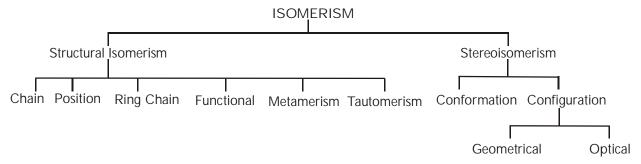


ISOMERISM

Isomerism name was given by Berzilius. Two or more than two organic compounds having the same molecular formula and molecular weight but different physical and chemical properties are called isomers and the phenomenon is called isomerism.



Structural Isomerism:

When two or more number of organic compounds have same molecular formula but different structural formula these are called structural isomers.

S.No.	Isomers	Characteristics	Conditions	
1	Chain Isomers	They have different size of main chain or side chain	They have same functional group	
2	Positional Isomers	They have different position of locant	They should have same carbon skeleton and same functional group	
3	Ring Chain Isomers	They have difference in open & close chain structure	Different mode of linkage (open chain or closed chain)	
4	Functional Isomers	Different functional group	Chain and positional isomerism is not considered	
5	Metamerism Different nature of alkyl group along a polyvalent functional group on either side		They should have same nature of functional group, chain & positional isomerism is ignored	
6	Tautomerism	Different position of an atom usually hydrogen atom	The two isomers remains in dynamics equilibrium with each other	

1. Chain Isomerism (CI):

The compounds which have same molecular formula, same functional group, same position of functional group or multiple bond or substituent but different arrangement of carbon chain (main chain or side chain) shows chain isomerism.

Example :

$$CH_3-CH_2-CH_3$$
 $CH_3-CH_2-CH_3$

 Butane(4C)
 CH_3

 2-Methyl propane (3C)

 Example :
 $CH_3-CH_2-CH_2-CH_2-OH$
 $CH_3-CH_2-CH_2-OH$

 1-Butanol (4C)
 CH_3

 2-Methyl-1-propanol (3C)

Pentanoic acid

3-Methyl butanoic acid

2.2-Dimethyl propanoic acid

2. **Position Isomerism (PI):**

The compounds which have same molecular formula, same functional group, same parent carbon chain but different position of functional group or multiple bond or substituents, are position isomers.

Example: CH₂=CH-CH₂-CH₃

But-1-ene

But-2-ene

Example : CH₃—CH₂—CH₂—CH₂—OH CH₃—CH₂—CH—CH₃ OH

1–Butanol

2–Butanol

Example:

$$CH_3-CH_2-CH_2-CI$$
 $CH_3-CH_2-CH-CH_3$ CI 1-Chlorobutane 2-Chlorobutane

2-Chlorobutane

Illustrations ———

Illustration 1. How many structural isomers are possible for molecular formula C_4H_{10}

Solution C_4H_{10} have two isomers: Both butane and isobutane are chain isomers.

$$CH_3 - CH_2 - CH_2 - CH_3$$

$$CH_3 - CH_2 - CH_2 - CH_3$$
 $CH_3 - CH_3 - CH_3$

Butane

Isobutane

Illustration 2. How many structural isomers are possible for molecular formula C_5H_{12}

 C_5H_{12} have three isomers : All of three structures are chain isomers because only carbon **Solution** chain (parent) is different.

$$\mathsf{CH_3} - \mathsf{CH_2} - \mathsf{CH_2} - \mathsf{CH_2} - \mathsf{CH_3} \ , \ \mathsf{CH_3} - \mathsf{CH_2} - \mathsf{CH} - \mathsf{CH_3} \ , \mathsf{CH_3} - \mathsf{C} - \mathsf{CH_3} \ \\ \mathsf{CH_4} \ \\ \mathsf{CH_5} \ \\ \mathsf$$

Pentane

2–Methyl butane 2,2–Dimethylpropane

Illustration 3. How many structural isomers are possible for molecular formula C_6H_{14}

C₆H₁₄ has 5 isomers: **Solution**

(a)
$$CH_3CH_2CH_2CH_2CH_3$$
 (b) $CH_3-CH_2-CH_2-CH_3-CH_3$

Hexane

(c)
$$CH_3 - CH_2 - CH_3 - CH_3$$

3-Methyl pentane

2,3-Dimethyl butane

(e)
$$H_3C - C - CH_2 - CH_3$$

 CH_3

2,2-Dimethyl butane

a & b, b & d, a & c, c & d \longrightarrow Chain Isomers

b & c, d & e

→ Position Isomers

Illustration 4. How many structural isomers are possible for molecular formula C₃H₆Cl₂

Solution C₃H₆Cl₂ has 4 isomers: Position of chlorine atom is different in all the structure, so these are position Isomers.

(i)
$$H_3C - CH_2 - CH - CI$$

1,1-Dichloropropane

1,3-Dichloropropane

1,2-Dichloropropane

Illustration 5. How many benzenoid isomers are possible for molecular formula C₈H₁₀

Solution C₈H₁₀ has 4 aromotic isomers

Illustration 6. How many structural isomers are possible for molecular formula C_7H_{16} **Solution** C_7H_{16} have nine isomers

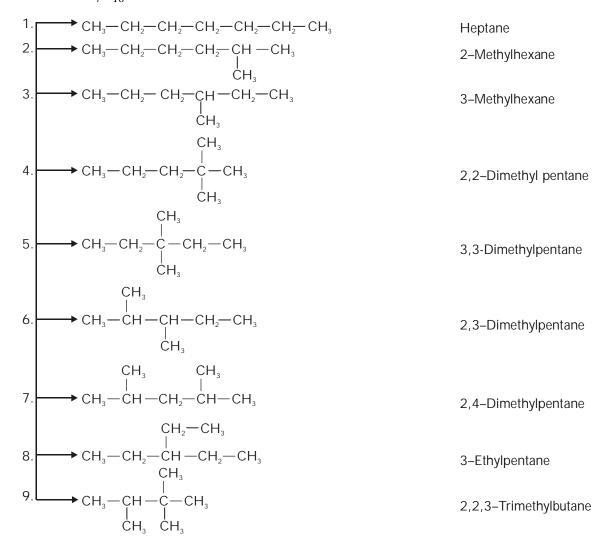


Illustration 7. Molecular formula No. of Structural Isomers

	-	
C_4H_{10}		2
C_5H_{12}		3
$C_{6}H_{14}$		5
$C_{7}H_{16}$		9
C_3H_6		2
C_4H_8		5
$C_{5}H_{10}$		10
2 10		

3. Ring chain isomerism (RCI):

Same molecular formula but different mode of linking (open chain or closed chain) of carbon atoms.

$$C_3H_6$$
 CH₃-CH=CH₂ [open chain]
$$C_3H_6$$
 [closed chain or ring]

They have same molecular formula so they are Ring chain isomers.

(a)
$$H_3C-C \equiv CH$$

(b) $CH_2=C=CH_2$
(c) $CH_2=CH_2$

Q.1
$$CH_3 - CH_2 - CH_2 - CH_2$$
 and $CH_3 - CH_2 - CH_3$ are ?

$$^{4}_{CH_{3}}$$
 $^{3}_{CH_{2}}$ $^{2}_{CH}$ $^{C}_{CH_{3}}$ are ?

Pentanenitrile

2-Methyl butanenitrile

- **Sol.** Molecular formula same, Functional group same, position of Functional group same but different parent carbon atom chain so both are Chain isomers
- Q.2How many minimum carbons required for Chain isomerism and Position isomerism in alkanes?
- **Sol.** 4, 6
- **Q.3** How many minimum carbons required for Chain isomerism and Position isomerism in alkenes?
- **Sol.** 4, 4
- **Q.4** How many minimum carbons required for Chain isomerism and Position isomerism in alkynes?
- **Sol.** 5, 4

4. **Functional Isomerism:**

Same molecular formula but different functional groups.

Following compounds show Functional isomerism, as they have same molecular formula and different functional group.

- (i) Alcohol and ether \longrightarrow CH₃—CH₂—OH and CH₃—O—CH₃
- Aldehydes and ketones \longrightarrow CH₃-CH₂-C-H and CH₃-C-CH₃ \parallel O (ii)
- Acids and ester \longrightarrow CH₃—C—OH and H—C—O—CH₃ (iii)
- Cyanide and isocyanide \longrightarrow CH₃—CH₂—CH₂—CN and CH₃—CH₂—CH₂—NC
- Nitro and Nitrite \longrightarrow $CH_3-CH_2-N_{QO}$ and $CH_3-CH_2-O-N=O$ (v)
- (vi) Amide and Oxime \longrightarrow CH₃—C-NH₂ and CH₃—CH=NOH and CH₃CH₂-N=O

(vii) 1°, 2°, 3° amines

(i)
$$CH_3$$
— CH_2 — CH_2 — NH_2 (ii) CH_3 — NH — CH_2 — CH_3 (iii) CH_3 — CH_3 CH_3 — CH_3

(ix) 1° , 2° , 3° amide

5. Metamerism:

Same molecular formula, same polyvalent Functional group but different alkyl groups attached to polyvalent Functional group on either side.

Polyvalent Functional group [More than one valency] are:

$$-O-\ , \ -S-\ , \ -C-\ , \ -C-O-\ , \ \ -C-O-\ , \ \ -C-O-\ , \ \ -C-O-\ , \ \ \ \ \ \$$

Example:
$$CH_3 - O - CH_2 - CH_3 - CH_3 - CH_3 - CH_3 - CH_2 - CH_3 + CH_3 - CH_3 -$$

Both are metamers.

N–Ethyl ethanamine N–Methyl propanamine

They are only metamers not CI

Example :
$$CH_3-C-CH_2-CH_2-CH_3-CH_3$$
 $CH_3-CH_2-C-CH_2-CH_3-CH_3$

2–Hexanone 3–Hexanone

Both are metamers and Position isomer

Propyl ethanoate Methyl–2–methyl propanoate

Both are Metamers

Sol. Both are metamers.

Q.2 3°Amines of M.F.C₅H₁₃N(All metamers)

Sol.

KEY POINTS

- Parent carbon chain and functional group must be same in chain isomers.
- Polyvalent functional group must be present for metamerism.
- 1°, 2° and 3° amines are considered as different type of functional group.
- 1° , 2° and 3° alcohols are considered as same functional group.
- 6. **Tautomerism or Desmotropism:**

Tautomerism was introduced by "Laar". It's also called desmotropism.

Defination of tautomerism → Arises due to rapid oscillation of an atom usually hydrogen between 2 polyvalent atoms in a molecule.

The tautomerism is also called kryptomerism or allotropism or desmotropism or dynamic isomerism.

Example:

Example:

 \rightarrow It involves σ -bond shifting

- → Tautomers remain in dynamic equilibrium with each other
- → More stable isomer is present in higher concentration.
- → Tautomerism Involve intramolecular acid-base reaction.
- → The process can be catalysed by acid as well as base

Ε

TYPE OF TAUTOMERISM

(1) Diad tautomerism:-

If the migration take place in between adjacent atoms then system is known as diad tautomerism.

$$H-C \equiv N \rightleftharpoons H-N \equiv C$$
 $WA SA$

(2) Triad tautomerism:-

If migration take place between first atom to third atom.

$$CH_2 - CH_2 \longrightarrow CH_2 = CH_1$$
Keto enol

(3) Space tautomerism:

If distance of migration is more than 3 atom then it is known as space tautomerism.

□ Condition for Tautomerism :

(a) For carbonyl compounds: Carbonyl compounds having at least one α -H show tautomerism

3 α H,

show tautomerism.

6 α H,

show tautomerism

(iii)
$$CH_3$$
— CH — C — H CH_3 O

1 α H,

show tautomerism

No α H,

No tautomerism

$$(v) \bigcirc \bigcirc \stackrel{\parallel}{\bigcirc} C-H$$

Νο α Η.

No Tautomerism

(vi)
$$\overset{O}{\underset{C-CH_3}{\parallel}}$$

3 α H,

shows tautomerism (Acetophenone)

No α H,

No tautomerism (Benzophenone)

- (viii) Ph—C—CH₂—C—Ph
- 2 α H,
- shows tautomerism

(ix) H

- 4 α H,
- shows tautomerism

(x)

- $\alpha ext{-H}$, attached sp 2 carbon does not take part in tautomerism
- Q.1 Which of the following show keto enol tautomerism.









- **Sol.** (A), (B) and (D)
 - (b) For nitro compounds: Nitro compounds having at least one α H show tautomerism

$$CH_2-N$$
 O
 $CH_2=N$
 O
 OH

Nitro form

Aci nitro form

MECHANISM

(I) Acid catalysed Mechanism:-

$$CH_3 \xrightarrow{C} CH_3 \xrightarrow{H^+} CH_3 \xrightarrow{C} CH_3 \xrightarrow{C} CH_3 \xrightarrow{C} CH_3 \xrightarrow{C} CH_3 \xrightarrow{C} CH_2 \xrightarrow{C} CH_3$$

→ More stable product is major product in case of more than one enol

$$CH_3-CH_2-C-CH_3 \stackrel{\text{H}^+}{\rightleftharpoons} CH_3-CH \stackrel{\text{OH}}{=} C-CH_3 + CH_3-CH_2$$

$$(major) \qquad \qquad (Minor)$$

(II) Base catalysed mechanism

Q.1 Draw the tautomer which is present in more amount (major).

$$(a) \overset{\bigcirc}{\longleftarrow} \overset{H^{+}}{\longleftarrow}$$

Ans. (a) (b) OH

Q.2 Draw tautomers:-

(1)
$$CH_3 - C - H \Longrightarrow$$

(2)
$$CH_3 - C - CH_3 \rightleftharpoons$$

(4)
$$CH_3$$
— C — C — H
 CH_3
 CH_3
 CH_3
(Pivaldehyde)

$$(6) \bigcirc C - CH_3 \longrightarrow$$

$$(11) CH_3 - CH = NH$$

(13)
$$CH_3 - CH_2 - N = O$$

(15)
$$Ph - N = N - NH - Me$$

 $Ph - N = N - CH_2 - Ph$

(16)
$$Ph-N = N - OH$$

ENOL CONTENT: Generally keto form is more stable than enol form

- \rightarrow % amount of enol at equilibrium is known as enol content.
- → enol content ∞ stability of enol
 - ∞ aromatization of enol
 - ∞ stability of enolate ion
 - ∞ Intramolecular H-bonding
 - ∝ Stability of anion

Que. Arrange following in decreasing order of enol content.

Ans. || > | > ||

Ans. || > || > ||

Ans. | > | > ||

Sol. Due to strong chelate in I

Ans. Aromatic

$$\uparrow$$
 $|||>||>| \rightarrow Anti$

Non aromatic

Ans. |<||

$$\rightleftharpoons$$

"keto" (≈ 1%)

"enol" (stable by resonance and aromatic nature)

7.
$$CH_3-C-CH_2-C$$

$$\rightleftharpoons$$

Aceto acetic ester (AAE)

In aqueous solution

Keto from is stablised by intermolecular H–Bonding.

In liquid state

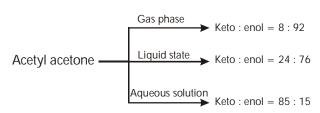
$$CH_3-C = CH - C - OC_2H_5$$

$$\begin{matrix} & & \parallel & & \parallel \\ & & -H \cdot \cdot \cdot \cdot O \end{matrix}$$

Enol form is stabilised by intramolecular H-Bonding.

- (i) Enol content \propto number of >C=O group.
- (ii) If number of >C=O groups are equal then proportional to number of α -H.

Acetyl acetone: (On same pattern)



KINETIC ISOTOPIC EXCHANGE:

1.
$$CH_3$$
 H $\xrightarrow{\Theta_{OD}}$ CD_3 H

2.
$$CH_3$$
 CH_3 CD_3 CD_3 CD_3

4.
$$\frac{\Theta_{OD}}{D_2O}$$
 $\frac{\Theta_{OD}}{D_2O}$

5.
$$\bigcirc_{\Theta_{OD} \atop \overline{D_2O}} \bigcirc_{D_2O} \bigcirc_{D} \bigcirc_{D}$$

9.
$$\bigoplus_{O}^{H} \xrightarrow{\Theta_{OD}} CD_3 \swarrow CD$$

- 1. Arrange the following in correct order of enol content.

(C) $CH_3 - C - CH_2 - C - H$ 0 0

- (D) $CH_3 C CH_2 C CH_3$
- 2. Which have maximum stable enol form

- **3.** Arrange the following in correct order of enol content.
 - I:
- $CH_3CH = O$ \rightleftharpoons $CH_2 = CH OH$
 - $CH_3 CH_2 CH = O \iff CH_3 CH = CH OH$ Π :
- 4. Arrange the following in correct order of enol content.
 - $\begin{array}{cccc} \operatorname{CH}_3 \operatorname{C} \operatorname{CH}_3 & \Longrightarrow & \operatorname{CH}_2 = \operatorname{C} \operatorname{CH}_3 \\ & || & & | \\ \operatorname{O} & & \operatorname{OH} \end{array}$
 - $\begin{array}{cccc} \mathsf{CH_3} \mathsf{C} \mathsf{C} \mathsf{CH_3} & \Longrightarrow & \mathsf{CH_2} = \mathsf{C} \mathsf{C} \mathsf{CH_3} \\ & || & || & & | & || \\ & \mathsf{O} & \mathsf{O} & & \mathsf{OH} \; \mathsf{O} \end{array}$
- 5. The compounds C₂H₅OC₂H₅ and CH₃OCH₂CH₂CH₃ are
 - (A) chain isomers

(B) geometrical isomers

(C) metamers

- (D) conformational isomers
- 6. The number of primary, secondary and tertiary amines possible with the molecular formula C₃H₀N respectively.
 - (A) 1, 2, 2
- (B) 1, 2, 1
- (C) 2, 1, 1
- (D) 3, 0, 1

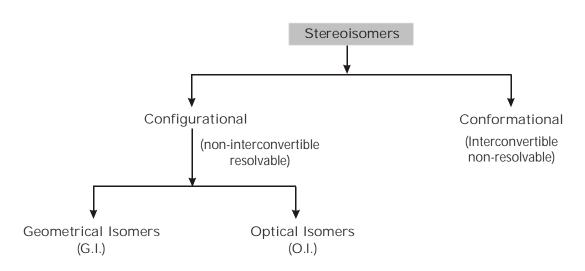
7. Which of the following has **incorrect** relation

$$(B) \begin{picture}(60,0) \put(0,0){\line(1,0){100}} \put(0,0){\line(1,0)$$

- **8.** How many structural isomers are possible for C_5H_{10} (excluding stereoisomers)
 - (A) 10
- (B) 11
- (C) 12
- (D) 13
- **9.** How many benzonoid isomers are possible for C_7H_8O
 - (A) 4

- (B) 5
- (C) 6
- (D) 3

STEREO ISOMERISM



Stereo-Isomerism:-

Two or more than two compounds having same molecular formula, same structural formula but different arrangements of atoms or groups in space.

Geometrical isomerism:

Stereo-isomers which are obtained due to different orientation of atoms or group in the space around restricted rotation are known as G.I.

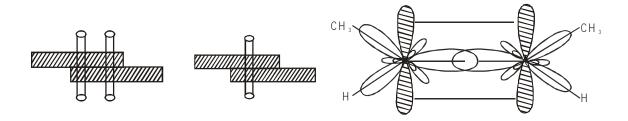
Ε

Condition for G.I.:

Condition 1: Restricted rotation must be present.

Restricted Rotation

Free Rotation



Example :
$$\overset{CH_3}{\overset{}_{H}} C = C \overset{CH_3}{\overset{}_{H}} = \overset{CH_3}{\overset{}_{H}} C = C \overset{H}{\overset{}_{CH_3}}$$
 $cis-2$ -butene $trans-2$ -butene

Note : cis \rightleftharpoons trans is possible only when π bond break.

Condition 2

(i) The two groups at each end of restricted bond must be different.

$$a \neq b$$
 $C = C A a \neq b$

Example G.I.

$$C_{aa} = C_{aa}$$
 ×

$$C_{aa}=C_{bd}$$
 ×

$$C_{aa} = C_{b2}$$
 ×

$$C_{ab} = C_{ab}$$

$$C_{ab} = C_{bd}$$

Condition 3

Terminal valency should be present in the same plane.

1. Geometrical isomerism in alkene C = C

Example

G.I.

$$\sum_{H} c = c < \sum_{H}^{CI}$$

Yes

$$CI$$
 $C = C$ CI CH_3

Yes

No

Yes

- 2. Geometrical isomerism in $\supset C = \ddot{N} -$

Imine compounds are produced from carbonyl compounds on reaction with ammonia.

$$R = O + H_2 - \ddot{N} - H \xrightarrow{-H_2O} R = \ddot{N} - H$$
Imine

$$R = O + H_2 - N - H \xrightarrow{-H_2O} R = N - H$$

Imines prepared from unsymmetrical aldehydes and ketones, always show geometrical isomerism.

Q. Which of the following compounds show geometrical isomerism after reaction with NH₃.



Ans. c,d,e,g,i

(b) Oximes ($>_{C=N-OH}$):

They are prepared by reacting carbonyl compuond with hydroxyl amine (NH₂–OH)

$$R > C = O + H_2 N - OH \xrightarrow{-H_2O} R > C = N - OH$$
(Aldoxime)

$$\begin{array}{c}
R \\
R'
\end{array}
C =
\begin{array}{c}
O + H_2
\end{array}
N - OH \xrightarrow{-H_2O}
\begin{array}{c}
R \\
R'
\end{array}
C = N - OH$$
(Ketoxime)

- → Except formaldehyde (CH₂O). All other aldehyde forms two oximes.
- → Unsymmetrical ketone forms two oximes.
- **Q.1** Which of the following ketones will show G.I. after raction with H_2N-OH .
 - (1) Propanone

(2) Butanone

(3) 3-pentanone

$$\begin{array}{c} CH_{\overline{3}}-CH_{\overline{2}}-C-CH_{\overline{2}}-CH_{\overline{3}}\\ \\ O\end{array}$$

(4) Acetophenone

(5) Benzophenone

$$C_6H_{\overline{5}}CCC_6H_5$$

(6) Cyclo hexane



Ans. 2,4,7

Q. The lowest molecular weight of acyclic ketone and its next homologue are mixed with excess of NH2 . OH

to react. How many oximes are formed after the reaction?

Ans. 3

(3) Geometrical isomerism in azo compounds (-N=N-)

(i) $H-N=N-H(H_2N_2)$

$$H = \frac{H - \ddot{N} = \ddot{N} - H}{M}$$
and
$$H = \frac{H}{M} = \frac{H}$$

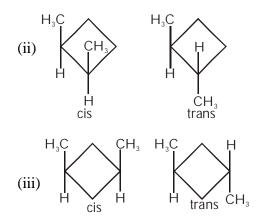
(ii) Ph₂N₂ (Azobenzene)

$$Ph \xrightarrow{\text{N=N}} Ph \xrightarrow{\text{Ph}} N=N \xrightarrow{\text{Ph}} Ph$$
syn anti

(4) Geometrical isomerism in cyclic compound

$$(i) \overset{CH_3}{\overset{}_3} \overset{CH_3}{\overset{CH_3}{\overset{}_3}} \overset{CH_3}{\overset{CH_3}{\overset{}_3} \overset{CH_3}{\overset{}_3} \overset{CH_3}{\overset{}_3$$

Restricted rotation



$\textbf{(5)} \quad \textbf{Geometrical isomerism in cycloalkenes in double bonds:} \\$

In cycloalkenes, G.I. exists across double bonds with ring size equal to or greater then 8 carbon atoms (due to ring strain)

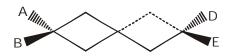
(6) G.I. in spiro compounds:

Example

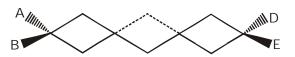


Yes

G.I.



No



(7) G.I. in cummlenes

Example

G.I.

Yes

$$A = C = C = C$$

No

$$A = C = C = C$$

Yes

Note: Even π -bond – don't show G.I. Odd π -bond - show G.I.

Q.1 Which of the following shows G.I.

$$(i) \qquad \frac{H}{V} \qquad V$$

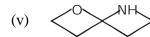
- No



-Yes

<>> −No

- Yes



- Yes

$$(vi) \quad \begin{array}{c} A \\ C = C = C \\ H \end{array}$$

-No

-Yes

(viii)
$$CH_3$$
— CH — CH — CH — H — H — H — V

– Yes

(Any no. of π bond replaced by ring \Rightarrow still G.I.)

$$(x) \qquad \bigvee_{V} \qquad \bigoplus_{H} \qquad \bigoplus_{H} \qquad \bigoplus_{H} \qquad \bigvee_{V} \qquad \qquad -Yes$$

(xiii)
$$\sqrt{\frac{1}{H}}C\sqrt{\frac{1}{V}}\sqrt{\frac{1}{V}}\sqrt{\frac{1}{H}}\sqrt{\frac{1}{V}}$$
 $-No$

(8) G.I. in Biphenyl Compound

A,B,D &E : small \Rightarrow Conformation (Not show G.I.)

 $large \Rightarrow due to SIR (Not show G.I.)$

$$\perp \Rightarrow$$
 no. G.I.

→ Triphenyl Compound

Not in plane \Rightarrow as due to most stable.

$$(A \neq B) \cap (D \neq E)$$

(B) NOMENCLATURE SYSTEMS OF GEOMETRICAL ISOMERS:

(a) **Cis–Trans System :** If similar groups at same side then cis and if same groups at different side then trans.

$$a > C = C < a$$
 $b > C = C < a$

[Same groups, same side] [Same groups different side]

Example: x > C = C < xcis x > C = C < xcis x > C = C < xcis

Example: $CH_3 \rightarrow C=C < CH_2 \rightarrow CH_3$ $CH_2 \rightarrow CH_3$ $CH_3 \rightarrow C=C$ $CH_3 \rightarrow C$ $CH_3 \rightarrow$

trans-2-pentene It does not show Geometrical isomers So no cis-

trans

(b) E - Z System:

E (Entgegen): When high priority groups are opposite side.

Z (**Zussaman**): When high priority groups are same side.

$$\begin{array}{ccc} LP \\ LP \\ E' \end{array} \qquad \begin{array}{cccc} HP \\ LP \\ \end{array} \qquad \begin{array}{ccccc} HP \\ LP \\ \end{array} \qquad \begin{array}{ccccc} TZ' \\ \end{array}$$

HP – High priority and LP – Low priority

Priority Rules:

Chann, Ingold, Prolog (CIP Rule)

Rule 1. Priority α Atomic no. of atom which is directly attached to restrided rotatory system.

$$C = C \xrightarrow{\text{Br}}$$

Rule 2. Priority α Atomic weight (in case of isotopes)

Br
$$CH_2$$
 H_3C-O D $C=C$

Rule3. If at the first directly attached, R-1 fails move to next atom and atoms attached to it.

(HHC) (HHC
$$\ell$$
)
$$I-H_2C-CH_2$$

$$C=C$$

$$CH_2-CH_2-CH_3$$

$$CH_2-CH_3$$

$$CH_3$$

$$CH_3$$

$$CH_3$$

$$CH_3$$

$$CH_3$$

Rule4. If directly attached groups contain double bond then duplicate them by dummy atoms.

Ex.4:
$$N \equiv C$$
 $CH = O$
 $C \equiv CH$
 $C \equiv CH$

022 Onor

Rule-5 If after converting a multiple bond, it converts identical to a original, higher priority to original one.

$$\begin{array}{c} H_2C=CH \\ CH_3-CH \\ CH_3-CH \\ CH_3 \end{array} \begin{array}{c} C \equiv CH \\ CH_3 \\ CH_3 \end{array} \begin{array}{c} CH_3 \\ CH_3 \\ CH_3 \end{array} \begin{array}{c} After converting \\ it turns \end{array}$$

Rule-6

$$\begin{array}{c|c}
E \\
\hline
Z
\end{array}$$

$$\begin{array}{c|c}
E \\
\hline
Z
\end{array}$$

$$\begin{array}{c|c}
CZ
\end{array}$$

cis/trans ⇒ cis

$$Z/E \Rightarrow Z$$

$$R/S \Rightarrow R$$

Example: Assign E-Z nomenclature

(i)
$$H_{[HP]} = C = C < CH_3 CH_2 - CH_3 [HP]$$
 'Z'

(ii)
$$CH_3 > C = C < H_5 = CH_3 = CH$$

(iii)
$$CH_3 > C = C < CH_3$$
 'E'

(v)
$$CH_3 C C CH_2 CH_3 CH_3 CH_3$$
 [I, H, H]

(vi)
$$CH_2 = CH$$
 $C = C$ $C(CH_3)_3$ $CH - CH = CH_2$

$$N \equiv C$$
 $C = N$
 CH_3
'Z'

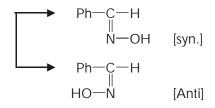


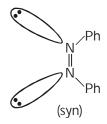
(C) Syn-Anti Nomenclature

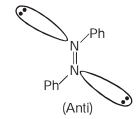
Example: Acetaldoximes has two Geometrical isomers –

$$\begin{array}{cccc} CH_3-C-H & CH_3-C-H \\ \parallel & \parallel & \parallel \\ N-OH & HO-N \end{array}$$
 syn anti

When H and OH are on the same side When H and OH are on the opposite side







Ex. Which of the following show Geometrical isomerism –

(A)
$$CH_3$$
— CH_2 — $CH=N$ — OH

(B)
$$H_2C=N$$
—OH

Sol. (A), (D)

□ NUMBER OF GEOMETRICAL ISOMERS : (For compounds not showing optical isomerism)

Calculation of GI:

n = no. of unit which can show GI

Case I : Compound is unsymmetrical -2^n

Case II: Compound is symmetrical $2^{n-1} + 2^{p-1}$ (p is $\frac{n}{2}$ if n is even and $\frac{n+1}{2}$ if n is odd)

Que. Calculate total number of G.I. in following compounds.

1.
$$CH_3 - CH = CH - CH_3$$
 _____ 2

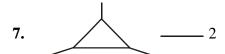
2.
$$CH_3 - CH = CH - CH = CH_2$$
 2

3.
$$CH_3 - CH = CH - CH = NH - 4$$

4.
$$CH_3 - CH = CH - CH = CH - CH_3$$
 3

5.
$$CH_3 - CH = CH - CH = CH - CH_2 - Cl$$
 4

6.
$$CH_3 - CH = C = C = CH - CH = CH - CH_2 - CH = NH _____ 8$$



12.
$$CH-CH_3 = 2$$

PHYSICAL PROPERTIES OF GEOMETRICAL ISOMERS:

Physical Properties of Cis-Trans Isomers:

S.No.	Physical properties	Comparison	Remarks
1	Dipole moment	cis > trans	cis-isomer has resultant of dipoles while in trans isomer dipole moments cancel out
2	Boiling point	cis > trans	Molecules having higher dipole moment have higher boiling point due to larger intermolecular force of attraction
3	Solubility (in H ₂ O)	cis > trans	More polar molecules are more soluble in H ₂ O
4	Melting point	trans > cis	More symmetric isomers have higher melting points due to better packing in crystalline lattice & trans isomers are more symmetric than cis.
5	Stability	trans > cis	The molecule having more vander wall strain are less stable. In cis isomer the bulky group are closer they have larger vander waal strain.

Dipole moment $[\mu]$:

Example:

Example:

$$H_3$$
—C—H
 H —C—C H_2 —C H_3

trans $\mu \neq 0$

cis
$$\mu \neq 0$$

Example:

$$\begin{array}{c} \overrightarrow{C}H_{3} - C - H \\ \parallel \quad \rightarrow \\ H - C - CI \end{array} \quad trans \quad \mu \neq 0$$

Illustrations ——

Illustration 7. Which of the following show Geometrical isomerism –

(A) 1,1–diphenyl–1–butene

(B) 1,1–diphenyl–2–butene

(C) 2,3-dimethyl-2-butene

(D) 3-phenyl-1-butene

Soltuion (B)

Illustration 8. If dipole moment of chlorobenzene is μ , then dipole moment of is –



Solution Zero

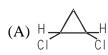
Illustration 9. Which of the following show Geometrical isomerism –

(A)
$$CH_3$$
— CH_2 — $CH=N$ — OH

(B)
$$H_2C=N$$
—OH

Solution (A), (D)

Illustration 10. Which of the following show Geometrical isomerism –



Solution

(A), (B) and (D)

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KEY POINTS

- Cyclo heptene and lower cyclalkenes cannot exist in trans form. So they can not show G.I.
- Allenes which have odd number of double bonds can show G.I.
- Double bond is not necessary condition for G.I. Restricted rotation is necesary condition for G.I.
- 1. Calculate the total number of open chain isomeric carbonyl compounds of molecular formula C_5H_8O which can't show geometrical isomerism.
- 2. Assign E & Z configuration?

(III)
$$\begin{array}{c} CH_2CH_2CH_3 \\ CH-CH_3 \\ CH_3 \end{array}$$

$$(V) \begin{array}{c} F \\ C - C - C \\ F \\ C - C - C \end{array}$$

(VI)
$$\frac{NC}{CH = CH_2}$$

(VII) OHC
$$C \equiv CH$$
 CH_3
 $C - CH_3$
 $C = CH_3$
 $C = CH_3$

$$(IX) \quad \underbrace{ \begin{array}{c} Me \\ \\ Et \end{array} } \quad \underbrace{ \begin{array}{c} OMe \\ \\ O^- \ Li^+ \end{array} }$$

$$(X) \quad \overset{H}{\underset{OH}{\bigvee}} \quad \overset{18}{\underset{OH}{\bigvee}}$$

(XII)
$$CH_{3} \\ CH - CH_{2} - CH_{3} \\ CH_{3} \\ H$$

Conformational Isomerism

The different arrangement of atoms in space that result from the free rotation arround C—C bond axis are called conformations. The phenomenon is called conformational isomerism

Some Important Terms:

- (i) **Dihedral or Torsional angle :** Angle between bonds of two adajecent atoms is knows as dihedral or Torsional angle.
- (ii) **Staggered Conformation :** Conformations in which valency triangle are opposite and most priority group are also opposite then known as staggered/anti conformation.
- (iii) Eclipsed Conformation: In which two valency triangle as well as most priority group (according to CIP) are superimpose then known as Eclipsed conformation.
- (iv) Skew Conformation: All other conformations are known as Skew Conformations.
- (v) Torsional Strain: Is the name given to the repulsion felt by the bonded electron of front carbon atom with the bonded electrons of back carbon atom.
- (vi)Steric Strain: Strain felt by the repulsion of atoms or groups of atoms of front carbon atom with back carbon atom. In most circumstances torsional strain dominates over steric strain.

• Conformers of ethane [CH₃—CH₃]

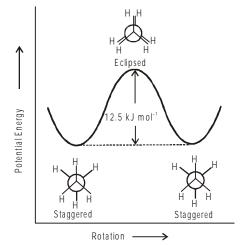
I = III (Eclipsed form) in this form distance between 2C–H bonds is minimum so maximum repulsion or minimum stable.

II = IV (Staggered form) in this form distance between 2C–H bonds is maximum so minimum repulsion so maximum stable.

There are infinite conformers between eclipsed and staggered forms which are called as skew forms

Stability order: Staggered > Skew > Eclipsed.

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

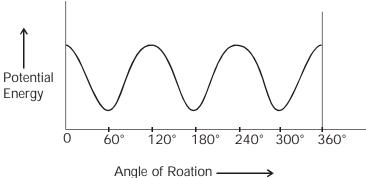
Conformation of propane:

$$\mathbf{E}_{\mathbf{X}}$$
 CH_3 CH_2 $-CH_3$

Saw horse projection formula

Newman Projection Formula

Propane:



Conformation of Butane $[CH_3-CH_2+CH_2-CH_3]$ (arround C_2-C_3 rotaion)

$$\begin{array}{c} CH_3 \\ CH_3 \\ CH_3 \\ H \end{array} \begin{array}{c} CH_3$$

I/VII = Fully eclipsed

II/VI = Gauche form

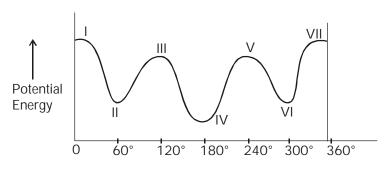
III/V = Partially eclipsed

IV = Anti form

Stability Order IV > II > III > I

P.E. Order IV < II < III < I

Potential Energy Diagram:



Angle of Roation ----->

1. Draw most stable conformation of following:

(i)
$$CH_2-CH_2 \longrightarrow H \longrightarrow H \longrightarrow H \longrightarrow H \longrightarrow H$$

Due to H-bonding gauche is more stable than anti

(ii)
$$CH_2-CH_2$$
 H CH_2-CH_2 H H H H

(iv)
$$CH_2 - CH_2 \longrightarrow H \longrightarrow H \longrightarrow H$$

$$\begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \end{array}$$

$$(v) \quad \begin{array}{c} CH_2 \longrightarrow CH_2 \\ I \quad I \\ COOH \ COOH \end{array} \longrightarrow$$

$$(v) \quad \begin{array}{c} CH_2 - CH_2 \\ \hline \\ COOH COOH \end{array} \longrightarrow \begin{array}{c} OH \\ \hline \\ H \end{array} \longrightarrow \begin{array}$$

$$(vi) \quad \begin{matrix} CH_2 \longrightarrow CH_2 \\ I & I \\ NR_3^{\oplus} & COO^- \end{matrix} \longrightarrow$$

$$\begin{array}{ccccc}
CH_2 & CH_2 \\
COONa & COONa
\end{array}
\longrightarrow
\begin{array}{cccccc}
H & COO \\
H & H
\end{array}
\longrightarrow
\begin{array}{ccccc}
H & COO \\
H & H
\end{array}$$
(Repulsion)

GAUCHE EFFECT:

For most stable conformation across C-heteroatom bond bulkier group of C must placed at max. gauche position of lone pair.

Q.1 Draw most stable conformation:

(ii)
$$CH_3 - CH_2 \rightarrow OH$$

$$H \xrightarrow{CH_3} H \xrightarrow{H} CH_3$$

(More stable by Gauche effect)

(iii)
$$CH_3 - CH_2$$
 $\rightarrow NH_2$

$$H \xrightarrow{N} H \rightleftharpoons CH_3 \xrightarrow{N} H$$

(More stable by G.Effect)

Dipole moment in Conformational analysis

Dipole moment (μ) :

$$\mu_{\text{net}} = \sum \! \mu_{i} x_{i}$$

$$\mu_{net} = \mu_a x_a + \mu_g x_g$$

$$x_a + x_g = 1$$

.. Only stable conformers are considered.

 $a \Rightarrow anti \\$

 $g \Rightarrow gauche$

Q.2 Calculate μ for 1,2-dichloroethane.

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Q.3 Calculate μ_g if μ_{net} of $\begin{matrix} CH_2 - CH_2 \\ I \end{matrix}$ is 1D, mole fraction of anti conformation is 0.82.

[Given : $\mu_{net} = [\mu_i \times i$, where x_i is mole fractor of independent stable conforation]

Ans. $1 = 0.82 \times 0 + 0.18x \Rightarrow x = 5.55$ [by using above given formula]

Q.4 Compounds with $\mu = 0$,

$$(i) \qquad \int\limits_{CI}^{CI} \qquad \mu = 0$$

$$(ii) \bigcap_{Cl}^{Cl} \mu = 0$$

$$(iv) \bigcup_{CN}^{CN} \mu = 0$$

Q.5 Which has higher μ.



Q.6 Draw most stable conformers of

- (a) 3-methyl pentane $(C_2 C_3)$
- (b) 3-methyl hexane $(C_3 C_4)$

Ans. (1) (a)
$$CH_3$$
 CH_3 CH_3 (b) CH_3 CH_3

Q.7 Compare relative stabilities of given conformers:-

Ans. (2) (c) > (a) > (b)

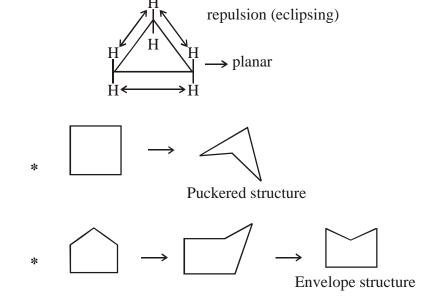
Conformational analysis of cycloalkane

Angle strain: When acyclic compound is converted into cyclic compound then deviation in bond angle is observed and per bond deviation is known as angle strain.

Angle strain =
$$\frac{\text{Total deviation}}{2}$$

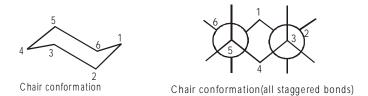
When size of ring increases then it becomes flexible and partial σ bond rotation is observed so larger ring acquire non-planar orientetion to avoid eclipsing.

Eclipsing:



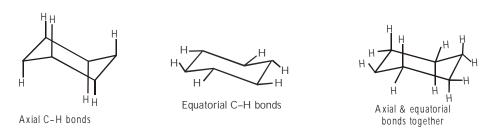
Conformational analysis of cyclohexane

(i) Chair form: Experimental evidences show that cyclohexane is non-planar. If we look to the models of the different conformations that are free of angle strain first there is chair conformation. If we sight along each of the carbon-carbon bonds in turn we see in every case perfectly staggered bonds.



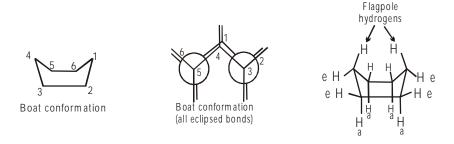
The conformation is thus free of all the strains, it lies at energy minimum and is therefore a conformational isomer. The chair form is the most stable conformation of cyclohexane.

Axial and equatorial bonds in chair form of cyclohexane:



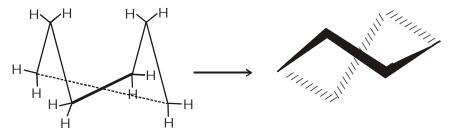
The 12 hydrogen atoms of chair conformation of cyclohexane can be divided into two groups. Six of the hydrogens, called axial hydrogens, hence their bonds parallel to a vertical axis that passes through the rings centre. These axial bonds are directed up & down on adjacent carbons. The second set of six hydrogens called equatorial hydrogens are located approximately along the equator of the molecule.

(ii) **Boat form :** Another conformation which is known as boat conformation has exactly eclipsed conformations.

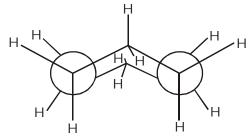


In boat form of cyclohexane 6 hydrogens are equatorial, 4 hydrogens are axial and two hydrogens are flagpoles. It is an unstable conformation of cyclohexane due to torsional strain among axial hydrogens and due to van der waals strain caused by crowding between the "flagpole" hydrogens.

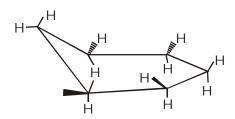
(iii) Twist Boat conformation



Newmann:

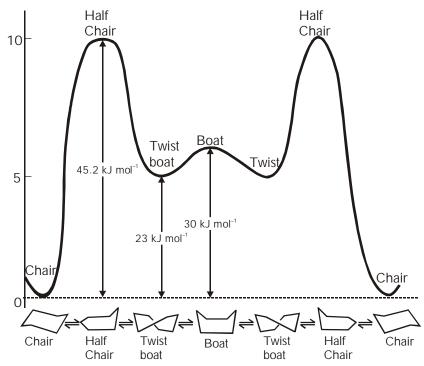


(iv) Half Chair Conformation



Stability order:

Chair > Twist boat > Boat > Half Chair



The relative energies of the various conformations of cyclohexane.

The positions of maximum energy are conformations called half-chair conformations, in which the carbon atoms of one end of the ring have become coplanar.

• Conformational inversion (Ring flipping) in cyclohexane

Like alkanes cyclohexane too is conformationally mobile. Through a process known as ring inversion, Chair-chair interconversion, or more simple ring flipping one chair conformation is converted to another chair.

By ring flipping all axial bonds convert to equatorial and vice-versa. The activation energy for cyclohexane ring inversion is 45 kJ/mol. It is a very rapid process with a half-life of about 10⁻⁵ sec at 25°C.

• Conformational analysis of monosubstituted cyclohexanes

In ring inversion in methylcyclohexane the two chair conformations are not equivalent. In one chair the methyl group is axial; in the other it is equatorial. At room temperature 95% of the methylcyclohexane exist in equatorial methyl group whereas only 5% of the molecule have an axial methyl group.

1,3-diaxial repulsion: A methyl group is less crowded when it is equatorial than when it is axial. The distance between the axial methyl groups at C-1 and two hydrogens at C-3 and C-5 is less than the sum of their vander waal radii which causes vander waal strain in the axial conformation this type of crowding is called 1,3-diaxial repulsions. When the methyl group is equatorial, it experience no significant crowding.

Q.8 Give ring flipping equilibrium constant for following compunds.



(ii)
$$\underbrace{K_c>1}_{Me}$$
 $\underbrace{K_c>1}_{Me}$

(iii)
$$Et \xrightarrow{E_{\downarrow}} Et$$

(iv)
$$Pr = K>1$$

$$(v) \qquad \underbrace{\qquad \qquad }_{tBu} \underbrace{K_c > 1}, \qquad \underbrace{\qquad \qquad }_{tBu}$$

$$(vi) \qquad \underbrace{\qquad \qquad Me}_{Et} \quad \underbrace{K_c < 1}_{Et} \qquad \underbrace{Me}_{Et}$$

(vii)
$$Me$$
 Me
 Me
 Me
 Me

$$(viii) \begin{picture}(100,0) \put(0.5,0){\ovalpha} \put(0.5,0){\ovalpha}$$

$$(ix) \qquad \stackrel{F}{\longleftarrow} OH \qquad \stackrel{K_c<1}{\longleftarrow} \qquad \stackrel{F}{\longleftarrow} OH$$

(x)
$$CH_3$$
 $K_c < 1$ CH_3

Ε

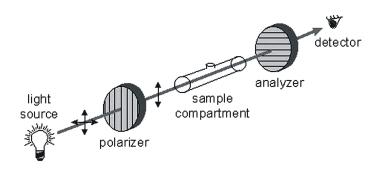
Optical Isomerism

Compounds which have same molecular and structural formula but have different optical activity are known as optical isomers.

Optical activity

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

Light has vibrations occur in all planes at right angles to the line of propagation. In plane polarized light the vibrations take place only in one plane. Plane polarized light can be obtained by passing ordinary light through a Nicol prism.



Certain organic compounds, when their solutions are placed in the path of a plane polarized light, have the remarkable property of rotating its plane through a certain angle which may be either to the left (or) to the right. This property of a substance of rotating the plane of polarized light is called optical activity and the substance possessing it is said to be optically active.

The observed rotation of the plane of polarized light [determined with the help of polarimeter] produced by a solution depends on:

- (a) The amount of the substance in tube;
- **(b)** On the length of the sample tube;
- (c) The temperature of the experiment and
- **(d)** the wavelength of the light used.

The instrument used to measure angle of rotation is called polarimeter. The measurement of optical rotation is expressed in terms of specific rotation $[\alpha]_D^t$; this is given by the following relation :

$$[\alpha]_D^t = \frac{\alpha_{obs}}{\ell \times C}$$
 [where $\alpha = observed$ angle of rotation]

 $[\alpha]_D^t$ = specific rotation determined at t°C, using D-line of sodium light.

 ℓ = length of solution in decimeters

C = concentration of the active compound in grams per millilitre.

The sign attached with the angle of rotation signifies the direction of rotation. Negative sign (–) indicates that the rotation is towards anti-clockwise, while positive (+) sign means that the direction of rotation is toward right clockwise.

If the substance rotates plane-polarised light to the right i.e. in clockwise direction it is called dextrorotatory and indicated by 'd' or (+)

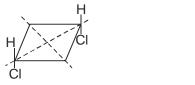
If the substance rotates plane-polarised light to the left i.e. in anti clockwise direction it is called laevorotatory and indicated by 'l' or (–)

• Condition of Optical Activity

Compound must be asymmetrical.

Types of Symmetry

(i) Plane of symmetry (POS): An imaginary plane which bisects any object or molecule into two equal parts which are mirror images of each other is known as POS.



Plane of symmetry

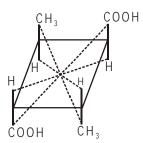


Plane of symmetry



Plane of symmetry

(ii) Center of Symmetry (COS): It is a point inside a molecule from which on travelling equal distance in opposite directions one takes equal time.



(iii) Axis of Symmetry (AOS) (C_n): Axis of symmetry is an axis such that if one rotates the molecule by $\frac{360^{\circ}}{n}$, the new position of molcule is superimposable with the original one.

Ε

(iv) Alternate axis of Symmetry (AAOS): An imaginary plane around which rotation by angle x gives its mirror image is known as AAOS. It is represented by S_n where $n = \frac{360}{x}$

• Chiral Compound

Compound which is not super imposable on its mirror image is known as Chiral Compound. All optically active compounds are Chiral.

• Asymmetric carbon (or) Chiral Carbon

If all the four bonds of carbon are satisfied by four different atoms/groups, it is chiral. Chiral carbon is designated by an asterisk (*).

Example:
$$H = \begin{bmatrix} B & F & F \\ A & F & F \end{bmatrix}$$

Optically Active Carbon Compounds:

If a carbon-atom is attached with four different group, then if does not have any element of symmetry. It is known as asymmetric carbon atom, which is represented as ${}^*C_{abde}$.

If a molecule contains only one asymmetric carbon atom, then the molecule as a whole becomes chiral and optically active and show optical isomers.

CIIII	Compound	Centre of symmetric		Optical active
(1)	H C H	Absent	Yes	No
(2)	H CI	Absent	Yes	No
	B C CI		Yes	No
(4)	B C CI	Absent	No	Yes

• Projection Formula of Chiral Molecules

(i) Wedge-Dash Projection formula

Example: (i) Butan-2-ol

$$CH_3$$
 C
 C
 C
 C_2H_5

(ii) Ficher Projection formula

Rules of writing Fisher Projection formula

- (a) Groups at Vertical line are away from observer.
- **(b)** Groups at Horizontal line are towards the observer.
- (c) Central 'C' atom of the cross is chiral.
- (d) High priority group lies at the top of vertical line (Numbering starts from top).

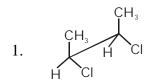
Ex 1:- Mark the chiral objects:

- (i) Cup
- (ii) Plate
- (iii) Letter A
- (iv) Letter G
- (v) Fan

- (vi) Door
- (vii) Shoe
- (viii) Glove

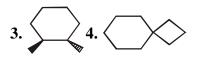
Ans. IV, VII, VIII

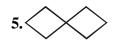
Q. 1 Identify POS if present:



Ans. 1. $\sqrt{\ }$ **2.** $x \$ **3.** $\sqrt{\ }$ **4.** $x \$ **5.** $x \$ **6.** $\sqrt{\ }$

Q. 1 Identify POS if present:







1. $\sqrt{2}$. $\sqrt{3}$. \times 4. $\sqrt{5}$. $\sqrt{6}$. $\sqrt{7}$. $\sqrt{8}$. $\sqrt{9}$. $\sqrt{10}$. $\sqrt{6}$.

Q. 2 Identify COS if present.

$$4. \begin{array}{c} CH_3 \\ H \\ CH_3 \end{array} CI$$

5.
$$CI = C$$

$$\begin{array}{c} CI \\ C \\ C \end{array} = C = C \begin{array}{c} C \\ C \\ C \end{array}$$

Ans. 1. $\sqrt{2}$ 2. X 3. X 4. $\sqrt{5}$ 5. $\sqrt{6}$ 6. X 7. $\sqrt{8}$ 8. X

• Optically active compounds having no asymmetric carbon

(i)
$$CH_3$$
 $C = C = C$

Enantiomers

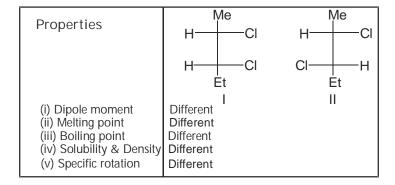
Stereoisomers which are mirror-image of each other are called enantiomers (or) enantiomorphs. Thus (i) and (ii) are enantiomers. All the physical and chemical properties of enantimoers are same except two:

- (i) They rotate PPL to the same extent but in opposite direction. One which rotates PPL in clockwise direction is called dextro-rotatory [dextro is latin word meaning thereby right] and is designated by d (or) (+). One which rotates PPL in anti-clockwise direction is called laevo rotatory [means towards left] and designated by l (or) (-).
- (ii) They react with optically active compounds with different rates.

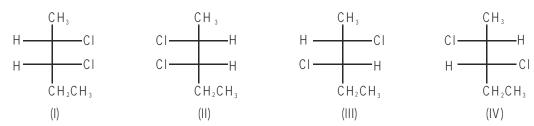


• Diastereomerism

The optical isomer which are not mirror images to each other are called diastereomers.



Example:



I, II = Enantiomers,

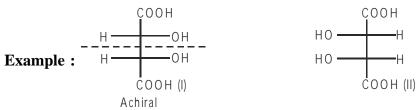
I, III = Diastereomers,

II, III = Diastereomers,

III, IV = Enantiomers

II, IV= Diastereomers

I, IV = Diastereomers



I and II are identical

• Stereoisomerism in Tartaric Acid

Tartaric acid exists in only three stereomeric forms. Two of them (1 and 2) are non superimposable mirror images of each other so they are enantiomers of each other. The 3rd isomer is non mirror image stereomers of (1) and (2) so it is diastereomer of (1) and (2). 3rd isomer containes plane of symmetry so, it is optically inactive. It is known as meso tartaric acid.

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Meso isomers

- (i) Achiral compound which have chiral centers is known meso compound.
- (ii) They are achiral (optical rotation = 0).
- (iii) They have $[\alpha] = 0$ due to internal compensation of optical rotation.
- (iv) They are diastereomer of $d \ell$ pair. So, it has different physical properties than $d \ell$ -pair.
- (v) Presence of more than one asymmetric 'C' atoms.
- (vi) They are non resolvable.

Internal compensation:

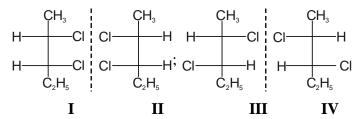
In meso tartaric acid the inactivity is due to effects within the molecule and not external. The force of rotation due to one of the molecule is balanced by the opposite and equal force due to the other half. The optical inactivity so produced is said to be due to internal compensation. It occurs whenever a compound containing two (or) more asymmetric carbon atoms has a plane (or) point of symmetry. Since the optical inactivity of such a compound arises within the molecule, the question of separating into active components does not arise.

• Racemic mixture (External compensation)

If equimolar amounts of d and ℓ -isomers are mixed in a solvent, the solution is inactive. The rotation of each isomer is balanced (or) compensated by the equal but opposite rotation of the other. Optical inactivity having this origin is described as due to external compensation. Such mixtures of (+) and (-) isomer (Racemic mixtures) can be separated into the active components.

A meso compound is optically inactive due to internal compensation

Que. Give the relationship between following compounds.



Analysis

I, II – Enantiomers

III, IV – Enantiomers

I, III – Diasteromers

I, IV – Diasteromers

II, III – Diasteromers

II, IV – Diasteromers

• Pseudo Chiral Centre

A chiral center which becomes achiral on changing the configuration of one of its substituents and vice versa

$$\begin{array}{c} \text{CH}_3 \\ \text{CH-OH} \\ \text{Pseudo chiral center} \longrightarrow \text{HC-Br} \\ \text{HC-OH} \\ \text{CH}_3 \end{array}$$

• Calculation of number of optical isomers

The number of optical isomers of an organic compound depends on its structure and number of asymmetric carbon atoms. Thus, the number of optical isomers may be determined from the knowledge of the structure of the compound as follows:

(a) When the molecule is unsymmetrical

No. of optically active isomers, $a = 2^n$

Number of meso forms (m) = 0

 \therefore Total no. of optically isomers = $(a + m) = 2^n$

(b) When the molecule is symmetrical and has even no. of asymmetric carbon atoms.

No. of optically active isomers, $a = 2^{(n-1)}$

No. of meso forms, $m = \frac{n}{2^{2}}$

 \therefore Total no. of optically isomers = a + m

(c) When the molecule is symmetrical and has an odd no. of asymmetrical carbon atoms.

no. of optically active isomers, $a = 2^{(n-1)} - 2^{\frac{n-1}{2}}$

No. of meso forms, $m = 2^{\frac{n-1}{2}}$

 \therefore Total no. of optically isomer = $(a + m) = 2^{(n-1)}$

Q.10 Calculate total number of stereoisomers of following: -

$$(1) \qquad \begin{matrix} Cl & I & Br \\ Br & I & Cl \end{matrix} \qquad (2) \qquad \begin{matrix} Cl & Br \\ Br & Cl \end{matrix} \qquad (3) \qquad \begin{matrix} Cl \\ Cl \end{matrix} \qquad (4) \qquad \begin{matrix} Cl \\ Cl \end{matrix}$$

Ans. (1) 36

(2) 10

(3)6

(4)4

• D - L System (Relative configuration) : Application on correct Ficher Projection Formula

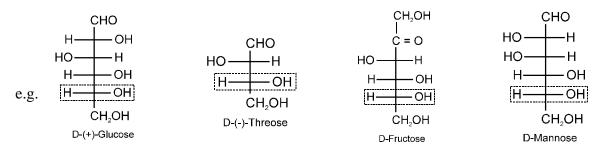
This method is used to relate the configuration of sugars and amino acids to the enantiomers of glyceraldehyde. The configuration of (+)-glyceraldehyde has been assigned as D and the compounds with the same relative configuration are also assigned as D, & those with (-) glyceraldehyde are assigned as L.

odeOs\BOBO-BA\Kota\JEE/Advanced\\Leader\Che\Shee\\somerism\Eng\01

Examples:

COOH COOH COOH
$$H_2N - H$$
 $H - NH_2$ $NH_2 - H$ CH_3 CH_2OH CH_2CH_2COOH CH_3 CH_2OH CH_2CH_2COOH CH_2CH_2COOH CH_2CH_2COOH CH_2CH_2COOH CH_2CH_2COOH CH_2CH_2COOH

Sugars have several asymmetric carbons. A sugar whose highest numbered chiral centre (the penultimate carbon) has the same configuration as D-(+)-glyceraldehyde (– OH group on right side) is designated as a D-sugar, one whose highest numbered chiral centre has the same configuration as L-glyceraldehyde is designated as an L-sugar.



• 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 configuration 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). (R) (S) nomenclature is assigned as follows:

- **Step 1:** Assign priority to the groups which are attached with chiral carbon.
- **Step 2 :** Bring the lowest priority group to dash by even simultaneous exchanges.
- **Step 3:** Draw an arrow from first priority group to second priority group till third priority group.
- **Step 4:** If the direction of arrow is clockwise the configuration is R and if anticlockwise it is S.

RS Nomenclature in fischer formula:

- **Step 1:** Assign priority to the groups which are attached with chiral carbon.
- **Step 2:** Bring the lowest priority group to vertical line.
- **Step 3 :** Draw an arrow from first priority group to second priority group till third priority group.
- **Step 4:** If the direction of arrow is clockwise the configuration is R and if anticlockwise it is S.

$$(2) C_2 H_5 \longrightarrow C C_2 H_5$$

$$(2) C_2 H_5 \longrightarrow C C_2 H_5$$

$$(3) C_2 H_5 \longrightarrow C C_2 H_5$$

$$(4) C_2 H_5 \longrightarrow C C_2 H_5$$

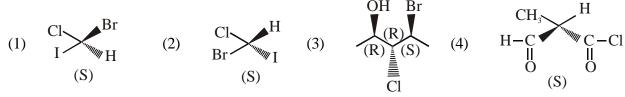
$$(4) C_3 H_5 \longrightarrow C C_2 H_5$$

$$(5) C_4 H_5 \longrightarrow C C_2 H_5$$

• Important

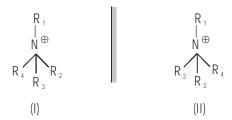
Note that the designation of a compound as R or S has nothing to do with the sign of rotation. the Cahn-Ingold rule can be applied to any three dimensional representation of a chiral compound to determine whether it is R or S only. For example in above case (i.e. lactic acid), R configuration is laevo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

Que. Give R/S configuration of following compounds.



• Amine inversion :

(i) Chiral nitrogen containing tetra alkyl ammonium ion show optical isomerism.



I and II enatiomers

(ii) Chiral nitrogen containing tertiary amine do not show optical isomerism **Reason:** Rapid umbrella inversion.



(iii) Energy required for this interconversion is available at room temperature so I and II are identical

• Optical Purity

Some times we deal with mixtures that are neither otpically pure nor racemic mixture. In these cases we specify the optical purity of the mixture. It is defined as the ratio of its rotation to the rotation of pure enantiomer.

$$\Rightarrow$$
 Optical purity = $\frac{\text{observed optical rotation}}{\text{optical rotation of pure enantiomer}} \times 100$

e.g. If we have some 2-butanol with observed rotation of +9.72, we compare this rotation with +13.5 rotation of the pure (+) enantiomer.

Optical purity =
$$\frac{9.72}{13.5} \times 100 = 72\%$$

That means 72% is pure (+) 2-Butanol and 28% is (± mixture)

Total (+) isomer =
$$72 + 14 = 86\%$$
, (-) isomer = 14%

Ε

Specific Rotation(∞):-

Rotation caused by 1gm/ml of solution in 1 dm length polarimeter tube at specific temperature and fixed wavelength of light.

Confusion
$$q = +180^{\circ} \text{ or } -180^{\circ}$$

If concentration is halfed and becomes $+90^{\circ}$ then d if -90° then ℓ

1. Observed rotation of 2gm/ml of solution placed in 25cm length polarimeter tube is +138°. Calculate its specific rotation.

Ans.
$$+27.6^{\circ}$$

50

Optical Purity (O.P.) or enantiomeric ecess (e. e.)

O.P. (e. e.) =
$$\frac{\text{excess of one enantiomer over other}}{\text{Total mix}} \times 100$$

 $\frac{|d-l|}{|d-l|} \times 100$

$$O.P. = \frac{observer\ specific\ rotation}{Sp.rotation\ of\ pure\ enantiomer} \times 100$$

	% of d	% of l	optical purity	% of Racemic mixture
1	100%	0%	100%	0%
2	99%	1%	98%	2%
3	90%	10%	80%	20%
4	75%	25%	50%	50%
5	10%	90%	80%	20%
6	1%	99%	98%	20%
7	0%	100%	100%	0%

Ex. In a lactic acid (+6 gm) d and 4 gm l Calculate observed specific rotation if specific rotation of pure lactic acid = +13.6

Sol. O.P. =
$$\frac{d\ell}{|d+\ell|} \times 100 = \frac{6-4}{10} \times 100 = 20\%$$

Observed sp. rot. = 20% of $13.6 = 2.72^{\circ}$

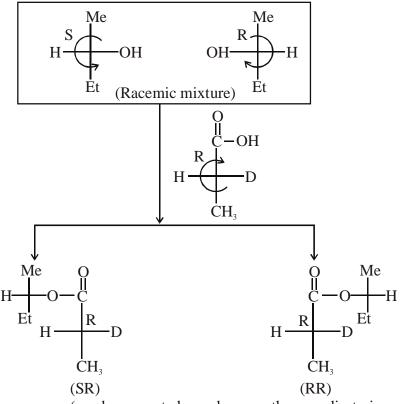
- **Ex.** Calculate the specific rotation of the following samples taken at 25° using the sodium D line.
- (a) 1.0 gm of sample is dissolved in 20.0 ml. of ethanol. Then 5 ml of this solution is placed in a 20.0 cm polarimeter tube. The observed rotation is 1.25° counterclockwise.
- (b) 0.050 gm of sample is dissolved in 2.0 ml of ethanol, and this solution is placed in a 2.0 cm polarimeter tuber. The observed rotation is clockwise 0.043°.

Ans. (a)
$$-12.5^{\circ}$$

(b)
$$+8.6^{\circ}$$

Resolution:- Separation of enantiomers from enantiomeric mixture is known as resolution.

When optically active compound is introducted in racemic mixture than we obtain diasteriomeric pair which is easily separated by fractional distillation.



(can be separated now because they are diasteriomers)

Resolvable and Non-Resolvable Compounds:-

Identify resolvable & non-resolvable compound.

Ans. 1. Resolvable **2.** Non-Resolvable **3.** Resolvable **4.** Resolvable **5.** Resolvable **6.** Non-Resolvable **Rigid body system :** If chiral center is present at bridge head then inversion at that position is not possible, so only two stereo isomer are possible.

Ans. 2

Ex.
$$CH_3$$

Ans. 8

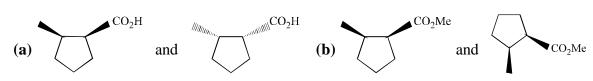
KEY POINT

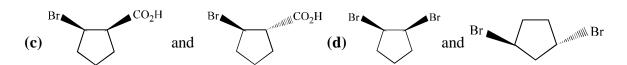
- If any stereo isomer is optically active of a compound then compound will show optical isomerism.
- Chiral amines are non resolvable at room temperature due to amine flipping.
- All physical properties of enantiomers except direction of optical rotation are same.

$$\begin{array}{c|c}
 & CH_3 \\
 & H - C \\
 & C \\
 & C_2H_5
\end{array}$$

The compound with the above configuration is called:

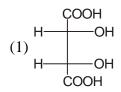
- (A) (2S, 3S)-2-chloro-3-hydroxypentane
- (B) (2S, 3R)-2-chloro-3-hydroxypentane
- (C) (2R, 3R)-2-chloro-3-hydroxypentane
- (D) (2R, 3S)-2-chloro-3-hydroxypentane
- 2. Find out the total number of cyclic isomers of C_6H_{12} which are optically active?
- 3. How many enantiomers are possible on monochlorination of isopentane.
- **4.** Write the structure of:
 - (i) (E) penta-1,3-diene
- (ii) (2Z, 4E)hexa-2,4-diene
- (iii) (2E, 4E)-3-ethylhexa-2,4-diene
- (iv) (R)-2-Bromopentane
- (v) (S)-3-bromo-3-chlorohexane
- (vi) (2S, 3R)-2,3-dibromobutane
- **5.** What are the relationships between the following pairs of isomers?

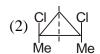




Illustrations

Illustration 11. Mark meso isomers among following







Solution

(1), (2), (4) and (5)

Illustration 12.Which of the following is optically active –

(A)
$$CH_3$$
— CH = C = CH — CH_3

(B)
$$CH_2 = C = CH_2$$

(C)
$$_{Br}^{Cl} > C = C < _{Br}^{Cl}$$

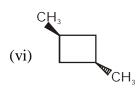
(D)
$$\underset{Et}{\text{Me}} > C = C = C < \underset{Br}{\text{Cl}}$$

Solution

(A), (C) and (D)

Q.1 Select chiral molecules out of following:-

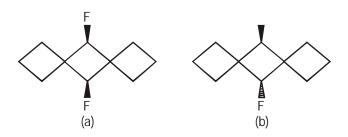
$$(v) = N = N$$



Ans.

(i) achiral (ii) achiral (iii) chiral (iv) chiral (v) achiral (vi) achiral (vii) chiral (viii) chiral (ix) achiral

Q. 2 Identify POS and COS if present:-



Ans. (a)
$$POS = \sqrt{COS} = x$$

(b) POS =
$$\sqrt{}$$

$$COS = \sqrt{}$$

Q. 3 Identify relationship between following molecules:-

$$(d) \underset{Et}{\overset{CH_3}{\longrightarrow}} CH_3 \qquad CH_3$$

(c) diastereomer (d) diastereomer

Q.4 Identify relationship:-

Q.5 Identify POS or COS if present

$$(A) \bigcup_{CI}^{H} C = C = C = C \bigcup_{H}^{CI}$$

(B)
$$C = C = C = C$$

Ans.

POS

COS

G.I.

Optically active

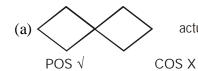
1.

2.

 \mathbf{X}

 \mathbf{X} X

Q.6 Spiro compound



actual 3D

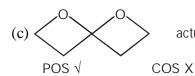


Optically inactive

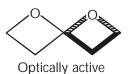
(b)
$$\bigcirc$$
 actor \bigcirc COS X

actual 3D





actual 3D

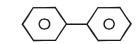




actual 3D



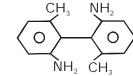
Q.7 (1)



(2)

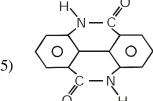
$$\begin{array}{c|c}
SO_3H & NO_2 \\
\hline
O & O \\
NO_2 & SO_3H
\end{array}$$

(3)



(4)

(5)



Ans. (1) inactive (2) active (3) active (4) inactive (COS present)

(5) inactive (planar)

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- (P) POS
- (Q) COS



(R) Resolvable



(S) Non-resolvable

Ans. (A) \rightarrow P, S;

- $(B) \rightarrow R; \quad (C) \rightarrow P, S \ (D) \rightarrow P, Q, S$

EXERCISE # O-I

Single Correct Type:

- 1. Minimum number of carbon atom required by a Hydrocarbon alkane, alkene and alkyne to show chain isomerism respectively are:
 - (A) 4, 4, 4
- (B) 4, 3, 3
- (C) 4, 4, 3
- (D) 4, 4, 5

SR0001

- How many structural isomers of primary amines are possible for the formula C₄H₁₁N? 2.
 - (A) 2

- (B) 3
- (C) 4
- (D) 5

SR0003

- **3.** Maximum potential energy is associated with which of the following conformers of n-butane:
 - (A) Anti
- (B) Gauche
- (C) Eclipsed
- (D) Partial eclipsed

SR0006

- 4. Which among the following will show geometrical isomerism:
- (A) $\stackrel{\text{H}_3\text{C}}{\smile}$ (B) $\stackrel{\text{H}}{\smile}$ OH $\stackrel{\text{CH}_3}{\smile}$ (C) $\stackrel{\text{C}}{\smile}$ CH=N-OH (D) All of these

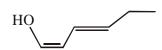
SR0008

- 5. Which one of the following is Z isomer:

- $(A) \xrightarrow{CH_3} C = C \xleftarrow{Br} (B) \xrightarrow{CH_3} C = C \xleftarrow{Cl} (C) \xrightarrow{CH_3} C = C \xleftarrow{Cl} (D) \xrightarrow{CH_3} C = C \xleftarrow{H} CH_3$

SR0009

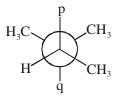
6. The correct stereochemical descriptions for the structure given below are:



- (A) 1 Z, 3Z
- (B) 1Z, 3E
- (C) 1E, 3E
- (D) 1E, 3Z

SR0010

7. What is the value of p & q of following conformer of 2,3-dimethyl butane?



(A)
$$p = H, q = H$$

(A)
$$p = H$$
, $q = H$ (B) $p = CH_3$, $q = CH_3$ (C) $p = CH_3$, $q = H$ (D) $p = H$, $q = CH_3$

(D)
$$p = H, q = CH_3$$

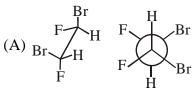
SR0011

8. Which of the following can not show geometrical isomerism:

$$(A) \begin{picture}(60,0) \put(0,0){\line(1,0){0.5ex}} \put(0,0){\line(1,0){0$$

SR0013

9. Which of the following pairs of compound is/are identical?



$$(B) \begin{array}{cccc} CH_3 & & I \\ Cl & H & CH \end{array}$$

$$(C) \begin{array}{c} Cl & CH_3 \\ H & CH_3 & Cl \\ H & CH_3 & Cl \\ Cl & CH_3 \end{array}$$

(D)
$$Br$$
 Cl
 H
 H
 H
 H
 H
 H
 H
 H

SE0078

10. Which of the following cannot be represent in E or Z



$$(D) \longrightarrow N \bigvee_{OH}$$

SR0018

11. H H H H H A C CH₂-CH=CH₂

(A) Geometrical isomer

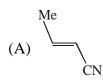
(B) Ring chain isomer

(C) Position isomer

(D) Chain isomer

SR0019

12. Which of the following will have lowest dipole moment?



SR0022

13. Which of the following compounds can show geometrical isomerism in its resonating structure.

SR0023

14. Which of the following represent Z-isomer?

(A)
$$C = C$$
 $O - CH_2 - CH_3$ $O - CH_3$

$$(B) \xrightarrow{CH_3-CH_2} C=C \xrightarrow{C} C$$

$$CH_3-CH_2 C=C$$

$$CH_3-CH_2 C=C$$

$$(C) \int_{F}^{C=C} c = C$$

$$(D) \int_{D}^{H} C = C \int_{HC = CH_2}^{C \equiv CH}$$

SR0024

15. Which of the following compound will not shows geometrical isomerism?

(A) Ph –CH =N –Me (B)
$$(C)$$
 (D) (D) (CH_3)

SR0030

Assertion / Reasoning Type:

16. Statement-1: All double bond containing compounds show geometrical isomerism. *and*

Statement-2: Alkenes have restricted rotation about the carbon-carbon double bond.

- (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.

SR0032

17. **Statement-1:** According to CIP sequence rule the priority of the groups is

$$-CH = CH_2 < -C \equiv CH < -C \equiv N < -CH = O$$

and

Statement-2: Priority of the given groups are based on molecular mass of groups.

- (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

SR0033

Ε

Comprehension Type:

Paragraph for Q. 18 to 19

Different spatial arrangements of the atoms that result from rotation about a single bond are conformers. n-Butane has four conformers eclipsed, partial eclipsed, gauche and anti. The stability order of these conformers are as follows:

Anti > gauche > Partial eclipsed > Fully eclipsed

Although anti is more stable than gauche but in some cases gauche is more stable than anti.

Which one of the following is the most stable conformer? **18**.

(D)
$$H \longrightarrow CH_3$$
 CH_3

SR0034

- Number of possible conformations of n-butane is: **19**.
 - (A) 2

- (B) 4
- (C) 6
- (D) infinite

SR0034

Matrix Match Type:

Match the column I with column II.

Column-I (reaction)

(A) & \rightarrow CI

Column-II (stereoisomers)

(P) Homologs

(Q) Functional isomers

- (R) Metamer
- $-O-CH_3$ & $CH_3-O-CH_2-CH_3$ (S) Position isomers

SR0035

21. Match the column I with column II.

Column-I

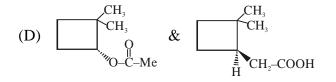
(A)
$$\underset{\text{Et}}{\overset{\text{Cl}}{\bigvee}}$$
 & $\underset{\text{Me}}{\overset{\text{Cl}}{\bigvee}}$

Column-II

(P) Identical

(Q) Functional isomers

(R) Geometrical Isomers



(S) Positional Isomers

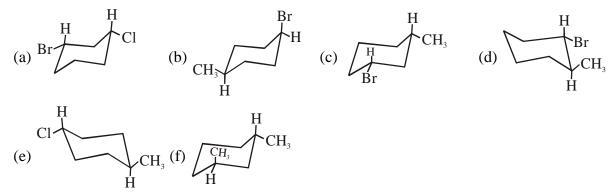
SR0036

Subjective Type:

- **22.** Considering rotation about the C_3-C_4 bond of 2-methylhexane :
 - (a) Draw the Newman projection of the most stable conformer
 - (b) Draw the Newman projection of the least stable conformer

SR0037

23. Determine whether each of the following compounds is a cis isomer or a trans isomer.

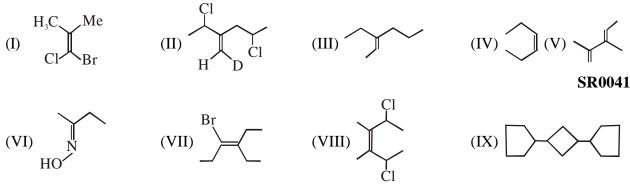


SR0038

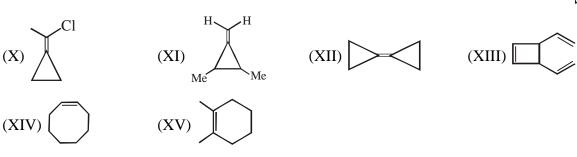
24. Draw the most stable conformer of N-methylpiperidine.

SR0039

25. Identify molecules which usually can show geometrical isomerism (at room temperature):



SR0042



SR0043

26. Calculate the number of Benzenoid isomers possible for C₆H₃ClBrI.

SR0044

Assign E or Z to the following compounds and write 1 for E and 2 for Z.

SR0045

Write answer of part (a), (b), (c) & (d) in the same order and present the four digit number as answer in OMR sheet. For example: If all these answer are 9 then fill 9999 in OMR sheet.

28. Number of geometrical isomers of the following compound.

$$C_{6}H_{5} - CH = CH - CH = CH - C = C = C = CH_{2}$$

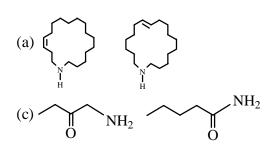
SR0046

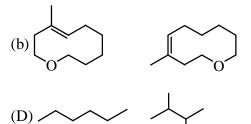
29. Total number 2° and 3° Alcohols possible for $C_5H_{11}OH$. without counting stereo isomers.

SR0046

Write answer of part (a) & (b) in the same order and present the four digit number as answer in OMR sheet. For example: If your Answer for (a) is 9 & (b) is 9 then fill 0909 in OMR sheet.

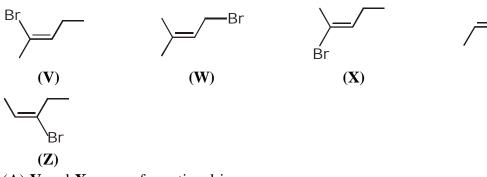
- **30.** Analyse the following pairs of compounds.
 - Write 1 if they are Geometrical isomers.
 - Write 2 if they are Chain isomers.
 - Write 3 if they are position isomers.
 - Write 4 if they are Functional group isomers.





SR0047

31. Which one of the following statements concerning compounds V-Z is true:



- (A) V and X are conformational isomers
- (B) Y and Z are constitutional isomers
- (C) **X** and **Y** are constitutional isomers
- (D) V and Y are stereoisomers

SE0001

- **32.** Which of the following compound has no isomer?
 - (A) CH₃CH₂CH₂Cl
- (B) CH₃CHO
- (C) CH₂=CH-Cl
- (D) ClCH,CH,Cl

(Y)

SE0002

- **33.** Compound CH₂Cl₂ contain :
 - (A) Plane of symmetry

(B) Centre of symmetry

(C) Axis of symmetry

(D) Both (A) & (C)

SE0003

- **34.** Number of POS present in CH₄:
 - (A) 3

- (B) 4
- (C) 5
- (D) 6

SE0004

35. How many stereoisomers of the following molecule are possible?

(A) Two optical isomers

- (B) Two geometrical isomers
- (C) Two optical and two geometrical isomers (D) None

36. The number of cis-trans isomer possible for the following compound.

(A) 2

- (B) 4
- (C) 6
- (D) 8

SE0006

- 37. $\stackrel{\text{N}}{\bigcup}$ has 'x' chiral centre then find the value of x :
 - (A) 7

(B) 8

- (C) 6
- (D) 5

SE0007

- 38. H OH C_2H_5 C_2H_5 C_2H_5 C_2H_5 C_2H_5 C_2H_5 C_2H_5 C_2H_5 C_2H_5 C_3
 - (A) Diastereomers
- (B) Enantiomers
- (C) Identical
- (D) Constitutional isomers

SE0008

- **39.** The number of optically active compounds in the isomers of C_4H_9Br is :
 - (A) 1

- (B) 2
- (C) 3
- (D) 4

SE0009

40. Compound have :

$$\begin{array}{c} CH_3 \\ H_{M_{H_0}} \\ H \end{array}$$

(A) Plane of symmetry

(B) Centre of symmetry

(C) Axis of symmetry

(D) None

SE0010

41. Br CHO
F H

COOH

Configuration of compound is:

- (A) 2S, 3S
- (B) 2R, 3S
- (C) 2R, 3R
- (D) 2S, 3R

- 42. Brillian & Climing F have configuration respectively:
 - (A) R, S
- (B) S, S
- (C) S, R
- (D) R, R

SE0012

- **43.** Minimum molecular weight of a hydrocarbon containing minimum number of C-atom to show optical isomerism:
 - (A) 100
- (B) 80
- (C) 68
- (D) 70

SE0013

44. For the given configuration :

Which of the compound/configuration are optically active:

(A) I

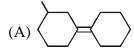
(B) II

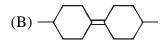
(C) III

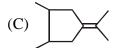
(D) IV

SE0014

45. Compounds which can show both optical as well as geometrical isomerism :



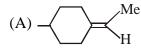


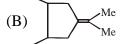


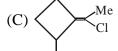
$$(D) \left\langle \bigcirc \right\rangle - \left\langle \bigcirc \right\rangle$$

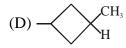
SE0015

46. Which of the following will not show optical isomerism :



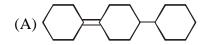


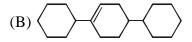


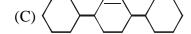


SE0016

47. Optical & geometrical isomerism both can be shown by :-







$$(D) \left\langle \begin{array}{c} \\ \\ \end{array} \right\rangle \left\langle \begin{array}{c} \\ \\ \end{array} \right\rangle$$

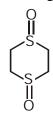
(A) Cl-CH=C=C=CH-Cl

(B) Cl-CH=C=C=CH-Cl

$$(D) \underbrace{\overset{Cl}{\underset{Me}{\bigvee}}^{H}}_{Me}$$

SE0018

49. The correct statement for the given compound is



- (A) It can shows geometrical isomerism
- (B) It can show optical isomerism

(C) It contain chiral centre

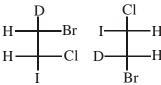
(D) None of these

SE0019

- 50. Meso-tartaric acid and d-tartaric acid are:-
 - (A) Positional isomers (B) Enantiomers
- (C) Diastereomers
- (D) Racemic mixture

SE0020

51. The two compounds given below are:



- (A) Enantiomers
- (B) Diastereomers (C) Optically inactive (D) Identical

SE0021

SE0022

52. Which of the following combinations amongst the four Fischer projections represents the same absolute configurations?

$$CH_3$$
 H
 OH
 $CH=CH_2$
 (I)

$$H \longrightarrow CH_3$$
 $CH = CH_2$
 (II)

$$H \longrightarrow CH_3$$
 $CH = CH_2$ $H \longrightarrow CH = CH_2$ $CH = CH_2$ $H \longrightarrow CH = CH_3$ (II) (IV)

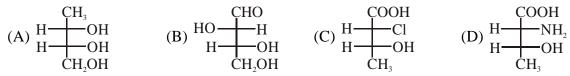
- (A) (II) and (III)
- (B) (I) and (IV)
- (C) (II) and (IV)
- (D) (III) and (IV)

53. The S-ibuprofen is responsible for its pain relveing property. Which one of the structure shown is S-ibuprofen:

(A)
$$\stackrel{\text{Me}}{\underset{\text{Me}}{\longleftarrow}}$$
 $\stackrel{\text{O}}{\underset{\text{C-OH}}{\longleftarrow}}$ $\stackrel{\text{O}}{\underset{\text{C-OH}}{\longleftarrow}}$

$$(B) \stackrel{Me}{\underset{Me}{\longleftarrow}} \underbrace{\bigcirc \stackrel{H}{\underset{CH_3}{\longleftarrow}}_{U}}_{CH_3} H$$

Which of the following is a 'threo' isomer:



$$(D) \stackrel{H}{\underset{CH_{3}}{\longleftarrow}} OH$$

SE0024

55. Number of possible stereoisomers of glucose are :-

SE0025

56. Which of the following is not D sugar:

SE0026

57. Number of chiral centres in [X] & [Y] is a & b respectively. The value of (a–b) is :

$$[X] = \bigcup_{Cl} O \quad [Y] = \bigcup_{Cl} OH \quad OH$$

$$[Y] = \bigcap_{Cl} OH$$

(A) 1

(C)3

(D) 4

SE0027

58. Which one of the following is resolvable:

(B)
$$\begin{array}{c} H \\ CH_3 \end{array}$$
 $\begin{array}{c} CH_3 \end{array}$

(C)
$$H H$$

 $CH_3 CH$

(A)
$$\stackrel{\text{H}}{\longleftarrow}$$
 COOH (B) $\stackrel{\text{H}}{\longleftarrow}$ (C) $\stackrel{\text{H}}{\longleftarrow}$ (D) $\stackrel{\text{H}}{\longleftarrow}$ COOH

SE0028

59. How many stereoisomers can exist for the following acid.

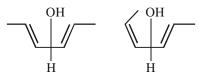
(A) Two

(B) Four

(C) Eight

(D) Six

60. Incorrect relationship between given compounds are



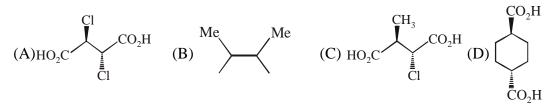
- (A) Both are geometrical isomers
- (B) Both are stereo isomers

(C) Both are enantiomers

(D) Both are diastereomers

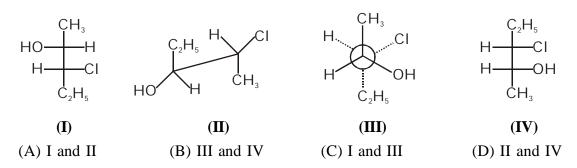
SE0030

61. Identify meso compound.



SE0031

62. The two projection formulae that represent a pair of enantiomers are :-



SE0032

- **63.** A pure sample of 2-chlorobutane shows rotation of PPL by 30° in standard conditions. When above sample is made impure by mixing its opposite form, so that the composition of the mixture becomes 87.5% d-form and 12.5% ℓ -form, then what will be the observed rotation for mixture.
 - $(A) 22.5^{\circ}$
- (B) $+ 22.5^{\circ}$
- $(C) + 7.5^{\circ}$
- (D) -7.5°

SE0033

- **64.** When an optically active compound is placed in a 10 dm tube is present 20 gm in a 200 ml solution rotates the PPL by 30°. Calculate the angle of rotation & specific angle of rotation if above solution is diluted to 1 Litre.
 - (A) $16^{\circ} \& 36^{\circ}$
- (B) $6^{\circ} \& 30^{\circ}$
- (C) 3° & 30°
- (D) $6^{\circ} \& 36^{\circ}$

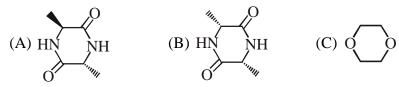
SE0034

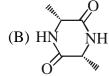
- **65.** Identify % optical purity if 6 gm (+)-2-butanol is mixed with 2 gm (-)-2-butanol.
 - (A) 50 %
- (B) 66.6 %
- (C) 33.3 %
- (D) 75 %

- A mixture of d and ℓ , 2-bromobutane contain 75% d-2-bromobutane. Calculate enantiomeric excess. 66.
 - (A) 75%
- (B) 25%
- (C) 50%
- (D) 100%

SE0036

67. Which of the following is example of meso compound?







$$(D) \left\langle \begin{array}{c} NH \\ NN \end{array} \right\rangle$$

SE0037

- Which of the following has $C_2 & C_3$ axis of symmetry? **68.**

SE0038

69. Configuration of I & II respectively will be:

- (A) D, D
- (B)L,D
- (C) D, L
- (D) L, L

SE0039

- (A) Enantiomers
- (B) Conformation
- (C) Identicle
- (D) Diastereomers

EXERCISE # O-II

Single correct Option Type:

- Molecular formula C₅H₁₀O can have :
 - (A) 6-Aldehyde, 4-Ketone

(B) 5-Aldehyde, 3-Ketone

(C) 4-Aldehyde, 3-Ketone

(D) 5-Aldehyde, 2-Ketone

SE0041

2. In the given halogenoalkene M, atoms X, Y and Z represents hydrogen or bromine or chlorine. To show cis-trans isomerism, what could be the identities of atoms X, Y and Z?

	X	Y	Z
1	Cl	Н	Cl
2	Н	Br	Cl
3	Н	Br	Н

- (A) 1, 2 and 3
- (B) 1 and 2 only
- (C) 2 and 3 only
- (D) 1 and 3 only

SE0042

Statement–1 : H—Et is a chiral resolvable molecule. **3.**

Statement–2: H—Et is non-superimposable on its mirror image.

- (A) Statement–1 is true, Statement–2 is true; Statement–2 is not the correct explanation of Statement–1
- (B) Statement–1 is true, Statement–2 is true; Statement–2 is the correct explanation of Statement–1
- (C) Statement-1 is true, Statement-2 is false
- (D) Statement–1 is false, Statement–2 is true

SE0043

4. Total number of stereoisomer of following compounds are respectively:-

(A) 4, 6

(B) 8

(C) 6,6

(D) 8, 8

- 5. Which of the following compounds are optically active?
 - (A) CH₃.CHOH.CH₂.CH₃

(B) $H_2C=CH.CH_2.CH=CH_2$

(C)
$$H \subset C = C = C \cdot H$$

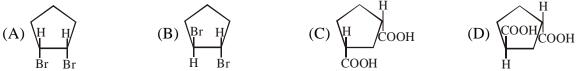
$$(D) \underbrace{ \begin{array}{c} HOOC & NO_2 \\ NO_2 & COOH \end{array}}_{NO_2 COOH}$$

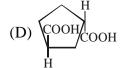
SE0045

Which out the following are Non-resolvable: 6.





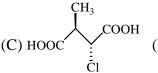


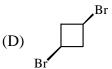


SE0046

7. Identify compound(s) which is/are not meso:

(A) HOOC
$$\stackrel{\text{Cl}}{\underset{\text{Cl}}{\underbrace{}}}$$
 COOH (B) $\stackrel{\text{Me}}{\underset{\text{Cl}}{\underbrace{}}}$ (C) HOOC $\stackrel{\text{CH}_3}{\underset{\text{Cl}}{\underbrace{}}}$ (D) $\stackrel{\text{Br}}{\underset{\text{Br}}{\underbrace{}}}$



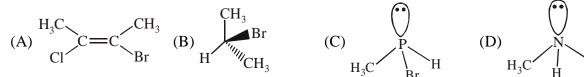


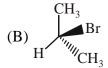
SE0047

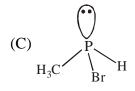
- 8. Which of the following statements for a meso compound is/are correct:
 - (A) The meso compound has either a plane or centre of symmetry
 - (B) The meso compound is optically inactive due to internal compensation.
 - (C) The meso compound is achiral
 - (D) The meso compound is formed when equal amounts of two enantiomers are mixed

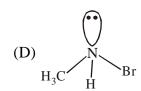
SE0048

9. Among the following the non-resolvable compound is/are:









SE0049

- Compound $\begin{array}{c|c} H & -NH_2 \\ HO & -H \end{array}$ is/are?
 - (A) (2R, 3S), L
- (B) L, Erythreo
- (C) Threo, D
- (D) (2R, 3S), D

11. Relation between compounds are :

(A) I & II = Enantiomers

(B) II & III = Enantiomers

(C) I & II = Identical

(D) II & III = Identical

SE0051

SE0052

13. Identify correct relation between pair of compounds?

Diastereomers

Identical

(C)
$$H$$
 Me
 Me
 OH
&

Diastereomers

Enantiomers

14. Which two of the following compounds represents a pair of enantiomers?

$$(I) \qquad \qquad \bigcup_{i,m} OH$$

(A) I & II

(C) III & IV

SE0054

15. Which two of the following compounds are diastereomers?

(A) I & II

(C) III & IV

(D) I & III

SE0055

16. The correct relation between the following compounds is:

$$C = C = C$$
HO
HO

C = C = C

(A) Enantiomers

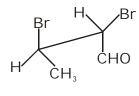
(B) Diastereomers

(C) Homomers (Identical)

(D) Constitutional isomers

SE0056

17. Identify the correct statement regarding following molecules?



(M)

H CHO
CH₃

(N)

Br—H Br—H

СП3

 (\mathbf{O})

(P)

- (A) M and O are diastereomers
- (C) M and N are identical

- (B) N and P are enantiomers
- (D) O and P are diastereomers

Matrix Match Type:

18. Column I

(P) Structural

(B)
$$H \xrightarrow{CH_3} Cl & H \xrightarrow{Cl} CH_3$$

(C)
$$H \longrightarrow OH$$
 & $H_3C \longrightarrow Et$ OH

$$(D) \xrightarrow[H_0]{H_0 C_2} & & \xrightarrow{H_0 C_2} & \\ HO & & & H & \\ HO & & HO & \\ HO & & H & \\$$

(S) Diastereomers

SE0058

19. Match the column

	Column-I		Column-II
(1)	✓ OH & ✓ OH	(P)	Position isomers
(2)	OH & OH	(Q)	Chain isomers
(3)	✓✓OH & ✓OH	(R)	Homologues
(4)	OH CH ₂ OH CH ₃	(S)	Functional isomers

20. Match the column–I

Column-I (Compounds)		Column-II (Total number of stereoisomers)		
(1)	\overline{C}	(P)	8	
(2)	CI	(Q)	4	
(3)	CICICI	(R)	3	
(4)	CI CI	(S)	2	

SE0060

Subjective Type:

21.

What is number of chiral centres present in Diosgenen is:

SE0061

22. Calculate the total number of chrial carbon atoms in.

SE0062

23. Total number of isomeric (including stereo) bromochlorofluoroiodo propadiene.

24. Re-orient the molecule at the left to match the partially drawn perspective at the right. Find the two missing substituents at their correct positions.

$$(A) CH_{2}CH_{3}$$

$$H_{3}CH_{2}CH_{3}$$

$$(B) H$$

$$CH_{2}CH_{3}$$

$$CH_{2}CH_{3}$$

$$H$$

$$CH_{2}CH_{3}$$

- (A) $\mathbf{M} = \mathbf{CH}_3 \mathbf{CH}_2 \mathbf{N} = \mathbf{CH}_3 \mathbf{M}_3 \mathbf{M}_3$
- (B) $\mathbf{X} = \mathbf{CH}_3 \mathbf{Y} = \mathbf{F} \mathbf{Y}$
- (C) $\mathbf{M} = \mathbf{CH}_3 \mathbf{N} = \mathbf{CH}_3 \mathbf{CH}_2 \mathbf{N} = \mathbf{CH}_3 \mathbf{CH}_2 \mathbf{N} = \mathbf{CH}_3 \mathbf{CH}_2 \mathbf{CH}_3 \mathbf{CH}_$
- (D) $\mathbf{X} = \mathbf{F} \mathbf{Y} = \mathbf{CH}_3 \mathbf{Y} = \mathbf{CH}_3 \mathbf{H}_3 \mathbf{H$

SE0064

25. Find out the total number of cyclic isomers of C_6H_{12} which are optically active ?

SE0065

26. How many of the given compounds are chiral:

(i) OH (iii)
$$COOH$$
 (iii) $COOH$ (viii) CO

SE0066

27. With reasons, state whether each of the following compounds I to VIII is chiral

$$(I) \overbrace{ \begin{array}{c} Cl \\ Cl \\ Cl \end{array} }$$

$$(IV) \begin{array}{c} Cl_{M_{N_{0}}} \\ Cl \\ Cl \end{array} C = C = C \\ CO_{2}H \\ Me \\ (V) \\ O \\ O$$

28. How many cyclopentane structures (including stereo) are possible for C_7H_{14} .

SE0068

29. The number of diastereoisomers (excluding enantiomers) for 1-bromo-2-chloro-3-iodocyclopropane.

SE0069

30. Identify total number of stereoisomers for the following compound:

SE0070

31. How many of the given molecule / species are chiral:

SE0071

32. Total geometrical isomers possible for :

(A) 3

(B) 4

(C) 5

(D) 8

SE0072

Ε

EXERCISE # S-I

Single Correct Type:

The correct statements describing the relationship between:

$$R_2CH - N \bigcirc O$$
 $R_2CH - N \bigcirc O$ $R_2CH - N \bigcirc O$

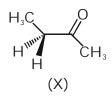
$$R_2CH - N O$$
(Y)

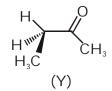
$$R_2C = N OH$$

- (A) X and Y are resonance structures and Z is a tautomer
- (B) X and Y are tautomers and Z is resonance structure
- (C) X, Y and Z are all resonance structures
- (D) X, Y and Z all are tautomers

SE0073

2. The correct statements about conformations X and Y of 2-butanone are:





- (a) **X** is more stable than **Y**
- (b) Y is more stable than X
- (c) Methyl groups in **X** are anti
- (d) Methyl groups in Y are gauche
- (A) a and d

(B) a and c

(C) b and c

(D) a, c and d

SE0074

Among the following, the number of molecules that possess C2-axis of symmetry is : **3.**

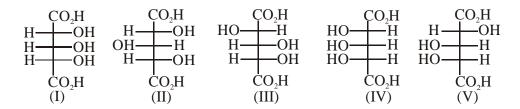




$$CH_4$$
, $CI = CI$, BF_3 ,

CHCl₃, 2,5-dimethylthiophene,
$$CI$$
H
 $C = C = C$

4. Observe the given compounds and answer the following questions.



- (i) Which of the above formulae represent identical compounds?
- (A) I and II
- (B) I and IV
- (C) II and IV
- (D) III and IV
- (ii) Which of the above compounds are enantiomers?
- (A) II and III
- (B) III and IV
- (C) III and V
- (D) I and V

SE0076

5. Which of the following option is correct regarding the given compounds :

(A) Both are identical

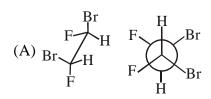
(B) Both are optically inactive

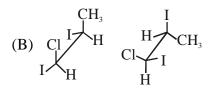
(C) Both are enantiomers

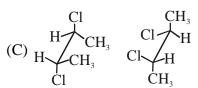
(D) Geometrical isomer

SE0077

6. Which of the following pairs of compound is/are identical?







 $(D) \xrightarrow{\text{Br}} Cl \xrightarrow{\text{H}} H \xrightarrow{\text{H}} H$

SE0078

Multiple Correct Type:

- **7.** Which of the following statements is/are not correct for D-(+) glyceraldehyde:
 - (A) The symbol D indicates the dextrorotatory nature of the compound
 - (B) The sign(+) indicates the dextrorotatory nature of the compound
 - (C) The symbol D indicates that (–OH) group lies left to the chiral centre in the conventionally correct Fischer projection diagram
 - (D) The symbol D indicates that (–OH) group lies right to the chiral centre in the conventionally correct Fischer projection diagram

SE0079

Ε

8. Which of the following are correct representation of L-amino acids:

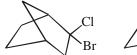
(A)
$$H_2N$$
 COOH CH_2OH

(A)
$$H_2N$$
 $\stackrel{COOH}{\longrightarrow}$ (B) H^{NH_2} $\stackrel{NH_2}{\longrightarrow}$ $\stackrel{OH}{\longrightarrow}$ \stackrel

(C) Diastereomers

SE0080

9. Identify relation between these two compounds:



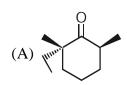
(B) Enantiomers



(D) Positional Isomers

SE0081

10. Which of the following undergoes racemisation in alkaline medium?



(A) Homomers

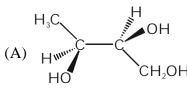






SE0082

Which compound is different from the others? 11.

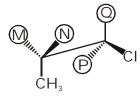


CH,OH

$$(D) \begin{array}{c} HOCH_2 \\ HOCH_3 \\ HOCH_4 \end{array}$$

SE0083

12.



(Y)

(X)

What would be the correct match to get (Y) as a diastereomers of (X)?

(A) $\mathbf{M} = -\mathbf{H}$

N = -Br

 $\mathbf{Q} = -\mathbf{Ph}$ P = -H

- (B) $\mathbf{M} = -\mathbf{H}$ N = -Br
- $\mathbf{P} = -\mathbf{Ph}$

- (C) $\mathbf{M} = -\mathbf{Br}$
- $\mathbf{Q} = -\mathbf{Ph}$

- (D) $\mathbf{M} = -\mathbf{Br}$
- $\mathbf{Q} = -\mathbf{H}$

- N = -H

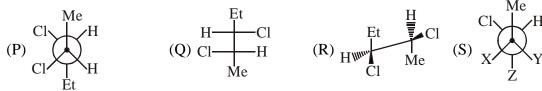
- N = -H
- $\mathbf{P} = -\mathbf{Ph}$

ALLEN

Comprehension Type:

Paragraph for Question 13 to 14

Four compounds are given below 'S' is a stereoisomer of P.



- **13.** P & Q are related as:
 - (A) Identical
- (B) Enantiomer
- (C) Diastereomer
- (D)Positional isomerism

SE0085

- 14. Which of the above structures represented is Sawhorse projection:
 - (A) P

- (B) Q
- (C) R
- (D) S

SE0086

Paragraph for Question 15 to 17

S(+) Mono sodium Glutamate (MSG) is a flavour enhancer used in many foods. Fast foods often contain substantial amount of MSG and is widely used in Chinese food. If one mole of above MSG was placed in 845 ml solution and passed through 200 mm tube, the observed rotation was found to be $+9.6^{\circ}$.

- **15.** Find out the specific rotation of (–) MSG:
 - $(A) + 24^{\circ}$
- $(B) + 56.8^{\circ}$
- $(C) 48^{\circ}$
- (D) None of these

SE0087

- **16.** Find out the approximate percentage composition of (–) MSG in a mixture containing (+) MSG and (–) MSG whose specific optical rotation is -20° :
 - (A) 83.3%
- (B) 16.7%
- (C) 91.6%
- (D) 74%

SE0088

- **17.** If 33.8 g of (+) MSG was put in 338 ml solution and was mixed with 16.9g of (-) MSG put in 169 ml solution and the final solution was passed through 400 mm tube. Find out observed rotation of the final solution :
 - $(A) + 1.6^{\circ}$
- (B) $+4.8^{\circ}$
- (C) $+3.2^{\circ}$
- (D) None of these

82

Paragraph for Q.18 to Q.19

Among the following structures?

$$(V) \underbrace{ \begin{pmatrix} Cl \\ V \\ Cl \end{pmatrix} }_{Cl}$$

$$(VII) \prod_{I}^{F} C = C = C = C \left\langle \begin{array}{c} Cl \\ Br \end{array} \right.$$

- 18. Optically active compound is -
 - (A) III
- (B) IV
- (C) V
- (D) VII

SE0090

- **19.** Which of the following will not show optical isomerism -
 - (A) I

- (B) II
- (C) V
- (D) VIII

SE0091

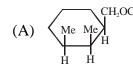
Matrix Match Type:

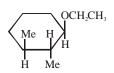
20. Column-I

(Compounds)

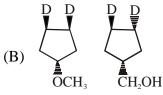
Column-II

(Relation)

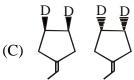




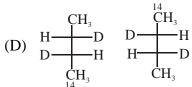
(P) Metamers



(Q) Functional Isomer



(R) Geometrical isomer



- (S) Enantiomer
- (T) Diastereomer

List - I

List - II

(A)
$$\begin{array}{c} Br \longrightarrow H \\ HO \longrightarrow H \\ CH_3 \end{array}$$

(1)
$$HO \longrightarrow CH_3$$
 CH_3
 Br

(B)
$$HO \xrightarrow{CH_3} H$$
 $Br \xrightarrow{CH_3} H$
 CH_3

(B)
$$HO \xrightarrow{CH_3} H$$
 (2) $Br \xrightarrow{CH_3} CH$ CH_3 CH_3

(C)
$$H \xrightarrow{CH_3} OH$$
 CH_3

(C)
$$H \longrightarrow OH$$
 (3) $OH \longrightarrow CH_3$ (iii) (2S,3R)

(D)
$$HO \xrightarrow{CH_3} H$$
 CH_3 CH_3

(D)
$$HO \xrightarrow{CH_3} H$$
 $H \xrightarrow{Br} CH_3$ (4) $H \xrightarrow{Br} C \xrightarrow{CH_3} CH_3$

SE0093

Subjective Type:

In what stereoisomeric forms would you expect the following compounds to exist?

(a) EtCH(CO₂H)Me

(b) MeCH(CO₂Et)CO₂H



(e)
$$H$$
 C=C=C=C H

(f) Et(Me)C=C=C(Me)Et

$$(h) \bigotimes_{Br}^{I} \bigotimes$$

$$(J) \bigoplus_{H}^{CH^3}$$

SE0094

Calculate the number of Benzenoid isomers possible for C₆H₃ClBrI. 23.

24. What are the relationships between the following pairs of isomers?

SE0096

SE0097

$$(g) \overset{H}{\underset{CH_{3}}{\longleftarrow}} \overset{H}{\underset{Ph}{\longleftarrow}} \text{ and } \overset{H}{\underset{H}{\longleftarrow}} \overset{Cl}{\underset{Ph}{\longleftarrow}} \text{ (h)} \overset{H}{\underset{HO}{\longleftarrow}} \overset{H}{\underset{OH}{\longleftarrow}} \text{ and } \overset{HO}{\underset{H}{\longleftarrow}} \overset{OH}{\underset{H}{\longleftarrow}}$$

SE0098

$$25. \quad X \xrightarrow{2H_2}$$

Find out total number of structures of X.

SE0099

26. Calculate the number of chiral center in the molecule Ethyl 2,2-dibromo-4-ethyl-6-methoxy cyclohexane carboxylate.

SE0100

27. Calculate the total number of stereoisomers possible for

SE0101

(iii)
$$H$$
 C=C=C CH =CH-CH₃

SE0103

85

SE0104

SE0105

(ix)
$$EtO-P$$

$$OEt$$

$$(x)$$

$$OH$$

$$(xi)$$

SE0106

28. How many different chloroethanes are there from the formula $C_2H_{6-n}Cl_n$ (where n can be any integer from 1 to 6)?

SE0107

Ε

EXERCISE # J-MAINS

1. Geometrical isomerism is not shown by-

[AIEEE-2002]

- (1) 1,1–dichloro–1–pentene
- (2) 1,2-dichloro-1-pentene
- (3) 1,3–dichloro–2–pentene
- (4) 1,4-dichloro-2-pentene

SR0048

2. Recemic mixture is formed by mixing two: [AIEEE-2002]

(1) Isomeric compounds

(2) Chiral compounds

(3) Meso compounds

(4) Enantiomers with chiral carbon

SE0108

3. Following types of compounds I and II [AIEEE-2002]

- (I) CH₃CH=CHCH₃
- (II) CH_3 —CH—OH, are studied in terms of isomerism in CH_2CH_3
- (1) Chain isomerism

(2) Position isomerism

(3) Conformers

(4) Stereo isomerism

SE0109

4. Among the following four structures I to IV [AIEEE-2003]

It is true that-

- (1) All four are chiral compounds
- (2) Only I and II are chiral compounds
- (3) Only III is a chiral compound
- (4) Only II and IV are chiral compounds

SE0110

5. Which of the following will have a meso-isomer also[AIEEE-2004]

(1) 2–chlorobutane

(2) 2,3–dichlorobutane

(3) 2,3–dichloropentene

(4) 2-hydroxy propanoic acid

(1)
$$CH_3$$
— CH_2 — $C \equiv CH$

[AIEEE-2004]

(3)
$$CH_3 - C - C_2H_5$$

SE0112

7. Which of following compounds is not chiral [AIEEE-2005]

(1) 1-chloropentane

- (2) 2-chloropentane
- (3) 1-chloro-2-methyl pentane
- (4) 3-chloro-2-methyl pentane

SE0113

8. Of the five isomeric hexanes, the isomer which can give two monochlorinated compounds is:

(1) 2-methyl pentane

(2) 2,2–dimethyl butane

[AIEEE-2005]

(3) 2,3–dimethyl butane

(4) n-hexane

SE0114

9. Which types of isomerism is shown by 2,3–dichloro butane[AIEEE-2005]

- (1) Structural
- (2) Geometric
- (3) Optical
- (4) Diastereo

SE0115

10. Increasing order of stability among the three main conformations (i.e. Eclipse, Anti, Gauche) of 2-fluoroethanol is [AIEEE-2006]

(2) Eclipse, Anti, Gauche

(1) Gauche, Eclipse, Anti (3) Anti, Gauche, Eclipse

(4) Eclipse, Gauche, Anti

SR0049

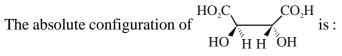
Which one of the following conformations of cyclohexane is chiral? 11.

[AIEEE-2007]

- (1) Twist boat
- (2) Rigid
- (3) Chair
- (4) Boat

SE0142

12.



[AIEEE-2008]

- (1) S, S
- (2) R, R
- (3) R, S
- (4) S, R

SE0116

The alkene that exhibits geometrical isomerism is:-**13.**

[AIEEE-2009]

(1) 2-butene

(2) 2-methyl-2-butene

(3) Propene

(4) 2–methyl propene

SR0051

(1)4

- (2) 6
- (3) 3
- (4) 2

SR0117

- 15. Out of the following, the alkene that exhibits optical isomerism is :-
- [AIEEE-2010]

(1) 2-methyl-2-pentene

(2) 3-methyl-2-pentene

(3) 4-methyl-1-pentene

(4) 3-methyl-1-pentene

SE0118

16. Identify the compound that exhibits tautomerism:

[AIEEE-2011]

- (1) 2-Pentanone
- (2) Phenol
- (3) 2-Butene
- (4) Lactic acid

SR0052

17. The IUPAC name of the following compounds is :

[JEE-MAIN-2012]

- (1) (Z) 5 hepten -3 yne
- (2) (Z) 2 hepten -4 yne
- (3) (E) -5 hepten -3 yne
- (4) (E) 2 hepten 4 yne

SR0053

[JEE-MAIN 2012]

[JEE-MAIN 2012]

- **18.** Dipole moment is shown by :-
 - (1) trans-2, 3-dichloro- 2-butene
 - (3) 1, 4-dichlorobenzene

- (2) 1, 2-dichlorobenzene
- (4) trans-1, 2-dinitroethene

SR0054

- 19. Maleic acid and fumaric acids are:-
- 0) (1) :-- :-- :--

(1) Tautomers

(2) Chain isomers

(3) Geometrical isomers

(4) Functional isomers

SR0055

20. Monocarboxylic acids are functional isomers of :

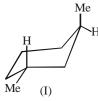
[JEE-MAIN 2013]

- (1) Esters
- (2) Amines
- (3) Ethers
- (4) Alcohols

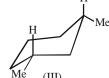
SR0056

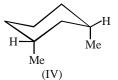
21. Arrange in the correct order of stability (decreasing order) for the following molecules:

[JEE-MAIN 2013]



H Me Me





- (1) (I) > (II) > (III) > (IV)
- (II)
- $(2) (IV) > (III) > (II) \approx (I)$

(3) (III) > (I) \approx (II) > (IV)

 $(4) (I) > (II) \approx (III) > (IV)$

SR0057

22. For which of the following molecule significant $\mu \neq 0$

[JEE-MAIN 2014]







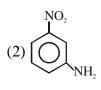


- (1) Only (III)
- (2) (III) and (IV)
- (3) Only (I)
- (4) (I) and (II)

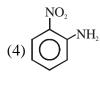
SR0058

23. Which compound exhibits maximum dipole moment among the following :-[JEE-MAIN 2015]









SR0059

24. The number of structural isomers for C_6H_{14} is:

[JEE-MAIN 2015]

- (1)6
- (2) 4
- (3) 3
- (4) 5

SR0060

25. The optically inactive compound from the following is:-

[JEE-MAIN-2015]

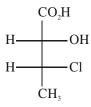
(1) 2-chloropropanal

- (2) 2-chlorobutane
- (3) 2-chloro-2-methylbutane
- (4) 2-chloropentane

SE0119

26. The absolute configuration of :

[JEE-MAIN-2016]



- (1)(2R, 3R)
- (2)(2R, 3S)
- (3)(2S, 3R)
- (4)(2S, 3S)

90

EXERCISE # JEE-ADVANCED OBJECTIVE

1. The H_3C C=C H shows: [IIT-1995]

(A) Geometrical isomerism

- (B) Optical isomerism
- (C) Geometrical & optical isomerism
- (D) tautomerism

SE0125

2. When cyclohexane is poured on water, it floats, because :

[IIT-1997]

- (A) cyclohexane is in 'boat' form
- (B) cyclohexane is in 'chair' form
- (C) cyclohexane is in 'crown' form
- (D) cyclohexane is less dense than water

SR0063

- 3. How many optically active stereoisomers are possible for butane -2,3-diol: [IIT-1997]
 - (A) 1

- (B) 2
- (C) 3
- (D) 4

SE0126

- 4. The number of possible enantiomeric pairs that can be produced during monochlorination of 2-methyl butane is:

 [IIT-1997]
 - (A) 2

- (B) 3
- (C) 4
- (D) 1

SE0127

- 5. Which of the following compounds will show geometrical isomerism: [IIT-1998]
 - (A) 2-butene

(B) propene

(C) 1-phenylpropene

(D) 2-methyl-2-butene

SR0064

- **6.** Which of the following compound will exhibits geometrical isomerism : [IIT-2000]
 - (A) 1-phenyl-2-butene

(B) 3-phenyl-1-butene

(C) 2-phenyl-1-butene

(D) 1, 1-diphenyl-1-propene

SR0065

- 7. The number of isomers for the compound with molecular formula C₂BrClFI is : [IIT-2000]
 - (A) 3

- (B) 4
- (C) 5
- (D) 6

SR0066

- **8.** Which of the following has the lowest dipole moment : [IIT-2000]
 - $(A) \xrightarrow{CH_3} C = C \xrightarrow{CH}$

(B) CH_3 –C=C– CH_3

(C) $CH_3CH_2C\equiv CH$

(D) CH₂=CH−C≡CH

SR0067

$$CH_3$$
 CH_3 $HO \longrightarrow H$ $HO \longrightarrow H$ OH CH_3 CH_3 III

[IIT-2000]

SE0128

Which of the following compounds exhibits stereoisomerism-**10.**

[IIT-2002]

(A) 2-Methylbutene-1

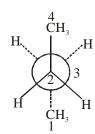
(B) 3–Methylbutyne–1

(C) 3-Methylbutanoic acid

(D) 2-Methylbutanoic acid

SE0129

In the given conformation, If C_2 is rotated about C_2 – C_3 bond anticlockwise by an angle of 120° then 11. the conformation obtained is: [IIT-2004]



- (A) Fully eclipsed conformation
- (B) Partially eclipsed conformation

(C) Gauche conformation

(D) Staggered conformation

SR0068

- **12.** On monochlorination of 2-methylbutane, the total number of chiral compounds formed is :
 - (A) 2

- (B) 4
- (C) 6
- (D) 8

[IIT-2004]

SE0130

13. (i)
$$\mu_{obs} = \sum_{i} \mu_{i} x_{i}$$

where μ_i is the dipole moment of a stable conformer of the molecule, Z–CH $_2$ –CH $_2$ –Z and \boldsymbol{x}_i is the [IIT- 2005] mole fraction of the stable conformer.

Given: $\mu_{obs} = 1.0 \text{ D}$ and x (Anti) = 0.82

Draw all the stable conformers of Z-CH₂-CH₂-Z and calculate the value of $\mu_{(Gauche)}$

(ii) Draw the stable conformer of Y-CHD-CHD-Y(meso form), when $Y = CH_3$ (rotation about C_2 – C_3) and Y = OH (rotation about C_1 – C_2) in Newmann projection.

SR0069

The number of structural isomers of C_6H_{14} is: **14.**

[IIT-2007]

(A) 3

- (B) 4
- (C) 5
- (D) 6

SR0070

15. Statement-I: Molecules that are not superimposable on their mirror images are chiral

Statement-II: All chiral molecules have chiral centres.

[IIT-2007]

- (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.

SE0131

16. The correct statement(s) concerning the structures E, F and G is (are)

[IIT-2008]

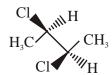
$$H_3C$$
 OH CH_2

$$H_3C$$
 CH_3 OH

- (A) **E**, **F** and **G** are resonance structures
 - (B) **E**, **F** and **E**, **G** are tautomers
- (C) **F** and **G** are geometrical isomers
- (D) **F** and **G** are diastereomers

SE0132

17. The correct statement(s) about the compound given below is (are): [IIT-2008]



- (A) The compound is optically active
- (B) The compound possesses centre of symmetry
- (C) The compound possesses plane of symmetry
- (D) The compound possesses axis of symmetry

SE0133

- **18.** The correct statement(s) about the compound $H_3C(HO)HC - CH = CH - CH(OH)CH_3$ (X) is (are):
 - (A) The total number of stereoisomers possible for X is 6

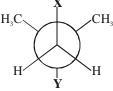
[IIT-2009]

- (B) The total number of diastereomers possible for X is 3
- (C) If the stereochemistry about the double bond in X is trans, the number of enantiomers possible
- (D) If the stereochemistry about the double bond in X is cis, the number of enantiomers possible for X is 2

SE0134

In the Newman projection for 2,2-dimethylbutane **19.**

[IIT-2010]



X and **Y** can respectively be –

- (A) H and H

- (B) H and C_2H_5 (C) C_2H_5 and H (D) CH_3 and CH_3

20. In the Newman projection for 2,2-dimethylbutane [IIT-2010]

X and Y can respectively be -

- (A) H and H

- (B) H and C_2H_5 (C) C_2H_5 and H (D) CH_3 and CH_3

SE0135

21. Amongst the given option, the compound(s) in which all the atoms are in one plane in all the possible conformations (if any), is (are) -[IIT-2011]

(A)
$$H_{,C} - C$$
 CH

(A) $H_{2}C - C_{CH_{2}}$ (B) $H - C = C - C_{CH_{2}}$ (C) $H_{2}C = C = O$ (D) $H_{2}C = C = CH_{2}$

SR0032

Which of the given statement(s) about N,O,P and Q with respect to M is (are) correct? 22.

[JEE-2012]

- (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

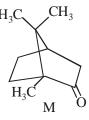
SE0136

23. The total number(s) of **stable** conformers with **non-zero** dipole moment for the following compound is (are) [JEE-2014]

$$\begin{array}{c} Cl \\ Br \longrightarrow CH_3 \\ Br \longrightarrow Cl \\ CH_3 \end{array}$$

SE0137

24. The total number of stereoisomers that can exist for M is: [JEE-2015]



25. In the following monobromination reaction, the number of possible chiral products is: [JEE-2016]

$$H \xrightarrow{CH_2CH_2CH_3} Br \xrightarrow{Br_2(1.0 \text{ mole})} Br$$
 CH_3
 (1.0 mole)
(enatiomerically pure)

SE0139

26. For the given compound X, the total number of optically active stereoisomers is _____.

[IIT-JEE 2018]

This type of bond indicates that the configuration at the specific carbon and the geometry of the double bond is fixed

This type of bond indicates that the configuration at the specific carbon and the geometry of the double bond is NOT fixed

SE0140

27. Total number of isomers, considering both structural and stereoisomers, of cyclic ethers with the molecular formula C₄H₈O is ____[IIT-JEE 2019]

ANSWER-KEY

EXERCISE # O-I

Single Correct Type:

Ans. (C)

- 1. Ans. (D)
- 2. Ans. (C)
- 3. Ans. (C)
- 4. Ans. (D)
- 5. Ans. (A)

6. Ans. (B)

11.

- 7. Ans. (C) 12. Ans. (B)
- 8. Ans. (C) 13. Ans. (D)
- Ans. (C)
 Ans. (B)
- 10. Ans. (D)
 15. Ans. (C)

Assertion / Reasoning Type:

- 16. Ans. (D)
- 17. Ans. (C)

Comprehension Type:

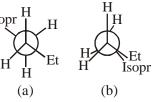
- 18. Ans. (C)
- 19. Ans. (D)

Matrix Match Type:

- 20. Ans. (A) \rightarrow P; (B) \rightarrow R; (C) \rightarrow Q; (D) \rightarrow R
- 21. Ans. (A) \rightarrow R; (B) \rightarrow S; (C) \rightarrow P; (D) \rightarrow Q

Subjective Type:

22. Ans.



23. Ans. (a) cis (b) cis (c) cis (d) trans (e) trans (f) trans

- 24. Ans. CH₃
 - 25. Ans. II, III, IV, V, VI, VIII, IX, XI, XIII, XIV,
- 26. Ans. (10)
- 27. Ans. (2112)
- 28. Ans. (4)
- 29. Ans. (0404)

- **30.** Ans. (a) Geometrical isomers so (1)
- (b) Position isomers so (3)
- (c) Functional isomers so (4)
- (d) Chain isomers so (2)

- 31. Ans. (C)
- 32. Ans. (C)
- 33. Ans. (D)
- 34. Ans. (D)

- 35. Ans. (A)
- **36.** Ans. (A)
- 37. Ans. (A)
- 38. Ans. (D)

39. Ans. (B)

$$C_{4}H_{9}Br \Longrightarrow CH_{3}-CH_{2}-CH_{2}-CH_{2} \\ Br \\ Br \\ CH_{3}-CH_{2}-CH_{3} \\ CH_{3}-CH_{3} \\ CH_{3}-CH_{2}-CH_{2} \\ Br \\ Br \\ Br \\ CH_{3}-CH_{3} \\ CH_{3}-CH_{2}-CH_{2} \\ Br \\ Br \\ Br \\ CH_{3}-CH_{3} \\ CH_{3}-CH_{2}-CH_{2} \\ Br \\ CH_{3}-CH_{3} \\ CH_{3}$$

(Optically active)

Optically active isomers \Rightarrow 2

- **40. Ans. (B)**
- 41. Ans. (D)
- 42. Ans. (A)

43. Ans. (C)

$$H_3C$$

$$C = C = C$$

$$H$$

- 44. Ans. (B)
- 45. Ans. (C)
- 46. Ans. (D)

47. Ans. (C)

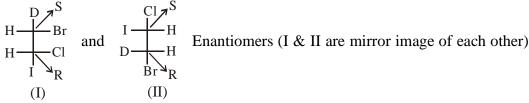
48. Ans. (A)

Cl-CH=C=C=CH-Cl is a planar structure

- 49. Ans. (A)
- 50. Ans. (C)

Meso tartaric acid and d-fartaric acid and not mirror image of each other so they are diastereomers.

51. Ans. (A)



- 52. Ans. (C)
- 53. Ans. (D)
- 54. Ans. (B)

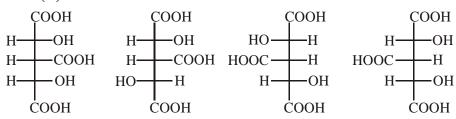
55. Ans. (C)

$$2^n \Rightarrow 2^4 \Rightarrow 16$$

- 56. Ans. (B)
- 57. Ans. (B)
- 58. Ans. (B)

Optically active compounds are resolvable.

59. Ans. (B)



- 60. Ans. (C)
- 61. Ans. (A)

- 62. Ans. (C)
- 63. Ans. (B)

e.e =
$$87.5 - 12.5 \implies 75 \%$$
 of

$$ee = \frac{Rotation by mixture}{Rotation by pure isomer} \times 100$$

$$75 = \frac{X}{30} \times 100$$

$$X = \frac{75 \times 30}{100} = +22.5^{\circ}$$

64. Ans. (B)

$$\ell = 10 \text{ dm}$$

$$c = 20 \text{ gm}/200 \text{ ml}$$

$$\alpha = 30^{\circ}$$

$$\left[\alpha\right]_{\text{specific}} = \frac{\alpha_{\text{obs}}}{c.l} = \frac{30}{\frac{20}{200} \times 10} \implies 30^{\circ}$$

 $\alpha_{\mbox{\tiny obs.}}$ after dilution

$$\alpha_{obs} = \alpha_{sp} c.p.$$

$$\alpha_{\text{obs}} = 30 \times \frac{20}{1000} \times 10 \implies 6^{\circ}$$

65. Ans. (A)

% optical purity =
$$\frac{|d-\ell|}{d+\ell} \times 100 = \frac{4}{8} \times 100 = 50\%$$

Ans. (C) **66.**

67. Ans. (A)

68. Ans. (**D**)

69. Ans. (C)

70. Ans. (A)

EXERCISE # O-II

Single correct Option Type:

1. Ans. (B)

 $C_5H_{10}O:$

Ketones

Total \Rightarrow 5 aldehyde

Total \Rightarrow 3 ketones

2. Ans. (C)

4. Ans. (A)

OH OH OH (Trans, Trans)
$$(ii) \qquad OH \qquad (Cis , Cis)$$

$$(iii) \qquad OH \qquad (Cis , Trans) Two \Rightarrow R + S$$

Total is isomers = 4

$$\Rightarrow$$
 (i) OH OH

(ii)
$$OH$$
 OH $(\underline{+})$ Two

(iii)
$$\underbrace{\hspace{1cm}}^{OH}_{OH}$$
 ($\underline{\pm}$) Two

Total = 6 isomer

- 5. Ans. (A,C,D)
- 6. Ans. (A,C)

Optically active compounds are resolvable and A & C are optically inactive

- 7. Ans (B,C,D)
- 8. Ans. (A,B,C)
- 9. Ans. (A,B,D) 10. Ans. (C,D)

- 11. Ans. (A,D)
- 12. Ans. (A,C)
- 13. Ans. (A,B,C,D) 14. Ans. (C)

- 15. Ans. (D)
- 16. Ans. (C)
- 17. Ans. (D)
- 18. Ans. $A \rightarrow P$; $B \rightarrow R$; $C \rightarrow Q$; $D \rightarrow R$
- 19 Ans. $1 \rightarrow R$; $2 \rightarrow P$; $3 \rightarrow Q$; $4 \rightarrow S$
- 20. Ans. $1\rightarrow S$; $2\rightarrow R$; $3\rightarrow Q$; $4\rightarrow Q$

21. Ans. (11)

22. Ans. (i) 6, (ii) 8

23. Ans. (6)

$$Br$$
 $C = C = C$
 F
 CI
+ Enantiomer

$$CI$$
 Br^{WW}
 $C = C = C$
 I
+ Enantiomer

24. Ans. (A, B)

25. Ans. (8)







4 Optically Active Isomers 2 Optically Active 2 Optically Active

$$2 + 2 + 4 = 8$$

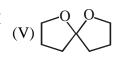
26. **Ans.** (6)





(III)
$$HO_2C$$
 CO_2H

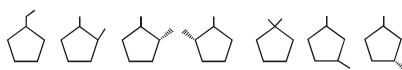
$$(IV) \begin{array}{c} Cl_{M_{I_{n_{i}}}} C = C = C \\ CO_{2}H \end{array} (V) \begin{array}{c} O \\ O \end{array}$$





27. Ans. Achiral: I, III, IV; chiral: II, V, VI, VII

28. Ans. (8)



Ans. (4) **29.**









30. Ans. (8)

Stereogenic centre = 3

total number of stereoisomer = $2^3 = 8$

Ε

EXERCISE # S-I

Single Correct Type:

1. Ans. (A)

2. Ans. (D)

3. Ans. (8)

4. Ans. (i) (B); (ii) (C)

5. Ans. (C)

6. Ans. (C)

Multiple Correct Type:

7. Ans. (A,C)

8. Ans. (A,C,D)

9. Ans. (C)

10. Ans. (C)

11. Ans. (B)

12. Ans. (A,D)

Comprehension Type:

13. Ans. (B)

14. Ans. (C)

15. Ans. (D)

M.W. of MSG = 169

$$C = \frac{169 \text{ gm}}{845 \text{ ml}}$$

$$\ell=200~mm=2~dm$$

$$\alpha_{obs} = +9.6^{o}$$

$$[\alpha]_{sp} = \frac{\alpha_{obs}}{C.\ell.} = \frac{9.6}{\frac{169}{845} \times 2} = -24^{\circ}$$

16. Ans. (C)

ee =
$$\frac{\left[\alpha\right]_{\text{mixture}}}{\left[\alpha\right]_{\text{pure}}} \times 100 = \frac{-20^{\circ}}{-24^{\circ}} \times 100 = 83.3^{\circ}$$

$$\therefore$$
 RM = 100 - 83.3 \Rightarrow 16.7 % $-$ 1 = 8.35

17. Ans. (C)

$$C = \frac{33.8 - 16.9 \text{ g}}{338 + 169 \text{ ml}} = \frac{16.9 \text{ g}}{507 \text{ ml}}$$

$$\ell = 400 \text{ mm} = 4 \text{ dm}$$

$$\alpha_{\rm obs} = \left[\alpha\right]_{\rm sp.} \, c.\ell = \, 24 \times \frac{16.9}{507} \times 4$$

$$= + 3.2^{\circ}$$

18. Ans. (A)

19. Ans. (C)

Matrix Match Type:

20. Ans. $A \rightarrow P$; $B \rightarrow Q$; $C \rightarrow R,S$; $D \rightarrow S$

21. Ans. $A \rightarrow 4 \rightarrow iii$; (B) $\rightarrow 3 \rightarrow iv$; (C) $\rightarrow 2 \rightarrow ii$; (D) $\rightarrow 1 \rightarrow i$

Subjective Type:

22. Ans. Optical: a,b,c,d,f,g,i,j,k; Geometrical isomer: c,g,j; None: e, h

23. Ans. (10)

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

25. Ans. (7)

- 26. Ans. (3)
- 27. Ans. (i) 24 (ii) 9 (iii) 4 (iv) 4 (v) 3, (vi) 4 (vii) 25, (viii) 24, (ix) 2, (x) 4, (xi) 3

28. Ans. (9)

EXERCISE # J-MAINS

- Ans. (1) 1.
- 2. Ans. (4)
- 3. Ans. (4)
- 4. Ans. (2)
- 5. Ans. (2)

- 6. Ans. (3)
- Ans. (1) 7.
- 8. **Ans.**(3)
- 9. Ans. (3)
- 10. Ans. (2) 15. Ans. (4)

- 11. Ans. (1)
- 12. Ans. (2)
- 13. Ans. (1)
- 14. Ans. (1)

- **16.** Ans. (1)
- 17. Ans. (4) 22. Ans. (2)
- 18. Ans. (2) 23. Ans. (3)
- 19. Ans. (3) 24. Ans. (4)
- 20. Ans. (1)

- 21. Ans. (3) 25. Ans. (3)
- Sol.



It achiral \ optically inactive

26. Ans. (3)

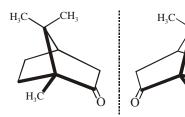
EXERCISE # JEE-ADVANCED OBJECTIVE

- 1. Ans. (B)
- 2. Ans. (D)
- **3.** Ans. (B)
- 4. Ans. (A)

- 5. Ans. (A,C)
- 6. Ans. (A)
- 7. Ans. (D)
- 8. **Ans.** (**B**)
- 9. Ans. Enantiomers - I and III; Diastereomers - I & II and II & III
- 10. Ans. (D)
- 11. Ans. (C)
- **12.** Ans. (B)
- **Ans.** (i) $\frac{1}{0.18}$ D, (ii) Anti form when Y = CH₃ & Gauche when Y = -OH 13.
- **14.** Ans. (C)
- 15. Ans. (C)
- **16.** Ans. (B,C,D)
- 17. Ans. (A,D)

- **18. Ans.** (**A**,**D**)
- 19. Ans. (B,D)
- **20. Ans.** (**B**,**D**)
- 21. Ans. (B,C)

- 22. 23. Ans. (3) Ans. (A,B,C)
- 24 Ans. (2)
- **Sol.** M is a organic compound known as camphor. M contains two <u>rigid</u> chiral centre so it can exist only in two enantiomeric forms.



- Ans. (5) 25
- **26.** Ans.(7)
- Ans. (10.00) 27.