VINAYAKA MISSION'S RESEARCH FOUNDATION - DU FACULTY OF ARTS AND SCIENCE/DEPARTMENT OF CHEMISTRY Course & Branch: <u>B.Sc. – CHEMISRY</u>; Sem: I<u>I Sem.</u> <u>Subject Name: DSC – 1B: General Chemistry – II – Question and Answer</u> <u>UNIT – IV: Stereochemistry</u> Part – A (2 Marks)

1. What is stereoisomerism?

The phenomenon in which different compounds have the same molecular formula and structural formula but have different configuration i.e. different arrangement of atoms and groups in space is called stereoisomerism.

eg: d and l – lactic acid

2. Write the two types of stereoisomerism.

Stereoisomerism is divided into two types,

- (i) Optical Isomerism
- (ii) Geometrical isomerism.
- 3. Draw the structure of d and l lactic acid.



4. Define optical isomerism.

Optical isomerism is the phenomenon in which different compounds have the same molecular formula and structural formula but have different configuration i.e. different arrangement of atoms and groups in space. They rotate the plane of the plane polarized light in different directions.

5. What is optical activity?

Solution of some organic compounds have an unique property of rotating the plane of the plane polarized light. This is property is called optical activity.

- What is the condition for optical activity?
 The molecule must be chiral i.e. it must have two structures which are mirror images and which cannot be superimposed on one another.
- 7. Write a short note on chirality.

According to Vant Hoff and Le Bel theory, in a molecule like methane, the carbon atom is at the centre of a regular tetrahedron and the four atoms or groups present at the four corners. If the four groups attached to a central atom of molecules are different, then the molecule is not superimposable on its mirror image such a molecule is called Chiral molecule and that carbon is called chiral carbon or asymmetric carbon. This phenomenon is called chirality.

8. Define racemization.

Racemization is the process of converting an optically active compound in to racemic modification. Racemic modifications are also called racemic mixtures or racemates. e.g.; dl mixture

9. Define resolution in stereochemistry.

The separation of racemic mixture in to its enantiomers (dextro and laevo compounds) is termed as resolution.

Methods used for resolving racemic compounds

- (i) Mechanical separation (ii) Bio-chemical separation (iii) By salt formation
- 10. What are enantiomers?

Optical isomers which are mirror images are called enantiomers. Chirality is the necessary condition for the existence of enantiomers

e.g. Lactic acid



Lactic acid - chiral (not superimposable) - Enantiomers

11. What is conformation?

The different arrangements of atoms that result from rotation about a single bond is called conformation.



12. Draw the Newmann projection for ethane.



13. What is torsional strain of ethane?



The 12 kJ/mol of extra energy present in the eclipsed conformation of ethane is called torsional strain.

Torsional strain is due to repulsion between electron clouds in the C-H bonds as they pass close by each other in the eclipsed conformer

14. Draw the chair conformation of cyclohexane.

Conformations of Cyclohexane is unstrained

chair conformation: bond angle 111.5° (close to the ideal 109.5° tetrahedral angle)



chair



15. Draw the E & Z structure of 1,2-dichlroethene.



(E)- : the higher priority groups are on opposite sides of the double bond.(Z)- : the higher priority groups are on the same side of the double bond.

(<u>For remembrance</u>: E is for "Enemies", which are on opposite sides. In Z isomers, the higher priority groups are on *zee zame zide*.)

Part – B (5 Marks)

1. Briefly explain stereoisomerism with one example.

The phenomenon in which different compounds have the same molecular formula and structural formula but have different configuration i.e. different arrangement of atoms and groups in space is called stereoisomerism.

eg: d and l – lactic acid

d and l – lactic acids are two different compounds. Both have the **same molecular** formula, i.e. C₃H₆O₃. Both have the same structural formula, viz CH₃CH(OH)COOH.

But, they have **different configurations** i.e. the arrangement of various atoms and groups in space of the two acids are different. The structure of one compound is **the mirror image of the other.**



Thus, d- and l- lactic acids are a pair of stereoisomers.

2. Write a note on optical isomerism.

Optical isomerism is the phenomenon in which different compounds have the same molecular formula and structural formula but have different configuration i.e. different arrangement of atoms and groups in space. They rotate the plane of the plane polarized light in different directions.

The two compounds which have the same molecular and structural formula but have different configuration and which rotate the plane of the plane polarized light in different directions are called optical isomers.

eg: d and l – lactic acid



3. Explain briefly about chiral and achiral molecules.

Chiral molecule

According to Vant Hoff and Le Bel theory, in a molecule like methane, the carbon atom is at the centre of a regular tetrahedron and the four atoms or groups present at the four corners. If the four groups attached to a central atom of molecules are different, then the molecule is not superimposable on its mirror image such a molecule is called Chiral molecule and that carbon is called chiral carbon or asymmetric carbon. This phenomenon is called chirality.

Chirality is the necessary condition for the existence of enantiomers. e.g. Lactic acid



<u>Achiral molecule</u>

Molecule that are superimposable or their mirror images are called achiral. Achiral molecules possess symmetry.

e.g. Isopropyl chloride



4. Give any two methods to bring about racemization.

Racemization is the process of converting an optically active compound in to racemic modification. Racemic modifications are also called racemic mixtures or racemates.

e.g.; dl mixture

Methods to bring about racemeization

- (i) Action of heat (ii) Treatment with chemical reagents
- (iii) Substitutions and rearrangements (iv) Auto-racemization.
- (i) Action of heat When d or 1 -isomer is heated, we get the dl mixture.
- (ii) Treatment with chemical reagents

Many substances undergo racemization when treated with chemical reagents e.g. Mandelic acid ($C_6H_5CH(OH)COOH$) form (±)bromo-acid when treated with hyrdrobromic acid.

(iii) Auto-racemization

In some cases, racemization occurs spontaneously at room temperature, e.g. dimethyl bromo succinate undergoes racemization on standing at room temperature. This type of racemization is termed as auto-racemization.

5. Explain any one method used for resolving racemic compounds.

<u>**Resolution**</u>: The separation of racemic mixture in to its enantiomers (dextro and laevo compounds) is termed as resolution.

Any attempt to prepare an optically active form of a compound ends up in a racemic mixture only. So, they have to be separated into d and l forms. The process of such separation is called resolution.

Methods used for resolving racemic compounds

(ii) Mechanical separation (ii) Bio-chemical separation (iii) By salt formation

(i) <u>Mechanical separation:</u>

When the enationmers (+) and (-) forms of the optically active compounds or their salts form well-defined crystals, showing hemihedral faces, they can be separated by simple hand-picking. *Pasteur* separated in this manner crystals of sodium ammonium recemate, Na.NH₄C₄O₆.2H₂O.

6. Briefly explain the conformation of ethane and energy barrier for rotation.

<u>Conformation</u>: The different arrangements of atoms that result from rotation about a single bond is called conformation.

<u>**Conformers**</u>: a specific conformation (conformational isomer); same connections of atoms





Energy barrier for rotation: Not perfectly free rotation about σ -bonds



The 12 kJ/mol of extra energy present in the eclipsed conformation of ethane is called torsional strain.

Torsional strain is due to repulsion between electron clouds in the C-H bonds as they pass close by each other in the eclipsed conformer 7. Draw the graph of potential energy versus bond rotation in ethane with different conformations.



8. Discuss different conformations of butane and explain its torsional strain.

Different conformations of butane

Anti conformation: two large groups are in the opposite side

Eclipsed conformations

Gauche conformation: two large groups are 60° apart



Torsional strain on eclipse conformation:



Torsional strain on Gauche conformation:

3.8 kJ/mol (0.9 kcal/mol) unstable due to steric strain between two methyl groups



9. Draw the graph of potential energy versus bond rotation in butane with different conformations.



10. Briefly explain how to arrive E-Z nomenclature for 1,2-dichloroethene.

We look at what is attached to each end of the double bond in turn, and give the two groups a "priority".

If the two groups with the higher priorities are on the same side of the double bond, that is described as the (Z)- isomer. The symbol Z comes from a German word (zusammen) which means together.

If the two groups with the higher priorities are on opposite sides of the double bond, then this is the (E)- isomer. E comes from the German entgegen which means opposite.



(E)- : the higher priority groups are on opposite sides of the double bond.

(Z)- : the higher priority groups are on the same side of the double bond.(For remembrance: E is for "Enemies", which are on opposite sides.In Z isomers, the higher priority groups are on zee zame zide.)

Part – C (10 Marks)

1. Explain stereoisomerism with examples.

The phenomenon in which different compounds have the same molecular formula and structural formula but have different configuration i.e. different arrangement of atoms and groups in space is called stereoisomerism.

Example (i):- d and l – lactic acid:-

d and *l* – lactic acids are two different compounds. Both have the **same molecular** formula, i.e. $C_3H_6O_3$. Both have the same structural formula, viz CH₃CH(OH)COOH.

But, they have **different configurations** i.e. the arrangement of various atoms and groups in space of the two acids are different. The structure of one compound is **the mirror image of the other.**



Thus, *d*- and *l*- lactic acids are a pair of stereoisomers.

Example (ii) Maleic and fumaric acids are two different compounds. Both have the same formula, viz, $C_4H_4O_4$. But, they have different configurations i.e. the arrangement of various atoms and groups in space, of the two acids, are different as shown below.



2. Give the detail explanation on optical isomerism.

Optical isomerism is the phenomenon in which different compounds have the same molecular formula and structural formula but have different configuration i.e. different arrangement of atoms and groups in space. They rotate the plane of the plane polarized light in different directions.

The two compounds which have the same molecular and structural formula but have different configuration and which rotate the plane of the plane polarized light in different directions are called optical isomers.



Optical activity:-

Solutions of some organic compounds have an unique property of rotating the plane of the plane polarized light. This property is called optical activity. Such substances are called optically active substances. If they rotate the plane of plane polarized light towards the **right (clockwise)**, they are called **dextro-rotatory**. If they rotate the plane of plane polarized light towards the **left (anti-clockwise)**, they are called **laevo-rotatory**.

The amount of rotation depends, for a given substance, on a number of factors like

- (i) The thickness of the layer
- (ii) The nature of solvent
- (iii) The temperature, and
- (iv) The wavelength of the light used.

Conditions for optical activity:

The molecule must be **chiral** i.e. it must have two structures which are mirror images and which **cannot** be superimposed on one another.

Asymmetric Centre:

Any structural feature of a molecule which gives rise to optical activity may be called asymmetric centre. In many reaction, a new asymmetric centre is created.

3. Explain in detail about racemization.

Racemization is the process of converting an optically active compound in to racemic modification. Racemic modifications are also called racemic mixtures or racemates. e.g.; dl mixture

Methods to bring about racemeization

- (i) Action of heat
- (ii) Treatment with chemical reagents
- (iii) Substitutions and rearrangements
- (iv) Auto-racemization.
- (*i*) <u>Action of heat</u> When d or 1 -isomer is heated, we get the dl mixture.

(ii) *<u>Treatment with chemical reagents</u>*

Many substances undergo racemization when treated with chemical reagents e.g. Mandelic acid ($C_6H_5CH(OH)COOH$) form (±)bromo-acid when treated with

hyrdrobromic acid.

(iii) <u>Substitutions and rearrangements</u>

Substitutions and rearrangement reactions which takes place via S_N^1 type stepwise mechanism end up in racemized products. e.g.

(iv) Auto-racemization

In some cases, racemization occurs spontaneously at room temperature, e.g. dimethyl bromo succinate undergoes racemization on standing at room temperature. This type of racemization is termed as auto-racemization.

Mechanism of racemization

Compounds which racemize readily are found to contain an asymmetric carbon atom joined to a hydrogen atom and a negative group.

For e.g.



The intermediate enol form is not asymmetric. When it reverts to the stable form, there are equal chances to produce the dextro and laevo forms. So it gives a racemic mixture.

In the case of a compound which can not undergo tautomeric change, mechanism of racemisation is uncertain. However the racemisation is said to take place via the formation of a planar intermediate which when reverts to the stable form, there are equal changes to produce the dextro and laevo forms. So it gives a racemic mixture,

This can be illustrated by taking the base catalysed racemisation of (--) lactic acid.

	H	OH	+	OH
	CH3-C-COOH	\rightleftharpoons	CH3-C-COOH	ОК СН, −С − СООН
	ОН		Óн	, H
	(-) form			(+) form
NO.	DECOLUTION		and the second	

 What is resolution? Explain different methods used for resolving racemic compounds. <u>Resolution</u>: The separation of racemic mixture in to its enantiomers (dextro and laevo compounds) is termed as resolution.

Any attempt to prepare an optically active form of a compound ends up in a racemic mixture only. So, they have to be separated into d and l forms. The process of such separation is called resolution.

Methods used for resolving racemic compounds

(i) Mechanical separation (ii) Bio-chemical separation (iii) By salt formation

(i) <u>Mechanical separation:</u>

When the enationmers (+) and (-) forms of the optically active compounds or their salts form well-defined crystals, showing hemihedral faces, they can be separated by simple hand-picking. *Pasteur* separated in this manner crystals of sodium ammonium recemate, Na.NH₄C₄O₆.2H₂O.

(ii) <u>Bio-chemical separation</u>

(please refer the image)

(iii) By Salt formation:

(please refer the image)

Bio - chemical separation :

Certain bacteria or fungi when allowed to grow in a solution of the racemic compounds destroy one of the optical isomers at much quicker rate than the other due to selective assimilation. For example, when penicillium glaucum is allowed to grow in a solution of ammonium racemate, it destroys the d-tartrate by assimilation leaving behind the *l*-tartrate practically unaffected. However, the separation is not always complete and one component is always lost. Some other side-products may also be formed and the sample may be difficult to purify.

(ii) By means of salt formation :

This method is the best of all methods of resolution. In this method the active constitutents of a racemic mixture are converted into diastereoisomers [salts] with another active base or acid.

[down + Incid]	+ 2dhave	$[d_{acid} d_{base}] + [I_{acid} d_{base}]$
Racemic mixture	Active	Optically active salts
[acid]	base	[Diastereo - isomers]

The two salts thus obtained often differ in their solubilities and can be separated by fractional crystallizaton. The salts can be hydrolysed with inorganic acids or alkalis to get the original active compounds. For example, racemic tartaric acid is separated by this method. The optically active bases used for this purpose are mainly alkaloids like quinine, brucine, cinchonine, and morphine. Similarly racemic bases can be separated by using optically active acids like tartaric acids, comphor sulphonic acid, etc.

5. Explain different conformations, torsional strain and graph of potential energy versus bond rotation in butane.

Different conformations of butane

Anti conformation: two large groups are in the opposite side

Eclipsed conformations

Gauche conformation: two large groups are 60° apart



Torsional strain on eclipse conformation:



Torsional strain on Gauche conformation:

3.8 kJ/mol (0.9 kcal/mol) unstable due to steric strain between two methyl groups





<u>Graph of potential energy versus bond rotation in butane with different</u> <u>conformations.</u>