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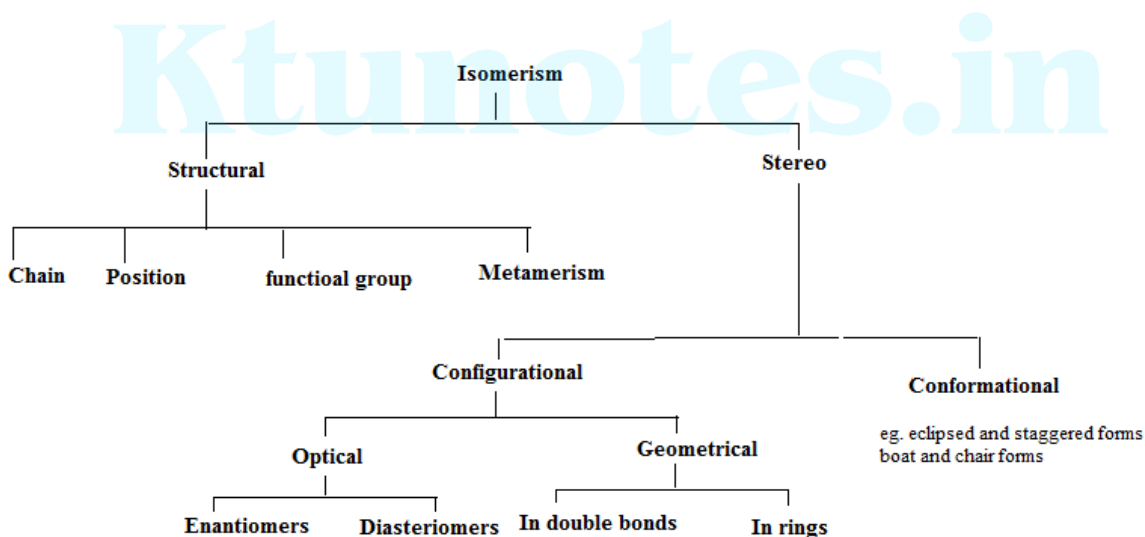
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# Chapter 4

## Stereochemistry and Polymer Chemistry

### 4.1 Isomerism

Organic compounds with same molecular formula but different structures are called isomers. The phenomenon is called isomerism. Isomers differ in their physical or chemical properties.



#### Classification

##### 4.1.1 Structural isomers

Isomers that have different bonding pattern.

##### Chain isomers

Isomers differ in carbon chain or skeleton, for example in (1)  $C_4H_{10}$  has two chain isomers possible (2)  $C_5H_{12}$  has three chain isomer possible.(fig. 4.1)

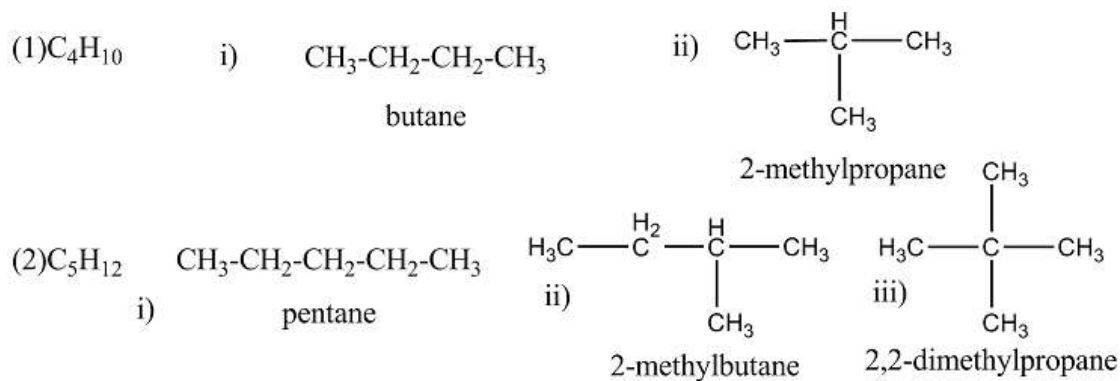


Figure 4.1: Chain isomers

**Position isomers**

Isomers differ in the position of attachment of functional group, for example in (1)  $C_3H_7Cl$  the position of functional group  $-Cl$  can be at  $C_1$  or  $C_2$ . (2) In  $C_4H_8$  the position of double bond can be at  $C_1$  or  $C_2$ . (fig. 4.2)

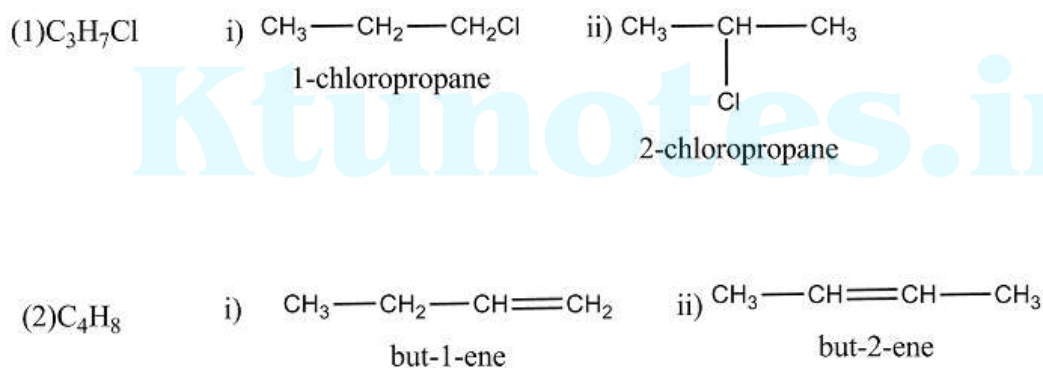


Figure 4.2: position isomers

**Functional group isomers**

Here isomers differ in the type of functional group, for example in

1. In  $C_2H_6O$ , the possible functional groups are  $-OH$  (alcohol) and  $-O-$  (ether)
2. In  $C_3H_6$  the possible functional groups are (i)  $C=C$  (ii) ring
3. In  $C_2H_4O$  The possible functional group combination are (i) aldehyde (ii)  $C=C$  and  $-OH$  (iii) ring and  $-O-$

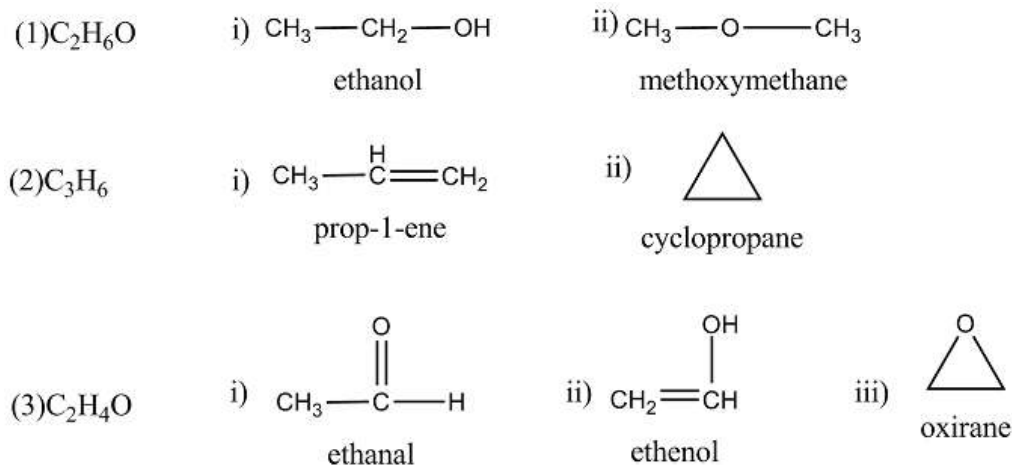
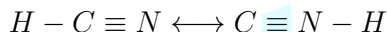


Figure 4.3: Functional group isomers

**Tautomerism** It is a special type of functional group isomerism in which isomers are rapidly inter changeable and maintains a dynamic equilibrium. For example hydrogen cyanide is rapidly converted to hydrogen isocyanide by rapid exchange of hydrogen atom between polyvalent carbon and nitrogen atoms.



Since hydrogen cyanide (HCN) is more stable than hydrogen isocyanide (HNC) the fraction of hydrogen isocyanide in the equilibrium mixture is very small.

**Keto-enol tautomerism** It is a special kind of functional group isomerism in which keto form rapidly interchanged to enol-form by exchange of hydrogen atom between oxygen atom and carbon atoms. For example (1) ethanal and eth-en-ol are keto and enol forms. Since keto-form is more stable enol form exists only in traces. (2) similarly propanone (acetone) also exhibits keto-enol tautomerism as shown below.

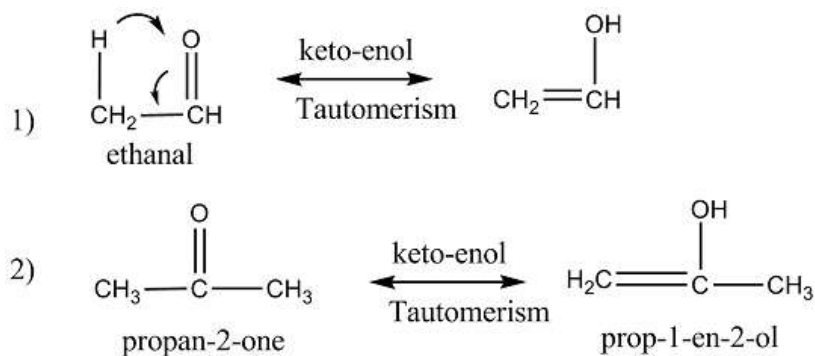


Figure 4.4: Keto-enol tautomerism

### Metamerism

Here isomers differ in the number of carbon atom on the either side of the hetero atom. For example diethyl ether has two carbon each on either side of the hetero atom oxygen, where as its metamer methoxy(1-propane) has three and one carbon atoms on the either side of oxygen atom.

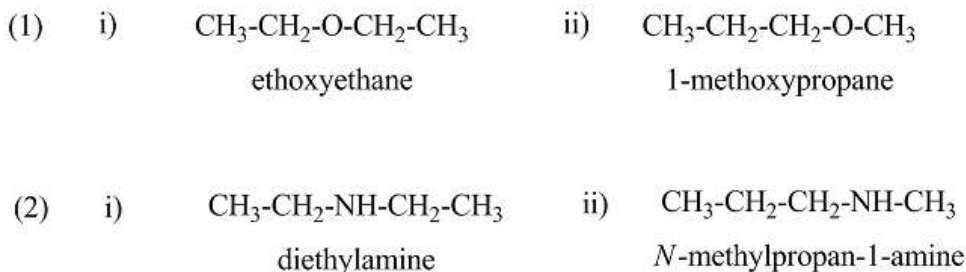


Figure 4.5: Metamers

#### 4.1.2 Three dimensional representation of organic molecules

Three denominational representation of structures are important in depicting stereo isomers. The  $sp^3$  hybridized C-atom has tetrahedral structure with bond angle of  $109.5^\circ$ . Wedge formula, Fischer projection formula, Saw-Horse formula, Newman's projection formula etc are used to represent 3D structures.

**Wedge formula for substituted methane** The wedge formula for substituted methane is as shown in fig.4.6. Thick line represents the groups which are projecting towards us. and broken lines represents the groups which are projecting away from us. Ordinary lines represents the groups in plane of the paper.

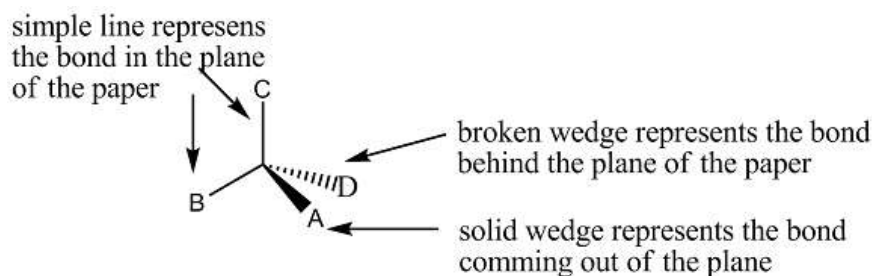


Figure 4.6: Wedge formula

**Fischer Projection Formula for substituted methane** In this method the asymmetric carbon atom is taken at the center with bonds are attached to this by crossed horizontal and vertical lines. The horizontal bonds represents the groups which are oriented towards us and vertical bonds represents the groups which are away from us .

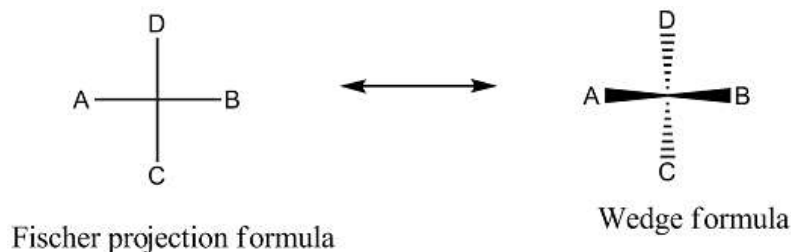


Figure 4.7: Fischer projection formula

**Conversion of wedge formula of substituted methane to Fischer projection:**

The scheme for conversion is as shown in fig.4.8. Here thick bond and any of the bond in plane of the paper are brought to horizontal direction.

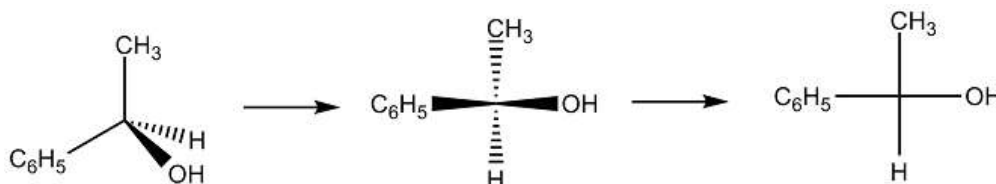


Figure 4.8: Conversion of wedge formula into Fischer projection formula

**Conversion of wedge formula of substituted ethane to Fischer projection:**

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 into Fischer projection formula, first transform staggered wedge formula to eclipse wedge formula and then to Fischer projection formula. The scheme is as shown below.

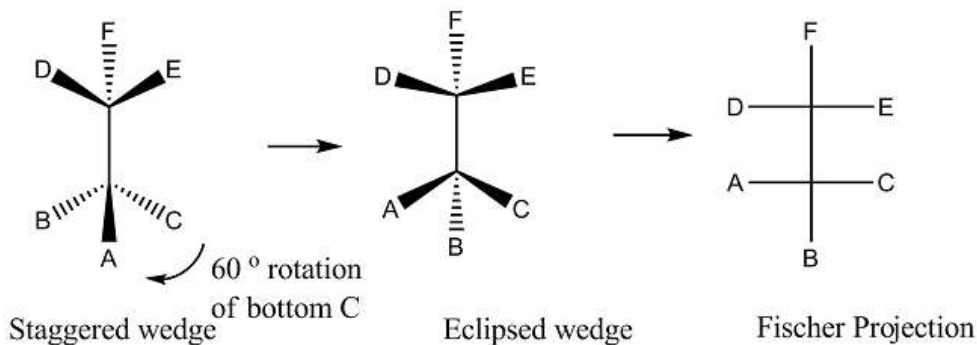


Figure 4.9: Conversion of wedge formula into Fischer projection formula

**Newman projection formula:** New man projection formal is used only for substituted ethane and not for substituted methane. The eclipse and staggered conformation of ethane can be represented using the formula. The bonds originating from the circumference of a circle is the back carbon atom and bonds origination from the center of the circle represented front carbon atom (orienting towards us).

**Conversion of Newman formula of substituted ethane to Fischer projection:**

Newman's formula for substituted ethane can be drawn either in staggers confirmation or eclipsed conformation. But Fischer projection formula can represent only eclipsed conformation of ethane. Thus in order to convert staggered Newman's formula into Fischer projection formula, fist transform staggered Newman's formula to eclipse Newman's formula and then to Fischer projection formula. The scheme is as shown below.(fig 4.10)

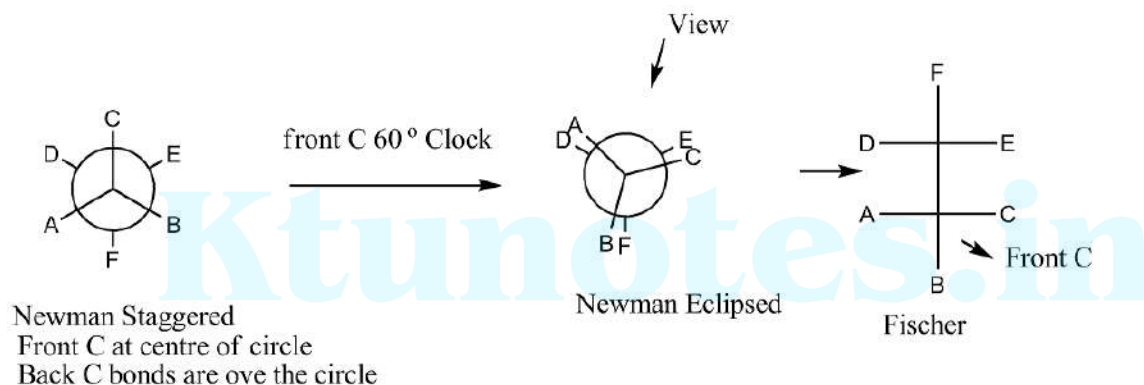


Figure 4.10: Conversion of Newman formula into Fischer projection formula

**Saw-Horse Formula:** Saw-Horse formula can represent either eclipsed or staggered conformations of ethane. Boat and chair forms of cyclohexane are represented using this formula. In this formula carbon atom oriented downwards represent front carbon atom.

**Conversion of Saw-Horse formula of substituted ethane to Fischer projection:**

Saw-Horse 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 Saw-Horse formula into Fischer projection formula, fist transform staggered Saw-Horse formula to eclipse Saw-Horse formula and then to Fischer projection formula. The scheme is as shown in fig. 4.11.

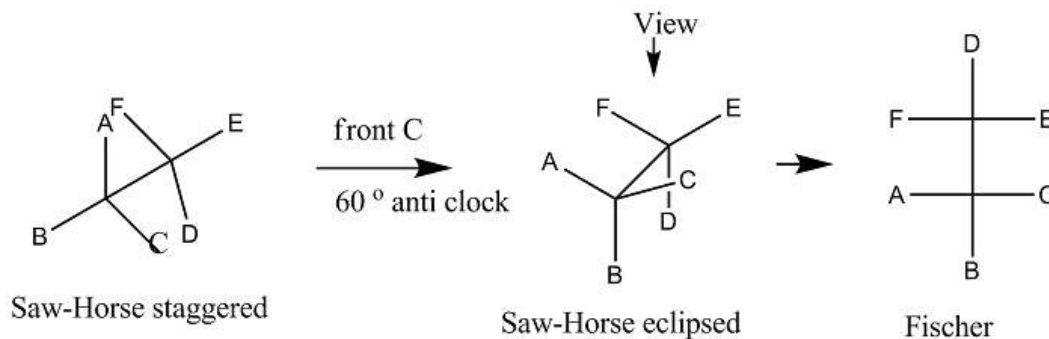


Figure 4.11: Conversion of Saw-Horse formula into Fischer projection formula

**Conversion of Saw-Horse formula of substituted ethane to Newman's formula:**

A conversion scheme is given in fig. 4.12.

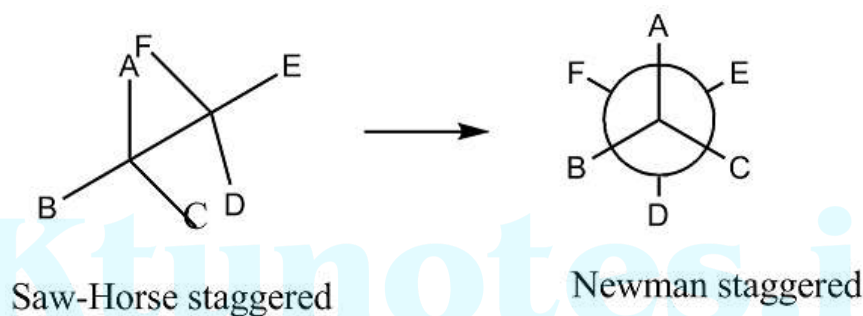


Figure 4.12: Conversion of Saw-Horse formula into Newman projection formula

**4.1.3 Stereo isomerism**

Stereo isomerism exists in organic molecules due to the difference in spacial arrangement of atoms. This can be divided into geometrical and optical isomerism.

**Geometrical isomerism**

**Geometrical isomerism in double bonds:** When carbon atoms are joined by a double bond ( $\sigma$  and  $\pi$  bonds), free rotation about this bond is restricted. Geometrical isomerism arises when the two substituents on each carbon atom are different. when all the four groups around a double bond are different (eg A,B,C,D) E,Z notations are given (see section 4.1.6).

**Geometrical isomerism in rings:** Geometrical isomerism is also possible in ring structures like cyclopropane, cyclobutane, cyclohexane etc., due to restricted rotation of  $C - C$  bonds involved in rings. In molecules like cyclohexane though bond rotation is there called "flipping", '*cis*' isomer never transform into '*trans*' isomer and the isomers can be separated.



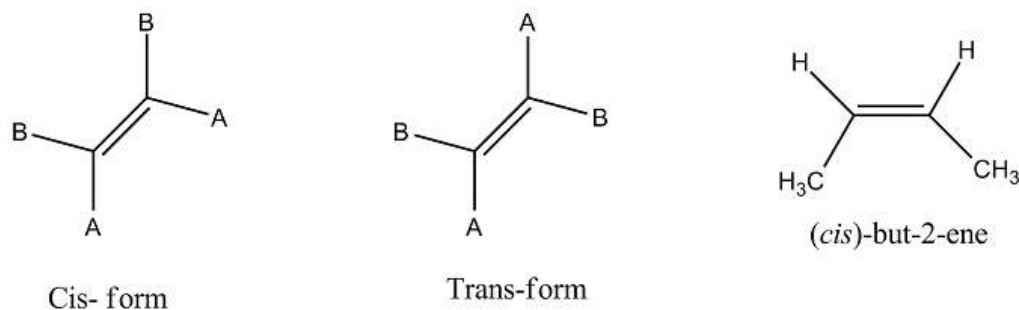
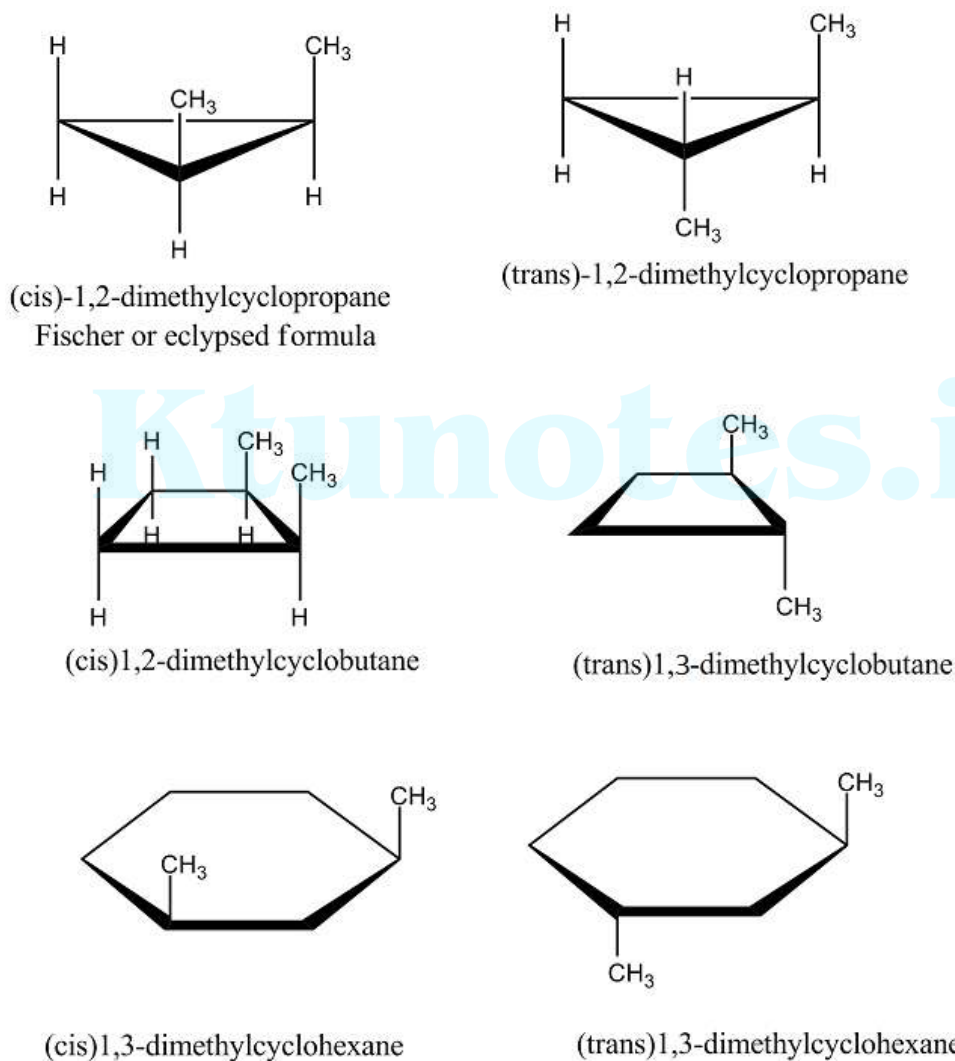
Figure 4.13: *cis* – *trans* isomerism in double bonds

Figure 4.14: Cis-trans isomerism in rings

#### 4.1.4 Optical isomerism

Certain substances possess the property to rotate plane polarised light . Such substances are called optically active substances and the phenomenon is called **optical activity**.

The substance which rotate plane polarised light clockwise is called dextrorotatory (indicated as *d* or +) while one which rotate plane polarised light anticlockwise is called levorotatory (*l* or -). The *d* and *l* isomers have same degree of rotation but opposite sign. These molecules are related to each other as their mirror images and are called **enantiomers**. The optically active isomers which are not related as mirror images are called **diastereomers**. The phenomenon is called **optical isomerism**.

**Condition for optical activity:** Non-superimposability of mirror image of a molecule with the original molecule is the only condition for optical activity. A molecule having **Chiral carbon atom** (All four groups attached to the C-atom are different) is having non-superimposable mirror image and thus optically active. Non-superimposability of mirror image can be easily checked by looking for the plane of symmetry. If a molecule possess plane of symmetry its mirror image will be superimposable and optically inactive.

All planar molecules are optically inactive since they possess plane of symmetry. 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. If two groups around a carbon atom are the same, the mirror image is superimposable and the molecule is not optically active example ethanol.

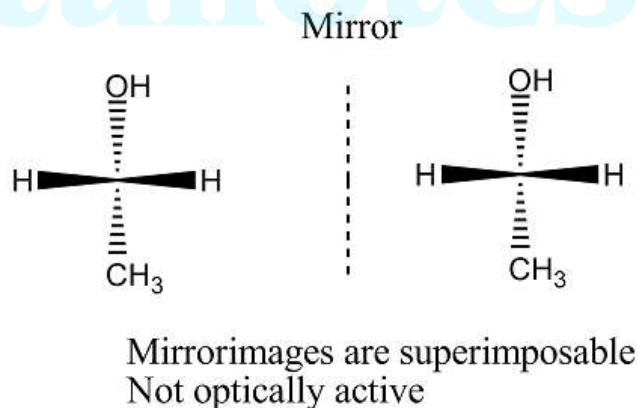


Figure 4.15: Ethanol

**Molecule having one asymmetric carbon atom:** If a molecule possess 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  $+2.67^\circ$  where as its mirror image (-) lactic acid has  $-2.67^\circ$ . Lactic acid present in sour milk is (+) lactic acid. If we have equimolar mixture of + and - forms of lactic acid net optical rotation will be zero, such mixtures are called racemic mixture.

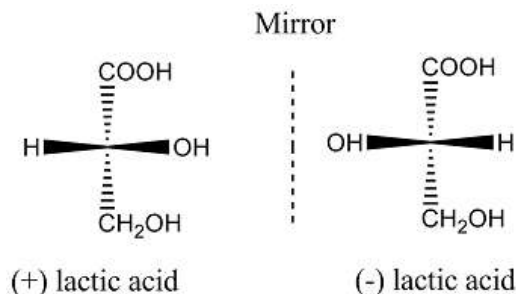


Figure 4.16: Optical isomerism in lactic acid

**Properties of enantiomers:** Physical properties like melting point, boiling point, refractive index etc are same for enantiomers but only optical rotation will be opposite. Chemical properties are also same with optically inactive reagents, but shows some differences in reactivity with optically active reagents. Biological properties like smell, taste, drug action etc show marked difference. For example *R*-limonene has the characteristic smell of orange while *S*-limonene smells like lemon. If one form of an enantiomer acts as a drug the other form may acts as a poison. For example *S*-thalidomide is a sedative drug while *R*-thalidomide is a teratogen (causes birth defects).

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

Consider 2,3-dihydroxy butanoic acid ( $\text{CH}_3 - \text{*CH}(\text{OH}) - \text{*CH}(\text{OH}) - \text{COOH}$ ), here carbon atoms marked by star are asymmetric. If there are two asymmetric carbon atoms  $2^2 = 4$  optical isomers are possible, they are shown in fig. 4.17; here (I,II) and (III,IV) are enantiomeric pairs, (I,III), (I,IV), (II,III), (II,IV) are diastereomeric pairs.

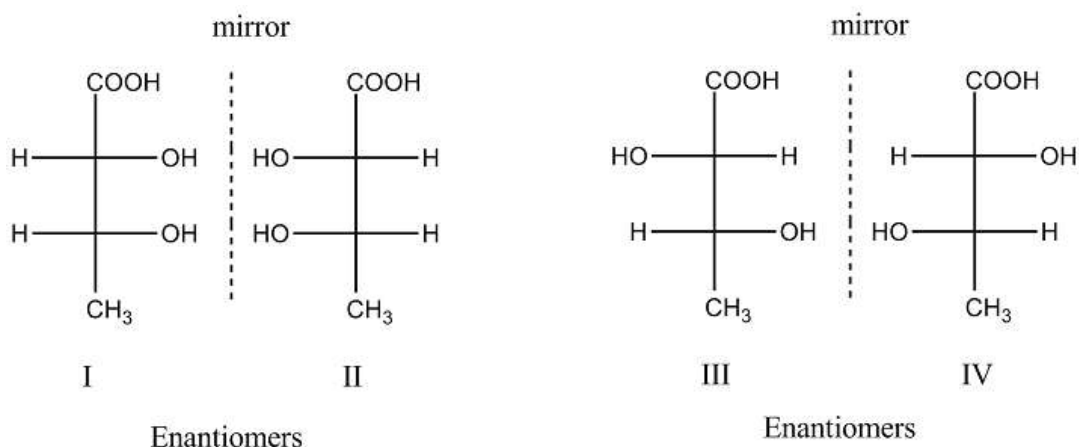


Figure 4.17: Optical isomerism in 2,3-dihydroxy butanoic acid

**Molecules having two asymmetric carbon atoms with same terminal groups.**

Consider tartaric acid ( $\text{HOOC} - \text{*CH}(\text{OH}) - \text{*CH}(\text{OH}) - \text{COOH}$ ) Here there are two chiral carbon atoms,  $2^2 = 4$  isomers are expected but since terminal groups are identical

only one enantiomeric pair and an optically inactive form called meso exists (total 3 forms).

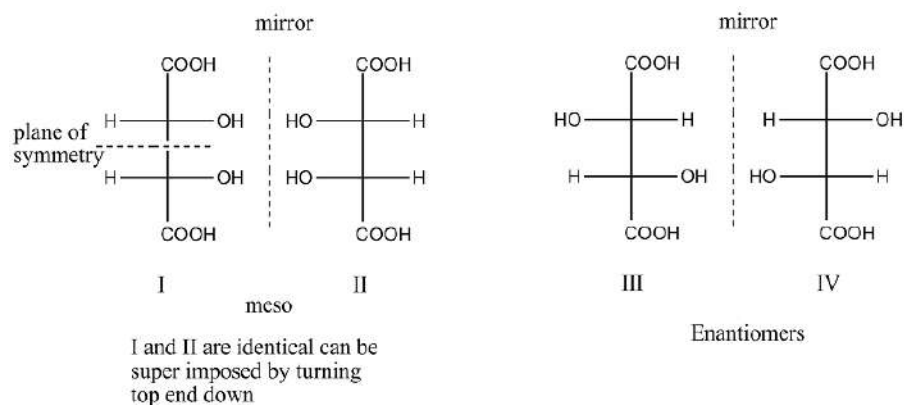


Figure 4.18: Optical isomerism in tartaric acid

**Problem 4.1.1.** How many optical isomers are possible for  $\text{CH}_3 - (\text{CHOH})_3 - \text{CH}_3$

*Ans:* There are only two asymmetric carbon atoms. The middle C-atom is not asymmetric.  $2^2 = 4$  optical isomers are possible, They are shown in fig.4.19. There are two meso forms (meso I and meso IV) and an enantiomeric pair II and III.

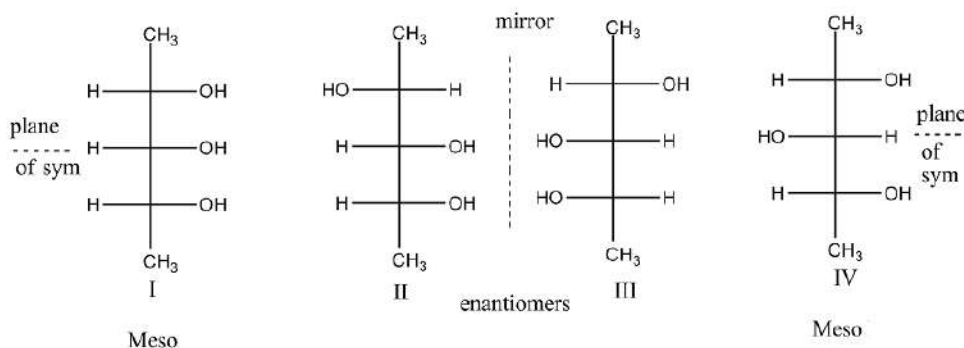


Figure 4.19: Optical isomerism in  $\text{CH}_3 - (\text{CHOH})_3 - \text{CH}_3$

**Problem 4.1.2.** 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

*Ans:* (b) and (c) (b)  $\text{CH}_3 - ^*\text{CH}(\text{NH}_2) - \text{CHO}$  Here all the four groups around the \* marked carbon atoms are different.

(c) 2-butanol  $\text{CH}_3 - \text{CH}_2 - ^*\text{CH}(\text{OH}) - \text{CH}_3$  Here all the four groups around the \* marked carbon atoms are different.

**Problem 4.1.3.** How many isomers are possible for  $C_6H_{14}$

Ans:

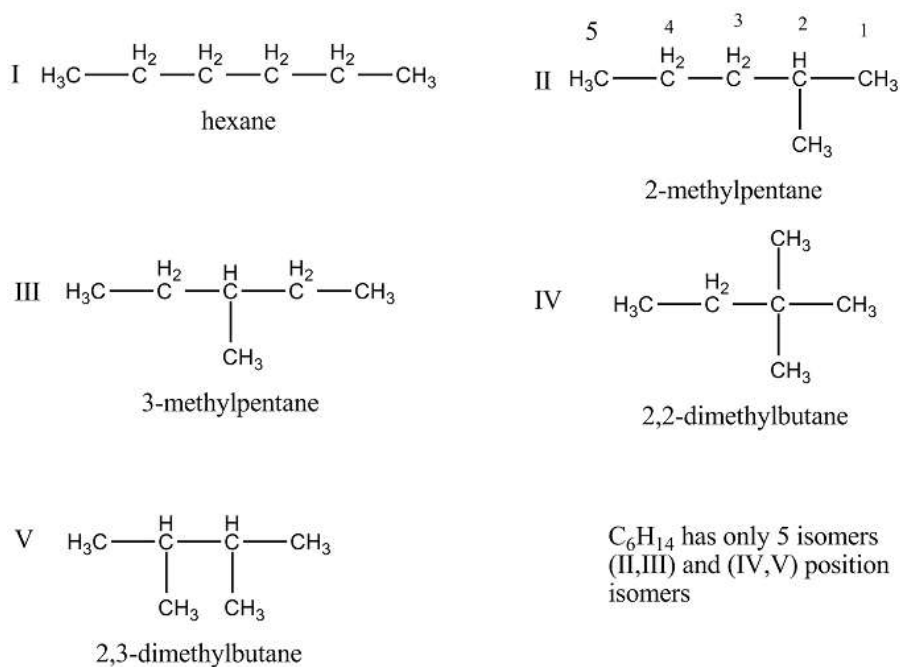


Figure 4.20: Isomers of  $C_6H_{14}$

**Problem 4.1.4.** How many isomers are possible for  $C_4H_8$

Ans:

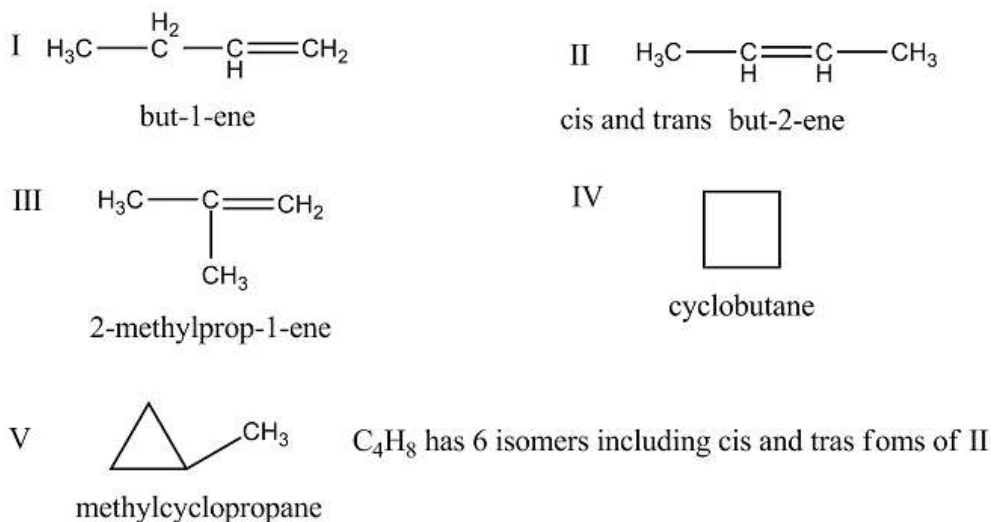
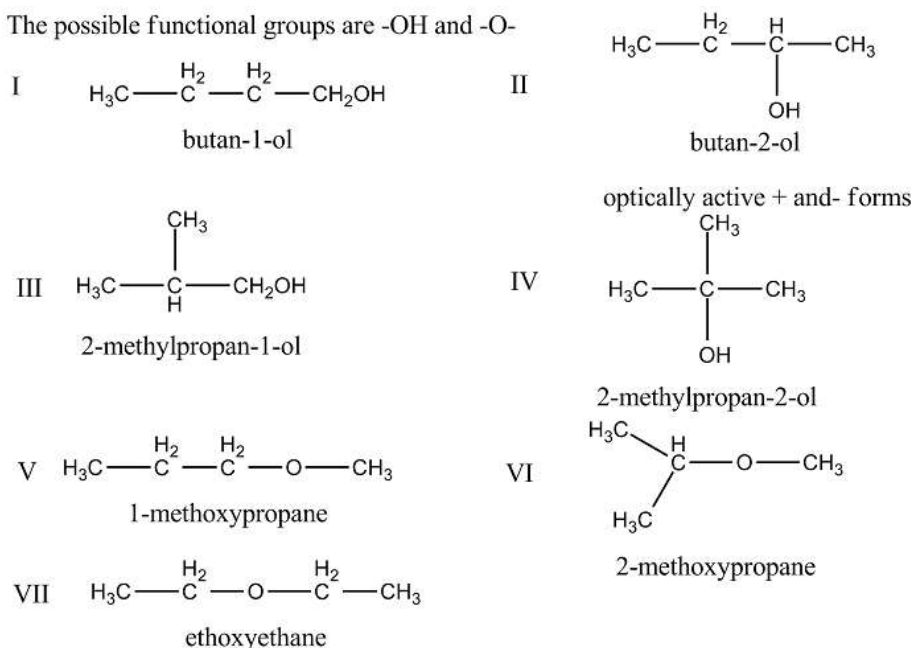


Figure 4.21: Isomers of  $C_4H_8$

**Problem 4.1.5.** How many isomers are possible for  $C_4H_{10}O$

Ans:

The possible functional groups are -OH and -O-



optically active + and- forms

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

Figure 4.22: Isomers of  $\text{C}_4\text{H}_{10}\text{O}$

**Problem 4.1.6.** Which of the following compounds are optically active?

- (cis)1,2-dimethylcyclopropane
- (trans)1,2-dimethyl cyclopropane
- (cis)1,3-dimethyl cyclobutane
- (trans)1,3-dimethyl cyclobutane
- (cis)1,2-dimethylcyclohexane
- (trans)1,2-dimethylcyclohexane.

Ans: fig. 4.23, (b) and (f)

#### 4.1.5 R and S configuration for optical isomers

This nomenclature is applied to chiral molecules based on a priority sequence assigned to groups around an asymmetric carbon atom. The rules are as follows.

- The directly attached atom having highest atomic number has highest priority for example when  $-\text{OH}$  and  $-\text{COOH}$  groups are ranked  $-\text{OH}$  has higher priority since atomic number of the first atom oxygen is 8 where as it is 6 for carbon ( $-\text{COOH}$  group)
- When two directly attached atoms are same then look for the atomic number of the next linked atom, for example when  $-\text{COOH}$  and  $-\text{CHO}$  groups are ranked  $-\text{COOH}$  has higher priority since both the second atoms are oxygen.
- For double bonds like  $-\text{C}=\text{O}$ ,  $-\text{C}=\text{C}$  are treated as two oxygen attachment and two carbon attachment respectively to first atom

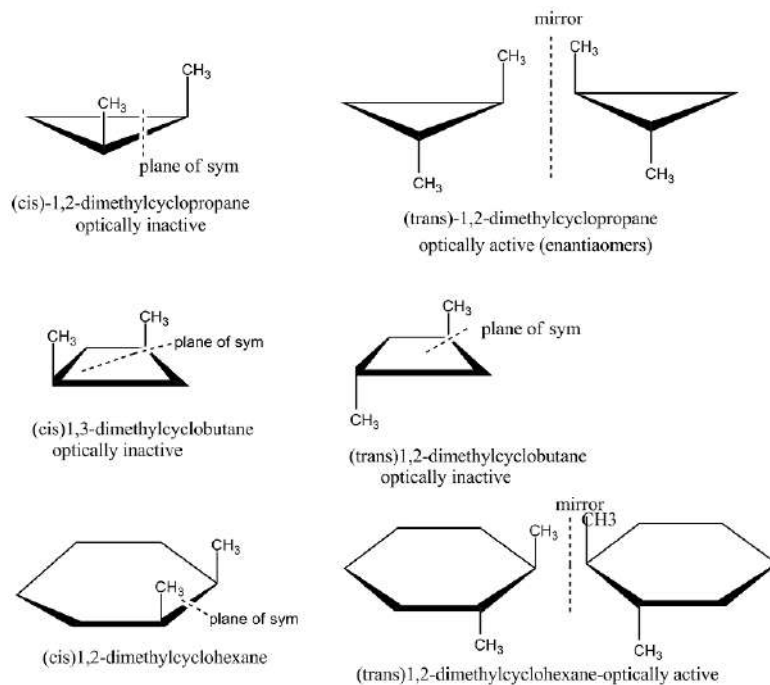
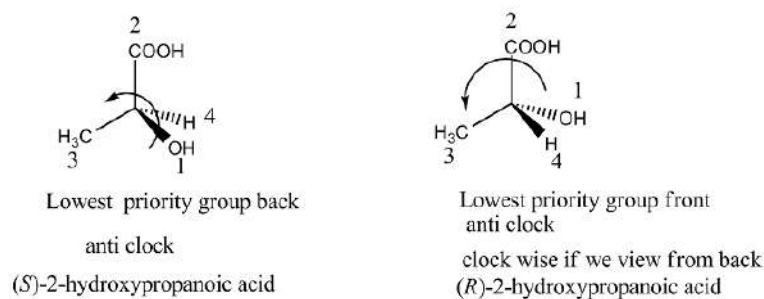


Figure 4.23: Optical isomerism in substituted rings

- The molecule is viewed such that the lowest priority group is away from us and look for priority order, if the sequence is clockwise the notation 'R' is given, if it is anti clock notation 'S' is given.
- If lowest priority group given in a structure is towards us take opposite rotation of what obtained from front side. (Or we have to perform two inter changes such that the lowest priority group is made away from us)

**Problem 4.1.7.** Assigning *R,S* notation to wedge formulaFigure 4.24: Assigning *R,S* notation to wedge formula

**Problem 4.1.8.** Assigning *R,S* notation to Fischer formula fig. 4.25

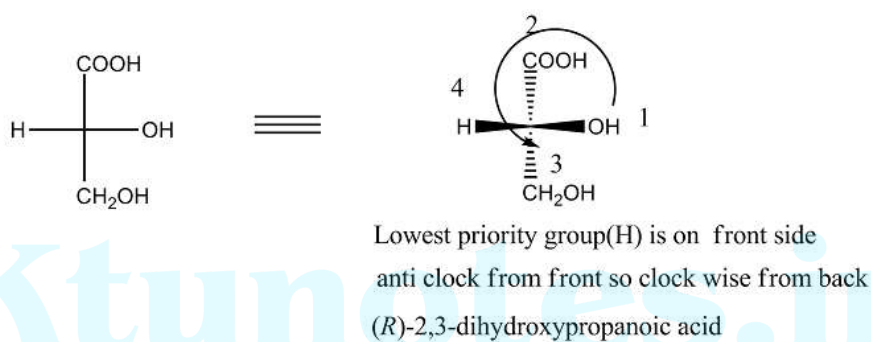
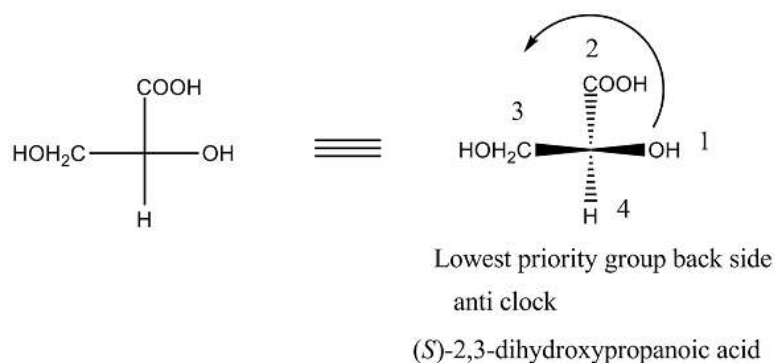


Figure 4.25: Assigning *R,S* notation to Fischer formula

**Problem 4.1.9.** Assigning *R,S* notation to Fischer projection formula for two chiral Carbon molecule fig. 4.26

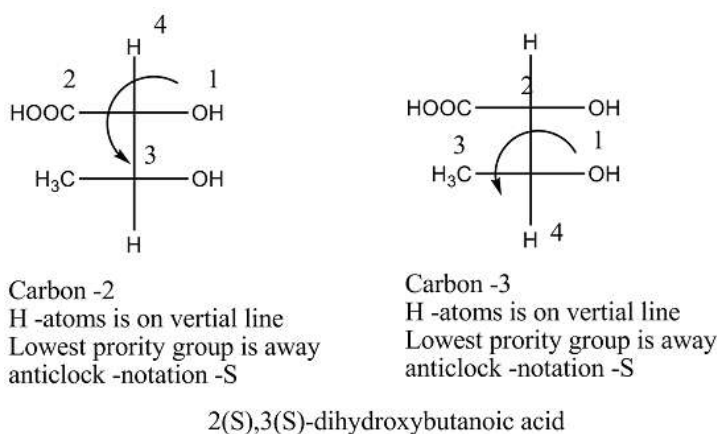
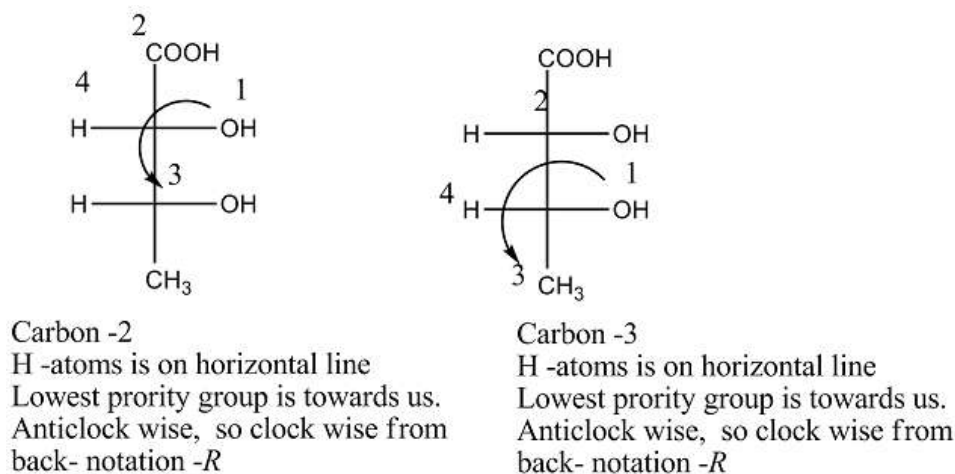


Figure 4.26: Assigning *R,S* notation to Fischer projection formula for two chiral Carbon molecule



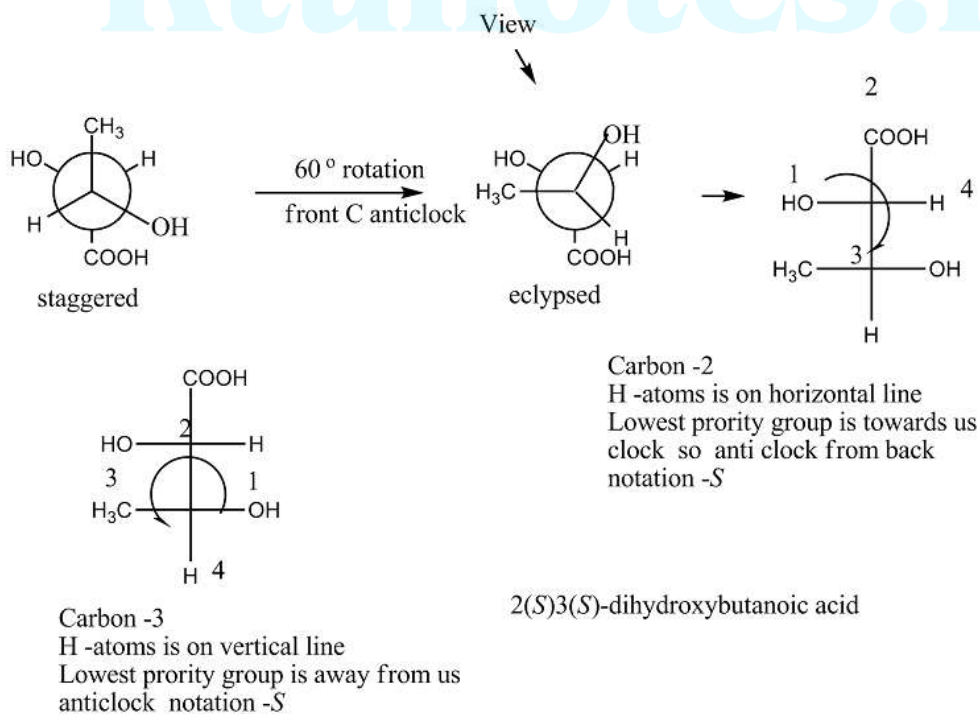
**Problem 4.1.10.** Assigning *R,S* notation to Fischer projection formula for two chiral Carbon molecule fig. 4.27



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

Figure 4.27: Assigning *R,S* notation to Fischer projection formula for two chiral Carbon molecule

**Problem 4.1.11.** Assigning *R,S* notation to Newman projection formula fig. 4.28



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

Figure 4.28: Assigning *R,S* notation to Newman projection formula

### 4.1.6 E and Z Nomenclature of geometrical isomers

The cis-trans nomenclature can not be applied to if all the four groups around double bonded carbon atoms are different. Here E-Z notation is used to assign geometrical isomerism. The rules are as follows

1. Groups around the two double bonded carbon atoms are separately given priority based on the rules used for R-S notation.
2. In first priority groups are on same side the notation 'Z' is given and if first priority groups are on opposite side the notation 'E' is given in fig. 4.29

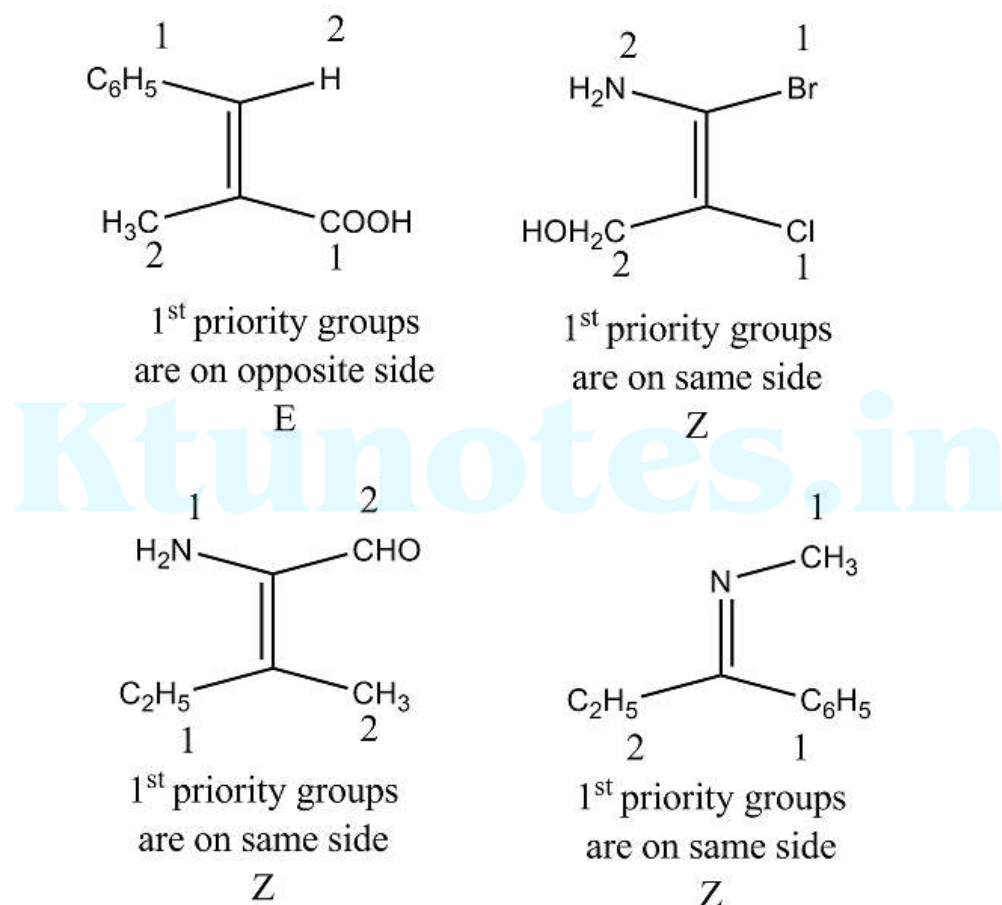


Figure 4.29: E-Z notations

### 4.1.7 Conformational analysis

The different spatial arrangement of atoms that results from 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 the other, low energy conformer is more populated than high energy conformer at room temperature.

### Conformation of ethane

The conformations of ethane ( $\text{CH}_3 - \text{CH}_3$ ) result from the rotation of back  $-\text{CH}_3$  about a  $\text{C} - \text{C}$   $\sigma$  bond while keeping front  $-\text{CH}_3$  fixed. The conformations can be better shown with Newman's projection formula. According to Newman's projection formula front carbon atom is shown at the center of the circle with the three  $\text{C} - \text{H}$  bonds placed at projection angle of  $120^\circ$ . The back carbon atom  $\text{C} - \text{H}$  bonds are shown over the circle which is also placed at projection angle of  $120^\circ$ . In eclipsed conformation the dihedral angle between the  $\text{C} - \text{H}$  bond of front and back carbon atom is zero, where as in staggered conformation it is  $60^\circ$ . In between these two extreme conformations there are infinite number of conformations possible depending on the dihedral angle. Experiments show that there is a 12 kJ/mol barrier between staggered and eclipsed conformations. The most stable (low energy) conformation is the one in which all six  $\text{C} - \text{H}$  bonds are as far away from each other as possible (staggered), so that  $-\text{C} - \text{H}$  bond repulsion between the two  $-\text{CH}_3$  groups is minimum. The least stable (high energy) conformation is the one in which the six carbon-hydrogen bonds are as close as possible (eclipsed). All other conformations lie in between these two limits.

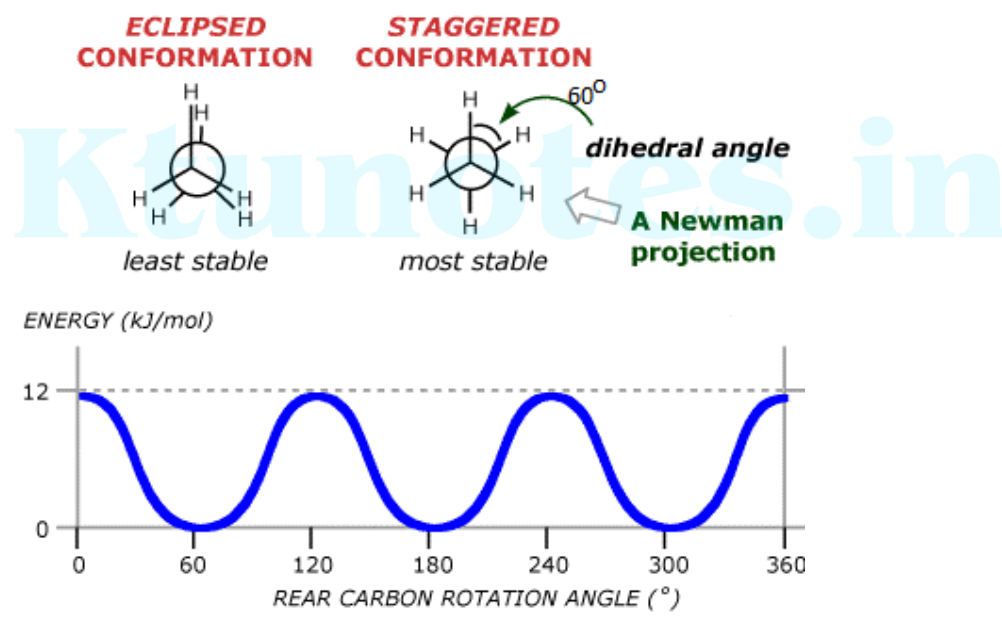


Figure 4.30: Conformation of ethane

### Conformations of butane

Conformations of butane about  $\text{C}_2 - \text{C}_3$  bond is important. Here the structure D in fig.4.31 has the highest energy with zero dihedral angle. The structure D is called fully-eclipsed conformation, it has high torsional strain energy because of bulky  $-\text{CH}_3$  groups are close to each other. When the front carbon atom of structure D is rotated through  $60^\circ$  (while keeping back carbon fixed) in clockwise or anti clock wise direction structure

B is obtained, it is called skew or Gauche form. The Gauche form is stable by an energy of 14.2 kJ/mol from fully eclipsed form D. When the front carbon atom of structure D is turned through  $120^\circ$  in clockwise or anti clockwise direction another eclipsed form is obtained, called eclipsed form (structure C). When structure D is turned through an angle of  $180^\circ$  in clockwise or anti clockwise direction fully staggered form A is obtained. It is also called Anti-form, it is the lowest energy form. The energy difference between the extreme conformations A and D is 19 kJ/mol.

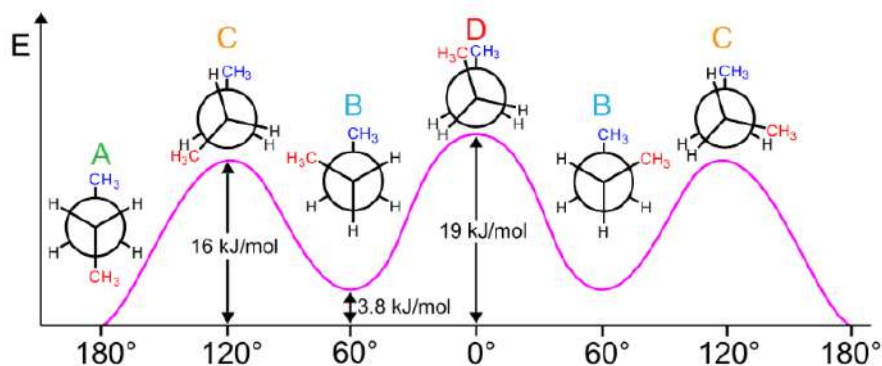


Figure 4.31: Conformation of butane

### Conformations of cyclohexane

In cyclohexane if we assume planar geometry the C-C-C bond angle become  $120^\circ$ , there is large bond angle strain due to high deviation from tetrahedral bond angle of  $109.5^\circ$ . Chair and boat forms are the two conformation of cyclohexane in which tetrahedral bond angle is maintained. In chair form all the C-H bonds are staggered where as in boat form  $C_2 - C_3$  and  $C_5 - C_6$  bonds are in eclipsed state.

**Chair form** In chair form all the C-H bonds are staggered. There are two types of C-H bonds in cyclohexane axial and equatorial. Axial bonds are shown in vertical direction and equatorial bonds are shown in slightly inclined from horizontal direction (fig. 4.32). Axial bonds are converted into equatorial bonds by C-C bond rotation in ring called flipping. The presence of axial and equatorial hydrogen atoms are confirmed from NMR spectrum at  $-60^\circ\text{C}$  which gives two different chemical shifts (At low temperature the flipping is arrested).

**Boat form** In chair form all C-H bonds are staggered where as in boat form  $C_2 - C_3$  and  $C_5 - C_6$  bonds are in eclipsed state. Boat form is less stable than chair form by 28 kJ/mole, due to eclipsing at  $C_2 - C_3$  and  $C_5 - C_6$  bonds and flagpole interactions. Boat conformation is stabilized in certain molecules like (cis)1,4-dihydroxy cyclohexane, due to hydrogen bonding through flagpole bonds and in bridge head compound like camphor.

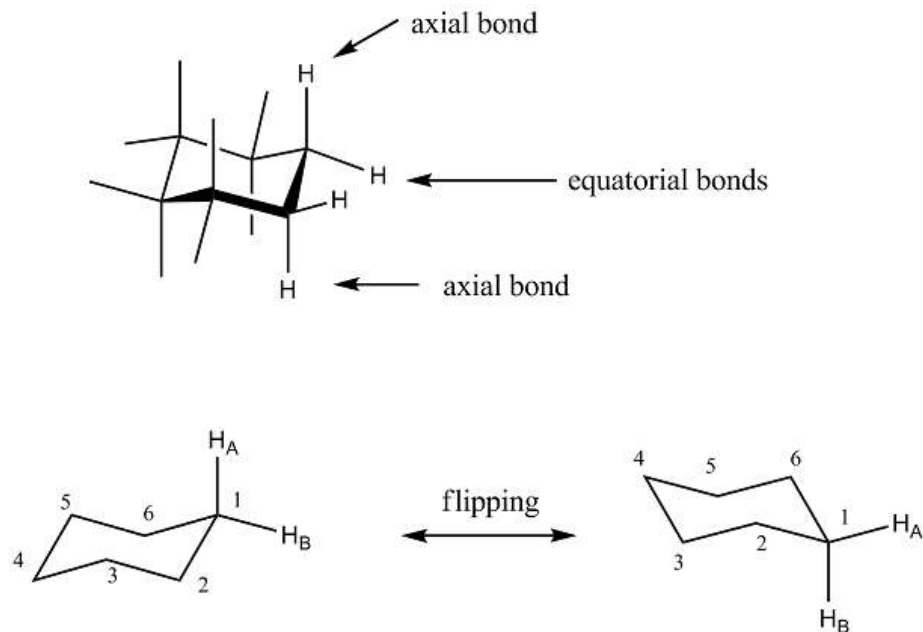


Figure 4.32: Chair Conformation of cyclohexane

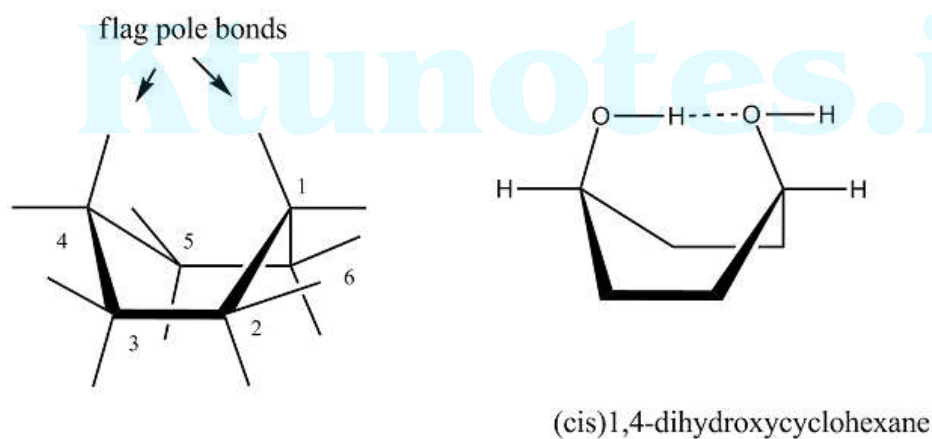


Figure 4.33: Boat Conformation of cyclohexane

**Conformations of mono methyl substituted cyclohexane** Methyl group can be placed at axial or equatorial positions of cyclohexane. Axial methyl bond rapidly changes to equatorial bond by carbon-carbon bond rotation in ring, called flipping. Thus axial methyl cyclohexane cannot be separated from equatorial methyl cyclohexane. Axial methyl group has two Gauche interactions (see conformations of butane) about  $C_1 - C_2$  bond and  $C_1 - C_6$  bond with  $-CH_2-$  groups of the ring where as equatorial methyl has no such interactions. Thus equatorial methyl cyclohexane is more stable than axial methyl cyclohexane and population of equatorial methyl cyclohexane is slightly more in the equilibrium mixture of the two conformers.

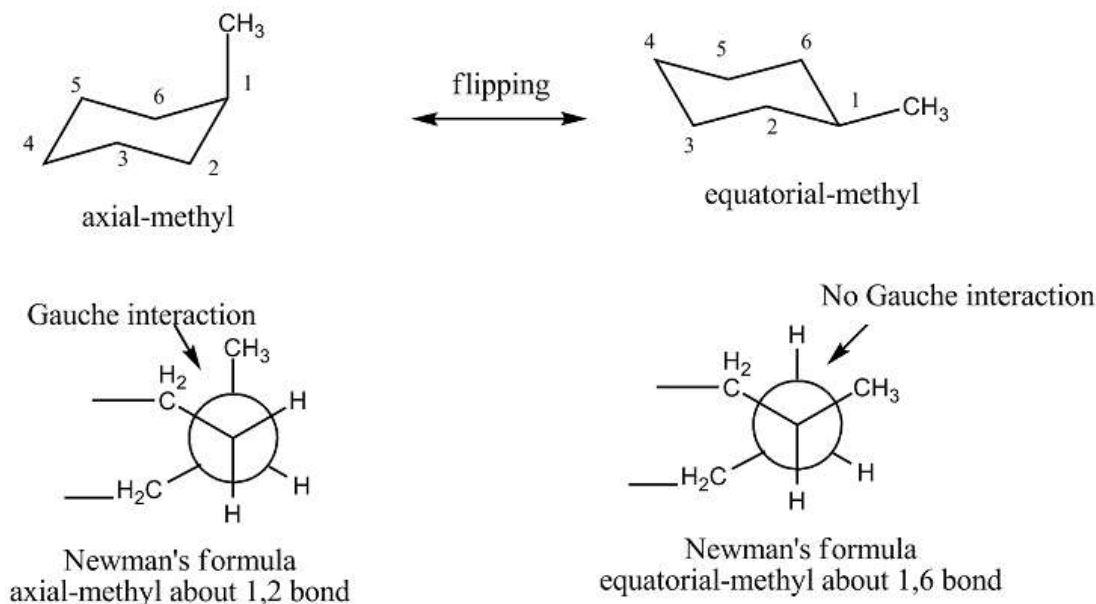


Figure 4.34: Conformations of mono methyl substituted cyclohexane

### Conformations of dimethyl substituted cyclohexane

There are four possible position isomers for dimethyl substitution, namely (1,1), (1,2), (1,3) and (1,4)

**1,1-dimethyl cyclohexane** When there are two methyl groups,  $-CH_3$  groups are substituted at axial and equatorial position of  $C_1$ . On flipping axial bonds are converted to equatorial bonds and vice-versa, thus only one conformer exists.

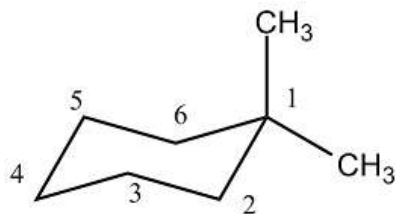


Figure 4.35: Conformations of 1,1-dimethyl cyclohexane

**1,2-dimethylcyclohexane:** 1,2-dimethyl cyclohexane has two geometrical isomers cis and trans, they will not inter convert each other by flipping.

**(cis)1,2-dimethyl cyclohexane** has two conformers (1a,2e) and (1e,2a), here 'a' refers to axial and 'e' to equatorial bonds. Both (1a,2e) and (1e,2a) forms are equally stable as they have equal number of Gauche interactions (three). (fig.4.36)

**(trans)1,2-dimethyl cyclohexane** has two conformers (1a,2a) and (1e,2e). They inter convert each other by flipping. In (1a,2a) form each axial methyl group has two Gauche

iterations with the ring  $CH_2$  groups, thus there are 4 gauche interactions whereas as (1e,2e) form has only one Gauche interaction in  $C_1 - C_2$  between  $-CH_3$  groups. Thus (1e,2e) conformer is more stable in (trans)1,2-dimethyl cyclohexane (fig 4.36).

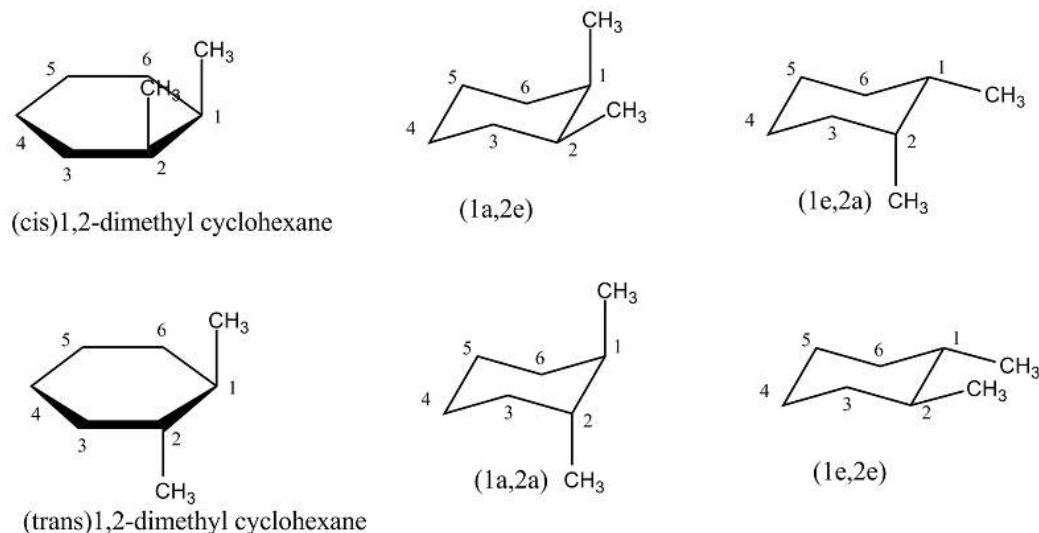


Figure 4.36: Conformations of 1,2-dimethyl cyclohexane

**1,3-dimethylcyclohexane:** 1,3-dimethyl cyclohexane has two geometrical isomers cis and trans and they will not inter convert each other by flipping.

**(cis)1,3-dimethyl cyclohexane** has two conformers (1a,3a) and (1e,3e), here 'a' refers to axial and 'e' to equatorial bonds. They inter convert each other by flipping. In (1a,3a) conformer each axial methyl group has two Gauche interactions with the ring  $CH_2$  groups, thus there are 4 gauche interactions, whereas (1e,3e) conformer has no Gauche interactions. Thus (1e,3e) conformer is more stable in (cis)1,3-dimethyl cyclohexane (fig 4.37).

**(trans)1,3-dimethyl cyclohexane** has two conformers (1a,3e) and (1e,3a). They inter convert each other by flipping. Both (1a,3e) and (1e,3a) forms are equally stable as they have equal number of Gauche interactions (two) (fig 4.37).

**1,4-dimethylcyclohexane** 1,4-dimethyl has geometrical isomers cis and trans forms and they will not inter convert each other by flipping. **(cis)1,4-dimethyl cyclohexane** has two conformers (1a,4e) and (1e,4a). Both (1a,4e) and (1e,4a) forms are equally stable as they have equal number of Gauche interactions (two).

**(trans)1,4-dimethyl cyclohexane** has two conformers (1a,4a) and (1e,4e). They inter convert each other by flipping. (1a,4a) form each axial methyl group has two Gauche interactions with the ring  $CH_2$  groups, thus there are 4 gauche interactions, whereas (1e,4e) form has no Gauche interaction. Thus (1e,4e) conformer is more stable in (trans)1,4-dimethyl cyclohexane



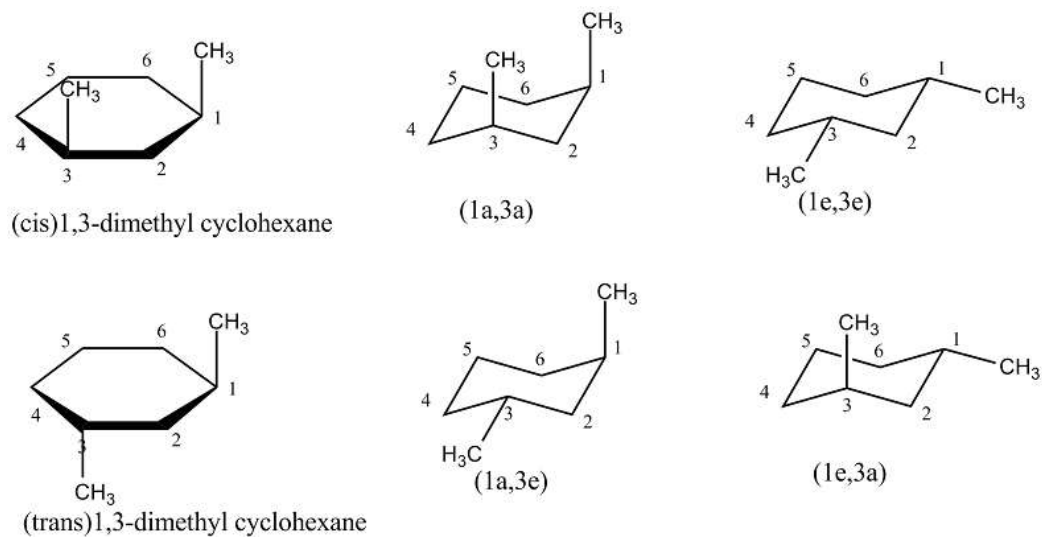


Figure 4.37: Conformations of 1,3-dimethyl cyclohexane

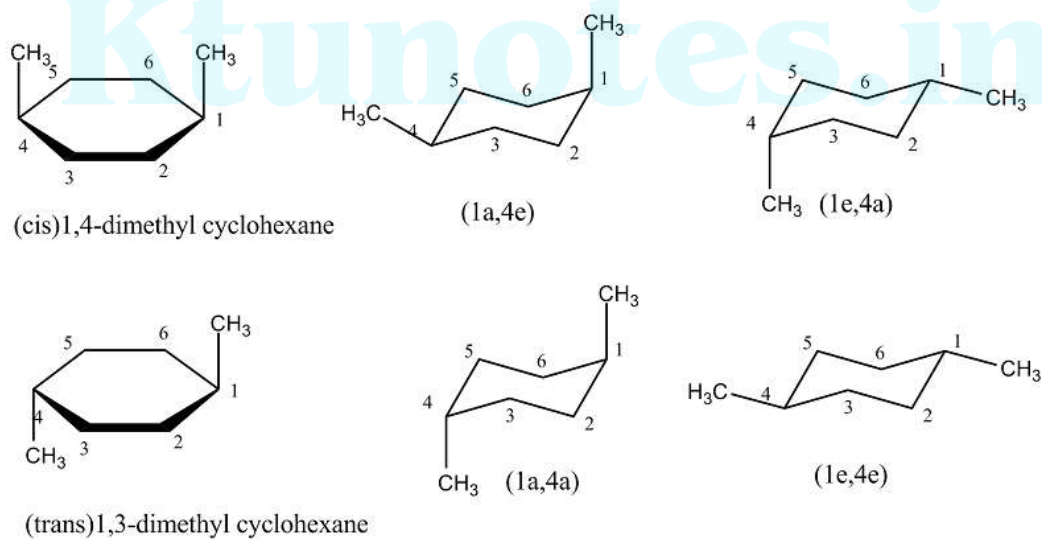


Figure 4.38: Conformations of 1,4-dimethyl cyclohexane

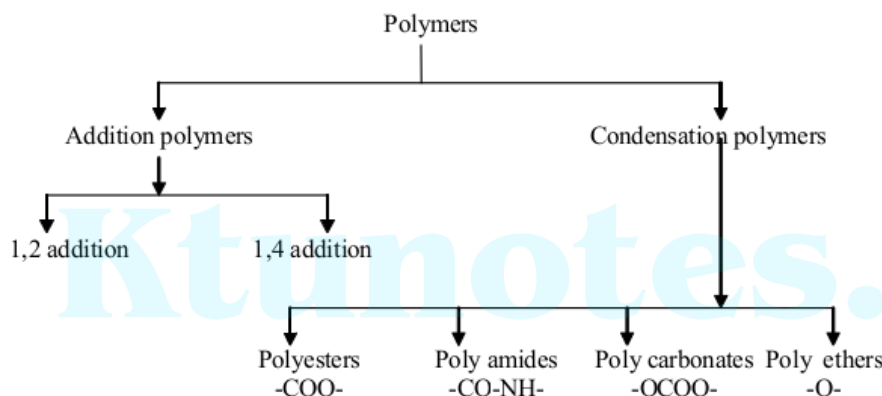


## 4.2 Polymers

Polymers are molecules with large molecular masses obtained by the covalent linkage of several small repeating chemical units called monomers. The repeating chemical unit may be same or different. A homo polymer is made of only one type of monomer e.g. Polyethylene, Poly propylene, PVC, etc. The number of repeating units is called the degree of polymerization. A co-polymer is made of two or more different monomeric species. e.g. butadiene-styrene (BS), Acrylonitrile butadiene-styrene (ABS ),etc.

### 4.2.1 Classification Based on Types of polymerization.

Based on the types of polymerization, polymers can be broadly divided into addition and condensation polymers.



### Addition Polymers

Addition polymers are formed by linking together simple unsaturated molecules. The driving force of addition polymerization is the conversion of weak carbon-carbon  $\pi$ -bonds into strong carbon-carbon  $\sigma$ -bonds. There are two types of addition polymers i.e. 1,2-addition and 1,4- addition. Addition polymerization is brought about by adding a small amount of substance called initiators. These substances help in the formation of free radicals, cations or anions. The monomer units are added to the free radicals or active species and chain growth takes place. Therefore addition polymerization is also called chain growth polymerization.

**1,2 Addition Polymers** In 1,2 addition each monomer consists of a  $\pi$ -bond, during polymerisation it is converted to a  $\sigma$ -bond, joining 1,2 positions of each monomer unit. Example: polymerisation of ethylene, propene, polyvinyl chloride, which are summarized in table 4.1. In addition polymerisation each monomer unit is added to growing chain therefore called chain growth polymerisation.

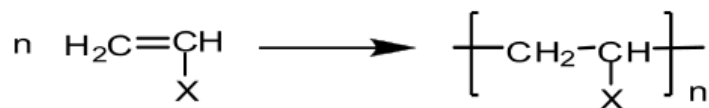


Figure 4.39: 1,2 Addition Polymers

Table 4.1: Comparison between 1,2-addition and 1,4-addition polymerisation

1,2-addition	1,4-addition
$X = -H$ Polyethylene(P.E)	$X = H$ Polybutadiene rubber
$X = -CH_3$ Polypropylene (P.P)	$X = CH_3$ Polyisoprene; cis form: Natural rubber, trans form: Synthetic Polyisoprene and gutta-percha
$X = -C_6H_5$ Polystyrene (P.S)	$X = -Cl$ Chloroprene rubber or Neoprene
$X = -Cl$ Polyvinyl Chloride (PVC)	
$X = -OH$ Polyvinyl alcohol	
$X = -CN$ Poly acrylo nitrile(PAN)	
$X = -COOH$ Poly acrylic acid	
$X = -COOCH_3$ Poly methacrylate (PMA)	
$X = -O-CO-CH_3$ Poly vinyl acetate (PVA)	

**1,4 addition Polymers** In 1,4 addition each monomer unit consists of two  $\pi$ -bonds, during polymerisation one new  $\pi$ -bond is formed at the middle (2,3 ) position and a  $\sigma$ -bond is formed by connecting 1,4 positons of each monomer unit. Example: polymerisation of butadiene, isoprene, chloroprene.

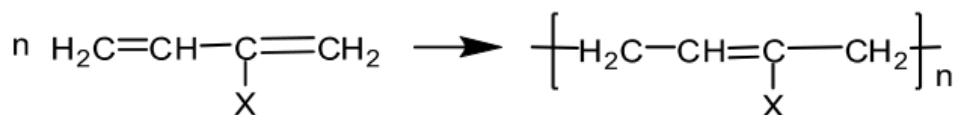


Figure 4.40: 1,4 addition Polymers

### 4.2.2 Condensation Polymers

Condensation polymerization takes place by linking together monomer molecules and is accompanied by elimination of simple molecules like water, ammonia, HCl etc. In condensation polymerization, monomer units used are generally different. In condensation polymerization, the degree of polymerization depends on the availability of the reactive groups at the ends of a growing chain. The condensation polymerization is also called step growth polymerization as the process of chain growth takes place from all parts in a step by step manner. For example condensation of terephthalic acid with ethylene glycol gives polyethylene terephthalate(PET).

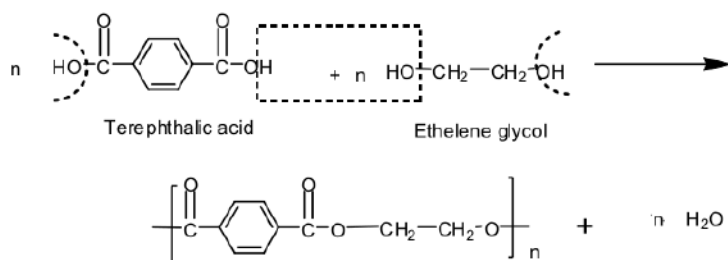


Figure 4.41: Polyethylene terephthalate(PET)

### 4.2.3 Co-polymers

Copolymerization is the polymerization of two or more different monomeric species together. e.g. Acrylonitrile-vinyl chloride, Butadiene-styrene(BS), Acrylonitrile-butadiene-styrene (ABS). Here composition of monomers can vary and can make polymers having wide range of properties.

Co-polymerization is also possible in condensation polymers by choosing combination

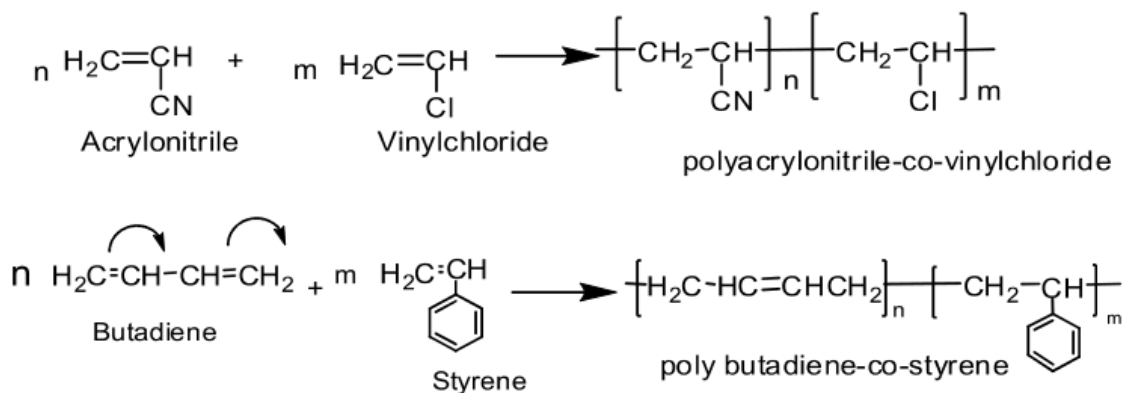


Figure 4.42: Co-polymers

of analogous molecules. For example poly ester can be prepared by taking a mixture of ethylene glycol and propan-1,3-diol for condensing with terephthalic acid in appropriate combinations.

### Types of Co-polymers

The repeating units of a co-polymer can be structurally arranged in different forms.

1. **Random co-polymers:** During co-polymerization, if a mixture of monomers are allowed to polymerize, only a random co-polymer is obtained. For example when a mixture acrylonitrile (A) and vinylchloride (B) is allowed to polymerize the random co-polymer obtained can be depicted as flows



Figure 4.43: Random co-polymers

2. **Alternating co-polymers** An alternating co-polymer comprising two species of monomeric units distributed in alternating sequence. The arrangement **-A-B-A-B-A-B-A-B-** or (AB)<sub>n</sub> represents an alternating co-polymer. For example an alternating polymer of styrene and butadiene can be produced reacting styrene and butadiene to form an adduct which contain one molecule from each, which further polymerized giving an alternating co-polymer.
3. **Block co-polymers:** This type of co-polymers can be synthesized by partially polymerizing each monomer into a resin or semi polymer. The semi-polymer obtained, on further combination results in a block copolymer. Here the monomers form long blocks.

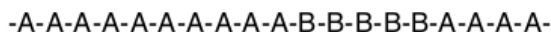


Figure 4.44: Block co-polymers

4. **Graft co-polymers:** It is a type of block Copolymer. Here the semi polymers of one monomer (B) are grafted to the high polymer main chain (A). Here the main chain is formed of one monomer and the grafted chain of another monomer.

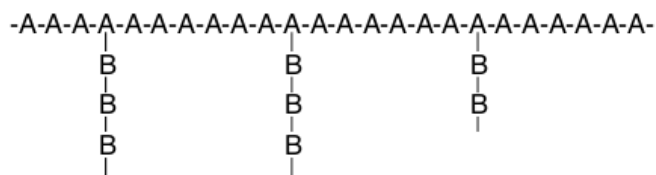


Figure 4.45: Graft co-polymers

### ABS-Acrylonitrile butadiene styrene

ABS is a terpolymer made by polymerizing styrene and acrylonitrile in the presence of polybutadiene. The proportions can vary from 15 to 35 percentage acrylonitrile, 5

to 30 percentage butadiene and 40 to 60 percentage styrene. The polymer is a long chain of polybutadiene blocks criss-crossed with random shorter chains of poly(styrene-co-acrylonitrile). The nitrile groups from neighbouring chains, being polar, attract each other

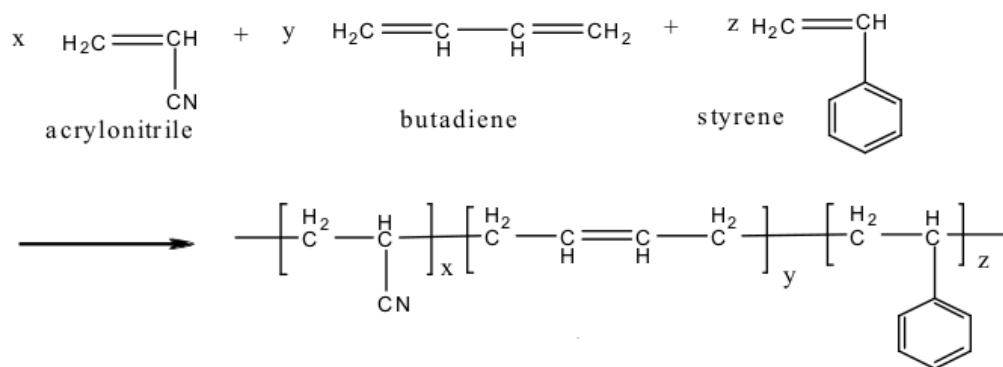


Figure 4.46: ABS

and bind the chains together, making ABS stronger than pure polystyrene. The styrene gives the plastic a shiny, impervious surface. The polybutadiene, a rubbery substance, provides resilience even at low temperatures. For the majority of applications, ABS can be used between  $-20^\circ\text{C}$  and  $80^\circ\text{C}$  as its mechanical properties vary with temperature.

**Properties:** ABS is an amorphous thermoplastic polymer having a glass transition temperature of  $105^\circ\text{C}$ . It can be engineered to give a range of physical properties depending on the ratio of the monomeric constituents. It has the strength and rigidity of acrylonitrile and styrene with added toughness of polybutadiene. It is considered superior for its hardness, gloss, toughness and electrical insulation properties. It has high impact resistance and resistant to aqueous acids and alkalies. The electrical properties are fairly constant over a wide range of frequencies. These properties are little affected by temperature and humidity. The important characteristics are

1. Medium strength
2. Tough, hard and rigid
3. Good chemical resistance
4. Dimensional stability
5. Creep resistant
6. Electroplatable
7. Outstanding formability
8. Very high impact strength
9. High tensile strength and stiffness

10. Excellent high and low temperature performance
11. Excellent ductility

**Applications:** ABS is light weight and has ability to be injection moulded and extruded make it useful in manufacturing products such as TV cabin, computer monitor body, computer key board, mobile phone body, kitchen appliances like mixer grinder, musical instruments, golf club heads (because of its good shock absorbance), automotive trim components, automotive bumper bars, medical devices for blood access, enclosures for electrical and electronic assemblies, Household and consumer goods.

#### 4.2.4 Kevlar<sup>®</sup> (Poly-paraphenylene terephthalamide)

Kevlar brand fiber is an innovative technology from DuPont that combines high strength with light weight was invented by Polish-American chemist Stephanie Kwolek. Kevlar is synthesized in solution from the monomers 1,4-phenylene-diamine (para-phenylenediamine) and terephthaloyl chloride in a condensation reaction yielding hydrogen chloride gas as byproduct. The result is a polymeric aromatic amide (aramid) with alternating benzene rings and amide groups. When they are produced, these polymer strands are aligned randomly. To make Kevlar, they are dissolved and spun, causing the polymer chains to orient in the direction of the fibre.

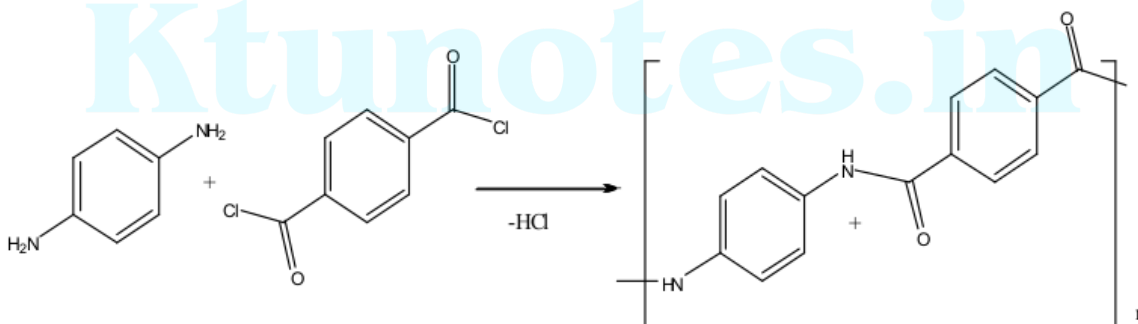


Figure 4.47: Kevlar

**Properties:** When Kevlar is spun, the resulting fiber has a tensile strength of about 3,620 MPa, and a relative density of 1.44. The polymer owes its high strength to the many inter-chain bonds. These inter-molecular hydrogen bonds form between the carbonyl groups and NH centers. Additional strength is derived from aromatic stacking interactions between adjacent strands. These interactions have a greater influence on Kevlar than the van der Waals interactions and chain length that typically influence the properties of other synthetic polymers and fibers. Kevlar's structure consists of relatively rigid molecules which tend to form mostly planar sheet-like structures.

Kevlar maintains its strength and resilience down to cryogenic temperatures ( $-196^{\circ}\text{C}$ ); in fact, it is slightly stronger at low temperatures. At higher temperatures the tensile

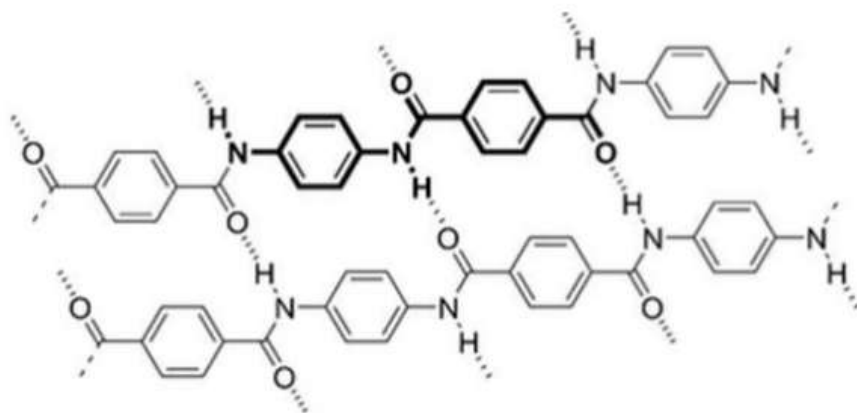


Figure 4.48: Molecular structure of Kevlar: bold represents a monomer unit, dashed lines indicate hydrogen bonds

strength is immediately reduced by about 10-20 percentage, and after some hours the strength progressively reduces further. For example at  $160^{\circ}\text{C}$  about 10 percentage reduction in strength occurs after 500 hours. At  $260^{\circ}\text{C}$  50 percentage strength reduction occurs after 70 hours.

### Applications

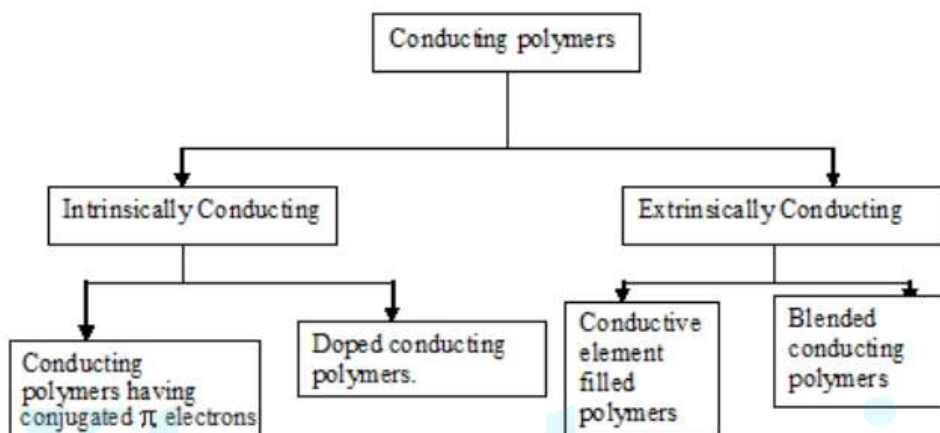
1. Kevlar is often used in the field of cryogenics for its low thermal conductivity and high strength at low temperature. Kevlar composites are used as thermal insulator for liquid  $\text{H}_2$  storage tanks of cryogenic rockets.
2. Kevlar shows high strength to weight ratio comparable to that of steel; therefore used in aerospace applications.
3. Kevlar is a well-known component of personal armor such as combat helmets, ballistic face masks, and ballistic vests. Kevlar is used to manufacture gloves, sleeves, jackets and other articles of clothing designed to protect users from cuts, abrasions and heat.
4. Kevlar has also been found to have useful acoustic properties for loudspeaker cones, specifically for bass and midrange drive units.
5. Kevlar has been used as a strength member in fiber optic cables such as the ones used for audio data transmissions.

## 4.3 Conducting Polymers

**Introduction:** In general, polymers are found to be insulators. With in the past few years, a new class of organic polymers have been synthesized which possess remarkable ability to conduct electrical current. A polymer which can conduct electricity is termed as conducting polymer. Among many polymers known to be conductive, poly acetylene,

poly aniline and poly pyrrole have been studied most. However, the conductive polymer that was actually launched this new field was poly acetylene.

**Classification:** Conducting polymers can be classified into following types

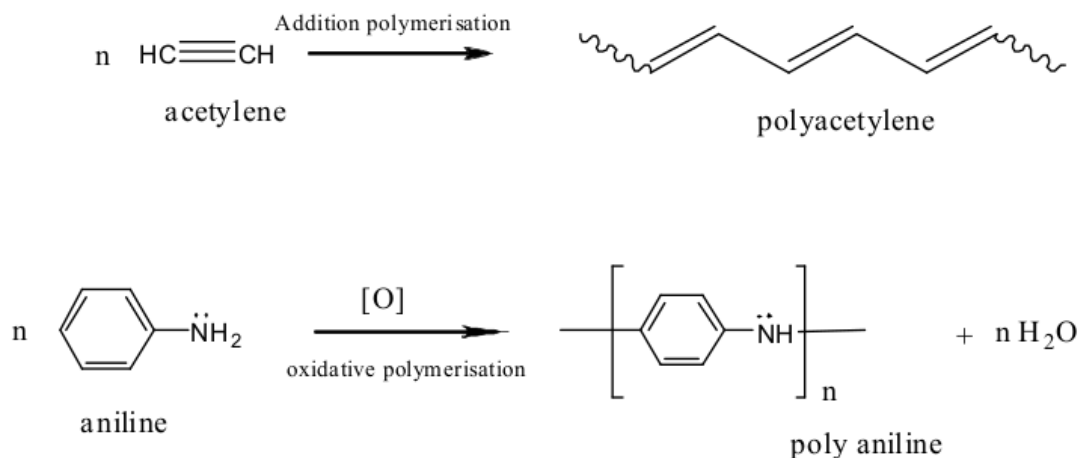


#### 4.3.1 Intrinsically conducting polymers

These polymers have extensive conjugation in the backbone which is responsible for conductance. This is again classified as

1. **Conjugated  $\pi$ -electron conducting Polymers:** A key property of a conducting polymer is the presence of conjugated double bonds along the backbone of the polymer. The orbitals of conjugated  $\pi$ -electrons overlap over the entire backbone of the polymer, resulting in the formation of valence bands and conduction bands, which extends over the entire polymer molecule. The highest occupied band is called valence band and lowest unoccupied band is the conduction band. These bands are separated by significant band gap. Thus electrical conduction would occur when electron from valence band are excited to conduction band either thermally or photolytically eg. polyacetylene and polyaniline





2. **Doped conducting polymers:** In comparison to conventional polymers the conducting polymers with conjugated  $\pi$ -electrons in their backbone can be easily oxidized or reduced as they have low ionization potentials and high electron affinities, i.e., their conductivities can be increased by creating positive or negative charge on polymer backbone by oxidation or reduction. This process is referred to as 'Doping' and are of two types

- (a) **p-doping:** It is done by oxidation process. In this process some electrons from  $\pi$ - bond of the conjugated double bonds are removed and the holes so created can move along the molecule. i.e., the polymer becomes electrically conductive. The radical cation produced is called 'polaron'. The polarons are mobile and can move along the polymer chain by rearrangement of double and single bonds and hence the polymer become conducting. The oxidation process is generally brought about by Lewis acids such as  $\text{FeCl}_3$ .

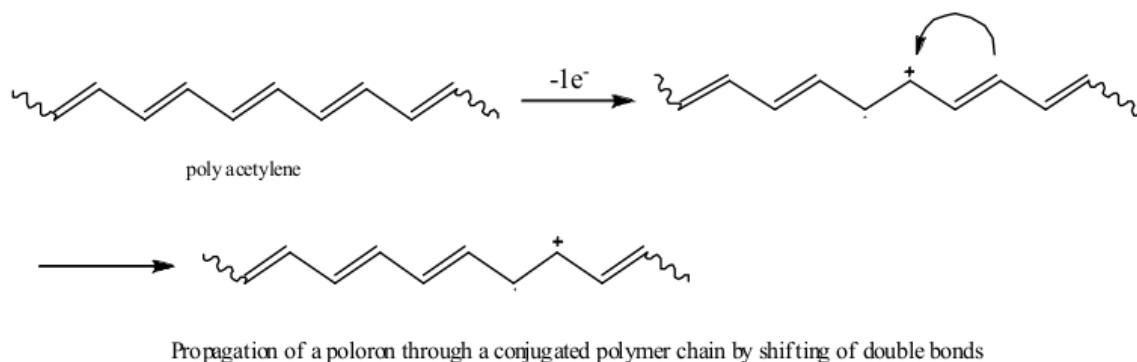


Figure 4.49: p-doping(polaron movement)

- (b) **n-doping:** In this type of doping some electrons are introduced into the polymer having conjugated double bonds by reduction with Lewis bases like lithium, sodium naphthalide etc. The reduction of polyacetylene by a Lewis base leads to the formation of anion called 'polaron' and bipolaron in two steps.

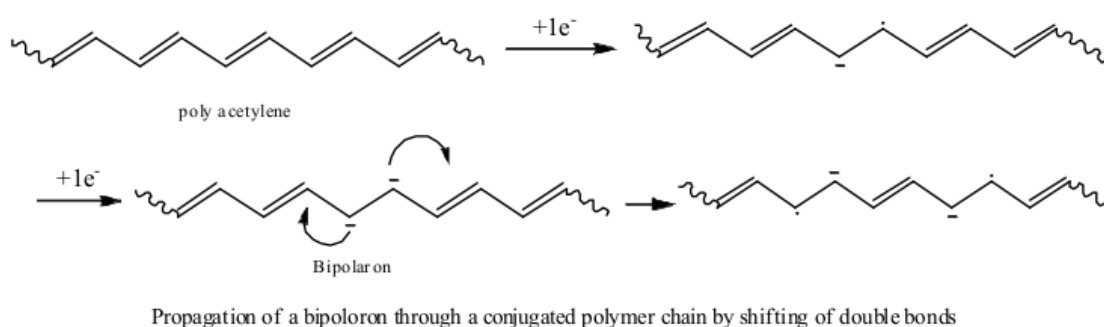


Figure 4.50: n-doping (polaron movement)

Conductive polymers	Repeating unit	Dopent		Scm <sup>-1</sup>
		n type	p-type	
Trans-poly acetylene		Li, AsF <sub>5</sub>	I <sub>2</sub> , Br <sub>2</sub>	10 <sup>4</sup>
Poly aniline			HCl	200
Poly pyrrole			BF <sub>3</sub>	
			HClO <sub>4</sub>	500-7500

#### 4.3.2 Extrinsically conducting polymers:

There are conducting polymers whose conductivity is due to the presence of externally added ingredients in them.

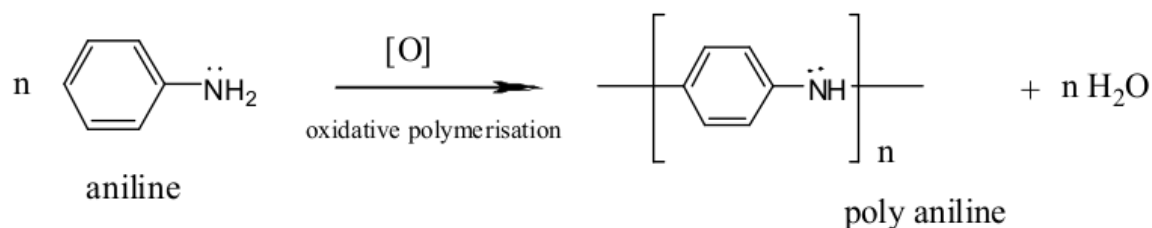
1. **Conductive element filled polymer:** These are polymers which are filled with conducting elements such as carbon black, metallic fibers, metal powders etc. The polymer acts as a binder to hold the conducting elements together. These polymers are, (i) low in cost, (ii) light in weight (iii) mechanically durable and strong, (iv) easily processable in different forms, shapes and sizes. This type is used in making computer key boards.
2. **Blended conducting polymers:** These polymers are obtained by blending conducting polymers with conventional polymers. These polymers possess better physical, chemical and mechanical properties.

#### 4.3.3 Polyaniline (PANI)

The oxidative product of aniline under acidic conditions is known as aniline black from 1862. Since 1980s polyaniline captured the intense attention of the scientific community due to the rediscovery of high electrical conductivity.

### Chemical synthesis

1. **Chemical method:** Aqueous solution of ammonium per sulphate is added slowly to a solution of aniline dissolved in dilute hydrochloric acid at a temperature of  $5^{\circ}\text{C}$  under agitation. After an hour a precipitate is formed, which can be removed by filtration. The polymer thus obtained is washed with ammonium hydroxide solution and dried.
2. **Electro-chemical method:** When thin film or better ordered polymer is required an electrochemical oxidation method is preferred. It is done by dipping platinum foil electrodes on acidified aqueous solution of aniline and a potential of 0.7 V is applied, then polyaniline film is formed on the surface of the positive electrode.



### Properties

Among various conducting polymers, polyaniline (PANI) is a unique and promising candidate for potential applications because of its stability in air and solubility in some organic solvents. It also exhibits dramatic changes in its electronic structure and physical properties on protonation. Recently PANI has attracted much attention for its magnetic behaviour as it exhibits high spin density and ferromagnetic spin-spin interaction.

The colour change associated with polyaniline in different oxidation states can be used in sensors and electrochromic devices. Polyaniline is more noble than copper and slightly less noble than silver which is the basis for its broad use in printed circuit board manufacturing and in corrosion protection. Doped poly aniline is a good conductor comparable to copper, whereas the original foam is a semiconductor.

### Applications

1. As electrode material for rechargeable batteries.
2. In the dissipation of static electric charges in metallic containers.
3. As shield in complex electronic circuits and electromagnetic radiations.
4. In biosensors and solar energy absorption.

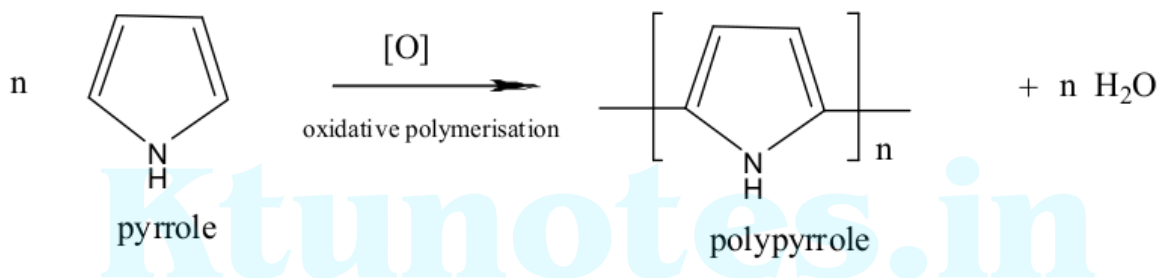
#### 4.3.4 Polypyrrole(PPy)

Polypyrrole is one of the most promising material with multifunctionalised application. It is an intrinsic conducting polymer with conjugated double bonds.

### Preparation

It can be prepared by electrochemical or chemical polymerization.

1. **Electro-chemical method:** Polypyrrole can be synthesized by electrochemical technique as follows. By the electrolysis of pyrrole (0.06M) in aqueous acetonitrile solution using platinum electrodes and tetraethyl ammonium boron tetrafluoride as the supporting electrolyte(0.01M). The polymer will be precipitated as a blue black film on the anode.
2. **Chemical method:** Polypyrrole can be synthesized by chemical oxidative polymerization technique using monomer pyrrole and ammonium per sulfate as oxidant in the ratio 1:1. The chemical polymerization can be carried out in a beaker by mixing 0.1M aqueous solution of pyrrole and 0.1M of ammonium per sulfate in 1:1 ratio for 3hrs. The polymer precipitates out. The PPy films can also be deposited on pre-cleaned glass substrate.



### Properties

PPy has excellent electrical, thermal and mechanical properties. It has good environmental stability and higher conductivity. The electrical resistance was found to decrease as temperature increases and hence conductivity increases. The decrease of resistance is due to the increase of efficiency of charge transfer in PPy with increase in temperature. PPy films are yellow but darken in air due to oxidation. Doped films are blue black depending on the degree of polymerisation and film thickness. They are amorphous and give weak diffraction. Pure PPy is an insulator while its oxidative derivatives are good electrical conductors.

### Applications of Polypyrrole (PPy)

1. Polypyrrole is used mostly in biosensors and immunosensors, because of its biocompatibility
2. Compared with metal and inorganic materials, doped PPy has better mechanical match with live tissue, resulting in its many applications in biomedical field.
3. It have applications in tissue engineering.
4. It is also employed as counter electrodes in dye-sensitized solar cells.

### 4.3.5 Applications of conducting polymers

1. In Rechargeable Batteries: The conducting polymers can be used as cathodes and solid electrolytes in batteries for automotive and other applications. These batteries have high reliability, light weight, non leakage of electrolytic and are small in size.
2. Some conducting polymers like polyaniline show different colours in different oxidation forms. This electro chromic property show different colours in different oxidation forms. This electrochromic property can be used to produce “smart windows” and electrochromic displays. [Smart windows are the windows which change colour in response to sunlight or temperature changes.]
3. These are also used in electro-luminascence OLED displays like TV, mobile phone etc.
4. In analytical sensors: These polymers are used for making sensors for  $pH$ ,  $O_2$ ,  $NO_x$ ,  $SO_2$  and glucose detection.
5. In photovoltaic devices: eg. In Al, polymer/Au photovoltaic cells.
6. In electronics: It can be used in Light Emitting Diodes (LEDs), electromagnetic shielding, electron beam lithography, etc.

### 4.3.6 OLED (Organic Light Emitting Diode)

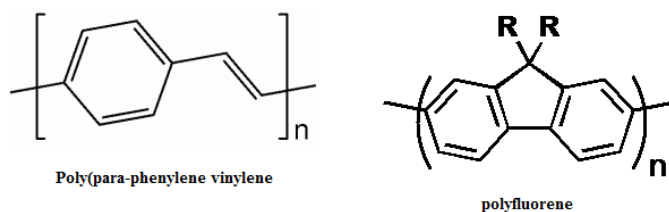
An organic light-emitting diode (OLED) is a light-emitting diode (LED) in which the emissive electroluminescent layer is a film of organic compound which emits light in response to an electric current. This layer of organic semiconductor is situated between two electrodes; , at least one of these electrodes is transparent. There are two main families of OLED:(i) those employing conducting polymers (ii) those based on small molecules.

**Principle:** The principle of conjugated polymer OLED is HOMO- LUMO transitions. The basic principle of small molecule OLED is the creation of a light-emitting electrochemical cell (LEC) on adding mobile ions to an OLED.

#### OLED employing conducting polymers

A typical OLED is composed of a layer of organic materials situated between two electrodes, the anode and cathode, all deposited on a substrate. The organic molecules are electrically conductive as a result of delocalization of  $\pi$  -electrons caused by conjugation of the molecule. These materials have conductivity levels ranging from insulators to conductors, and are therefore considered organic semiconductors. The highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) of organic semiconductors are analogous to the valence and conduction bands of inorganic semiconductors like silicon.

The organic compounds used in OLED's include derivatives of poly(p-phenylene vinylene) (PPV) and polyfluorene. Substitution of side chains onto the polymer backbone may determine the colour of emitted light.



**Construction:** Many modern OLEDs incorporate a simple bilayer structure, consisting of a conductive layer and an emissive layer. A typical organic light emitting diode (OLED) structure consisting of a glass substrate, a indium tin oxide (ITO) anode, and an organic bilayer diffused into a metallic cathode, as given below: The organic bilayer consists of

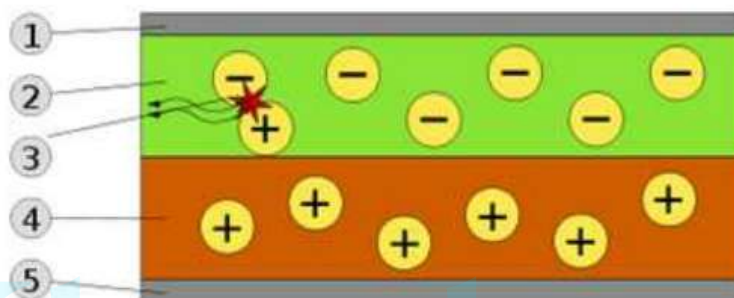


Figure 4.51: Schematic of a bilayer OLED 1. ITO cathode(-), layer, 2. Emissive Layer, 3. Emission of radiation, 4. Conductive Layer, 5. Metal anode (+)

a hole transport layer (HTL) and an emitting/electron transport layer (EML/ETL). As the emissive layer and the conducting layer is made up of organic molecules (both being different), The emissive layer used in an OLED is made up of n-type polymer molecules, out of which the most commonly used is polyfluorene. The conducting layer is made up of p-type polymer, and the commonly used component is polyaniline.

**Working** To make an OLED light up, we simply attach a voltage (potential difference) across the anode and cathode. As the electricity starts to flow, the cathode receives electrons from the power source and the anode loses them. Now we have a situation where the added electrons are making the n-type emissive layer negatively charged, while the p-type conductive layer is becoming positively charged. Positive holes are much more mobile than negative electrons so they jump across the boundary from the conductive layer to the emissive layer. When a hole (a single electron  $\pi$ -bond) meets an electron, the two things cancel out and release a brief burst of energy in the form of a quantum of light or a photon, in other words. This process is called recombination, and because it's happening many times a second the OLED produces continuous light for as long as the current keeps flowing.

**Note:** In conventional LED like GaAs and GaN electrons are more mobile than holes so p-region is the emissive layer.

### Small-molecule OLED

It consists of three organic layers sandwiched between electrodes. The organic layers adjacent to cathode and anode are the electron transport layer (ETL) and the hole transport layer (HTL), respectively. Emissive layer (EML) usually consists of light-emitting dyes or dopants dispersed in a suitable host material. Molecules like quinacridone derivatives are often used. Aluminium quinacridone (Alq3) has been used as a green emitter (fig. 4.50).

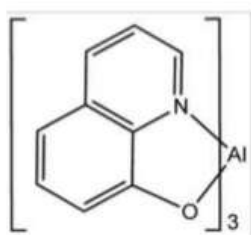


Figure 4.52: Aluminium quinacridone (Alq3)

### Advantages of OLED

1. The manufacture of OLED is highly economical and is more efficient than LCD and flat panel screens.
2. OLED display can be printed cloths and fabrics by ink jet printing. This technology will help in carrying huge displays in our hands.
3. There is much difference in watching a high-definition TV to a OLED display. As the contrast ratio of OLED is very high (even in dark conditions), it can be watched from an angle nearly 90 degrees without any difficulty.
4. No backlight is produced by this device and the power consumption is also very less.
5. OLED has a refresh rate of 100,000 Hz which is almost 9900 Hz greater than an LCD display.
6. The response time is less than 0.01 ms. LCD needs a response time of 1 ms.

## 4.4 Solved Problems

1. Which of the following objects has non-superimposable mirror images  
 (a) A cube with all six sides painted in different colors (b) A palm (c) A man not having left hand (d) A cube with 4 sides painted in different colors but opposite pair of faces in same color (e) A screw

Ans: a, b, c and e

2. Which of the following are enantiomers?

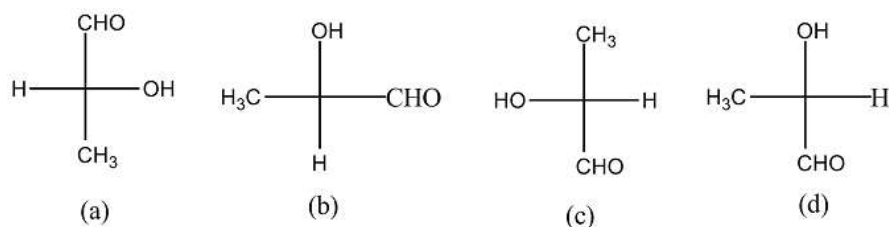


Figure 4.53:

Ans: Structures (a)(b)(c) are having the same notation R, hence one and the same. But (d) is having notation S. R and S forms are enantiomers.

3. Find out whether the following molecules are enantiomers, diastereomers or one and the same

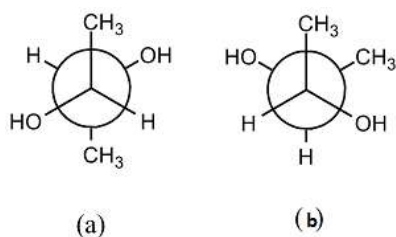


Figure 4.54:

Ans: (a) is meso form and (b) is + or - form or d, l form. Thus they are diastereoisomers. (Rotate front carbon atom of (a) through  $180^\circ$  such that  $-CH_3$  groups are on same side then  $-OH$  groups are on same side which is meso. Rotate front carbon atom of structure (b) clockwise  $60^\circ$  such that  $CH_3$  groups are on same side then  $-OH$  groups come opposite side which is + - form or d l form (fig. 4.53)



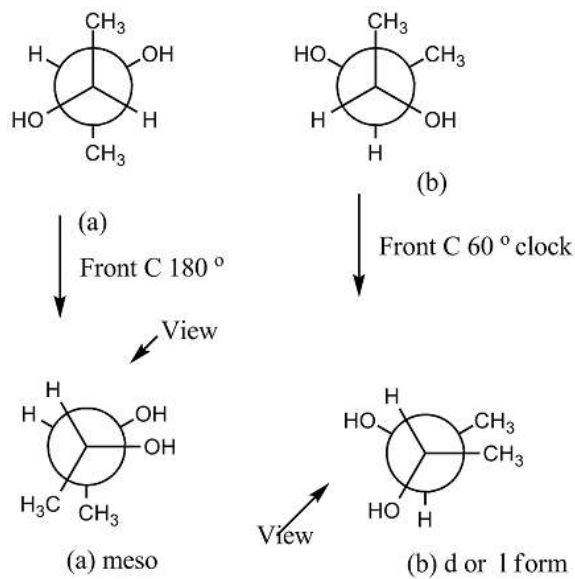


Figure 4.55:

4. Find out whether the following molecules are enantiomers, diastereomers or one and the same

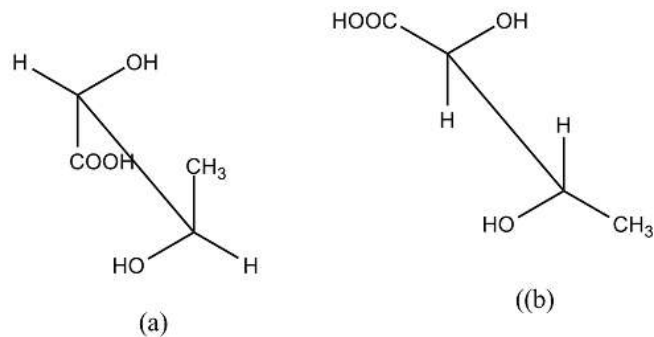


Figure 4.56:

Ans: The molecules (a) and (b) are the enantiomers (rotate front carbon atom of (a)) through  $180^\circ$  while keeping back fixed, such that  $-COOH$  and  $-CH_3$  group eclipsing. Rotate front carbon atom of (b) clockwise  $60^\circ$  and back carbon atom  $120^\circ$  anti clock such that  $-COOH$  and  $-CH_3$  group eclipsing. Then an enantiomeric structure as shown in the following figure is obtained (fig. 4.57).

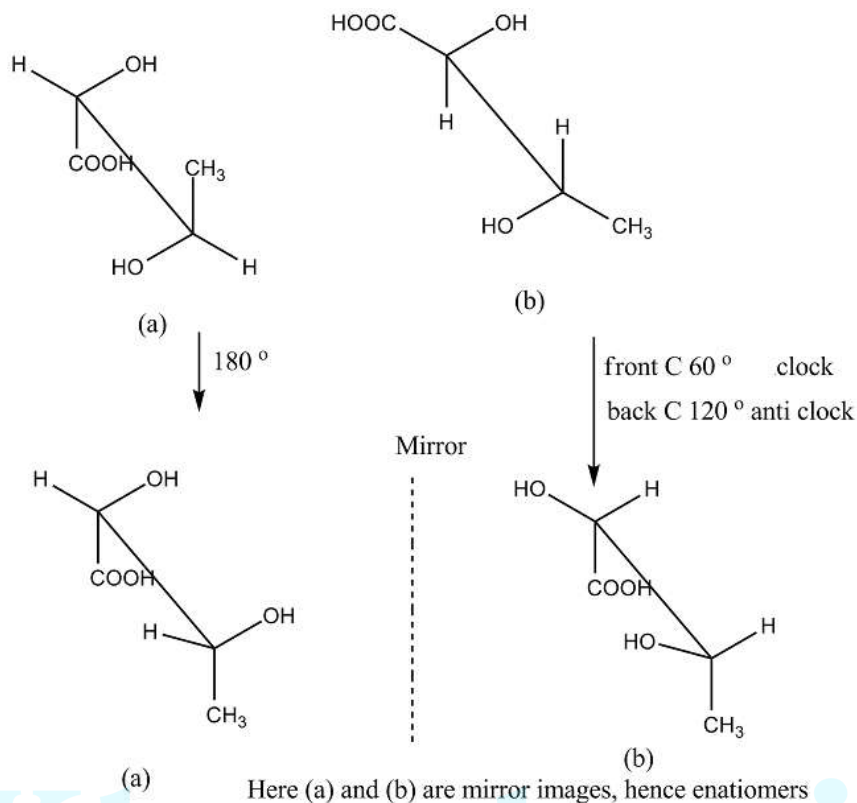


Figure 4.57:

5. Find out whether the following molecules are enantiomers, diastereomers or one and the same (fig. 4.56). Assume that priority decreases from A to F

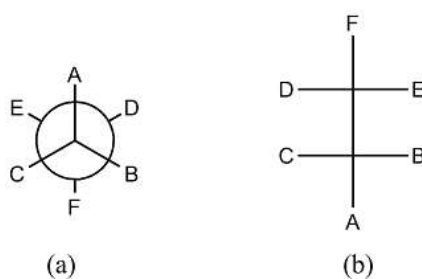


Figure 4.58:

Ans: Convert structure (a) to Fischer projection formula such that A and F are on vertical line. Rotate front carbon of (a) through 180° and observe from top. Fischer projection formula of (b) is obtained. Thus structures (a) and (b) are related to each other as mirror images or enantiomers (fig. 4.57).

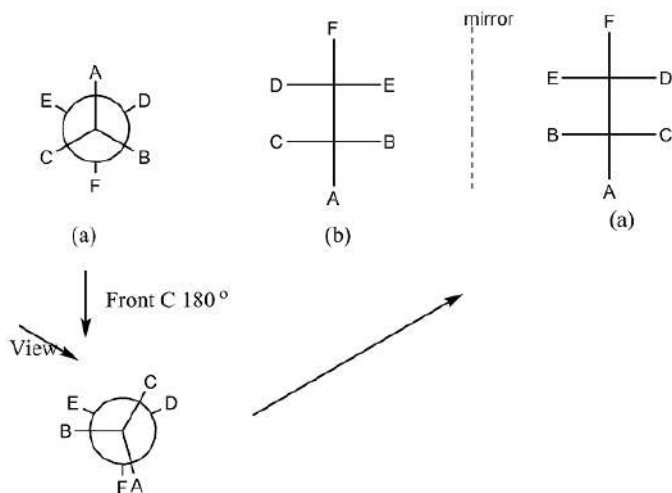


Figure 4.59:

## 4.5 Questions

1. what are chain isomers? give an example
2. What are position isomers? give an example
3. what are functional isomers? give an example
4. Which type of isomers are characterized by tautomerism give an example
5. What is keto-enol tautomerism? give an example
6. What are geometrical isomers?
7. Explain cis trans isomerism in substituted cyclopropane
8. Draw the structure of cis-2-butene
9. Draw the structure of R-Lactic acid
10. Find the asymmetric carbon atom and give the R,S notation of the following drug molecule (thalidomide) (Ans: S)

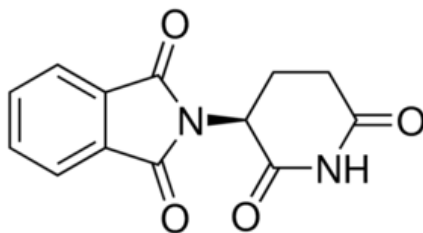


Figure 4.60:

11. Draw the mirror image, find the asymmetric carbon atom and give the R,S notation for original and mirror image of the following molecule (limonene) (Ans: original: S mirror image: R)

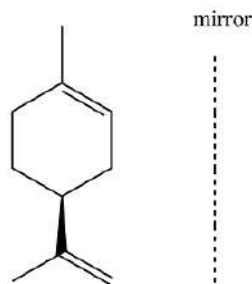


Figure 4.61:

12. Draw the mirror image, find the asymmetric carbon atom and give the R,S notation for original and mirror image of the following molecule (camphor) (Ans: original: R mirror image: S)

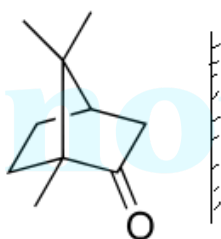


Figure 4.62:

13. Draw the structure of 2R,3S-dihydroxy butanoic acid
14. How many isomers (including stereo) are possible for  $C_4H_8$ ?
15. How many isomers (including stereo) are possible for  $C_4H_{10}O$ ?
16. How many isomers are possible for  $C_3H_6O$  ?. Draw the structure of each.
17. How many optical isomers are possible for  $CH_3 - (CHOH)_3 - COOH$  ?. Draw the structure of each.
18. Write the rule of assigning E-Z notation
19. Write the rule of assigning R,S-notation
20. Which of the following molecules can show optical activity (a) cis-1,3-dimethyl cyclohexane (b) trans-1,3-dimethyl cyclohexane (c) cis-1,4-dimethyl cyclohexane (d) trans-1,4-dimethyl cyclohexane

21. Why planar molecules do not show optical activity ?
22. What are the similarities and differences between properties of enantiomers
23. Discuss the conformations of ethane
24. Discuss the conformations butane
25. Why chair form is more stable than boat form
26. Among axial and equatorial mono methyl cyclohexane which conformer is more stable why?
27. Draw the geometrical isomers of 1,2 and 1,4-dimethyl cyclohexane, Draw their conformers, Which conformer is stable in each case?
28. What are co-polymers discuss different types
29. What are block co-polymers?
30. How co-polymerization is possible in condensation polymers?
31. what is ABS how it is prepared?
32. Discuss the properties and applications of ABS
33. What is Kevlar how it is prepared. Discuss its properties and applications?
34. How Kevlar is used in cryogenic application
35. What are conducting polymers give its classification
36. What is doping in conducting polymers?
37. Why conducting polymers like poly aniline and poly pyrrole can be doped only with p type dopents?
38. Show how polaron moves in a conducting polymer
39. What are polaran and bipolaran?
40. What are OLEDs ? What are different types of OLEDs? discuss their basic principles
41. Write a note on the construction and working of an OLED
42. Why n-region acts as emissive layer in contrast conventional inorganic LEDs
43. What are the advantages of OLEDs?