CHAPTER 6
STEREOCHEMISTRY AND POLYMER CHEMISTRY

6.1 INTRODUCTION

The properties of molecules depend on the arrangement of atoms in a molecule. Based on many experimental observations, Van't Hoff and Le Bel in early 1900s concluded that the spatial orientation of groups around carbon atoms are tetrahedral when a carbon atom is bonded to four other atoms. Over the years, the structural arrangement of atoms around carbon in three dimensions has gained much significance and attention and developed into a separate branch of study called stereochemistry. Stereochemistry is the study of the static and dynamic aspects of the three-dimensional shapes of molecules. It has long provided a foundation for understanding structure and reactivity. At the same time, stereochemistry constitutes an intrinsically interesting research field in its own right. Many chemists find this area of study fascinating simply due to the aesthetic beauty associated with chemical structures, and the intriguing ability to combine the fields of geometry, topology, and chemistry in the study of three-dimensional shapes. Stereoisomerism, chirality, conformational analysis, enantiomers etc. are some essential components of stereochemistry which will be discussed in this chapter. The goal is for the student to gain a fundamental understanding of the basic principles of stereochemistry and the associated terminology.

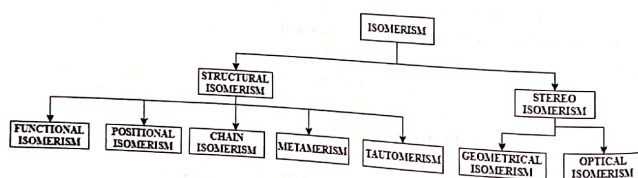## 6.2 ISOMERS AND ISOMERISM

Fig.6.1 Classification of Isomerism

Isomers are compounds having the same molecular formula but different properties due to different structural arrangements. There are broadly two different types of isomers
1. Structural isomers.
2. Stereoisomers.

6.3 STRUCTURAL ISOMERISM

Structural isomerism occurs when two or more compounds have the same molecular formula but different structures. These differences in structure will give the molecules different chemical and physical properties. Structural isomers have the same molecular formula but different structures due to different numbers and kinds of chemical bonds. The physical properties of these compounds may be different. For example $CH_3- O - CH_3$ and $CH_3 - CH_2 -OH$ are two different organic compounds having same molecular formula C_2H_6O; the former is an ether while the latter is an alcohol. Similarly the inorganic compound $Cr(H_2O)_6Cl_3$ can exists in three different forms.

$[Cr(H_2O)_6]Cl_3$ is a violet colored compound reacts readily with $AgNO_3$ to precipitate all chlorine atoms as $AgCl$. Also it is to be noted that this particular compound do not loss any mol of water when exposed to drying agents.

$[CrCl(H_2O)_5]Cl_2.H_2O$ is a light green coloured compound, reacts less readily with $AgNO_3$ to precipitate two-thirds of chlorine to $AgCl$. When exposed to drying agents this compound may lose 1 mol of water due to dehydration.

The third compound $[CrCl_2(H_2O)_4]Cl.2H_2O$ is a dark green coloured compound, reacts less slowly with $AgNO_3$ to precipitate one-third of chlorine to $AgCl$. When exposed to drying agents this compound may lose 2 mols of water due to dehydration.

There are five different types of structural isomerism

1. Chain Isomerism.
2. Functional Isomerism.
3. Position Isomerism.
4. Tautomerism.
5. Metamerism.

1. Chain or Skeletal Isomerism

1-Bromobutane   1-Bromo-2-methylpropane   2-Bromo-2-methylpropane
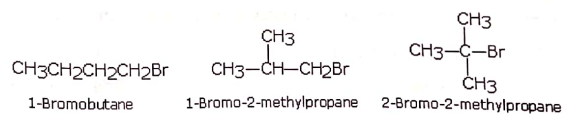
Chain or skeletal isomers have the same molecular formula but differ in the order in which C-atoms are bonded to each other. This is also known as skeletal isomerism. For example, C_4H_9Br can exist in three isomeric forms as shown above.

2. Functional Group Isomerism

Isomerism exhibited by compounds differing in functional groups is known as functional isomerism. As the functional group largely determines the properties of a compound, such compounds differ in their physical and chemical properties. Compounds exhibiting this type of isomerism are called functional isomers.

1. Dimethyl ether and ethyl alcohol have the same formula (C_2H_6O) but belong to two different classes of compounds.

C_2H_5-OH (Ethyl alcohol)

CH_3-O- CH_3 (Dimethyl ether)

2. Propionic acid and methyl acetate are functional isomers (molecular formula $C_3H_6O_2$) having acid and ester functional groups respectively.

CH_3-COO- CH_3 Methyl acetate

$CH_3 – CH_2$-COOH Propionic acid

3. Propionaldehyde and acetone both have the same molecular formula (C_3H_6O) but propionaldehye has an aldehydic group (-CHO) where as acetone has a ketonic group

$CH_3 – CH_2$-CHO Propionaldehyde

CH_3-CO- CH_3 Acetone

3. Position Isomerism

In compounds containing similar carbon chain, the difference in position occupied by a particular atom or group in the carbon chain, give rise to position isomerism. These isomers which differ only in the position of a group or atom in the carbon atom chain are known as position isomers. Position isomers has the same molecular formula but may differ in the position of multiple bond or functional group on the carbon chain. Generally position isomers may belong to the same homologous series and functional groups.
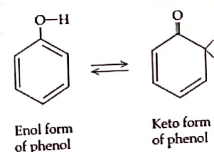
1. CH_3-CH_2- CH_2-OH Propyl alcohol

   CH_3-CHOH- CH_3 Isopropyl alcohol

2. CH_3-CH_2- CH_2-CH_2-OH Butan-1-ol

   CH_3-CHOH- CH_2-CH_3 Butan-2-ol
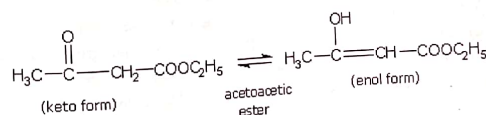
4. Tautomerism

When two structural isomers are mutually interconvertible and exist in dynamic equilibrium, they are called Tautomers and the phenomenon is termed Tautomerism. It is a kind of dynamic isomerism wherein one isomer is constantly changing into other and vice-versa. Tautomerism is caused by the wanderings of a labile hydrogen atom between two polyvalent atoms.
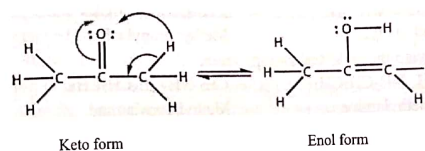
Keto form   Enol form

For example, acetone exhibits tautomerism and may be represented as an equilibrium mixture of two isomers. Here the keto form changes to the enol form by the migration of a proton to the carbonyl oxygen. Then a pair of electrons shifts from the C-H bond to the C-C bond. Phenol exhibits tautomerism as follows.

Enol form   Keto form
of phenol   of phenol

Keto-Enol Tautomerism

(keto form)   acetoacetic   (enol form)
                   ester

Generlly aldehydes, ketones and other carbonyl compounds such as esters exhibit this type of isomerism. It involves the migration of a proton (H⁺) from α- carbon atom to the carbonyl oxygen as outlined in the case of acetoacetic ester, acetone etc. The tautomer containing the carbonyl group (C=O) is designted as keto form. The other one containing a hydroxy group attched to a doubly bonded carbon is referred to as enol form. This kind of tautomerism is called Keto-Enol Tautomerism.

5. Metamerism

This type of isomerism is exhibited by members belonging to the same homologous series. Metamerism is due to the unequal distribution of carbon atoms on either side of the functional group.

Example 1: Diethyl ether and Methyl propyl ether

       $CH_3CH_2\text{-}O\text{-}CH_2CH_3$ $CH_3\text{-}O\text{-}CH_2CH_2CH_3$
         Diethyl ether   Methyl propyl ether
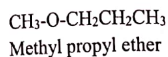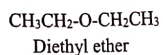
Example 2: Dimethylamine and Methylpropylamine

       $CH_3CH_2\text{-}NH\text{-}CH_2CH_3$ $CH_3\text{-}NH\text{-}CH_2CH_2CH_3$
         Diethylamine   Methylpropylamine
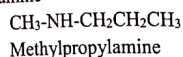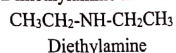
6.4 STEREOISOMERISM

Stereochemistry is the 'chemistry of space', i.e., stereochemistry deals with the spatial arrangements of atoms and groups in a molecule. The phenomenon exhibited by two or more compounds with the same molecular and structural formulae, but different three-dimensional arrangements of their atoms or groups in space is called stereoisomerism. Stereoisomerism can be classified in to two groups

     1. Geometrical isomerism
     2. Optical isomerism

1. Geometrical Isomerism

This type of isomerism is due to the different geometrical arrangement of two different groups about the carbon-carbon double bond. Geometrical isomerism is also called *cis-trans* isomerism. When similar groups are attached to the same side of the molecule, it is called cis (*or syn*) isomer; while in *trans* (or anti) isomer similar groups lie on the opposite side. Physical properties such as melting point, boiling point, density, solubility may be different in the case of geometrical isomers, but possess same chemical properties.

Origin / Reason for Geometrical Isomerism: Two carbon atoms joined together by a single bond can be freely rotated around the axis. But when two carbon atoms are joined by a double bond (consisting of a sigma-bond and a pi-bond), the free rotation around the axis will be restricted and may not be possible on certain cases. In this way, the atoms or groups attached to carbon atoms in compound containing C=C double bond become locked up in space.
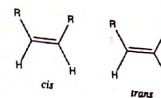

The alkene molecule has planar shape with two carbon atoms of the double bond and the four atoms attached to these carbons, all lie in one plane, and their positions in space being fixed. Rotation, if any would break the π bond which is impossible (since the energy required is not available from molecular collisions at ordinary temperatures), so the rotation about the double bond is prevented. This restriction in the rotation around the double bond leads to Geometrical Isomerism. In short, in order to show geometrical isomerism,

     1. The molecule must have restriction in rotation
     2. Restricted atoms must have different substituents

Characteristic properties of Geometrical Isomers

     1. In the *trans* form the molecules are closely packed. Hence trans isomers are more stable and have a higher melting point.
     2. The trans- isomers have a dipole moment zero because of cancellation of effect where as cis- isomer always shows some value.
     3. The cis- isomer have a greater solubility, dipole moment, heat of combustion, refractive index and density.
     4. The cis- isomer has the tendency to yield cyclic compounds due to the closeness of reacting groups to each other.
     5. The ring structure is more or less rigid and may be compared to the double bonds in olefinic compounds. There can be no rotation around C-C bonds forming the ring. Hence, cyclic compounds can also exhibit Geometrical Isomerism.
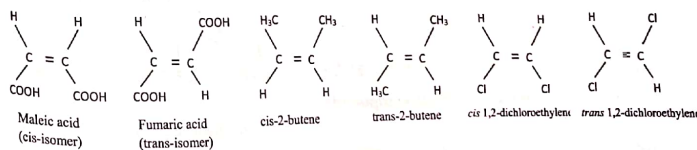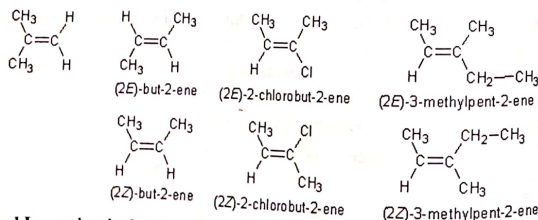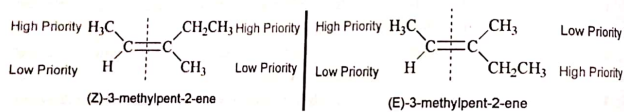

Examples of Geometrical Isomerism

E and *Z* Notation of Geometrical Isomers

The term *cis-trans* are being widely used to describe geometrical isomers. However, in compounds where all four atoms or groups attached to carbon atoms of double bond are different, the *cis* and *trans* nomenclature cannot be followed. Such geometrical isomers are designated by *E* and *Z* nomenclature. The labels *E* and *Z* have been derived from the German words entgegen (meaning opposite) and zusammen (meaning follow together). The following simple steps need to be followed for specifying the configuration.

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 the same side of the double bond. If the priority groups are on the opposite sides of the double bond, the configuration is E.

Atoms or groups are assigned priority by the following rules:

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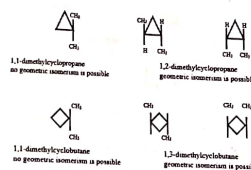

(Z)-3-methylpent-2-ene   (E)-3-methylpent-2-ene

(2E)-but-2-ene   (2E)-2-chlorobut-2-ene   (2E)-3-methylpent-2-ene

(2Z)-but-2-ene   (2Z)-2-chlorobut-2-ene   (2Z)-3-methylpent-2-ene

Geometrical Isomerism in Cyclic compounds

Geometrical isomerism is also possible in cyclic compounds. Requirement for geometrical isomerism in cyclic compounds is that there must be at least two other

groups besides hydrogen on the ring, and these must be on different carbon atoms. It is a general rule that a ring and double bond are stereochemically equivalent, since in both cases substituent is located above and below the plain containing the π- orbital or the ring atoms: thus *cis-trans* isomerism can occur in cyclic systems. There can be no rotation about carbon-carbon single bonds forming a ring because rotation would break the bonds and break the ring. Thus, there are two conditions for geometrical isomerism in cyclic compounds.

1. There must be at least two other groups besides hydrogen on the ring.
2. These groups must be on different carbon atoms.

For instance no geometrical isomers are possible for 1, 1-dimethyl cyclopropane and 1, 1-dimethyl cyclobutane

1,1-dimethylcyclopropane   1,2-dimethylcyclopropane
no geometric isomerism is possible   geometric isomerism is possible

1,1-dimethylcyclobutane   1,3-dimethylcyclobutane
no geometric isomerism is possible   geometric isomerism is possible

To understand geometric isomerism in cyclic compounds, we presume that the carbon atoms of a cyclic structure such as cyclohexane form a plane. The plane of the ring is considered being horizontal with the edge of the ring projected towards us, shaded more heavily. In a cyclic compound, each carbon atom is joined to its neighboring ring carbon atoms and also to two other atoms or groups which are shown by vertical lines.
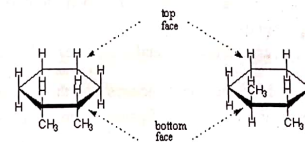
cis-1,2-dimethyl cyclohexane   *trans*-1,2-dimethyl cyclohexane

Fig. 6.2 Geometrical Isomerism in Cyclohexane

When an atom (or a group) is placed at the top of the vertical line, it is said to be above the plane of the ring and when an atom (or a group) is attached to the bottom of a vertical line it is said to be below the plane of the ring. Usually, hydrogen atoms attached to the ring and their bonds are not shown. Sometimes, a broken wedge is used to indicate a group below the plane of the ring, and a solid line represents a group above the plane. The important point is that the two methyl groups are on opposite sides of the plane of the ring. Just as in the case of *cis-* and *trans-* alkenes, when two groups are on opposite sides of the ring, they are *trans-* and when they are on the same side they are *cis-*. These compounds are geometric isomers of each other.
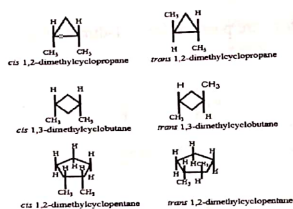

cis 1,2-dimethylcyclopropane   trans 1,2-dimethylcyclopropane

cis 1,3-dimethylcyclobutane   trans 1,3-dimethylcyclobutane

cis 1,2-dimethylcyclopentane   trans 1,2-dimethylcyclopentane

Fig. 6.3 Geometrical Isomerism in various cyclic compunds

6.5 REPRESENTATION OF THREE DIMENSIONAL STRUCTURES

In stereochemistry molecules are to be visualized in three dimensions, appropriate modes of representation of three- dimensional molecules on two- dimensional paper is essential. Various representations commonly used are discussed below. The chemistry of most of the compounds comes under two predominant structures.

1. The tetrahedron: It is found whenever a carbon atom is bound to four groups through four single bonds.
2. Octahedron: Most of the transition metal complexes fall within this category.

Since both tetrahedron and octahedron structures are three dimensional, they cannot easily be drawn on two dimensional piece of paper. Chemists have adopted a number of conventions to overcome this difficulty.
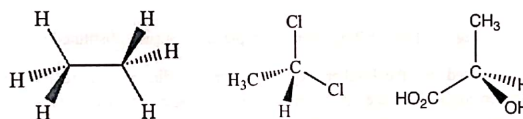
1. **Wedge – hash Projection**

Wedge-hash (Wedge - dash) diagrams are the most popular representation used to represent the 3D shape and are ideally suited to show the structure of SP^3 hybridized

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(tetrahedral) atoms. A wedge-hash projection is a means to represent a molecule (drawing) in which three types of lines are used to represent the three-dimensional structure.

1. Solid lines to represent bonds which are in the plane of the paper.
2. Dashed lines to represent bonds that extend away from the viewer.
3. Wedge (dark thick lines) shaped lines to represent bonds oriented facing the viewer.

Wedge- Hash Projection of Methane and dichloromethane molecules

Wedge- Hash Projection of a) Ethane molecule b) 1,1 Dichloro ethane c) Lactic acid

Fischer Projection

The Wedge-hash representation of stereochemistry can be cumbersome on many molecules, particularly in the case of molecules with a number of stereocenters. The German chemist Emil Fischer introduced another method to represent the stereochemistry known as Fischer projection. Fischer projections are abbreviated structural forms to represent the stereochemical representation to a chemist without drawing a 3D structural representation of the molecule. These representations are only used for molecules that contain chirality centers. Fischer projections use perpendicular lines to represent a stereo-center. The point of intersection of lines represents the asymmetric carbon atom. The horizontal lines represent the bonds that project forwards (coming out of the plane of the paper), while the vertical lines represent the bonds that project backwards (going behind the plane of the paper).

Reading Fischer Projections

1. The bonds that are written horizontally are pointed towards the viewer (wedge)
2. The bonds that are written vertically are pointed away from the viewer (dash)
3. Typically the carbon atom is written vertically with C_1 of the chain at the top.
4. Molecules with multiple chiral centers are written in an eclipsed conformation.
5. In the case of carbohydrates, OH points to the right when the center is R (Rectus Latin means right) and OH points to the left when the center is S (Sinister Latin means left) .

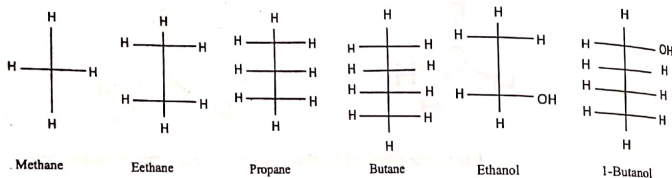Methane　　Eethane　　Propane　　Butane　　Ethanol　　1-Butanol

Fig. 6.4 Fischer Projection of simple alkanes and substituted alkanes

It is to be noted that the Fischer projections are two dimensional representations of a three dimensional molecule. In order to identify whether two or more structures are identical or not the projections can be manipulated in certain specified ways.

Importance of Fischer projections

1. It is easy to recognize enantiomers and mesocompounds from the appropriate Fischer projections because planes of symmetry in the actual molecules reduce to lines of symmetry in their projections.
2. It is easy to determine the configuration of a chiral carbon by applying the R,S - system to a Fischer projection.

Newman projection

In Newman projections the two carbon atoms having the σ bonds are represented by two circles, one behind the other, so that only the carbon in the front is visible. The hydrogen atoms attached to the front carbon are represented by C- H bonds from the center of the circle. The C- H bonds of the back carbon redrawn from the circumference of the circle.

Ethane　　　　　　　　　　　　　　Butane
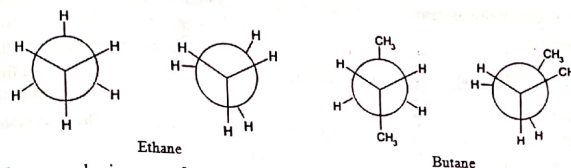
For example, in case of ethane, a point represents the front carbon atom and three lines emerging from it are the three bonds attached to three hydrogen atoms. The circle in the Newman projection represents the rear atom, and the lines radiating from the circle are the bonds of the rear carbon atom. Newman projections are characterized by the angles formed between bonds on the front and rear atoms. Such angles are called dihedral angles.
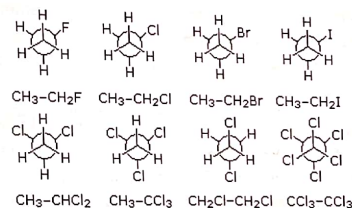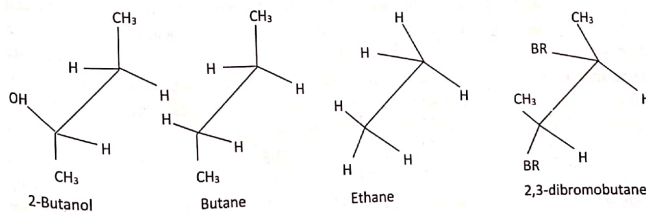

CH_3–CH_2F　　CH_3–CH_2Cl　　CH_3–CH_2Br　　CH_3–CH_2I

CH_3–$CHCl_2$　　CH_3–CCl_3　　CH_2Cl–CH_2Cl　　CCl_3–CCl_3

Fig.6.5 Newman projection for various halogen substituted ethane

Sawhorse Projections

2-Butanol　　　　　Butane　　　　　Ethane　　　　　2,3-dibromobutane

This is a three dimensional convention in which two atoms under consideration are taken as two points where four lines intersect and the remaining groups are attached to six free ends. The bond linking these two carbon atoms is considered to be in the plane of the paper and the remaining lines (bonds) project above or below that plane. There is a free rotation about the carbon-carbon bond and three groups attached. The front atom may be rotated clockwise or anticlockwise with respect to the groups attached to the rear atom. Few examples for sawhorse projections are shown above.

6.6 OPTICAL ISOMERISM

Light may be considered as wave motion containing oscillating magnetic and electric fields. These electric and magnetic fields oscillates in planes which are perpendicular to each other and to the direction of propagation of the light wave. When a beam of light is passed through a tube containing a polarizer (NICOL prism), the emerging light has vibrations only in plane. All the waves vibrating in other planes are either absorbed or rejected. This light having wave motion in one plane only is called plane polarized light and the plane perpendicular to the plane of vibration is called the plane of polarization.

Optical activity: It is the phenomenon exhibited by compounds which, when placed in the path of a beam of plane –polarized light, are capable of rotating the plane of polarization to right or left. Such substances that rotate the plane of polarized light are known as optically active (chiral), and the phenomenon is referred to as optical activity. Those substances that rotate the plane to the right (clockwise) are called *dextro-rotatory* indicated by *d* or (+), and those that rotate to the left (anti-clockwise) are called *levo-rotatory* indicated by *l* or (-). A mixture of these two substances in equal proportions will be optically inactive and is called the *racemic mixture*.

The instrument for studying the interaction between plane polarized light and optically active molecules are known as a polarimeter. Initially a beam of light from a source is passed through a polaroid sheet called polarizer, then through a sample tube. By rotating the analyzer, another polaroid sheet, minimal light transmission can be achieved. Then the sample tube is filled with a solution containing an optically active compound. As the plane polarized light passes through the sample, its plane of polarization is rotated either to the right or to the left by certain amount. The direction of rotation depends on the nature of the optical isomer (*d* or *l* form). This rotation can be measured readily by turning the analyzer in the appropriate direction, until minimal light transmission is again achieved. The angle of rotation in degrees, α, depends not only on the nature of the molecules, but also on the concentration of the solution and the length of the sample tube.
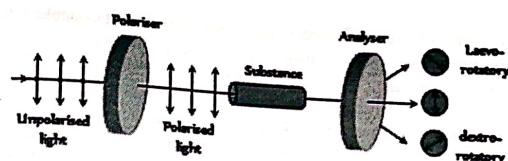
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Fig.6.6 Schematic representation of a polarimeter

Specific rotation: When an optically active liquid is placed in the path of a plane polarized light, the plane of polarization of light is rotated. The extent of rotation (alpha) of the plane of polarization depends on (i) nature of the solution (ii) its temperature (iii) length ' l' through which light passes (iv) density 'd' of the substance (v) wave length of the light employed. In order to standardize the conditions so that the comparisons are meaningful, the observed rotation is converted to specific rotation. The measurement of optical activity is reported in terms of specific rotation. It can be defined as the observed rotation when a polarized light is passed through1decimeter (10 cm) of the solution with a concentration of 1gm/ml. The specific rotation is a characteristic property of the compound as its melting point, boiling point, density or refractive index. Mathematically specific rotation can be written as

$$[\alpha]_D^t = \frac{\theta}{l \times c}$$

Where θ is the observed rotation in degrees, ' l' is the length in decimeters of the sample tube, 'c' is the concentration of the solution in gms / ml or density of the liquid, D is the line of sodium vapor light and 't' is the temperature. The unit of specific rotation is deg.(decimeter)$^{-1}$ (gm/cc)$^{-1}$.
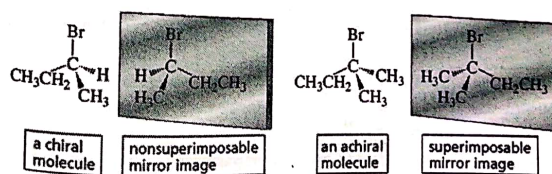
6.7 CHIRALITY

Fig.6.7 Mirror images and chirality

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Stereoisomers cannot be superimposed on their mirror images. For example, a right hand is a non-superimposable mirror image of left hand. An object which is non-superimposable on its mirror images is called chiral. Any molecule which cannot be superimposed on its mirror image is said to possess chirality. The reason for chirality is the tetrahedral carbon structures with 4 different constituents attached to it. In other words chirality is due to the presence of an asymmetric carbon atom. A carbon atom with four different groups attached to it is called stereocenter or chiral center. When molecule is superimposable on its mirror image it is symmetric and is said to be achiral. Achiral compounds have a plane or center of symmetry.

Enantiomerism

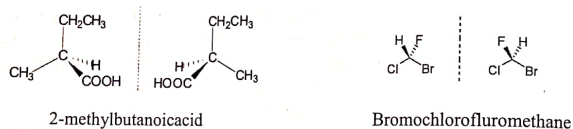| 2-methylbutanoicacid | Bromochlorofluromethane |

Fig 6.8 Examples of Enantiomers

If two stereoisomers are related to each other as an object and mirror image which are not superimposable, (like the right and left hand) they are called enantiomers (from the Greek word 'enantio' meaning opposite) or optical isomers and the phenomenon is known as enantiomerism or optical isomerism. The optical isomerism is exhibited by compounds containing asymmetric carbon atoms. Thus an asymmetric object and its mirror images are called enantiomers. Some of the examples are as given in this section.
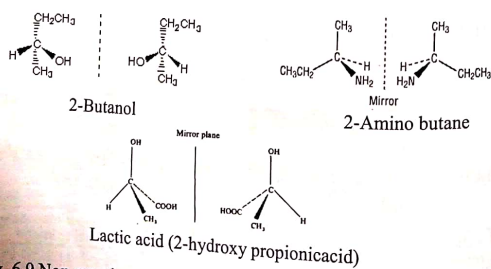

2-Butanol   2-Amino butane

Lactic acid (2-hydroxy propionicacid)

Fig. 6.9 Non superimposable compounds shows enantiomerism.

Properties of Enantiomers

1. Enantiomers have identical physical properties such as melting point, boiling point, density and refractive index, except in optical rotations which are of equal magnitude but opposite sign.
2. Their odors may be different, for example, (+) limonene has a smell of oranges whereas (-) limonene smells like lemons.
3. They have identical chemical properties except in their behavior towards chiral reagents and chiral solvents, where their rate of reactions and nature of products formed are different.
4. They may show different physiological properties, for example, (-) nicotine is more poisonous than (+) nicotine.
5. They can be separated only by the use of a chiral column agent.

Racemic mixture: A mixture of enantiomers with equimolar (50/50) quantity of two enantiomers is called racemic mixture. A racemic modification will be optically inactive, since the rotation caused by one half of the mixture is exactly cancelled by the opposite rotation displayed by the other half. In other words, a racemic mixture is optically inactive by external compensation. A racemic mixture is denoted by the prefix *dl-* or *(±).*

Preparation of racemic mixture

1. **By mixing equal amounts of the two enantiomers**: It is the most common method of forming a racemic modification and is achieved by the intimate mixing of equal amounts of the two enantiomers.
2. **By synthesis**: The syntheses of chiral compounds from achiral compounds in the absence of optically active reagents always produce racemic mixture.
3. **By racemisation**: It is the process of converting an optically active compound into the racemic modification by the application of heat, light or chemical reagents.

Resolution or Separation of Racemic Modification: The process of separation of enantiomers is known as resolution. The following methods are commonly used for resolution.

1. **Mechanical separation**: It involves separation of two sets by hand picking with the help of a pair of tweezers and a lens. This is a painstaking method applicable to those cases which give well defined crystals on crystallization that can be distinguished as enantiomers.
2. **Biochemical method**: This method involves the use of micro-organisms such as penicillium glaucum which consumes only one type of enantiomer (d-tartaric acid)

leaving behind l- tartaric acid. This method is not satisfactory as one enantiomer is completely destroyed.

3. **Chemical method:** In this method, a racemic modification is reacted with an optically active reagent to give a pair of non-identical derivatives known as diastereomers . These diastereomers differ in physical properties and can be separated by fractional distillation, crystallization etc.

Diastereomers

Diastereomers are stereoisomers that are not related to each other as an object and its mirror image. Due to the difference in free energy, they have different physical and chemical reactivity. Diastereomers generally have different melting points, boiling points, solubility, and chromatographic mobility and so on. Since they differ in physical and chemical properties, they can be separated by crystallization or chromatography. Any given structure can have only one enantiomer. All other stereoisomers of that molecule are diastereomeric. The relative configuration of diastereomeric molecules is frequently specified by the terms *syn* and *anti*. The molecules are represented as extended chains. Diastereomers with substituents on the same side of the extended chain are *syn* stereoisomers and those with substituents on the opposite sides are *anti* stereoisomers.

(+) tartaric acid   (-) tartaric acid

meso- tartaric acid
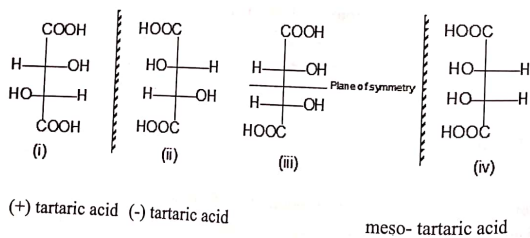
(1) and (2) being mirror images of each other, are enantiomers. However, (1) and (2) or (3) and (4) are not mirror images of each other and are termed as diastereomers.

Comparison between Enantiomers and Diastereomers

Table: 6.1 Differences between Enantiomers and Diastereomers

No	Enantiomers	Diastereomers
1	Have identical physical properties	Have different physical properties
2	Have identical chemical properties	Show similar but not identical chemical properties
3	Cannot be separated by physical methods	Can be easily separated by physical methods such as chromatography fractional distillation, etc.
4	Originates from chirality	May result from chirality or from *cis-trans* isomerism.
5	Basically *cis-trans* isomers are not enantiomeric	*cis-trans* isomers are always diastereomeric

Absolute configuration (R and S System)

Absolute configuration is the three-dimensional arrangement of groups or atoms in an asymmetrical molecule. To describe the absolute configuration of a chiral center, R and S nomenclature was suggested by Cahn, Ingold and Prelog. This nomenclature of configuration to an optically active compound is based upon the nature of groups attached to the asymmetric center and the priority assigned to them. The absolute configuration is defined by a prefix R (from the Greek word rectus, meaning right-handed) or prefix S (from the Greek word sinister, meaning left-handed) depending upon the sequence of the groups. The steps involved in assigning absolute configuration and the sequence rules to determine the order of priority of groups are as follows.

Step 1

Various groups attached to the chiral carbon are assigned priority based on the following sequence rules.

1. **Rule 1:** 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, higher is the priority. For example, if -H, -OH, $-CH_3$ and –Br are the groups attached to the chiral carbon then Br (atomic number 35) will have the highest priority, followed by –OH group (atomic number of O =12) then $-CH_3$ (atomic number of C = 6) and finally hydrogen (atomic number of H = 1). The order of priority will be Br > O > C > H.

2. **Rule2:** If two isotopes of same element are present, the heavier isotope has higher priority, that is, D > H and $C^{13} > C^{12}$.

3. **Rule3:** If two atoms directly linked to the chiral carbon are identical, then atomic numbers of the next atoms are used for assigning priority. If these atoms also have identical atoms attached to them, the priority is determined at the first point of difference along the chain. For example, between $-CH_3$ and $-CH_2OH$, the latter has a higher priority. Similarly for methyl, ethyl and n-propyl groups, the priority may be assigned as follows. The first carbon atom in methyl and ethyl is carbon and therefore atomic numbers of second atoms H (atomic number of H = 1) and C (atomic number of C= 6) decide the priority order, that is, ethyl > methyl. While considering ethyl and n-propyl, the second carbon atom is also identical and hence the third atoms (H,C) give the priority order as n-propyl > ethyl.

4. **Rule 4:** 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.

Step 2

The molecule is oriented in such a fashion that the group of the lowest priority is directed away from the viewer. It should be placed at the vertical bond as it lies behind the plane of the paper and is the farthest from the eye.

Step 3

If in moving from first, second and third priority groups, the eye travels in the clockwise or right handed direction, the configuration is assigned as R. If in going from first to second and then to third priority groups, the eye moves in counter
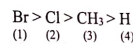
clockwise or left-handed direction, the configuration assigned is S. Consider the following examples.

Example 1:

1,1 – Chlorobromoethane CH(Cl)(Br). CH_3
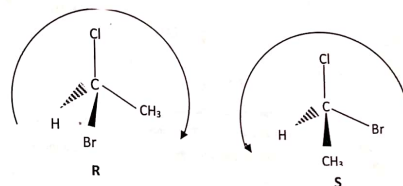
The four atoms directly bounded to the asymmetric carbon are Br, Cl, C, and H. Hence, priority order is

$$Br > Cl > CH_3 > H$$
$$(1) \quad (2) \quad (3) \quad (4)$$

Hence the configurations of two enantiomers are assigned as R and S

Example 2: Bromochlorofluromethane CHBrClF

The four atoms directly bonded to the asymmetric carbon are Br (atomic number of Br =35), Cl (atomic number of Cl =17), F (atomic number of F =9) and H (atomic number of H =1). Hence the priority order is Br > Cl > F > H.


S-enantiomer   R-enantiomer
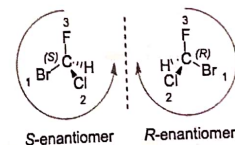
Assigning Configuration using Fischer Projections

If an atom or group of lowest priority occupies vertical position, in the Fischer projection then the configuration obtained gives the actual configuration of the molecule. If however, the atom or group of lowest priority occupies horizontal position in the Fischer

projection, then interchange to place the last priority bond at the vertical position. This should be done in pairs to avoid configuration change, since single interchange leads to an enantiomer of the compound and hence inverts the configuration.
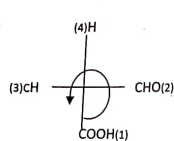
Anticlockwise H on
vertical line so S
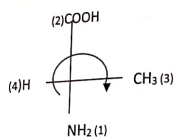
In 2-Amino propanoic acid
Clockwise should be R but since H
is on the horizontal line the
configuration is S
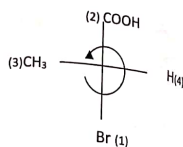
In 2-Bromopropanoic acid
Anticlockwise should be S but
since H is on the horizontal
line the configuration is R

In the case glyceraldehyde, while assigning priorities, we can write 1 to OH, 2 to CHO, 3 to CH_2OH and 4 to H. Configuration in B is S. This can be explained by properly assigning the priority groups. Here group with lowest priority H is on the vertical line; let us consider $1 \rightarrow 2 \rightarrow 3$. As the direction of movement is clockwise, the configuration is (R). In the case of A, the group with lowest priority H is on the horizontal line as shown in below. The configuration obtained for the sequence $1 \rightarrow 2 \rightarrow 3$ need to be reversed than that obtained. The sequence for the structure is clockwise and should be R, but it is to be reversed and hence must be stated as S.

(S)-Glyceraldehyde
A

(R)-Glyceraldehyde
B
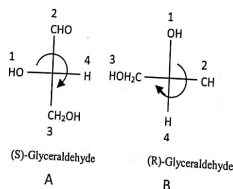
6.8 CONFORMATIONAL ANALYSIS

Groups bonded to a carbon–carbon single bond can rotate freely about the C-C bond axis. The rotation about the axis of rotation with respect to each other may form

temporary molecular shapes. The temporary molecular shapes resulting from such rotations are called conformations/ conformers' of the molecule. This type of isomerism is found in alkanes, cycloalkanes and their substituted derivatives. Unlike optical and geometrical isomers, the conformers are interconvertible easily by rotation around a single bond. But isolation of different conformers is not practically feasible due to the very low potential energy barrier for their interconversions. An energy barrier of about 16-20 kcal/mol is necessary for two conformers to exist independently at room temperature. Generally speaking, conformational isomers, are those which interconvert easily at room temperture through rotations about single bonds. An analysis of the energy changes that a molecule undergoes as groups rotate about a single bond is called conformational analysis.
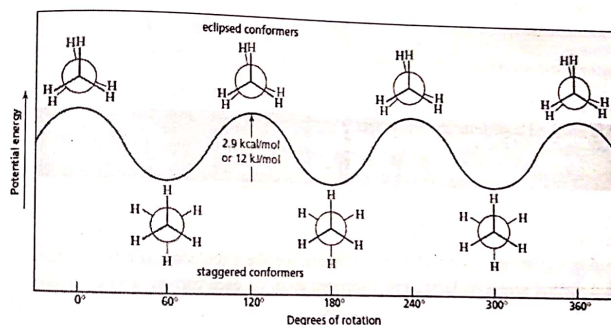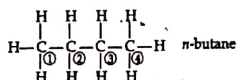
Conformational Analysis of Ethane

Fig 6.10 Potential energy changes that accompany rotation of H about the c-c bond of ethane

Let us consider the simple ethane molecule as an example. We can expect infinite number of different rotations of CH_3 groups about the carbon- carbon single (σ) bond. These different conformations may not have equal stability. The conformation in which the hydrogen atoms attached to each carbon atom with perfect staggering when viewed from one end of the molecule along the carbon – carbon bond axis will be having the lowest potential energy (i.e. most stable conformation). This can be easily explained in terms of the repulsive interactions between bonding pairs of electrons. The staggered 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 case, when viewed from one end of the molecule along the carbon – carbon bond axis, the hydrogen atoms attached to each carbon atom are directly opposite to each other. This conformation requires maximum repulsive interaction between electrons of six carbon–hydrogen bonds. It will be having the highest potential energy (i.e. least stable conformation). We represent this situation graphically by plotting the energy of an ethane molecule as a function of rotation about the carbon-carbon bond. The energy changes that occur are illustrated in Fig.6.10 In ethane the difference in energy between staggered and eclipsed conformations (ΔE) is 12kJmol^{-1}. The small barrier to rotation is called the torsional barrier of the single bond. Unless the temperature is extremely low (-250°C), many ethane molecules (at any given moment) will have enough energy to surmount this barrier. In short, when we discuss about a large number of ethane molecules, (a more realistic situation), we can say that at any given moment most of the molecules will be in staggered or nearly staggered conformations.

Conformational Analysis of Butane

The study of the energy changes that occurs in molecule when groups rotate about single bonds is called conformational analysis.

$$H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-H \quad \textit{n-butane}$$

Focusing our attention on C-2 and C-3 bonds, we see a molecule similar to ethane, but with a methyl group replacing one hydrogen atom on each carbon. The carbon- carbon single (σ) bond permits the free rotation of carbon atoms number 2 and 3 with respect to each other along their bond axis without breaking the bond. If one CH$_3$CH$_2$- group is kept stationary, and the other CH$_3$CH$_2$- group is allowed to rotate through 360° in six steps (60° each time), then the following six conformations of n-butane are obtained.

eclipsed I   gauche staggered   eclipsed II   anti
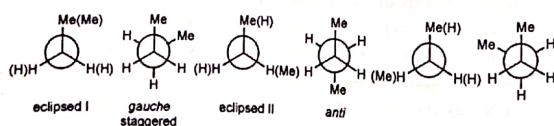
These different arrangements of groups in space that results from the free rotations along C-2 and C-3 bonds are called conformational isomers or conformations of n-butane and this phenomenon is called conformational isomerism. The potential energy changes taking place during the rotation resulting in these different conformations are shown in the Fig. 6.11 Regarding the conformational isomerism of butane, the following points are noteworthy.
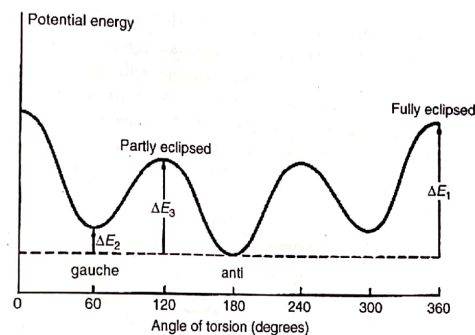

Fig 6.11 Potential energy changes in Butane conformations

1. **Anti conformation**: The fully staggered form in which the methyl groups are far apart with a dihedral angle of 180° is having the lowest potential energy and is the most stable conformation.
2. **Gauche conformation**: Here the methyl groups are only 60° apart (nearly staggered) with slightly higher energy than fully staggered form.
3. **Eclipsed conformation**: These forms of butane are having the highest energy and are the less stable conformation.

In general fully staggered **anti conformation** have the lowest energy and the highest population. The nearly staggered **gauche conformations** have an appreciable population than eclipsed conformations. The various conformational isomers usually cannot be isolated, since they are inter converted without breaking bonds by rotation about single bonds.

Conformational Analysis of Cyclohexane
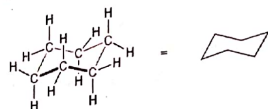
Cyclohexane is a saturated cyclic hydrocarbon (C_6H_{12}) in which all carbons are SP^3 hybridized and tetrahedral. Cyclohexane is an important component of many biological structures such as steroids and it is a stable molecule with strain less ring structure. Conformation analysis of cyclohexane represents the shape that the molecule will adopt due to the rotation around one or more single bond. The strain due to the deviation from one or more ideal bond angles and the strain caused by van der Waals repulsion which can be reduced or eliminated by rotation around a single bond need to be considered for conformational studies.
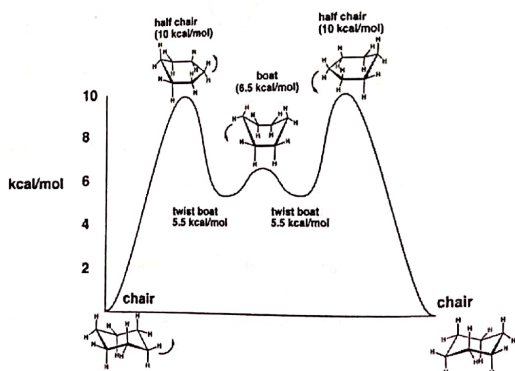

Fig.6.12 Energy diagram showing the interconversion of various conformations of cyclohexane

All the carbon atoms in cyclohexane are in the SP^3 hybridized state and the ideal bond angle is 109.5 degree. However, the planarity of the ring would force the carbons to have bond angles of 120 degree, which makes it unstable. There would be torsional strain also when the carbon atoms gets fully eclipsed. Cyclohexane has two stable forms, called chair and boat conformations (initially chair was called as Z and boat as C). Both the conformations are free from angle strain.However, due to the differences in steric strain
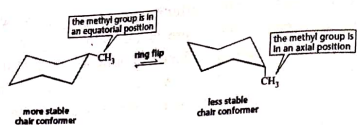
and bond opposition strain, the two forms differ in energy content. In the chair form, all the C-H bonds on adjacent carbon atoms are in the fully staggered position. These features make the chair conformation of cyclohexane most stable that minimizes strain. Half chair conformation lies 10 Kcal/ mol in energy above the chair conformation. It is the most unfavorable conformation due to the combination of ring and angle strain. In boat conformation, however, four of the C-H bonds are skew forms (1,2;3,4; 4,5 and 6,1) and 2 are eclipsed (2,3 and 5,6). At the same time, there will also be some bond opposition strain for these two pairs of eclipsed bonds and also steric repulsion between the hydrogen pointing towards each other at 1 and 4. Hence the total strain in the boat conformation is larger than that in chair conformation, and consequently boat form is less stable than chair form.
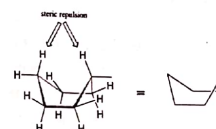

The chair form is rigid and resists distortion, and when it is changed in to the boat form, some angular deformation is necessary. The energy barrier for these transformations is about 6.5kcal/mol. Experimental data shows that a twist –boat contains less energy than the classical boat conformation. The chair conformation contains 5.5kcal/mol less energy than the twist conformation. It is to be noted that the energy barriers are not large enough to prevent interconversion of chair and boat conformations at room temperature. Due to the energy barrier for the chair to twist-boat is double that of reverse change, the chair will be the predominant form in an equilibrium mixture. A conformation versus energy diagram for cyclohexane showing how the various conformations interconvert is shown in Fig.6.12. It is to be noted that for cyclohexane the boat conformation is a transition state with maximum energy. Thus for the two chair conformations of cyclohexane to interconvert, the molecule must pass through two half chair conformations and a boat conformation, each of which are energy maxima as well as two twist boat conformations, which are at energy minima on the potential energy diagram

Conformational Analysis of Monosubstituted Cyclohexanes

Ring conversion in methylcyclohexane differs from that of cyclohexane in that the two chair conformations are not equivalent.

148

149

the methyl group is in an equatorial position

ring flip

the methyl group is in an axial position

more stable chair conformer

less stable chair conformer

Due to ring-flipping, methylcyclohexane is a mixture of a chair conformation with an equatorial methyl group and a chair conformation with an axial methyl group. A methyl group is less crowded when it is equatorial than when it is axial. The conformation with an equatorial methyl group is about 7kJ/ mol lower energy (more stable) than with an axial methyl group. When two conformations of a molecule are in equilibrium with each other, the one with the lower free energy predominates. At room temperature, approximately 95% of the molecules of methylcyclohexane are in the chair conformation that has an equatorial methyl group.   Although methylcyclohexane is a mixture of axial methyl and equatorial methyl conformations, we cannot separate these two conformations because they rapidly interconvert by ring-flipping. The mixture of these conformations is the single compound that we call methylcyclohexane.


steric repulsion
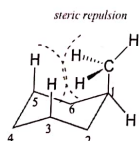
Conformational Analysis of Disubstituted Cyclohexane

In disubstituted cyclohexane, the preferred conformation will depend up on

1. The position of the two substituents on the ring (1,1-1,2- 1,3- and 1,4).
2. Stereochemical relationship (*cis or trans*).

In our discussion, only various isomers of dimethylcyclohexane will be considered, but the principles can be extended to other poly substituted cyclohexne derivatives. In the case of 1,1-disubstituted cyclohexanes, one of the substituents must necessarily be axial and the other equatorial, regardless of which chair conformer is considered. Since the substituents are the same in 1,1-dimethylcyclohexane, the two conformers are identical and present in equal concentration.In the cases of 1,2-, 1,3- and 1,4-disubstituted compounds the analysis is a bit more complex. It is always possible to have both groups

equatorial, but whether this requires a cis-relationship or a trans-relationship depends on the relative location of the substituents. As we count around the ring from carbon #1 to #6, the uppermost bond on each carbon changes its orientation from equatorial (or axial) to axial (or equatorial) and back. It is important to remember that the bonds on a given side of a chair ring-conformation always alternate in this fashion. Therefore, it should be clear that for cis-1,2-disubstitution, one of the substituents must be equatorial and the other axial; in the trans-isomer both may be equatorial. Because of the alternating nature of equatorial and axial bonds, the opposite relationship is true for 1,3-disubstitution (cis is all equatorial, trans is equatorial/axial). Finally, 1,4-disubstitution reverts to the 1,2-pattern.
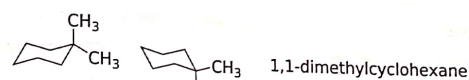
1,1-dimethylcyclohexane
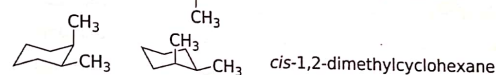
cis-1,2-dimethylcyclohexane
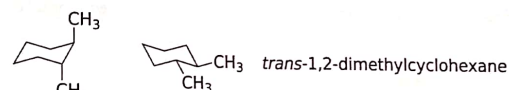
trans-1,2-dimethylcyclohexane
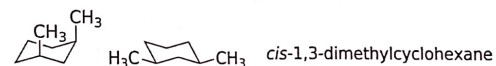
cis-1,3-dimethylcyclohexane
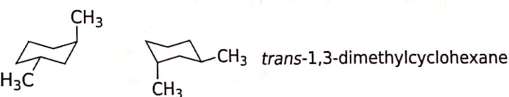
trans-1,3-dimethylcyclohexane
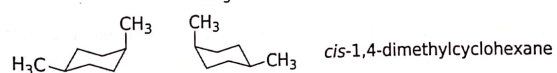
cis-1,4-dimethylcyclohexane
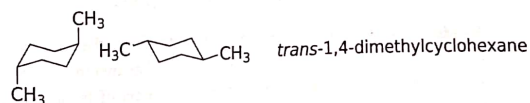
trans-1,4-dimethylcyclohexane

A summary of the various axial and equatorial relationships among methyl groups in the different possible *cis* and *trans* substituent patterns for dimethylcyclohexane is given in the following Table 6.2.

Table 6.2 Axial and Equatorial relationships in *cis*- and *trans*- dimethylcyclohexane

cis/trans substitution pattern	Axial / equatorial relationships		
1,1 dimethylcyclohexane	axial / equatorial	or	equatorial/axial
1,2-*cis* dimethylcyclohexane	axial / equatorial	or	equatorial/axial
1,2-*trans* dimethylcyclohexane	axial / axial	or	equatorial/ equatorial
1,3-*cis* dimethylcyclohexane	axial / axial	or	equatorial/ equatorial
1,3-*trans* dimethylcyclohexane	axial / equatorial	or	equatorial/axial
1,3-*cis* dimethylcyclohexane	axial / equatorial	or	equatorial/axial
1,4-*trans* dimethylcyclohexane	axial / axial	or	equatorial/ equatorial

6.9 COPOLYMERS

A polymer may consists of monomers of identical or different chemical structures, known as homopolymers or copolymers respectively. When a polymer is made by linking together only one type of small molecule, or monomer, it is called a *homopolymer*. When two different types of monomers are joined in the same polymer chain, the polymer is called a copolymer and its process is called copolymerization.

-A – A– A – A– A – A– A –   Homopolymers
-A – B– A– B– A– A – B–   Copolymers
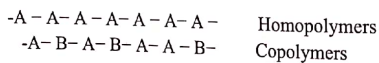
Let's imagine two monomers, A and B which can be made into a copolymer in many different ways. Depending upon the variations in distribution of monomer units within polymer chains, there are various types of copolymers such as

1. **Random copolymer:** In this type of copolymer, the monomer units are randomly distributed along the polymer chain. The two monomers may follow in any order. Most of the commercial copolymers of butadiene and styrene, butadiene and acrylonitrile etc. are random copolymers.
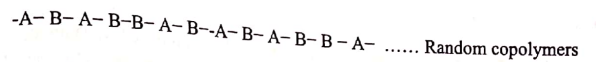
-A– B– A– B–B– A– B–-A– B– A– B– B – A– ...... Random copolymers

Table 6.3 Comparison of different copolymers

Random copolymers	Monomers are distributed randomly, and sometimes unevenly	Representation of copolymer
Alternating copolymers	Monomers are distributed in a regular alternating fashion, with nearly equal molar amounts of each in the chain	
Block copolymers	Monomers are segmented or blocked in a long sequence	
Graft copolymers	Branched copolymer with a backbone of one type of monomer and one or more side chains of another monomer	

2. **Alternate copolymer:** In this type, the monomers are arranged in a regular alternating fashion. These include polyesters, polyamides etc.
    -A– B– A– B–A– B– A–B– A– B– A– B– A– B– ......Alternate copolymer

3. **Block copolymer:** In this polymer a block of repeating unit of one kind of monomer is followed by a block of another kind of monomer, then again followed by the first kind and so on.
    -A– A– A– A–B– B– B–B– A– A– A– A– A–.........Block copolymers

4. **Graft copolymer:** In this type, a chain formed by one kind of repeating unit of monomer is grafted on to a chain of monomer units of another kind acting as a backbone of the polymer.
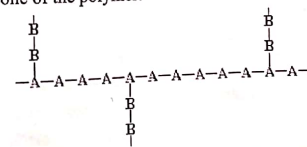
Graft copolymer

6.10 KEVLAR

Kevlar is a registered trade mark for a synthetic fiber Produced by DuPont, a chemical company. Kevlar was developed in 1965 and being used commercially since 1970. The chemical name for Kevlar is poly-para-phenylene terephthalamide. Kevlar is a fibrous aromatic polyamide formed by the polymerization of terephthalic acid dichloride and p-Aminoaniline. The reaction is a condensation polymerization yielding hydrochloric acid as the byproduct. Kevlar is an advanced polymer resembling nylons with wide ranging practical applications.

Terephthalic acid dichloride   p - Aminoaniline
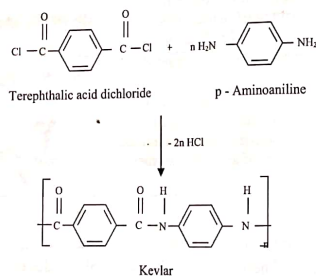
Kevlar

Properties

Kevlar is a classical example for an aromatic polyamide known as aramid polymer. There is stronger intermolecular force of attraction between adjacent polymer chains making it exceptionally stable and heat resistant. Important properties are:
1. High mechanical properties including strength.
2. Light weight.
3. Flexibility with heat stability.
4. More rigid than nylons.

Applications

1. Aerospace and aircraft industries.
2. Bullet-proof vests.
3. Motorcycle helmets.
4. Tyres, brakes, clutch lining and other car parts.
5. Protective clothing.

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6. Ropes and cables.
7. Other high performance materials.

6.11 ACRYLONITRILE BUTADIENE STYRENE (ABS) POLYMERS

Acrylonitrile Butadiene Styrene (ABS) is a terpolymer of acrylonitrile, butadiene and styrene. It was discovered during World War II. Usual compositions are about half styrene with balance divided between butadiene and acrylonitrile. Acrylonitrile contributes chemical resistance, heat résistance, and high strength; butadiene contributes toughness, impact strength and low-temperature property retention; styrene contributes rigidity, glossiness, and process ability. Considerable variations are possible resulting in different grades of ABS with a wide range of features and applications. Finished products of ABS have attractive appearance. Elecroplated ABS plastics have bright reflecting surface and used for making name plates, reflectors etc.

Preparation of ABS polymers: Two basic processes are used to prepare ABS polymers.

1. **Copolymerization:** In this method, acrylonitrile and styrene are polymerized in the presence of polybutadiene latex.

ABS
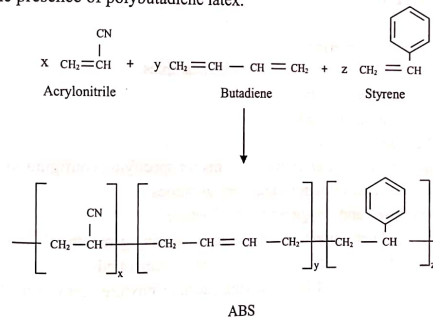
2. **Blending:** In this the two copolymers of styrene-acrylonitrile and acrylonitrile-butadiene are blended and the mixture is coagulated. The best method is by preparing a suitably cross-linked acrylonitrile butadiene rubber and mixing it with styrene-acrylonitrile copolymer. Depending on the ratio of the monomers and the pattern of their arrangements, a large variety of ABS polymers can be produced.

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Properties: ABS polymers have three monomers. Due to variations in relative amounts of these monomers, the final products can vary considerably. The important properties are:

1. High heat resistance.
2. Flame resistance.
3. Good process ability.
4. Very high impact resistance.
5. High glossiness.
6. Good chemical resistance.

Applications

1. They are used in automobile industry.
2. Molded articles.
3. Electrical/ electronic applications.
4. Household goods.
5. Sports goods.

IMPORTANT QUESTIONS

1. Write note on optical isomerism.
2. Describe geometrical isomerism with relevant examples.
3. Explain stereoisomerism with two examples.
4. Write note on resolution and recemisation.
5. Differentiate between enantiomers and diasteromers.
6. Describe 'sequence rules' used in R-S systems for specifying configurations.
7. Distinguish between conformations and configurations.
8. Write note on eclipsed and staggered form of butane.
9. Explain the essential conditions for a compound showing geometrical isomerism.
10. Write note on optical isomerism of chiral organic compounds.
11. Describe two methods used for resolving racemic mixtures into optically active compounds.
12. What is optical activity? How is it measured?
13. What is specific rotation?
14. Describe the conformal isomers of n-butane.
15. Explain with examples R-S system of configuration of optical isomers.
16. Write note on geometrical isomerism in cyclic compounds.
17. Write structural formula and important uses of Kevlar. (KTU 2016)
18. Write note on the preparations, properties and applications of Kevlar (KTU 2016)

19. Give the structure of ABS polymer. List two properties (KTU 2018 July)
20. What are copolymers? Give an example. (KTU 2016)
21. Discuss the classification of copolymers.
22. Discuss the chair and boat conformations in cyclohexane.
23. Write an essay on the conformational analysis of cyclohexane.
24. Discuss the conformational analysis of butane.
25. Draw the Newman projections for ethane and propane.
26. Draw the Wedge –hash projection for 1,1 Dichloromethane and Lactic acid.
27. Draw the Fischer projection for methane and ethane.
28. Enunciate the procedure for assigning R and S nomenclature for glyceraldehyde.
29. What is ABS? What are its properties and applications (KTU June 2019).

CHAPTER 7
CONDUCTING POLYMERS

7.1 INTRODUCTION

Polymers have long been used as insulating materials. For example, metal cables are coated in plastic to insulate them. Poor conductivity of polymers can be explained because of the non availability of the free electrons in conduction process.

Conducting polymers are much more electrically conductive than standard polymers but much less than metals such as copper. In practice, the conductivity of these materials are characterized by low –charge carrier mobility – a measure of how easily electric charge moves.

7.2 CLASSIFICATION

A polymer which can conduct electricity is termed as conducting polymer. Conducting polymers can be classified into following types.
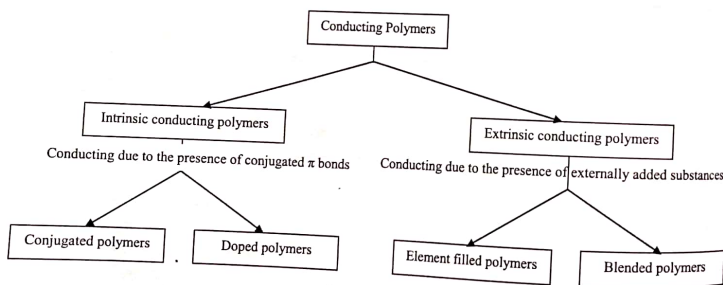

Fig 7.1 Classification of conducting

7. 3 INTRINSICALLY CONDUCTING POLYMER (ICP)

These polymers have extensive conjugation in the polymeric backbone which is responsible for conductance. The overlapping of π electrons over the centre backbone of the polymer result in the formation of valance bands (lowest occupied band) and the

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conductivity ,bands (highest occupied band) which extend over the entire polymer molecule.

1. Conjugated π-electrons conducting polymers

In this polymer, backbones or associated groups consists of localized electron pair or residual charge. Such polymers essentially contain a conjugated π-electron backbone, which is responsible for conducting electrical charge. In an electric field, conjugated π-electrons of the polymer get excited, and thereby can be transported through the solid polymeric material. Overlapping of orbital of conjugated π-electrons over the entire backbone result in the formation of valence bands as well as conduction bands, this extends over the entire polymer molecule. Generally, electrical conduction could occur only after thermal or photolytic activation of electrons to give them sufficient energy to jump the gap and reach the lower levels of the conduction band. Presence of conjugated π-electrons in a polymer increases its conductivity to a larger extent.

Trans- polyacetylene

Polyaniline(PANI)

Polythiophene

Polypyrrole
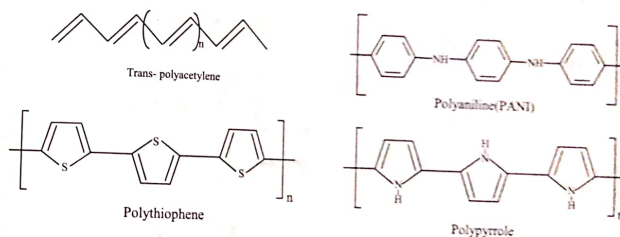
2. Doped conducting polymers

In comparison to conventional polymers, polymers with conjugated π-electrons can be easily oxidized or reduced as they have low ionization potentials and high electron affinities. Their conductivities can be increased by creating positive or negative charge on polymer backbone by oxidation or reduction. Doped conducting polymer is obtained by exposing a polymer to a charge transfer agent in either gas or solution phase. In general, doping increases the surface conductivity of the polymer.

By analogy with semiconductor technology, it is referred to as Doping. There are two different types of doping.
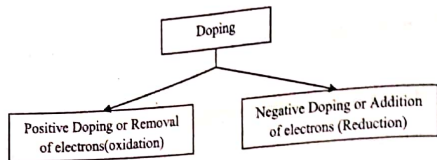
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Fig. 7.2 Types of Doping

a. Positive Doping (Oxidation)

It is done by treating an intrinsically conducting polymer with a Lewis acid; thereby oxidation process takes place by the formation of positive charges on the polymeric backbone. Some of the common P-dopant (Lewis acid) used are BF_3, $FeCl_3$ etc.
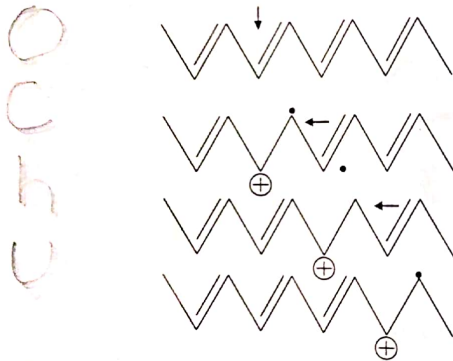

Fig.7.3 Propagation of polaron through a conjugated polymer chain by shifting the double bonds

The oxidation process (i.e. removal of an electron from the polymer π-backbone) leads to the formation of delocalized radical ion called **polaron**. These polarons are mobile, which can move along the polymer chain, by the rearrangement of double and single bonds. Thus, these polarons can act as current carriers for conduction.

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b. Negative Doping (Reduction)

It is done by treating an intrinsically conducting polymer with a Lewis base, thereby reduction process takes place by the formation of negative charges on the polymeric backbone. Some of the common N-dopant (Lewis base) used are Li, Na, Ca, tetrabutyl ammonium etc.

7.4 CONDUCTIVE ELEMENT FILLED POLYMERS

It is a resin or polymer filled with conducting elements such as carbon black, metallic fibers, metal oxides, etc. In this the polymers acts as the binder to hold the conducting elements together in the solid entity. These polymers possess reasonably good bulk conductivity, and are generally low cost, light weight, mechanically durable and strong, easily process able in different forms, shapes and sizes.

The minimum concentration of conductive filler which should be added so that the polymer starts conducting is known as percolation threshold. At this concentration of filler, a conducting path is formed in the polymeric material. Generally, special conducting grade C-black is used as filler, which has very high surface area, more porosity and more filamentous properties.

7.5 BLENDED CONDUCTING POLYMERS

These polymers are obtained by blending a conventional polymer with a conducting polymer. Such polymers possess better physical, chemical, electrical and mechanical properties and can be easily processed.

7.6 APPLICATIONS OF CONDUCTING POLYMERS

1. Analytical sensors: Conducting polymers are used for making sensors for O_2, NO_x, SO_2, NH_3, glucose, and P^H.
2. Rechargeable batteries: Conducting polymers are used for making button type rechargeable batteries. These batteries are small in size, long lasting and can produce current density up to 50 mA/cm^2. Moreover these batteries are environmentally friendly since they do not carry any toxic heavy metals.
3. In photovoltaic devices: They can be used in producing photovoltaic devices, e.g., in Al/polymer/Au photovoltaic cells.
4. Biosensors and chemical sensors: An emerging application for electrically conductive polymeric materials is biosensors and chemical sensors, which can convert chemical information in to a measurable electrical response.

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5. Electrochemical actuators: Conducting polymers are used as electro-chemical actuators.
6. Display systems: Used in optical display devices.
7. For making Ion-exchange membranes: membranes made up of conducting polymers can show boundary layer effects with selective permeability for ions, gases etc. and hence they are useful for ion-exchangers and controlled release of drugs.
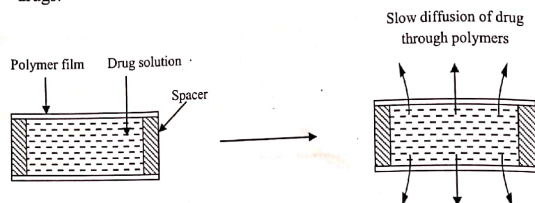

Fig.7.4 Slow, controlled release of drug by diffusion through polymer membrane

8. Used in wiring aerospace and aircraft components.
9. Used in variable transmission (smart) windows.
10. Used as conductive paints.
11. Used in antistatic coating for clothing.
12. Artificial nerves.
13. Microelectronic devices, telecommunication systems and biomedical equipments.
14. Used in electronic devices such as transistors and diodes.
15. The list of potential applications for conductive polymers remains a long one and includes radiation coatings, batteries, catalysts, electro chromic windows, fuel cells, nonlinear optics, radar dishes and wave guides.
16. Piezoceramics
17. Printed circuit boards.

7.7 FACTORS AFFECTING THE CONDUCTIVITY OF POLYMERS

The conductivity of organic polymers is influenced by the following factors.

1. Conjugation length of the polymer chain: with the increase in the extent of conjugation in a given polymer, its conductivity increases.

2. Doping level: the conductivity of polymers increases with doping level till a saturation point is reached.
3. Temperature: conductivity of a polymer increases with increase in temperature, and reaches a constant value at a particular high temperature.
4. Frequency of current: the conductivity of these polymers depends on the frequency of current..

Properties of conducting polymers

Conductive polymers have the following properties,

1. Good conductivity
2. High ability for charge storage
3. Ability to exchange ions.
4. They absorb visible light to give colored products.
5. They are transparent to X-rays.
6. The products are economical, recyclable, with dimensional stability.
7. These materials are environmentally friendly since it does not carry heavy metals.

7.8 POLYANILINE (PANI)

Polyaniline is one of the oldest conductive polymers known. It has been known as an electrically conductive polymer (ECP) for the past 35 years. Emeraldine (an oxidative form of polyaniline) is also known as "synthetic metal". It has conductivity like metals, metallic lusture and metallic sound. Although the compound itself was discovered over 150 years ago, only since the early 1980s has polyaniline captured the intense attention of the scientific community. This interest is due to the rediscovery of high electrical conductivity

Preparation

Polyaniline is made by the oxidative polymerization of aniline under acidic conditions. The most common oxidant is ammonium persulphate. The components are dissolved in 1 M HCl and the two solutions slowly combined. The reaction is very exothermic. The polymer precipitates as an unstable dispersion with micrometer-scale particulates.

Aniline → Polyaniline(PANI)
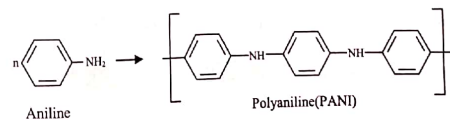
Conduction Mechanism of Polyaniline

Polyaniline is able to conduct electricity because of their conjugated π- bond system, which is formed by the overlapping of carbon π-orbital and alternating carbon-carbon bond lengths extending over large number of recurring monomer units. In polyaniline, nitrogen π-orbital and carbon rings are also part of the conjugated systems as shown in figure.
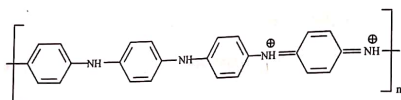
Chemical structure of doped emaraldinesalt (PANI)

The conjugated double bonds permit easy electron mobility throughout the molecule because the electrons are delocalized. Delocalization is the condition in which the π-bonding electrons are spread over a number of atoms rather than localized between two atoms. This condition allows electrons to move more easily, thus making polyaniline electrically conductive.

In addition, it has a conjugated double bond structure, the benzoid ring, between the quinoid imine and the benzoid amine structures, which renders polyaniline a conductive polymer. Polyaniline exists in three oxidation stages.

1. Leucoemeraldine
2. Emeraldine
3. Pernigraniline

The emeraldine- base form of polyaniline is the most stable of the three states and is the commonly accepted conductive polymer.

Properties of polyaniline

1. Polyaniline also known as "synthetic metal". It has conductivity like metals, metallic lusture and metallic sound.
2. Polyaniline has light weight and mechanical flexibility.
3. They can be doped for increasing the conductivity.
4. Poly anilines have three distinct oxidation states.
5. They can show different colors.
6. They are environmentally friendly with no heavy metals.

Applications of Polyaniline

Polyaniline due to their light weight, conductivity, mechanical flexibility and low cost can be used for various potential applications. The main uses of polyaniline are

1. Can be used in chemical vapor sensors, super capacitors and biosensors.
2. Corrosion protection.
3. Active electronic components such as non volatile memory.
4. The different colors, charges and conformations of the multiple oxidation states make the material promising for applications such as actuators, super capacitors and electrochromics.
5. They are suitable for manufacture of electrostatic dispersive (ESD) coatings and blends.
6. Rechargeable batteries: Polyaniline is used for making button type rechargeable batteries.
7. Microelectronic devices, telecommunication systems and biomedical equipments.

7.9 POLYPYRROLE

Polypyrrole (PPy) can be prepared by chemically or electrochemically through the oxidative polymerization of pyrrole monomer. Most commonly it is prepared by the oxidation of pyrrole using ferric chloride in methanol.

$$nC_4H_4NH + 2FeCl_3 \longrightarrow (C_4H_2NH)_n + 2FeCl_2 + 2HCl$$

Pyrrole   Polypyrrole
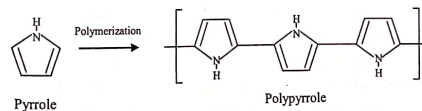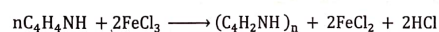
Properties

1. Polypyrrole films are yellow but darken in air due to oxidation. But some doped films are blue or black.
2. Undoped and doped films are insoluble in solvents but swellable. Doping of Polypyrrole makes the material brittle.
3. It has very high chemical resistance.

   4. Polypyrrole is an insulator. But oxidative derivatives are good electric conductors.

Applications

1. Polypyrroles are often used in biosensors, gas sensors, anti electrostatic coatings, smart windows and displays, light weight rechargeable batteries, electronic devices solid electrolytic capacitor etc.
2. Polypyrrole is a potential vehicle for drug delivery system.
3. Polypyrrole based polymer blends can be used to protect corrosion of metals.
4. In medical industry, it is used for testing blood lithium levels of patients.
5. Polypyrrole coatings have excellent thermal stability and can be used in carbon composites.

7.10 ORGANIC LIGHT–EMITTING DIODES (OLEDs)

Light emitting diodes (LEDs) are optoelectronic devices, which generate light when they are electrically biased in the forward direction. The early commercial LEDs devices, in 1960s were based on inorganic semiconductors such as gallium arsenide phosphide (GaAsP) as an emitter and the efficiencies were very low. After 40 years of research and development, the efficiencies of inorganic LEDs have been significantly improved and they are used in a wide range of applications such as telecommunications, indicator lights, and more recently in solid –state lighting.

Light emitting devices made with organic materials are called organic light-emitting diodes (OLEDs). Before the invention of OLEDs, organic based devices could be operated only in electroluminescence mode. The first organic electroluminescence device was demonstrated in the 1950s and very high operating voltages were required. These devices were made with anthracene single crystals doped with tetracene (a blue emitting fluorescence dye) sandwiching between two electrodes. Very high drive voltages were required and the efficiencies were very low. However, the new OLED devices are based on multilayer structure and they consists of a transparent anode, a hole transporting layer, an electron/ emitting layer, and a cathode. During operation, electrons and holes are injected from a cathode and anode, respectively, and recombination of electrons and holes leads to efficient light generation. The operation principles of LEDs are similar to that of LEDs.

OLEDs are used to create digital displays in devices such as television screens, computer monitors, portable systems such as mobile phones, handheld game consoles and PDAs and solid state lighting applications.

There are two main families of OLEDs

1. Those based on small organic molecules- e.g Organometallic chelates
2. Those based on organic polymers- e.g Polyfluorene and poly(p-phenylenevinylene)

OLED Structure

A typical OLED structure consists of the following five parts.

1. Substrate (clear plastic, glass, foil) supporting OLED.
2. Anode, adds electron holes (removes electrons) when a current flows through the device [Indium tinoxide (ITO), Au, LiF]
3. A hole transport layer (HTL), this is the conducting polymer layer that transport holes from anode. For example, poly aniline, Poly (p-phenylenevinylene) (PPV)
4. An electron transport layer (ETL). This is the emissive layer made of an organic molecule or polymer where light is made (different one from the conducting layer) e.g. polyfluorene.
5. A metallic cathode, injects electrons when a current flows through the device. (e.g Ag, Ca etc.)

Working principle

A typical OLED is composed of a layer of organic materials situated between an anode and a cathode deposited on a substrate. The organic molecules are electrically conductive as a result of delocalization of conjugated π electrons. These materials have conductivity levels ranging from insulators to conductors, and are therefore considered as 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.

When current is applied, electrons flow from the cathode to the anode. When these electrons go through the OLED layer, photons are released. The cathode "pushes" electrons in to the emissive layer, while the anode removes electrons from the conductive layer (which leads to "holes" in the conductive layer). The "new" electrons in the emissive layer combine with the holes in the conductive layer forming an exciton - releasing photons and light is created. Depending on the nature of the emissive materials the color can vary and the intensity of the light is controlled by the amount of current applied.
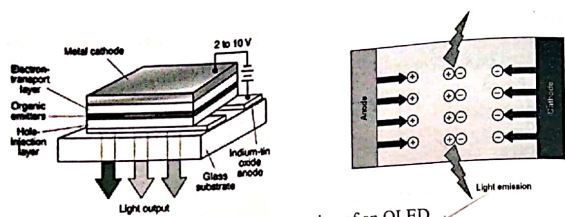
Figure 7.5 Operation of an OLED

By adding ions with mobility to an OLED can create a light–emitting electrochemical cell (LEC). OLEDs have a similar structure to inorganic LEDs. Unlike inorganic LEDs, OLEDs can be used to make emissive displays and area lighting panels.

OLED Advantages

1. Lightweight and flexible plastic substrates
2. Better power efficiency and thickness
3. Lower cost
4. They have greater efficiency levels than halogen and incandescent lights.
5. They are considered as cold lighting sources and do not generate excessive heat.

OLED Disadvantages

1. Low life span
2. Water damage- water can instantly damage the system

Applications

OLED technology is used in commercial applications such as

1. Displays for mobile phones
2. Portable digital media players
3. OLED cameras
4. Smart watch with OLED screens
5. Smart phones
6. OLED TV

In short, an OLED is simply an LED where the light is produced ("emitted") by organic molecules. Light-emitting diode of thin flexible sheets of organic electroluminescent material can be used for visual displays. Electrons are injected

from the cathode while Holes are injected from the anode. Transport and radiative recombination of electron hole pairs at the emissive polymer.

IMPORTANT QUESTIONS

1. How the conducting polymers are classified? Describe with examples. Explain its conductivity and applications. (KTU Dec.2017.
2. What are conducting polymers? Give two examples with structures (KTU 2016)
3. Explain the following
   (i)   Conducting polymers with conjugated π electrons.
   (ii) Doped conducting polymers.
   (iii) Conducting polymer blends.
4. Write the method of preparation of polyaniline and polyacetylene. Explain its conductivity.
5. Briefly explain the important applications of conducting polymers.
6. What is mean by doping in conducting polymers?
7. Explain the electrical conductivity of conducting polymers by using valance band theory.
8. Write a short note on OLED (KTU April 2018)
9. Explain the working of OLEDs
10. Write note on the structure of OLED
11. Write note on the applications of OLED
12. What is polypyrrole? How will you synthesize it? (KTU June 2019)
13. Which kind of doping is possible (p or n) in poly pyrrole why? Give two properties and applications?   (KTU June 2019)