyl groups are far apart with a dihedral angle of  $180^\circ$  is having the lowest PE and is the most stable conformation. It is called anti conformation.

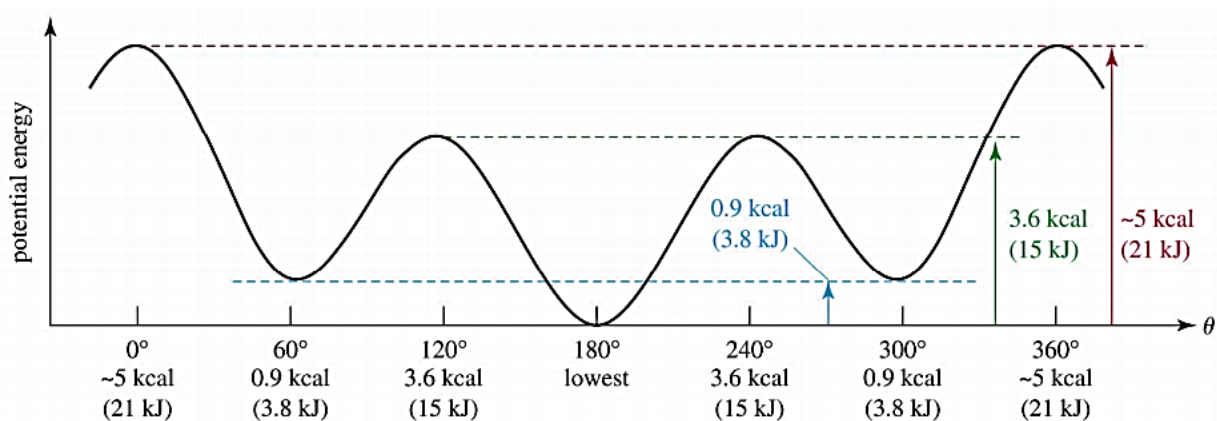
- The conformation in which the methyl groups are only  $60^\circ$  apart (nearly staggered) with slightly higher energy than fully staggered form and is called Gauche conformation.
- Eclipsed conformation is having the highest energy and is the less stable conformer.

In general full staggered anti conformation has the lowest energy and the highest population. The nearly staggered gauche conformation has an appreciable population than eclipsed conformation

## Conformations of Butane



## Conformational Analysis of Butane

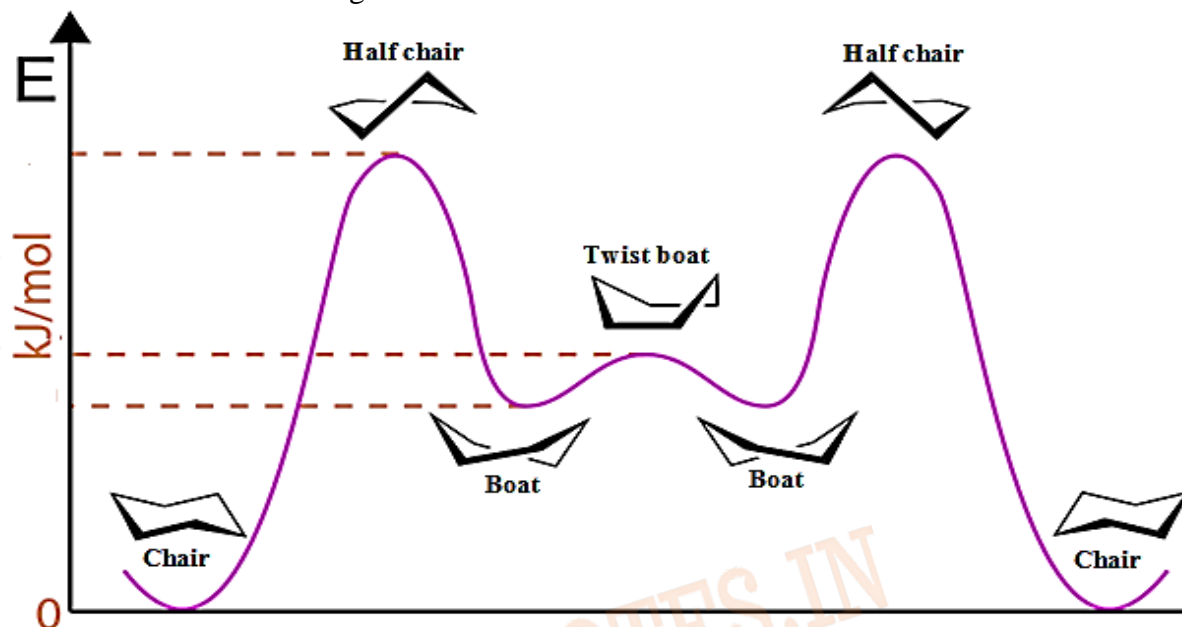


### Conformational analysis of cyclohexane

Cyclohexane is a saturated compound with all carbon atoms are  $sp^3$  hybridized and is tetrahedral, ideal bond angle is  $109.5^\circ$ . But the planarity of the ring would force the carbons to have bond angles of  $120^\circ$ , which makes it unstable. Cyclohexane has two stable forms, boat and chair form. Both the conformations are free from angle strain. In chair form all the C-H bonds on adjacent carbon atoms are in fully staggered position which minimizes strain makes it most

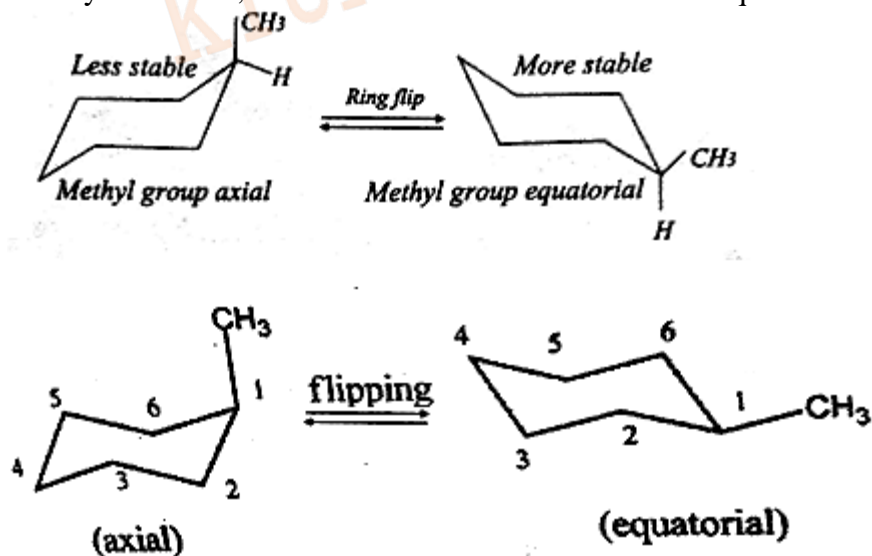


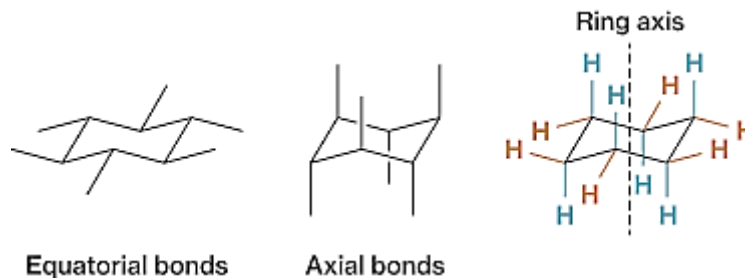
stable. A half chair conformation is also possible, but due to angle strain and ring strain, it is the most unfavorable condition. Its energy is 10Kcal/mol above the chair conformation. In the boat form conformation, total strain is larger than chair form and the boat form is also less stable than chair form. The chair form is rigid and resists distortion and when it is changed into boat form some angular deformation occurs. Its energy is 6.5Kcal/mol above the chair conformation. Twist boat conformation is also possible. Its energy is 5.5Kcal/mol above the chair conformation. The conformations involve following order of stability: chair > twist boat > boat > half-chair. All relative conformational energies are shown below



### Conformational analysis of monosubstituted cyclohexane

In monosubstituted cyclohexane, the two chair conformations are not equivalent.





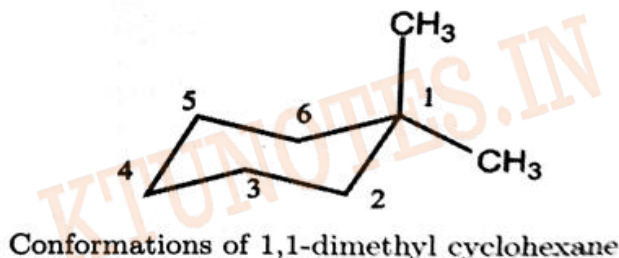
Due to ring flipping, mono substituted methyl cyclohexane is a mixture of chair conformation with an equatorial methyl group and a chair conformation with an axial methyl group. Methyl group is less crowded when it is equatorial than when it is axial. The conformation with axial methyl group has 7KJ/mol energy greater than those with axial methyl group. So at room temperature 95% of the molecules of methyl cyclohexane are in the chair conformation that has an equatorial methyl group. But we cannot separate the two conformations of methyl cyclohexane because they rapidly interconvert by ring flipping

### Conformational analysis of di-substituted cyclohexane

In di-substituted cyclohexane, there are four possible position isomers, namely (1,1), (1,2), (1,3) and (1,4).

#### 1) 1, 1-dimethyl cyclohexane

In this compound the two methyl groups are substituted at axial or equatorial position C1. On flipping axial bonds are converted as equatorial bonds and vice versa, thus only one conformer exists.

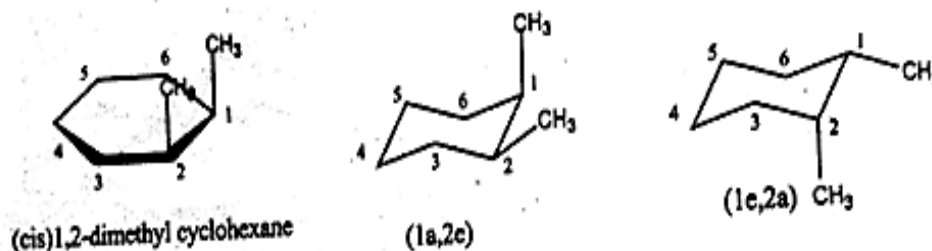


#### 2). 1, 2-dimethyl cyclohexane

This compound has two geometrical isomers cis and trans. They will not interconvert each other by flipping.

##### a). (Cis) 1, 2-dimethyl cyclohexane

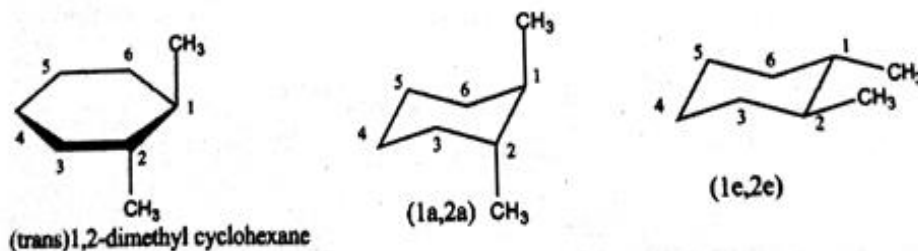
This compound has two conformers (1a, 2e) and (1e, 2a). Both are equally stable since they have equal number of gauche interactions.



##### b). (Trans) 1, 2-dimethyl cyclohexane

This compound has two conformers (1a, 2a) and (1e, 2e). They interconvert each other by flipping. (1a, 2a) has four Gauche interactions with the ring  $\text{CH}_2$  groups whereas (1e, 2e) has only one Gauche interaction. Thus (1e, 2e) conformer is more stable in (trans) 1, 2-dimethyl cyclohexane.



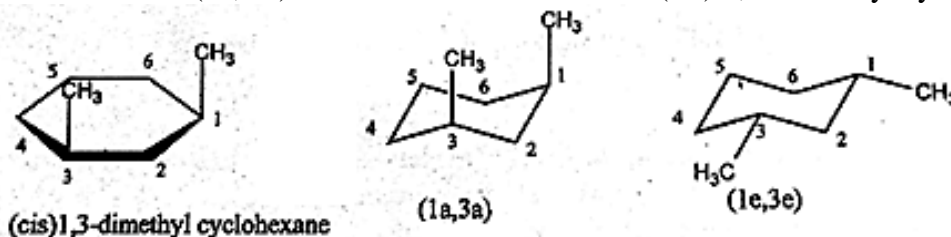


### 3). 1, 3-dimethyl cyclohexane

This compound has two geometrical isomers cis and trans. They will not interconvert each other by flipping.

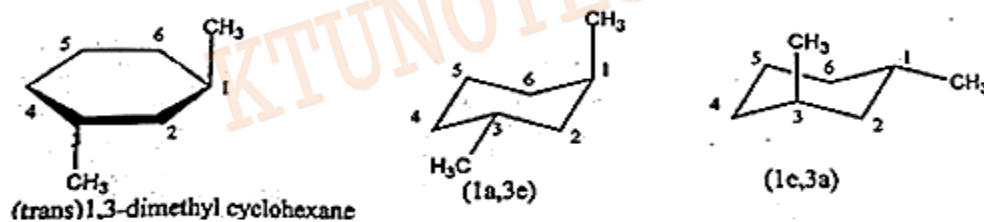
#### a). (Cis) 1, 3-dimethyl cyclohexane

This compound has two conformers (1a, 3a) and (1e, 3e). They interconvert each other by flipping. (1a, 3a) has two Gauche interactions with the ring  $\text{CH}_2$  groups whereas (1e, 3e) has no Gauche interaction. Thus (1e, 3e) conformer is more stable in (cis) 1, 3-dimethyl cyclohexane.



#### b). (Trans) 1, 3-dimethyl cyclohexane

This compound has two conformers (1a, 3e) and (1e, 3a). Both are equally stable since they have equal number of gauche interactions. They interconvert each other by flipping. Both are equally stable since they have equal number of gauche interactions.

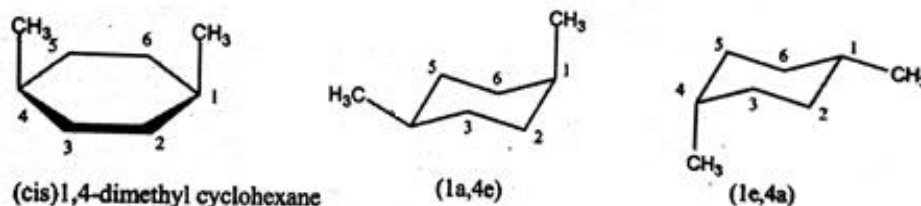


### 4). 1, 4-dimethyl cyclohexane

This compound has two geometrical isomers cis and trans. They will not interconvert each other by flipping.

#### a). (Cis) 1, 4-dimethyl cyclohexane

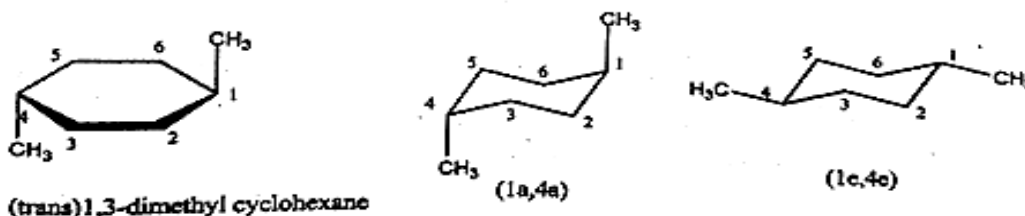
This compound has two conformers (1a, 4e) and (1e, 4a). Both are equally stable since they have equal number of gauche interactions.



#### b). (Trans) 1, 3-dimethyl cyclohexane

This compound has two conformers (1a, 4a) and (1e, 4e). They interconvert each other by flipping. In (1a, 4a) has four Gauche interactions with the ring  $\text{CH}_2$  groups whereas (1e, 3e) has

no Gauche interaction. Thus (1e, 4e) conformer is more stable in (trans) 1, 4-dimethyl cyclohexane.



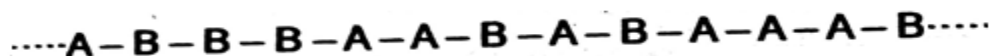
## Co- polymers

Polymers which are formed by the polymerization of two or more different monomers are called co-polymers. (Eg. BS, ABS co-polymers)

Types of co-polymers

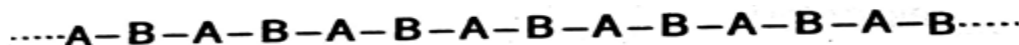
### 1. Random co-polymer:

If the monomeric units are arranged in a random fashion, then the co-polymer is known as random co-polymer.



### 2. Alternating co-polymer

If the monomers are arranged in a regular alternating fashion, then it is called alternating co-polymer.



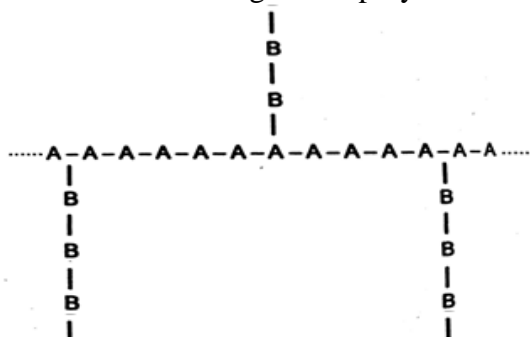
### 3. Block co-polymer

Co-polymer which can be formed with a long chain of homo polymer followed by a block of another homo polymer chain, then it is called block co-polymer.



### 4. Graft co-polymer

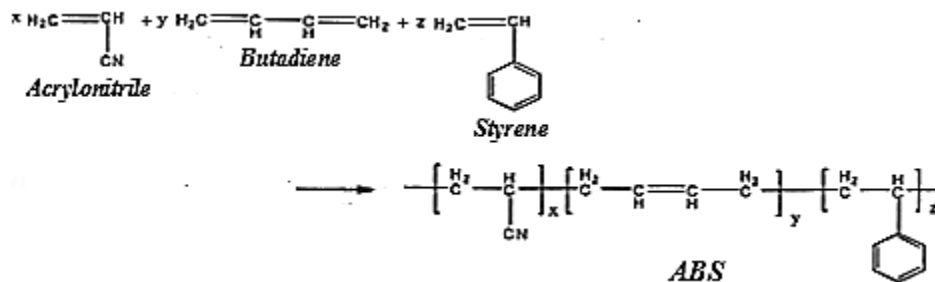
Co-polymers can be formed with homo polymers remaining grafted to the main chain of homo polymer at intervals, and then it is called graft co-polymer.



## ABS (Acrylonitrile Butadiene Styrene)

### Preparation:

It is obtained by dissolving poly butadiene in liquid acrylonitrile and styrene in presence of free radical initiator.



Properties:

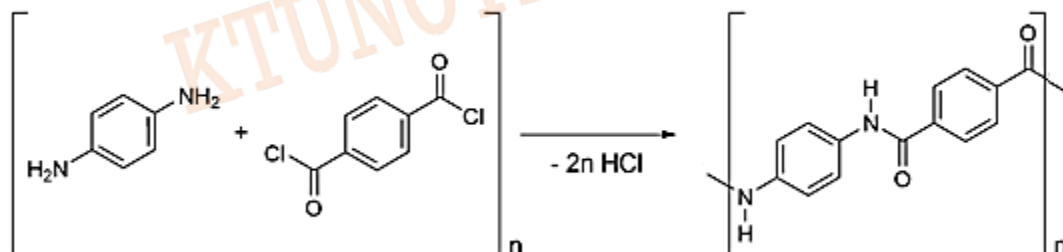
- Very hard, rigid and tough material.
- Resistant to impact, stretch, bent etc.
- Possess high tensile strength.
- Possess stiffness.
- Possess chemical resistance and heat resistance.
- Ductile in nature.

Uses:

- Used for making automobile parts.
- Used for making building materials.
- Used for making house wares such as refrigerator parts, parts of micro wave oven, coffee maker etc.

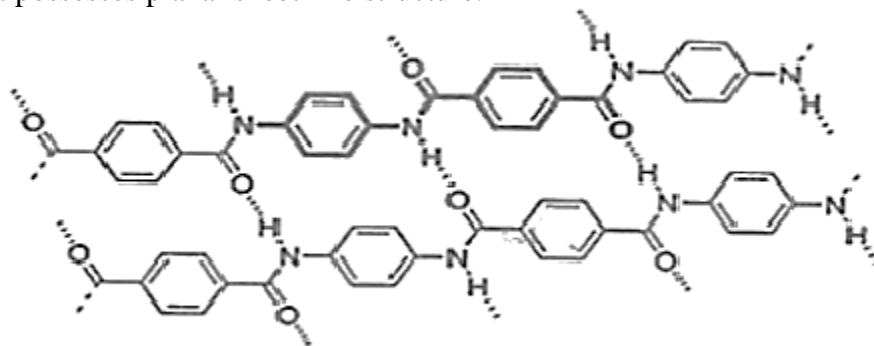
### KEVLAR (PPTA)

KEVLAR is poly para-phenylene terephthalamide. It is obtained by the condensation polymerization of para phenylene diamine and terephthaloyl chloride.



### Structure of KEVLAR

It possesses planar sheet like structure.



Three types of bonding are possible in Kevlar.

1. Covalent bonding

It is the strongest bonding in Kevlar.

These are weak bondings. Different chains in the Kevlar structure are held together by Vander Waals forces of interaction.

Hydrogen bondings are possible between amide linkages.

Due to the difference in the strength of covalent and Vander waals forces, Kevlar possesses anisotropy.

- It is five times stronger than steel.
- Possess high tensile strength and chemical resistance.
- Extremely light weight material.
- Possess heat resistance.

- For making bullet proof vests
- For making industrial gloves, helmets, body pads etc.
- For making sports equipments.
- For making industrial hoses.

Recently synthesized organic polymers are called organo electronic compounds. They can function as conductor or super conductor. Polymers are usually poor conductors of electricity, because of the absence of free electrons.

Polymers which can conduct electricity is called **conducting polymers**.

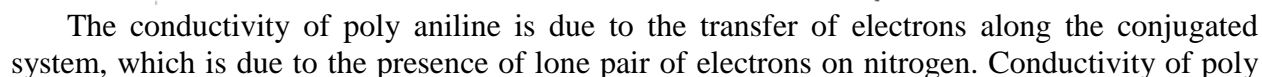
Eg. Polyacetylene, polyaniline, polypyrrole etc.

The first widely studied is polyacetylene. Its conductivity can be increased by a factor of  $10^{12}$  by doping it with an electron donor like alkaline earth metal ion or an electron acceptor like  $I_2$  or  $AsF_5$ .

Conductivity increases with decrease in band gap because in that case small amount of energy is required to promote an electron from valence band to the conduction band. In the case of polymeric insulators band gap is very large (1.5-4 eV) which obstruct the flow of electrons. But by the careful design of the chemical structure of polymeric back bone it is possible to reduce the band gap as low as possible (0.5-1 eV)



Poly aniline is a conducting polymer obtained by the oxidative polymerization of aniline. It is also obtained by the self-stabilized dispersion polymerization of aniline



aniline can be increased by protonation. At room temperature its conductivity is  $1000 \text{ Scm}^{-1}$ . It is soluble organic solvents.

Properties:

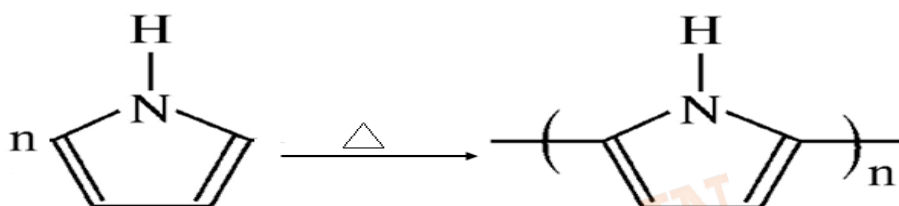
- It is highly flexible
- Possess high strength.
- Low cost material.
- It is stable both in air and water.
- Possess excellent anti-corrosion property.

**Applications;**

- 1) Used in LED, since the colour changes with the application of particular voltage and chemicals..
- 2) Used as electromagnetic shield and IR absorber.
- 3) Used for making rechargeable batteries.
- 4) Used as a corrosion resistive material.

**Poly pyrrole:**

Poly pyrrole is a conducting polymer obtained by the polymerization pyrrole under the influence of free radical, anionic or cationic initiator.



Poly pyrrole is a conjugated polymer. The conductivity of poly pyrrole is due to the electronic transfer along the conjugated  $\pi$  system.

**Properties:**

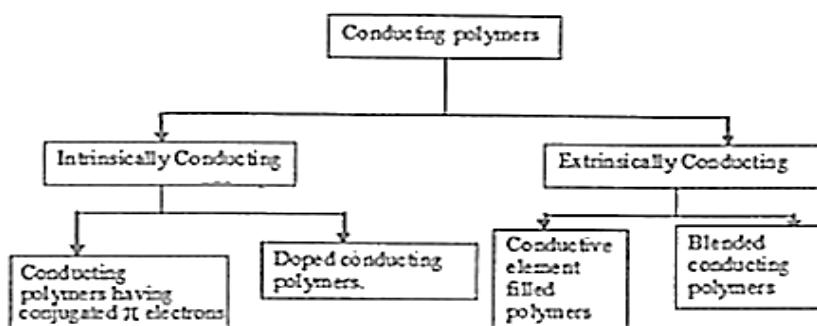
- It has excellent thermal, chemical and mechanical properties.
- It can be processed into any desired shape.
- It has good environmental stability.
- Electrical resistance decreases with increase in temperature. Hence conductivity increases.

**Applications:**

1. Used for making rechargeable batteries.
2. Used for making chemical carrying pipes.
3. Used as a very good electrical conductor.
4. It can be used as a tissue (cell) support substrate.

**Classification of Conducting Polymers:**

Conducting polymers can be classified into following types



Polymers which can conduct electricity are called conducting polymers. Polymers are usually pure conductors of electricity due to the absence of free electrons. In the case of polymers band gap is very large (1.5 – 4 eV). But by the careful design of the chemical structure of polymeric back-bone, it is possible to reduce the band gap as low as possible (0.5 – 1eV). Conducting polymers are classified into

1) Intrinsically conducting polymers

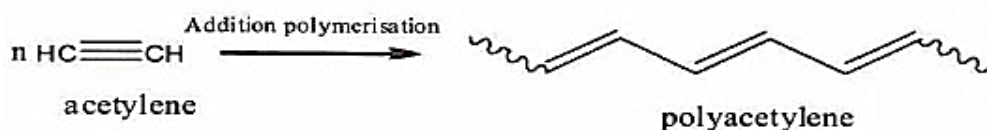
2) Extrinsically conducting polymers

1) Intrinsically conducting polymers

These are conducting polymers which have extensive conjugation in the polymeric back-bone which is responsible for conductance. These are again classified into

a) Conducting polymers containing conjugated  $\pi$  electrons:

These conducting polymers contain conjugated  $\pi$  electrons along the polymeric chain. The orbitals of conjugated  $\pi$  electrons overlap over the entire polymeric back-bone, resulting in the formation of valence band and conduction band, which extends over the entire polymeric back-bone. These bands are separated by a very small band gap. Thus electrical conduction would occur when electrons from valence band are excited to conduction band either thermally or photolytically. Eg. Poly acetylene



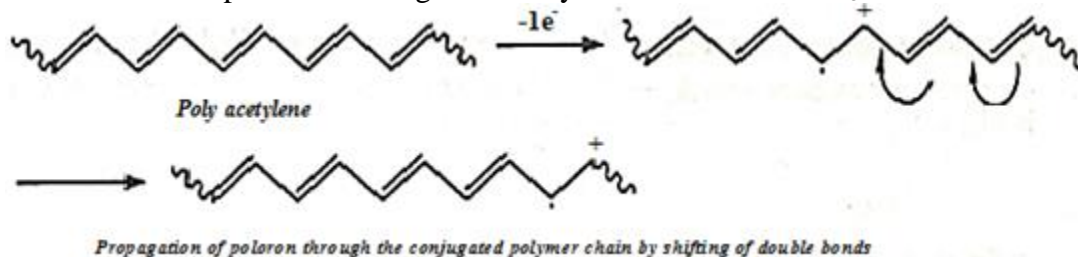
b) Doped conducting polymers:

Conductivity of intrinsically conducting polymers can be increased by creating a positive charge or negative charge by oxidation or reduction. This process is called doping. Conducting polymers obtained by this process is called doped conducting polymers. Doping is of two types.

p – doping & n - doping

#### Mechanism of conduction by p – Doping:

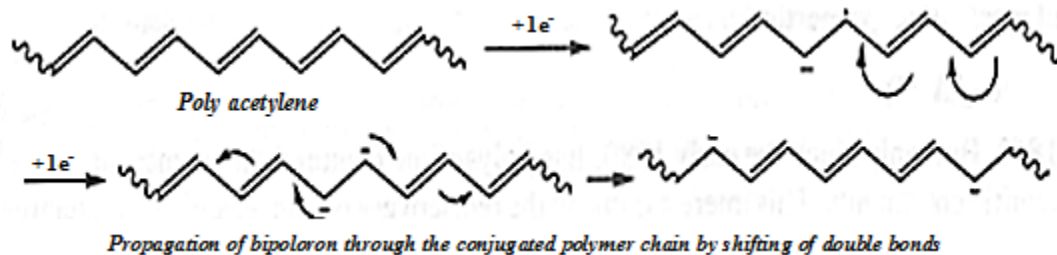
p – Doping is done by oxidation process. In this process some electrons of the  $\pi$ -bonds of the conjugated double bonds are removed and holes are created which can move along the polymer and the polymer becomes electrically conductive. The radical cation produced is called polaron. The polarons are mobile and can move along the polymer chain by the rearrangement of double and single bonds. Oxidation process is brought about by Lewis acid like  $\text{FeCl}_3$ .



#### Mechanism of conduction by n – Doping:

n – Doping is done by reduction process. In this process some electrons are introduced into the polymer having conjugated double bonds. Reduction can be done by using Lewis base like sodium naphthalide. This will lead to the formation of polaron and bipolaron in two steps.





## 2) Extrinsic conducting polymers:

These are conducting polymers whose conductivity is due to the presence of externally added ingredients in them. These are also classified into two.

### a) Conducting element filled conducting polymers.

These are polymers which are filled with conducting elements such as carbon black, metallic fibers, metal oxides etc. Here the polymers act as a binder to hold the conducting elements together. These polymers are low cost, light weight, mechanically durable and strong and can be easily processed into different shapes and sizes.

### b) Blended conducting polymers

These are polymers obtained by blending conducting polymers with conventional polymers. They possess better physical, chemical and mechanical properties.

### Distinguish between p-Doping & n-Doping

p-Doping	n-Doping
<ul style="list-style-type: none"> <li>• Done by Oxidation</li> <li>• Positive charge is created during the process.</li> <li>• Polaron are produced.</li> <li>• Single step process.</li> <li>• Lewis acid like <math>\text{FeCl}_3</math> is used as the reagent.</li> </ul>	<ul style="list-style-type: none"> <li>• Done by reduction</li> <li>• Negative charge is created during the process.</li> <li>• Polaron and bipolaron are produced.</li> <li>• Two step process.</li> <li>• Lewis base like sodium naphthalide is used as reagent.</li> </ul>

### OLED (Organic Light Emitting Diode)

OLED is an advanced form of LED and is made up of conducting polymer like polyaniline. Its thickness is 200 times smaller than human hair.

Parts of OLED:

1. Substrate:
2. Anode
3. Hole Transport Layer (HTL)
4. Electron Transport Layer (ETL)
5. Cathode

#### **Substrate:**

A clear plastic or glass that supports OLED is called substrate.

#### **Anode:**

When current passes through the OLED, it removes electrons and adds holes. Usually used anode is ITO (Indium Titanium Oxide)

#### **HTL:**

It is the conducting layer made of conducting polymer like polyaniline. It helps for the transport of holes from the anode through the OLED.

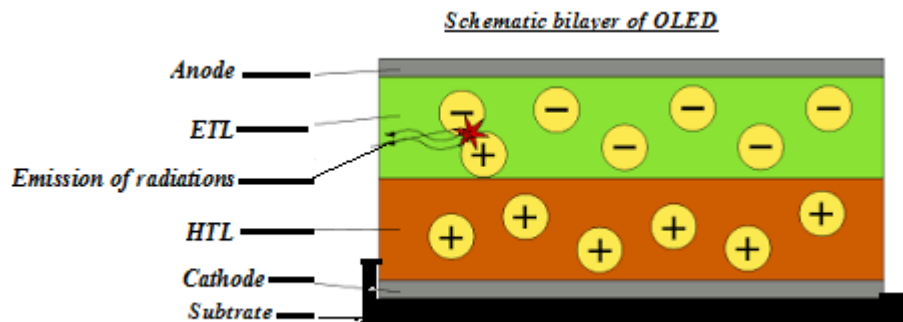


**ETL:**

It is the emissive layer made of polyfluorene. Light is produced in the ETL. It helps for the transport of electrons from the cathode through the OLED.

**Cathode:**

It ejects electrons when current flows through the OLED. Al or Ca is used as cathode.

**Working of OLED:**

When a voltage is applied across the OLED, a current of electrons flows from cathode to anode. During this current flow electron hole capture each other by electrostatic force of attraction. Recombination of electrons with holes produces light. The wave length of light produced depends on the band gap of the conducting polymer.

**Properties:**

- It is considered as a cold lighting source. Since no heat is generated during its working.
- Its power consumption is very less.
- It is flexible, very thin and small.
- It generates good quality light.
- More efficient than incandescent lamps and halogen lamps.

**Applications:**

1. They are used for making screens of smart watches, mobile phones, laptops and televisions.
2. They can be used for getting ambient lighting sources.

**Limitation:**

- Life time of the organic polymer is limited.

**Advantages**

- Manufacture OLED is highly economical and efficient.
- No backlight is produced by the device and its power consumption is very less.
- Its response time is less than 0.01 minutes.

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