STEREOISOMERISM

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Syllabus —

Geometrical isomerism; Optical isomerism of compounds containing up to two asymmetric centres, (R, S and E, Z nomenclature excluded). Conformations of ethane and butane (Newman projections)

Name :

_____Contact No. _____

STEREOISOMERISM

KEY CONCEPTS

STEREOISOMERISM

Stereoisomers have the same molecular formula and the same structure but they differ in configuration, i.e. in the arrangement of their atoms in space.

GEOMETRICAL ISOMERISM :

In this type of isomerism the compounds possessing same molecular formula differ in their properties due to the difference in their geometry.

H-C-COOH	Н–С–СООН
II	
H–C–COOH	HOOC-C-H
Maleic acid	Fumaric acid

CONDITIONS FOR GEOMETRICAL ISOMERISM

- **1.** There should be a double bond ring in the molecule.
- 2. The two atoms or groups attached to each doubly bonds carbon atom should be different. If one of the two doubly bonded carbon atoms carries two identical groups then the molecule does not exhabit geometrical isomerism.

Examples :

Alkenes

 $C_6H_5 - CH = CH - COOH$

In these cases both substitx Vuents on carbon-1 and carbon-2 are different hence they will show geometrical isomerism.

Cycloalkanes

Geometrical isomerism is possible in cyclic compounds also. There can be no rotation possible above C - C single bonds. In such compounds thus for rotation breakage in the bonds is required resulting to breakage in the ring, **e.g.**

1, 2-dimethyl cyclopropane exists in two isomeric forms written below :

 $CH_3 - CH = CH - CH_3$





A requirement for geometrical isomerism in cyclic compounds : There must be at least 2 other groups besides hydorgen on the ring and these must be on different ring C-atom. for example no geometrical isomers are possible for 1, 1-dimethyl cyclopropane.



1, 1-dimethyl cyclopropane (No isomers possible)



Oximes and Azo compounds

The oximes are formed by the reaction of carbonyl compounds (>C=O compounds i.e., aldehydes and ketones) with NH₂OH (hydroxyl amine) as :

>C = O + H₂ N-OH
$$\rightarrow$$
 >C=N-OH + H₂O
oxime
If -C- = aldehyde then oxime = aldoxime = $\stackrel{R}{\underset{H}{\longrightarrow}}C = N$ -OH or $\stackrel{H}{\underset{H}{\longrightarrow}}C = N$ -OH
If -C- = ketone then oxime = ketoxime = $\stackrel{R}{\underset{R}{\longrightarrow}}C = N$ -OH

(a) IN ALDOXIMES :



The first member of aldoximes does not show any geometrical isomer.

(b) IN KETOXIMES :

This compound is syn for ethyl group and anti for methyl group or this can be called anti compound. Similarly,

This compound is anti for ethyl group and syn for methyl group or this can be called syn compound.

(c) IN AZO COMPOUNDS i.e.,

$$\begin{array}{c} C_{\scriptscriptstyle 6}H_{\scriptscriptstyle 5} \\ \overbrace{} N = \ddot{N}_{\scriptscriptstyle C_{\scriptscriptstyle 6}}H_{\scriptscriptstyle 5} \\ \text{anti form} \end{array} \text{ and } \begin{array}{c} \ddot{N} = \ddot{N} \\ I = I \\ C_{\scriptscriptstyle 6}H_{\scriptscriptstyle 5} \\ C_{\scriptscriptstyle 6}H_{\scriptscriptstyle 5} \\ \text{syn form} \end{array}$$

E, Z SYSTEM FOR GEOMETRICAL ISOMERS :

The stereochemistry of highly substituted alkenes cannot be defined as cis or trans. For this purpose a new notation known as **E-Z notation** is used. Following a set of rules (Cahn-Ingold-Prelog rules) the substituents on a double bond are assigned priorities. The double bond is assigned the configuration **E (From entgegen, the German word for opposite)** if the two groups of higher priority are on the opposite sides of the double bond.

On the other hand the double bond is assigned the configuration **Z** (from zusammen, the German word for **together**) If the two groups of higher priority are on the same side of the double bond.



Cahn-Ingold-Prelog Rules

- 1. The higher the atomic number of the atom bonded directly to the stereocentre, the higher is the priority of the substituent. Among isotopes, the one with higher mass number gets the higher priority.
- 2. If two identical atoms are attached to the stereocentre, the relative priority of the two groups is decided by a similar comparison of the next atoms in the group moving away from the stereocentre.
- 3. A double is counted as two single bonds for both the atoms involved. Thus

$$c = 0 =$$

 $\begin{array}{l} \textbf{Priority Order:--I, -Br, -CI, -SO_{3}H, -SH, -F, -OCOR, -OR, -OH, -NO_{2}, -NR_{2}, -NHCOR, NHR, -CO_{2}R, -CO_{2}H, -CONH_{2}, COR, -CHO, -CH_{2}OH, -CN, -CR_{3}, -C_{6}H_{5}, -CHR_{2}, CH_{3}, D, H \end{array}$

Some examples are being given below :



The groups of higher priorities are on opposite sides. Hence it is (E) - 3-Bromopent-2-ene



The groups of higher priorities are on same side. Hence it is (Z) - 2-Methoxypent-2-ene



Groups of higher priority are on same sides (Z) -1-bromo-1-chloro-2-lodo propene



(Z)-But-2-ene-1, 4-dioic acid (Maleic acid)



OPTICAL ISOMERISM

The stereoisomerism which arises due to non-susperimposability of mirror image structure is called enantiomerism or optical isomerism. The mirror image isomers are called enantiomers.

Dissymmetry or chirality is the necessary and sufficient conditions for the enantiomerism. A carbon atom bonded to four different atom/groups in a molecule is called **chirality**. **A molecule is said to be dissymmetric or chiral if it is not superimposable on its mirror image**. On the other hand, a molecule which is superimopsable on its mirror image is called **non-dissymmetric or a chiral**. Non dissymmetric molecules do not show enantiomerism.



• Generally, the compounds containing an asymmetric carbon in their molecules are dissymmetric and hence show enantiomerism. But there are example where in spite of the presence of asymmetric carbons the compound does not show enantiomerism because its molecules are non-dissymmetric. For example, meso-tartaric acid.



meso-Tartaric acid

Superimposable : does not show enantiomerism

 There are compounds which do not contain any asymmetric carbon atom but still show enantiomerism and optical activity because their molecules are dissymmetric. For example, substituted allenes and substituted biphenyls.



Non-superimposable : shows enantiomerism

COOH NO₂ DISSYMMETRIC MOLECULE (Shows enantiomerism)

 NO_2

COOH

Representation of Enantiomers

1. **Perspective Formula :** In this method a normal line means bonds lying in the plane of paper and broken line means bonds going behind the plane of paper. A solid wedge represents bond projected out towards viewers.





2. **Projection Formula :** Here the molecule is imagined to be held in such a way that two of the bonds coming towards the viewer are in the horizontal plane and are represented by solid wedges. The other two bonds going behind the plane of paper are in vertical plane which are represented by broken lines. The formula of enantiomers of 2-butanol are



3. Fischer Projection Formulae : Envil Fischer devised a most simple and convenient method to represent the three dimensional arrangement of groups bonded to chirality centre. He used the point of intersection of two perpendicular lines to represent the chirality centre. Horizontal lines represent the bonds projected out of the plane of the paper towards viewer. Vertical lines on the other hand, represent the bonds projected back from the plane of the paper away from the viewer.



Characteristics of Enantiomers

Some of the important characteristics of enantiomers are as given below :

- 1. Enantiomers have chiral structures.
- 2. Enantiomers have identical physical properties such as melting point, boiling point, density, refractive index etc.
- **3.** Enantiomers are optically active substances. They rotate the plane of polarized light in opposite directions but to the equal extent.

	(+)-2-Methyl-1-butanol	(–)-2-Methyl-1-butanol
Specific rotation :	+ 5.90°	– 5.90°
Relative density :	0.8193	0.8193
Boiling point :	128.9°C	128.9°C
Refractive index :	1.4107	1.4107

4. Enantiomers have **identical chemical properties**. This means that they form same products as a result of chemical combination. However, their reactivity, i.e. rates of reaction with other optically active substances are different.

Stereoisomers with more than one chirality centres

We have already studied that organic compounds having one chirality centre always possess chiral structures and they exhibit enantiomerism. However, organic molecules having more than one chirality centres may have chiral as well as a chiral structures. The number of possible stereoisomers also increases with the increase in the number of chirality centres, in the molecule. In general, a compound having **n** chiral carbon atoms can have **2**ⁿ stereoisomers. In this section we shall study some aspects of organic compounds having two chirality centre.



Diastereomers

The stereoisomers which are non superimposable and do not bear mirror-image relationship are called **diastereomers**. Let us understand it by taking the example of 3-chloro-2-butanol. The molecule has two chirality centre. Thus, the number of possible stereoisomers are 2², i.e. 4. The four possible stereoisomers are shownbelow by Fischer projection formulae.



- Stereoisomers I and II are non-superimposable mirror images. Hence, they are called **enantiomers**.
- Stereoisomers III and IV are also non-susperimposable mirror images. They are also enantiomers.
- I and II also represent enantiomers in which similar groups (H atoms) are present on same side of carbon chain such enantiomers are called **erythro enantiomers**.
- In III and IV similar groups (H atoms) are present on opposite side of carbon chain. Such enantiomers are called **threo enantiomers**.
- Stereoisomers I and III are neither identical nor mirror images. Such stereoisomers are called **diastereomers**.
- In the similar way I and IV; II and III; II and IV also represent diastereoisomeric pairs. Thus, diastereomers are configurational isomers which are not enantiomers (It may be noted that cis-trans geometrical isomers which are configurational isomers but not enantiomers can also be called diastereomers).

Characteristics of Diastereomers

- (i) The diastereomers have different physical properties such as melting points, boiling points, densities, solubilities and values of specific rotation.
- (ii) They can be separated from one another by physical means like fractional distillation, fractional crystallization, chromatography, etc.
- (iii) They are generaly optically active. However, geometrical isomers are exceptions.
- (iv) They exhibit similar but not identical chemical behavior.

Meso compounds

According to 2^n rule each compound having two chirality centres should have ($2^2 = 4$) four stereoisomers. However, there are some compounds with two chiral carbons which have only three stereoisomers. For example, tartaric acid molecule has two chirality centres but it has only three stereoisomers. For example, tartaric acid molecule has two chirality centres but it has only three stereoisomers as shown below :





- Structure I and II are nonidentical mirror images and thus represent pair of enantiomers.
- Structure III is achiral inspite of the presence of two chirality centres. This is because of the presence of
 plane of symmetry in the molecule. If we draw the mirror image of structure III we shall find that it is
 superimposable on its mirror image (IV).



 Structure III or IV which are identical are called meso compounds (From Greek : meso means middle). Thus, the compounds containing two or more chirality centres but possessing a chiral molecular structure because of having plane of symmetry, are called meso compound.



MESO compound



• Meso compounds are optically inactive

Meso compounds do not rotate the plane of polarized light in any direction i.e. they are **optically inactive**. This is because of achiral nature of their molecules. Because of the present of plane of symmetry the optical rotation caused by half of the molecule is compensated by the rotation caused by the other half. T h i s cancellation of rotation within the molecule is referred to as internal compensation. In short, the **meso compounds are optically inactive due to internal compensation**.

It may be noted that if a compound with two chirality centres has the same four groups bonded to each of the chiral carbon, than one of its stereoisomer will be a meso compound.



RACEMIC MIXTURE

An equimolecular mixture of a pair of enantiomers is **called racemic mixture or racemic modification.** A racemic mixture is optically inactive. This is because of the fact that in equimolecular mixture of enantiomeric pair, that rotation caused by the molecules of one enantiomer is cancelled by the rotation caused the molecule of other enantiomer. This type of compensation of optical rotation in a racemic mixture is referred to as **external compensation**. Thus, **racemic mixture becomes optically inactive because of external compensation**.

Representation of a racemic mixture. The racemic mixture of a particular sample is indicated by using the prefix (dl) or (\pm) . For example, racemic mixture of lactic acid is represented as (\pm) **lactic acid**.

> Calculation of d-, ℓ -forms and meso forms

	For molecules having no plane of symmetry	For molecules having plane of symmetry		
No. of a symmetric carbon atoms = n No. of d- and ℓ -forms No. of meso forms Total no. of stereoisomers	n (even or odd) 2 ⁿ 0 2 ⁿ	when n is odd 2^{n-1} $2^{(n/2)-1}$ $2^{n-1} + 2^{(n/2)-1}$	When is even $2^{n-1} - 2^{(n-1)/2}$ $2^{(n-1)/2}$ 2^{n-1}	

Absolute Configuration (R, S configuration)

The actual three dimensional arrangement of groups in a molecule containing asymmetric carbon is termed **absolute configuration**.

System which indicates the absolute configurastion was given by three chemists R.S. Cahn, C.K. Ingold and V. Prelog. This system is known as (R) and (S) system or the Cahn–Ingold system. The letter (R) comes from the latin rectus (means right) while (S) comes from the latin sinister (means left).

It is batter system because in manycases configuration to a compound cannot be assigned by D, L method.

(R) (S) nomenclature is assigned as follows :

- 1. Each group attached to stereocentre is assigned a priority on the basis of atomic number. The group with the directly attached atom with highest atomic number out of the four groups gets top priority while the group with the atom of least atomic number gets the least priority.
- 2. If out of the four attached atoms in consideration, two are isotopic (like H and D), then priority goes to higher atomic mass i.e. D.
- **3.** If out of the four attached atoms in consideration, two or more are same, then priority is decided on the basis of the atom attached next to it in its group.
- **4.** While deciding the priority, if the atom in consideration is attached is further to an atom through a double bond then it is treated as if it is attached to two such atoms.

Thus, out of $-CH_2CH_3$ and $-CH = CH_2$, the $-CH = CH_2$ gets priority.

5. After assigning priorties, the lest priority group is written at remotest valency (going away), while the top priority group is written at the top directed valency (towards viewer). Remaining two groups now have two possibilities, giving two configuration. Thus, in the above compound (i.e. Bromochlorofluoriodo methane) we have





Now the order from top priority to the one of second priority and then to the one of third priority is determined.
 If this gives a clockwise direction then it is termed R configuration and if the anticlockwise direction is obtained then it is assigned S configuration. Eg.:



6. If we have to assign the configuration to a given structure and in that the lowest priority group is not on the remotest valency, then we have to first bring this lowest priority group at the valency by exchange rule. One mutual interchanging of the groups lead to reverse configuration and therefore to retain the given configuration the double exchange is to be performed.



Thus, the give structure hs R configuration. Note that the top priority group is not to be necessarily on top valency. We have to simply start the direction form top priority group.

Important : Note that the designation of a compound as R or S has nothing to do with the sign of rotation. the Cahn-Ingold rule can be applied to any three dimensional representation of a chiral compound to determine whether it is R or S only. For example in above case (i.e. lactic acid), R configuration is laevo rotatory is designated as R-(-)-lactic acid. Now the other configuration of it will have opposite sign of rotation i.e. S-(+)-lactic acid.

7. For the compounds containing more than one asymmetric carbon, again the same rules apply. Configuration to each asymmetric carbon is assigned separately. Thus, to assign configuration to first asymmetric carbon in (+)-tartaric acid, we have



CONFORMATIONS

• The different spatial arrangements of atoms which arise due to rotation around carbon-carbon single bond are called **conformations**.

Conformation of Ethane

• Out of infinite number of possible conformations of ethane, the two extreme conformations are **staggered** conformation and **eclipsed** conformation. The infinite intermediate conformations are known as **skew** conformations.



• The Sawhorse projection formula of the two extreme conformations of ethane are shown in figure.



The Newman's projection formula for staggered and eclipsed conformations of ethane are shown in figure.



Relative Stabilities of the Conformations of Ethane

The conformations of ethane do not have same stability. The **staggered conformations** is relatively more stable than the other conformations. It is because the repulsive interactions between the H-atom attached to the two carbon atoms are minimum due to the maximum distance between them. On the other hand, the **eclipsed conformation** is associated with maximum energy because the repulsive interactions between H-atoms adjacent carbon atoms are maximum due to minimum distance between them. The difference in the energy content of staggered and eclipsed conformations is 12.5 KJ mol⁻¹.

The variation of energy with rotation about the C–C bond in ethane has been shown in figure below :



Changes in energy during rotation about C-C bond in ethane

The difference in the energy of various conformers constitutes an energy barrier to rotation. The energy required to rotate the ethane molecule about carbon-carbon single bond is called **torsional energy**. But this energy barrier is not large enough to prevent the rotation. Even at ordinary temperature the molecules possess sufficient thermal and kinetic energy to overcome the energy barrier through molecular collisions. Thus, conformations keep on changing form one form to another very rapidly and cannot be isolated as separate conformers.



• Torsional energy :-

The energy required to rotate the ethane molecule about 'C–C' bond is called torsional energy **Conformations of Butane**

Butane molecule can be represented as derivative of ethane as given below :



Staggered conformations (I), in which methyl groups are as far apart as possible, is most stable due to minimum repulsion between methyl groups. This conformations is also called **anti** conformations. This on rotation through 60° gives eclipsed conformations (II), in which methyl group on one carbon is overlapped by the hydrogen atom on the other carbon.

Further rotation through 60° gives another staggered conformation (III). The conformation is also called **gauche** conformation. Gauche conformation on further rotation through 60° gives **fully elipsed conformation (IV)**. (IV) in which methyl groups on two carbons are just opposite each other. In this conformations steric strain is maximum hence this conformations is most unstable. Further rotation through 60° gives again gauche conformations (V) which is mirror image of gauche conformation (III). Conformation (V), on rotation through 60° gives conformation (VI) which is again eclipsed conformation.

The energy profile diagram for the conformation of butane is given below along with the difference of energy between various conformation of butane.





Energy changes that arise from rotation about the C2-C3 bond of butane.

Difference between conformation and configuration

	Conformation	Configuration
1.	It refers to different arrangement of atoms or groups relative to each other and raised due to	It refers to different arrangement of atoms or groups in space about a central atom.
	free rotation round a sigma bond.	
2.	The energy difference between two conformers is	The energy difference between two configuration forms
	lower.	is large.
3.	Conformers are not isomers and they can not be	These are optical isomers and can be separated form
	separated from each other.	each other.
4.	These are easily inter converted to one another.	These are not easily converted to one another.





PART - I : OBJECTIVE QUESTIONS



A-11. Geometrical isomerism will be exhibited by -(A) 1-Pentene (B) 3-Methyl-1-butene (C) 2-Pentene

(D) All of these compounds

- A-12. Which of the following compounds can show geometric isomerism (A) Vinyl chloride
 (B) 1, 1-Dichloroethene
 (C) 1, 2-Dichloroethene
 (D) Trichloroethene.
- A-13. The 'Z'-isomer is :
 - (A) $\underset{F}{Cl} = c < \underset{Br}{H}$ (B) $\underset{F}{Cl} = c < \underset{C_2H_5}{C_2H_5}$ (C) $\underset{C_2H_5}{C_2H_5} = c < \underset{COOH}{COOH}$ (D) $\underset{H}{HOOC} = c < \underset{H}{COOH}$
- A-14. The compounds X and Y in below reaction can be

$$Ph - NH \cdot NH_{2} + (X) + (Y) \xrightarrow{-H_{2}O} \xrightarrow{P+Q}_{organic}$$

$$(A) CH_{3} - CH_{2} - C - CH_{3} + CH_{3} - C - Ph \qquad (B) Ph - C - CH_{3} + CH_{3}CHO$$

$$(C) CH_{2} = O + CH_{3}CHO$$

$$(D) CH_{2} = O + CH_{3} - C - CH_{3}$$

A-15. Which of the following compound can not show geometrical isomerism ?



A-16. The correct stereochemical name of

(A) 2



- (A) Methyl 2-methylhepta (2E, 5E) dienoate (C) Methyl 2-methylhepta (2E, 5Z) dienoate
- (B) Methyl 2-methylhepta (2Z, 5Z) dienoate

2

(D) Methyl 2-methylhepta (2Z, 5E) dienoate

A-17. The total number of geometrical isomers possible in following compound is :

$$Ph - HC = HC - CH = CH - CH_{3}$$
(B) 1 (C) 6 (D) 8

- A-18. The number of geometrical isomers in the following compound is : $CH_3-CH = CH - CH = CH - C_2H_5$ (A) 4 (B) 3 (C) 2 (D) 5
- A-19. The total number of geometrical isomers possible in following compound is :

A-20. What characteristic is the best common to both cis-2-butene and trans-2-butene? (A) B.P. (B) Dipole moment (C) heat of hydrogenation (D) Product of hydrogenation

Section : (B) Optical Isomerism

 B-1.
 Optically active isomers but not mirror images are called -(A) Enantiomers
 (B) Meso
 (C) Tautomers
 (D) Diastereomers

B-2. Which of the following have asymmetric carbon atom?

$$\begin{array}{cccccc} \mathsf{Cl} \ \mathsf{Br} & \mathsf{H} \ \mathsf{Cl} & \mathsf{H} \ \mathsf{Cl} & \mathsf{H} \ \mathsf{H} \\ | & | & | & | & | \\ \mathsf{(A)} \ \mathsf{H} - \mathsf{C} - \mathsf{C} - \mathsf{H} & \mathsf{(B)} \ \mathsf{H} - \mathsf{C} - \mathsf{C} - \mathsf{Cl} & \mathsf{(C)} \ \mathsf{H} - \mathsf{C} - \mathsf{C} - \mathsf{H} & \mathsf{(D)} \ \mathsf{H} - \mathsf{C} - \mathsf{C} - \mathsf{CH}_{3} \\ | & | & | & | & | \\ \mathsf{H} \ \mathsf{H} & \mathsf{H} & \mathsf{H} & \mathsf{H} & \mathsf{H} & \mathsf{Br} \ \mathsf{OH} \end{array}$$

B-3. Two isomer are :



B-4. Number of chiral carbon atoms in the compound x, y and z respectively would be :



B-5. The number of optically active isomers possible for

B-6. Which of the following compounds can not exist as enantiomers -(A) CH_3 —CH(OH)COOH (B) CH_3 —CH₂—CH₂—CH₂OH

(C)
$$C_6H_5CH_2$$
—CH₃ (D) $C_6H_5CHCICH_3$

B-7. Which of the following compounds exhibit optical isomerism ?

(A)
$$(A)$$
 (B) $CH_2 = C = CH_2$ (C) $\begin{array}{c} CH_2 \\ I \\ CH_2 \end{array}$ (D) None of these

B-8. Which of the following will not show optical activity?







B.9.	Which of the following (A) CH_3COOH (B) CH	can exist as enantiomer I ₃ .CH(OH). COOH	s - (C) CH ₃ . CH ₂ . COOH	(D) HOOC. CH ₂ . COOH			
B.10.	A compound whose mo called :	lecules are optically inact	active even though they contain asymmetric carbon atoms is				
	(A) A threo compound (C) A dissymmetric cor	npound	(B) A erythro compoun (D) A meso compound	ld I			
B-11.	Number of chiral carbo CH ₃ – CH – CH ₂ I OH	on persent in the following $_2 - CH - CH - CH_3$ Br C_2H_5	compound :				
	(A) 2	(B) 3	(C) 4	(D) 5			
B-12.	The total number of op (A) 2	tically active isomer for C (B) 4	CH ₂ OH(CHOH) ₃ CHO is - (C) 8	(D) 12			
B-13.	Observe the following	structures I to III					
	C ₂ H ₅ – CH – C ₂ CH ₃ (I)	H ₅ (CH ₃) ₂ CH – CH OH (II)	– CH – CH ₃ CH ₃ – CH ₃	СН–СН–СН ₃ 			
	Correct statement is : (A) All three are chiral of (C) Only II is chiral	compounds	(B) I & II are chiral (D) Only III is chiral				
B-14.	Meso-tartaric acid and (A) positional isomers	d-tartaric acid are- (B) enantiomers	(C) diastereomers	(D) racemic mixture			
B-15.	Which of the following (A) Lactic acid	does not contain any as (B) 1, 3-Pentadiene	ymmetric carbon but car (C) Tartaric acid	n show enantiomers - (D) 2, 3-Pantadiene			
B-16.	The number of optically (A) 1	y active compounds in th (B) 2	e isomers of C ₄ H ₉ Br is (C) 3	(D) 4			
B-17.	Which of the following	compound has 'S' config	uration ?				
	(A) H Br	(B) Br - H CH ₃	(C) Br H OH	(D) HO HO H			
B-18.	Which of the following (A) 1, 2-Dichlorobutane (C) 2, 3-Dichlorobutane	compounds can exist in e e	meso-form- (B) 2, 3-DichloroPenta (D) 1, 2-DichloroPenta	ne			
B-19.	Which of the following	is responsible for the ina	ability of meso compound	d to show optical activity -			

- (A) Absence of chirality centre
- (B) Presence of more than one chirality centres
- (C) Dissymmetric nature of its structure
- (D) Internal compensation.



B-20. The correct configuration assigned for compound (I) & (II) respectively are :



B-27. The two compounds given below are :

(C) Meso compound

B-28. How many stereoisomers can exist for the following acid

$$H - C(OH).CO_{2}H$$

$$H - C.CO_{2}H$$

$$H - C(OH).CO_{2}H$$
(B) Four
(C) Eight

(D) Sixteen

8

B-29. Total number of stereoisomers of compound is :

 $\begin{array}{c} CH_3-CH-CH-CH-CH_3\\ | & | & |\\ Br & Br & Br \end{array}$ B-30.

(A) Two

Total number of stereoisomers in above compound : (D) 16 (A) 6 (C) 8 (B) 4

Section (C) Conformational Isomerism

C-1. Which of the following pairs of compound is/are identical ?

C-2. The eclipsed and staggered conformation of ethane is due to -(A) Free rotation about C-C single bond (B) Restricted rotation about C-C single bond (C) Absence of rotation about C-C bond (D) None of the above

- C-3. Increasing order of stability among the three main conformation (i.e. eclipse, anti, gauche) of ethylene glycol is: (A) Eclipse, gauche, anti (B) Gauche, eclipse, anti
 - (C) Eclipse, anti, gauche

- (D) Anti, gauche, eclipse
- C-4. Which of the following conformations of n-butane is the least stable -(A) Gauche (B) Anti (C) Eclipsed (D) Fully eclipsed
- C-5. In which of the following has minimum torsional strain and minimum Vander waal strain.

- C-6. The energy difference between staggered and eclipsed conformations of ethane is about -(A) 25 kJ/mole (B) 30 kJ/mole (C) 100 kJ/mole (D) 12.5 kJ/mole
- C-7. The two structures I & II represents :

C-8. Which of the following is represent the staggered conformation with dihedral angle $\phi = 60$?

- C-9. In the Newman projection formula of the least stable staggered form of n-butane, Which of the following reasons is the causes of its unstability ?

 (A) Vander-Waal's strain
 (B) Torsional strain
 (C) Combination of both.
 (D) None of these
- C-10. The dihedral angle between two methyl groups in partially eclipsed conformation of n-butane is (A) 180° (B) 120° (C) 90° (D) 109° 28'
- C-11. Which of the following is most stable ?

C-12. Which of the following is an achiral molecule ?

C-13*. Which of the following molecules is/are identical with that represented by

PART - II : MISCELLANEOUS QUESTIONS

Comprehensions Type :

Comprehension #1

Observe the following compound and answer the question 1 to 3

1. Which of the following cannot be its functional isomer,

Comprehension # 2

2.

3.

5.

6.

The simple axis of symmetry is defined as n fold axis of symmetry denoted as C_n . It is an axis such that if one rotates the molecule about the axis by 360/n , the new position of model is superimposable with original one.

It is clear that if molecule is turned by 360° (n = 1) along any axis new position is superimposable. Thus C₁ symmetry is universally present in all compounds.

4 Which of them contains C₁ axis of symmetry

(A) H_{axis} (B) H_{axis} (B) H_{axis} (C) H_{H} (C) H_{H} (D) None of these

STEREOISOMERISM # 20

Match the column Type

Assertion / Reasoning Type

DIRECTIONS:

Each question has 5 choices (A), (B), (C), (D) and (E) out of which ONLY ONE is correct.

- (A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
- (B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
- (C) Statement-1 is True, Statement-2 is False.
- (D) Statement-1 is False, Statement-2 is True.
- (E) Statement-1 and Statement-2 both are False.
- **10. Statement-1** : For the given compound the two isomers of configurations trans (R) and trans (S) are enantiomers.

Statement-2 : The two isomers in statement-1 are mirror image stereoisomers.

11. Statement-1: $\ln CH_3 - CH_3$ the conformations at all energy minima are degenerate. (degenerate = of same energy)

Statement-2 : At energy minima the torsional strain is minimum.

- Statement-1: An achiral molecule always has plane of symmetry as well as centre of symmetry.
 Statement-2: Molecular symmetry arises only when plane of symmetry & centre of symmetry both are present.
- **13.** Statement-1 : All the hydrogen atoms in $CH_2=C=CH_2$ lie in one plane. Statement-2 : All the carbon atoms in it are sp²-hybridised
- **14. Statement-1**: Benzaldehyde forms two oximes on reacting with NH₂OH. **Statement-2**: The two oximes arise due to geometrical isomerism.

PART - I : MIXED OBJECTIVE

16. Which will form geometrical isomers?

17.

18. Which of the following is most likely to show optical isomerism?

20. Fischer projection formula of compound $C_2H_5 - C_1$ can be represented as : $H_{W} - C_1 - C_1$ of $C_1H_2 - C_2$

21. Select 'cis' isomer among the following :

(B)

(D) None of these

24.

25.

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26. The IUPAC name of the compound CH_{e}

(A) (2E, 4E, 6Z)-octa-2,4,6-triene (C) (2Z, 4E, 6Z)-octa-2,4,6-triene (B) (2E, 4E, 6E)-octa-2,4,6-triene (D) (2Z, 4Z, 6Z)-octa-2,4,6-triene

(i) 2ⁿ⁻¹

(iii) 2ⁿ

(ii) $2^{n-1} + 2^{\frac{n-1}{2}}$

27. Match List I with List II and select the correct answer from the given codes : List I List II

(Compound)

(Number of optical isomers)

(A) A symmetrical compound with 'n' chiral carbon

(B) Symmetrical molecule with 'n' chiral carbon when n is even(C) Symmetrical molecule with 'n' chiral carbon when n is odd

•			-		
С	ο	de	es	1	

	Α	В	С
(A)	1	2	3
(B)	3	2	1
(C)	3	1	2
(D)	2	3	1

28. Select the optically inactive compound among the following :

29. Identify, which of the following molecule does not have 'R' configuration ?

(A) $CI \xrightarrow{F} D$ H
(B) $H_3C \xrightarrow{CH_2CI} CH_2OH$ H
(B) $H_3C \xrightarrow{H} CH_2OH$

30. Which of the following is the enantiomer of the structure C

(D) It does not have an enantiomer

(C) H ~ H

PART - II : SUBJECTIVE QUESTIONS

- 4. Mention the specific type of isomerism exhibited by each of the following pairs:
 - (a) 1,2-dichloro ethane and 1,1-dichloro ethane
 - (b) Propanoic acid and methyl acetate
 - (c) Methyl acetate and ethyl formate
 - (d) o-Nitrophenol and P-nitrophenol
 - (e) Anisole and o-cresol
 - (f) Phenol and Cyclohexa-2,4-dien-1-one
- 5. Find out the total number of cyclic isomers of C_6H_{12} which are optically active?
- **6.** How many cyclopentane structures (including stereo) are possible for C_7H_{14} .
- 7. With reasons, state whether each of the following compounds I to IX is chiral.

8. Find D/L configuration in the following molecules.

9. Find relationship between the given pairs.

- **10.** For the given compound $CH_3 CH CH = CH CH_3$.
 - (I) Find total number of stereoisomers.
 - (II) Number of optically active stereoisomers.
 - (III) Total number of fractions on fractional distillation of all stereoisomers.

Fischer projection formula of this compound can be represented as :

- **12.** What does D/L & d/ ℓ represent.
- 13. Optical purity or enantiomeric excess is given as

optical purity = $\frac{\text{excess of one enantiomer over other}}{\text{entire mixture}} \times 100$

If optical purity of a $d-\ell$ mixture is 72% and it is known that d isomer is in excess then what is the percentage of this excess isomer

14. (+)-Mandelic acid has a specific rotation of + 158 unit. What would be the observed specific rotation of each of the following mixture ?

(a) 25% (–)-mandelic acid and 75% (+)-mandelic acid

- (b) 50% (–)-mandelic acid and 50% (+)-mandelic acid
- (c) 75% (–)-mandelic acid and 25% (+)-mandelic acid.
- **15.** Write the newman projection formula along $C_1 C_2$ bonds in staggered form of following compounds.

(I)
$$\overset{1}{C}H_{3} - \overset{2}{C}H_{2} - CH_{3}$$
 (II) $\overset{1}{C}H_{3} - \overset{2}{C}H - CH_{3}$
 \downarrow
 CH_{3}

(III)
$$\begin{array}{c} CH_{3} & CH_{3} CH_{3} CH_{3} CH_{3} CH_{3} CH_{3} CH_{3} - CH_{2} CH_{3} CH_{3} - CH_{3} CH_{3} - CH_{3} CH$$

- **16.** Write the newman projection formula of the following compounds
 - (I) $CI-CH_2-CH_2-CH_3$ in its most polar form.
 - (II) $CI-CH_2-CH_2-CI$ in its most stable form.
 - (III) $HO-CH_2-CH_2-OH$ in its most stable form.
 - (IV) HOOC– CH_2 – CH_2 –COOH in its least stable staggered form.
- 17. Convert the following Fischer projection into Newmann & Sawhorse projection

PART - I : IIT-JEE PROBLEMS (PREVIOUS YEARS)

(A) M and N are non-mirror image stereoisomers (B) M and O are identical (C) M and P are enantiomers (D) M and Q are identical

10.	The alkene that exhibits (1) 2-methyl propene	geometrical isomerism i (2) 2-butene	is : (3) 2-methyl-2-butene	(4) prop	[AIEEE 2009, 4/144] Dene
11.	The number of stereoise CH ₃ -CH=CH-CH(OH)- (1) 2	omers possible for a com Me is: (2) 4	pound of the molecular f	ormula (4) 3	[AIEEE 2009, 4/144]
12.	Out of the following, the (1) 3-methyl-2pentene	(OH)–Me is: (2) 4 (3) 6 ng, the alkene that exhibits optical isomeris tene (2) 4-methyl-1-pentene (3) 3-meth bund that exhibits tautomerism. (2) Lactic acid (3) 2-Penta following statements is correct ? s except lysine are optically active s are optically active.		(4) 2-m	[AIEEE 2010, 4/144] ethyl-2-pentene
13.	Identify the compound to (1) 2-Butene	nat exhibits tautomerism. (2) Lactic acid	(3) 2-Pentanone	(4) Phe	[AIEEE 2011, 4/120] nol
14.	Which one of the follow (1) All amino acids exce (2) All amino acids are o (3) All amino acids exce (4) All amino acids exce		[AIEEE 2012, 4/120]		
15.	How many chiral compo	ounds are possible on mo	pnochlorination of 2 - met	hyl buta	ne?
	(1) 8	(2) 2	(3) 4	(4) 6	
16*.	Which branched chain is substituted alkyl halide ' (1) Tertiary butyl chloride	somer of the hydrocarbor ? e	with molecular mass 72 (2) Neopentate	u gives o	nly one isomer of mono [AIEEE 2012, 4/120]

(3) Isohexane

(4) Neohexane

EXERCISE #4

NCERT QUESTIONS

- **1.** How many acyclic structural isomers of C_5H_{10} can show geometrical isomerism ?
- **2.** How many cyclic structural isomers of C_5H_{10} can show geometrical isomerism.
- **3.** Find the total number of geometrical isomers of following compounds.
 - (I)
- 4. Write all carbonyl compounds with molecular formula C_3H_6O and then react with excess of NH_2OH and find out how many total isomeric oximes are formed.

(II)

5. Indicate whether each of the following compound is 'E' or 'Z'.

(i)
$$\underset{H}{C_{H_{3}}}C = C < \underset{Br}{C_{I}}$$

(ii) $\underset{H}{I_{2}}C = C < \underset{C_{3}H_{7}}{C_{3}H_{7}}$
(iii) $\underset{H}{D_{2}}C = C < \underset{D}{C_{H_{2}}}C$

- **6.** Carbonyl compounds react with NH₂OH forming oximes which represents geometrical isomersm. Which smallest carbonyl compounds forms oxime but does not show geometrical isomerism ?
- 7. Calculate total number of possible geometrical isomers of Ph CH = CH CH = CH COOH.

8. Find plane of symmetry and centre of symmetry (if possible) in the following compounds.

9. Find total number of chiral carbon atoms in the following compounds :

10. Find R/S configuration of following compounds.

11. Identify chiral and achiral molecules in each of the following pairs of compounds :

						ANS	WER	s 🧲					
						Exerc	ise #	‡ 1					
						PAF	<i -="" b="" i<=""></i>			• •			
A-1.	(B)	A-2.	(C)	A-3.	(B)	A-4.	(D)	A-5.	(C)	A-6.	(D)	A -7.	(C)
A-8.	(B)	A-9.	(A)	A-10.	(C)	A-11.	(C)	A-12.	(C)	A-13.	(D)	A-14.	(D)
A-15.	(A)	A-16.	(D)	A-17.	(D)	A-18.	(A)	A-19.	(C)	A-20.	(D)	B-1.	(D)
B-2.	(D)	B-3.	(C)	B-4.	(A)	B-5.	(D)	B-6.	(C)	B-7.	(A)	B-8.	(C)
B.9.	(B)	B.10.	(D)	B-11.	(B)	B-12.	(C)	B-13.	(D)	B-14.	(C)	B-15.	(D)
B-16.	(B)												
B-17.	(C)	B-18.	(C)	B-19.	(D)	B-20.	(C)	B-21.	(B)	B-22.	(C)	B-23.	(A)
B-24.	(D)	B-25.	(C)	B-26.	(C)	B-27.	(A)	B-28.	(B)	B-29.	(B)	B-30.	(B)
C-1.	(A)	C-2.	(A)	C-3.	(C)	C-4.	(D)	C-5.	(D)	C-6.	(D)	C-7.	(C)
C-8.	(B)	C-9.	(A)	C-10.	(B)	C-11.	(A)	C-12.	(A)	C-13*.	(AD)		
						PAF	RT - II						
1.	(D)	2.	(B)	3.	(B)	4	(D)	5.	(B)	6.	(B)		
7.	(A) r,	(B) p, (C)) s, (D) p	C	8.	(A) s,	(B) r, (C	;) q, (D) p)	9.	(A) p,	(B) r, (C)) s, (D) c
10.	(A)	11.	(B)	12.	(E)	13.	(C)	14.	(A)				
						Exerc	ise ‡	‡ 2					
						PAF	RT - I						
1.	(B)	2.	(D)	3.	(A)	4.	(B)	5.	(B)	6.	(A)	7.	(A)
8.	(A)	9.	(B)	10.	(C)	11.	(D)	12.	(A)	13.	(B)	14.	(A)
15.	(A)	16.	(D)	17.	(C)	18.	(B)	19.	(A)	20.	(A)	21.	(A)
22.	(D)	23.	(A)	24.	(B)	25.	(D)	26.	(C)	27.	(C)	28.	(D)
29.	(D)	30.	(D)										
						PAF	RT - II						

1. Z - I, II, III, VI, VII ; E - IV, V, VIII, IX, X, XI, XII

(a) Enantiomers, (b) Enantiomers, (c) Geometrical isomers & Diastereomers, (d) Positional,
 (e) Optical (Diastereomers), (f) Diastereomers, (g) Enantiomers, (h) Identical, (i) Geometrical isomers (Diastereomers)

- 4. (a) Positional (b) Functional (c) Metamerism (d) Positional (e) Functional (f) Tautomerim
- **5.** 8
- 6. 8
- 7. achiral : I, III, IV ; chiral : II,V, VI, VII
- 8. (I) D (II) (2D, 3D)

(III) Equivalent fischer projection is NH_2 H and configuration L.

(IV) Equivalent fischer projection is $H \xrightarrow{COOH} OH$ $H \xrightarrow{H} OH$ and configuration (2D, 3L). $H \xrightarrow{H} OH$

COOH

ĊH₃

9. (I) Enantiomers (II) Positional isomers (III) Identical (IV) Diastereomers

10. (I)
$$CH_3 - CH - CH = CH - CH_3$$

 $H = CH - CH_3$

Number of stereocentres = 2 so total number of stereoisomers = $2^2 = 4$

- (II) All 4 isomers are optically active.
- (III) Total enantiomeric pairs are 2, hence number of fraction will be 2.

11.
$$H \xrightarrow{OH} C_2 H_5$$

 $H \xrightarrow{C_2 H_5} CH_3$

- D/L represent nomenclature (relative configuration) while d/ℓ represents direction of optical rotation.
 86%
- **14.** (a) 79 unit
 - (b) 0 (c) – 79 unit

16. 86%

4. Least stable staggered form of n–butane is

This is due to Vander Waal's strain developed between the methyl groups at $C_2 \& C_3$. There is no torsional strain in the staggered form at torsional angle 60°.

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(a) In structure (i), the central carbon is bonded to four different substituents (H, OH, Br and CH₃) and hence (i) is chiral.
 Structure (ii) has two identical Br atoms attached to central carbon atom and hence it is achiral molecule.
 (b) (i) is chiral and (ii) is achiral.
 (c) (i) is chiral and (ii) is achiral

