## CHAPTER

# Isomerism

## DEFINITION

Compounds having same molecular formula (M.F.) but differ in thier properties are known as **isomers** and this phenomenon is known as **isomerism.** 

## Classification



## STRUCTURAL ISOMERISM

Compounds having same molecular formula but differ in connectivity of atom (Structure is different).

## **CHAIN ISOMERISM**

Compounds having same molecular formula but differ in the length of the parent chain.

Example 1  $CH_3 - CH_2 - CH_2 - CH_3$  Butane (n - Butane) and  $H_3C - CH - CH_3$  2-Methylpropane  $| CH_3$  (Isobutane)

## Example 2

 $CH_3 - CH_2 - CH_2 - COOH$  Butanoic acid and  $CH_3 - CH - COOH$  2-Methylpropanoic acid I $CH_3$ 

## SOLVED EXAMPLE

## Example 1

Find all the structural isomers of  $C_6H_{14}$ 

**Sol.** 
$$CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3$$

## **POSITION ISOMERISM**

Compounds having same molecular formula and same parent chain but differ in the position of functional group, multiple bond and substitutent group are known as position isomers.

**E.g.**,  $CH_3 - CH_2 - CH = CH_2$  and  $CH_3 - CH = CH - CH_3$ 1-Butene 2-Butene

C1E.g., CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-Cl and CH<sub>3</sub>-CH-CH<sub>3</sub> are position isomers 1-Chloropropane 2-Chloropropane

**E.g.,**  $CH_3 - CH_2 - CH_2 - OH$  and  $CH_3 - CH - CH_3$ 

1-Propanol

2-Propanol

ÓН

\* 
$$CH_2 - CH_3$$
  $CH_3$   $CH_3$  are chain isomer,

not position isomer.

The above example can be best understood taking the following example

$$CH_3 - CH_2 - CH_2 - CH_3$$
 and  
 $CH_3 - CH_4$   
 $CH_3 - CH_3$   
 $H_3 - CH_4$ 

In this, the last carbon has been placed to II position to form chain isomer the same has happened with above example and hence they are chain isomer to each other.

#### Example 2

Find the relation between the given compounds. (A)  $CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3$  $(B) \ CH_{\overline{3}} \ CH - CH_2 - CH_2 - CH_3$ ĊH,  $(D) CH_{3}-CH_{3} CH_{3}$ CH<sub>3</sub> (E)  $CH_3 - CH_2 - CH_2 - CH_3$ CH<sub>3</sub>

## Sol.

a, b  $\longrightarrow$  chain isomers. b, c  $\longrightarrow$  position isomers.

c, d $\longrightarrow$  chain isomers. d, e $\longrightarrow$  position isomers.

Monochlorination  $\rightarrow$  Replace one H by Cl

#### **Example 3**

How many monochloro derivative will be of  $C_4H_{10}$  (Only structural)?

Sol.

$$C_{4}H_{10} \xrightarrow{C_{1}/h_{\nu}} C_{4}H_{9}Cl$$

$$\downarrow$$
4 forms (product)

#### **Example 4**

An alkane having molecular formula  $C_5H_{12}$  can give only one product on monochlorination. Find the IUPAC name of the alkane.

Sol.

$$CH_{3}$$

$$CH_{3}-C-CH_{3}$$

$$CH_{3}-CH_{3}$$

$$CH_{3}$$

$$(2, 2-Dimethyl propane)$$



#### Example 6

Find the total structural isomer of  $C_5H_{10}$ .

Sol.

For solving these kinds of problem we should at once draw all the possible structures of corresponding alkane and then we should check how many possibilities are there to put double bond.

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$$CH_{3}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{3} = 2$$

$$CH_{3}-CH_{2}-CH_{2}-CH_{3} = 3$$

$$CH_{3}-CH_{2}-CH_{2}-CH_{3} = 3$$

$$CH_{3}-CH_{3}-CH_{3}-CH_{3} = 3$$

H<sub>3</sub>C-C-CH<sub>3</sub> I CH<sub>3</sub>

no double bond can be placed in this compound as valency of C will exceeds from 4

Total open chain structural isomers = 5 To form cyclic structural we should always start with 3 carbon ring.



#### Example 7

Sol.

Find the total structural isomers of  $C_4H_6$ . Total unsaturation of  $C_4H_6 = 2$ i.e. possibility = one triple bond, or 2 double bond or (one ring + one double bond)  $CH_3-CH_2-CH_2-CH_3$  ( $\downarrow$  indicate possible position of triple bond)  $CH_3-CH_2-CH_3 \rightarrow$ {No triple bond}  $CH_3-CH_2-CH_3 \rightarrow$ {No triple bond}  $CH_3-CH=C=CH_2$   $CH_3-CH=C=CH_2$  $CH_2=CH-CH=CH_2$ }

Total open chain = 2 + 2 = 4



## Example 8

 $C_{3}H_{8} \xrightarrow{\text{mono}} ?$  (Only structural in all) dichlorination ?? trichlorination ??

Sol.

For monochloroderivative,

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

$$(2 \text{ forms}) \quad CH_{2}-CH_{-}CH_{3}$$

$$CH_{3}-CH_{2}-CH_{2}-CH_{2}-CI_{1}$$

$$CH_{3}-CH_{2}-CH_{2}-CI_{2}-CI_{2}$$

$$CH_{3}-CH_{2}-CH_{2}-CI_{2}-CI_{2}$$

$$CH_{3}-CH_{2}-CH_{2}-CI_{2}-CI_{3}$$

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

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

$$CI_{1}$$

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

$$CI_{2}$$

$$CH_{3}-CH_{3}-CH_{3}$$

$$CI_{2}$$

$$CH_{3}-CH_{3}$$

$$CI_{2}$$

$$CH_{3}-CH_{3}$$

$$CI_{3}$$

$$CH_{3}-CH_{3}$$

$$CH_{3}-CH_{$$

Trichloroderivative,

1. 
$$CH_{3} - CH_{2} - CH_{2}$$

To find di or trichloroderivative: We place two or three chlorine at last carbon and after that rotate one Cl by keeping the other two at the same place.

#### Example 9

Find all the structural dichloroderivative of cyclopentane.

Sol.



## **FUNCTIONAL ISOMERISM**

Compound having same molecular formula but differ in functional group are known as functional isomers.



Aldehyde, Ketone, cyclic ethers, cyclic alcohol, unsaturated alcohol etc are functional isomers to each other.

Alcohol and ether functional isomers of each other.

**E.g.**, CH<sub>2</sub>CH<sub>2</sub>OH, CH<sub>2</sub>OCH<sub>2</sub>

0

Acids and ester are functional isomers to each other.

Eg.,

\*

\*

$$H - \ddot{C} - O - CH_3$$
 and  $CH_3COOH$ 

- Cyanide and Isocyanide are functional isomer to each other but HCN and HNC are tautomers of each other.
- \* 1°, 2° and 3° amine are functional isomer to each other.

#### Example 10

How many primary, secondary and tertiary alcohols are possible for  $C_5H_{13}O$  ?(Only structural)

**Sol.** For 1° alcohol (–CH<sub>2</sub>OH)

 $C_5H_{12}OH \Rightarrow C_4H_9 - CH_2 - OH (4 \text{ form})$  OH OH IFor 2° alcohol (-CH-)  $\rightarrow C_3H_7 - CH - CH_3 (2 \text{ form})$ 

Replace one C  
OH  

$$CH_3 - CH_2 - CH - CH_2CH_3$$
 (1 form)  
Total = 3  
For 3° alcohol  $\begin{pmatrix} OH \\ -C \\ -L \end{pmatrix}$   $CH_3 - C - CH_2CH_3 = C_{H_3} = C_{H_3}$ 

## Example 13

So

For molecular formula  $C_4H_9NO$ , how many amide will be there which will not form H-bond ?(Only structural)

$$\begin{array}{c}
 0 \\
 \parallel \\
 0 \\
 R - C - NH_2 \\
 R - C - NH - R'
\end{array}$$
(1° amide)
$$\begin{array}{c}
 0 \\
 \parallel \\
 R - C - NH - R'
\end{array}$$

$$R - C - N \begin{pmatrix} R' \\ R' \end{pmatrix} (3^{\circ} \text{ amide})$$

For 1° amide

$$C_{3}H_{7} - C - NH_{2}$$
 (2 form)

For 2° amide, 
$$H-C-N-C_3H_7$$
 (2 form)

$$CH_3 - C - NH - CH_2CH_3$$

$$CH_3 - CH_2 - C - NH - CH_3$$

For 
$$3^{\circ}$$
 amide = 2



3° amide will not form H-bond hence there will be 2 amides which will not form H-bond.

## Example 14

Find all 1°, 2° and 3° amides for  $C_3H_7NO$ . (Only structural)

## Sol.

For 1° amides

$$O \\ \parallel \\ C_2H_5 - C - NH_2$$
 (1 form) total 1° amide =

For 2° amide

$$\begin{array}{c} O & O \\ \parallel & \parallel \\ H-C-NH-CH_2CH_3 & CH_3-C-NH-CH_3 \\ = 2 \text{ form} \end{array}$$

- 2 101111

For 3° amide

$$H - C - N CH_{3}$$
 total 3° amide = 1

Total amides  $(1^{\circ} + 2^{\circ} + 3^{\circ}) = 1 + 2 + 1 = 4$ 

## Example 15

Find the total no. of acid and esters from  $C_4H_8O_2$ . (Only structural)

## Sol.



For ester, 
$$\begin{array}{c} O \\ II \\ R_1 - C - O - R_1 \\ \hline Acid part \end{array} \rightarrow alcohol part$$

$$CH_3 - C - OC_2H_5 CH_3COOH + C_2H_5OH$$

For ester,

$$\begin{array}{c} O \\ \parallel \\ CH_3 - C - O C_2H_5 \end{array} \qquad \begin{array}{c} O \\ \parallel \\ C_2H_5 - C - O CH_3 \end{array}$$
  
total esters = 4

 $H-\ddot{C}-OC_3H_7$  (2 form)

## Example 16



#### Example 17



### Sol.



## Example 18

Find the possible dichloroderivative of  $C_6H_4Cl_2$ . (Only structural)

Sol.





$$\bigcup_{\substack{\leftarrow\\Cl}} \longrightarrow \begin{array}{c} C_6H_3CI_3\\ (z \text{ isomer}) \end{array}$$

Find the value of x, y, z.

Sol.

CI (1,2,3) (1,2,4)

There are two possibilities placing Cl in place of H.



$$(1,2,4)$$
  $Cl$   $(1,2,4)$   $y=3$   $(1,2,4)$   $(1,2,4)$ 

There are one possibilities of placing Cl, therefore z = 1 $\therefore$  x = 2, y = 3, z = 1

## Example 20

Find the total carbonyl compound (aldehydes and ketones) formed by  $C_5H_{10}O$  and also find the relation between carbonyl compounds which have same no. of  $\alpha$ -hydrogen.(Only structural)

5

For ketones,  $C_3H_7 - C - CH_3$  and  $\begin{array}{c} ||\\ \mathsf{CH}_3 - \mathsf{CH}_2 - \mathsf{C} - \mathsf{CH}_2 - \mathsf{CH}_3 \end{array} \quad (2 \text{ form}) \end{array}$ Total ketones = 3For aldehydes  $C_4H_9-C-H$  total aldehydes = 4 (4 forms) total carbonyl compounds = 4 + 3 = 7 $CH_3-CH_2-CH_2-CH_2-CHO$  (2  $\alpha$  H)  $\begin{array}{c} \mathsf{CH}_3-\mathsf{CH}_2-\mathsf{CH}-\mathsf{CH}_3 \\ | \\ \mathsf{CHO} \end{array} \qquad (\text{one } \alpha \ \mathrm{H}) \\ \end{array}$  $\begin{array}{c} \mathsf{CH}_3-\mathsf{CH}-\mathsf{CH}_2-\mathsf{CHO} \\ | \\ \mathsf{CH}_3 \end{array} (2 \ \alpha \ \mathrm{H})$ CH<sub>2</sub>  $CH_3 - C - CHO$  (no  $\alpha$  hydrogen)  $\downarrow$  $CH_3$ metamers  $\begin{cases} CH_3 - CH - C - CH_3 & (4 \alpha H) \\ \\ CH_3 \\ CH_3 \\ CH_3 - CH_2 - C - CH_2 - CH_2 \end{cases}$ ketone,  $(5 \alpha H)$ Example 21 Find total acyclic structural isomer of  $C_6H_{12}$ . (Only structural) Sol.

1. 
$$CH_3-CH_2-CH_2-CH_2-CH_2-CH_3 = 3$$
  
2.  $CH_3-CH_2-CH_2-CH_2-CH_3 = 4$   
 $CH_3-CH_2-CH_2-CH_2-CH_3 = 4$ 

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3. 
$$CH_{3} - C - CH_{2} - CH_{3} = 1$$
  
 $CH_{3} - C - CH_{2} - CH_{3} = 1$   
 $CH_{3} - CH_{3} - CH_{3} + CH_{3} = 2$   
4.  $CH_{3} - CH_{2} - CH_{3} - CH_{3} = 2$   
5.  $CH_{3} - CH_{2} - CH_{2} - CH_{3} = 3$ 

Total = 13 isomers.

## Example 22

Find the total conjugated diene in  $C_5H_8$ . (Only structural)

$$CH_3-CH \stackrel{\downarrow}{=} CH-CH \stackrel{\downarrow}{=} CH_2 \longrightarrow \text{ one possibility}$$
  
$$\downarrow \qquad \downarrow \qquad \downarrow$$

$$H_2C \stackrel{\bullet}{=} C - CH \stackrel{\bullet}{=} CH_2$$
  
 $CH_3$ 

 $\longrightarrow$  one possibility

 $H_3C-C-CH_3 \longrightarrow$  no possibility as placing  $CH_3$ 

double bond the valency of C will be more than four.

#### Example 23

Find total cumulated diene in  $C_5H_8$ . (Only structural)

Sol.

$$\begin{array}{c} \mathsf{CH}_2-\mathsf{CH}_2-\mathsf{CH}_2-\mathsf{CH}_2-\mathsf{CH}_2\\ \mathsf{H}_3\mathsf{C}-\mathsf{CH}_2-\mathsf{CH}_2-\mathsf{CH}_2-\mathsf{CH}_2-\mathsf{CH}_2\\ \mathsf{CH}_2-\mathsf{CH}=\mathsf{C}=\mathsf{CH}-\mathsf{CH}_3\\ \mathsf{CH}_3-\mathsf{CH}-\mathsf{CH}_2-\mathsf{CH}_3 \longrightarrow \mathsf{CH}_3-\mathsf{C}=\mathsf{C}=\mathsf{CH}\\ \mathsf{CH}_3\\ \mathsf{CH}_3\\ \mathsf{CH}_3\\ \mathsf{CH}_3\end{array}$$

$$\begin{array}{c} \mathsf{CH}_{3}\\ \mathsf{H}_{3}\mathsf{C}-\mathsf{C}-\mathsf{CH}_{3} \longrightarrow \text{ no form cumulated diene}\\ \mathsf{CH}_{3}\\ \text{Total} = 3\\ \Rightarrow \text{ Isolated dienes,}\\ \mathsf{CH}_{3}-\mathsf{CH}_{2}-\mathsf{CH}_{2}-\mathsf{CH}_{2}-\mathsf{CH}_{3} \longrightarrow \mathsf{CH}_{2}=\mathsf{CH}-\mathsf{CH}_{2}-\mathsf{CH}=\mathsf{CH}_{2}\\ \downarrow\\ \mathrm{sp}^{3}\\ \mathsf{CH}_{3}-\mathsf{CH}-\mathsf{CH}_{2}-\mathsf{CH}_{3} \longrightarrow \text{ no form isolated}\\ \mathsf{CH}_{3}\\ \text{diene}\\ \text{Total} = 1\end{array}$$

## **METAMERISM**

This type of isomerism is found in those types of compounds which have polyvalent atoms or polyvalent functional group, e.g. ether, 2° amine, ester etc.

Compound having same molecular formula but differ from the nature of alkyl group directly attached with polyvalent atom or polyvalent functional group

$$CH_3OCH_2CH_2CH_3$$
  
 $CH_3CH_2OCH_2CH_3$  metamers

(a) 
$$CH_3 - CH_2 - CH - NH - CH_3$$
  
 $|$   
 $CH_3$ 

(b)  $CH_3 - CH_2 - CH_2 - NH - CH_2 - CH_3$ a & b are metamers

## TAUTOMERISM

Compound having same molecular formula but different due to oscillation of an atom (usually H<sup>+</sup>) are known as tautomers.

$$CH_{3} \xrightarrow{O} CH_{3} \xrightarrow{OH^{\ominus}} \xrightarrow{O} CH_{2} \xrightarrow{O} CH_{3}$$

as after removal of H<sup>+</sup>, the anion formed is resonance stabilised.

\*

## **Keto enol Tautomerism**



## Mechanism



 $OH^{\Theta}$  acts as catalyst.

## **Base Catalysed Tautomerism**

$$CH_3 - C - CH_3 \xrightarrow{OH^{\ominus}} CH_2 = C - CH_3$$

$$> 99\% < 1\%$$

## Mechanism

$$CH_{3} - C - CH_{3} \xleftarrow{OH}{} CH_{3} - C - CH_{2} \xleftarrow{OH}{} CH_{3} - C - CH_{2} \xleftarrow{OH}{} CH_{3} - C - CH_{2} \xleftarrow{OH}{} CH_{3} - C = CH_{2}$$

- enol is more acidic than keto. \*
- \* After removal of H<sup>+</sup> from both form.

In I-ve charge is on C and in II-ve charge is on O therefore (ii) is more stable than (i) hence enol form is more acidic than keto form.

## **Acid Catalysed Tautomerism**



## Example 24

$$\begin{array}{c} \uparrow \\ CH_{3} - C - CH_{2} - CH_{3} \\ \uparrow \\ H^{+} \\$$

(More stable) (Less stable due to +I of  $CH_2$ )

In case of base catalysed tautomerism the stability of carbanion is the deciding factor. For acid catalysed tautomerism the stability at the product will be the deciding factor.

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Example 26



Sol.



Generally, keto form is more stable than enol but in some cases the stability of enol form is greater than keto. This is due to:

- 1. Intramolecular H-bonding
- 2. Aromatic character
- **3.** Extended conjugation
- 4. Steric factor

## E.g.,

$$CH_{3} - C - CH_{2} - C - CH_{3} =$$

$$(keto)$$

$$OH^{\dots \dots \dots O}$$

$$CH_{3} - C = CH - C - CH_{3}$$

$$(enol)$$

$$(Intramolecular H-bond)$$

$$(10 - 80\%)$$

Due to intramolecular H-bonding formation of 6 member ring takes place which is the cause of stability.

This can be also summarised as

$$\begin{array}{c} O & O \\ H & G = C - CH_2 - C - G \end{array}$$
If  $G = H$  % of enol  $80 - 90\%$   
 $G = Ph$  % of enol  $90 - 99\%$   
 $G = CH_3$  % of enol  $70 - 80\%$   
 $G = OC_2H_5$  % of enol  $5 - 10\%$   
(one side)  
 $CH_3 - C - CH_2 - C - OC_2H_5 \longrightarrow CH_3 - C - CH - C - OC_2H_5$   
(After removal of H<sup>+</sup>) (Cross conjugation)  
Cross conjugation restricts the resonance.  
 $OH^{------O}_{L} = H - C - OC_2H_5$   
**Example 27**  
Compare the enol percent.  
(A) CH<sub>3</sub>CHO  
O

(B)  $CH_3 - C - CH_3$ 

(D) CH<sub>3</sub> - C - CH<sub>2</sub> - C - H

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Sol. After removing  $H^+$  (acidic-H) from the compounds



Enol percent  $\infty$  stability of carbanion A > B > D > C

Formation of carbanion is one by step process from keto to enol. Therefore can be calculated as enol percent  $\alpha$  stability of carbanion.

## Example 30

Find the enol form of



## NITRO AND ACINITRO FORM





 $(CH_3)_3 C - NO_2$  will not show nitro and acinitro form it has no  $\alpha$  H w.r.t to NO<sub>2</sub> group.

## **IMINE AND ENAMINE**



For this type of tautomerism, there must be  $\alpha$  H w.r.t. (-CH = NH) group.

## **AMIDE AND IMINOL**

$$R-C-NH_2 \rightleftharpoons R-C=NH$$

## NITROSO AND OXIME FORM

 $Ph - CH_2 - N = O \implies Ph - CH = N - OH$ (Nitroso) (Oxime) (I) (||)II > I (stability)

due to extended conjugation in (II)

## HYDRAZONE AND AZOFORM

NH<sub>2</sub>NH<sub>2</sub> (Hydrazine)

$$C = O + H_2 N - NH_2 \longrightarrow C = N - NH_2$$

$$CH_3 - CH = N - NH_2 \iff CH_3 - CH_2 - N = NH$$
  
(Azo)

 $CH_3 - CH = N - NH - Ph \implies CH_3 - CH_2N = N - Ph$ (extended conjugation) Azo > Hydrazone (stability)

Example 31

Compare enol percent.

(I) 
$$CH_3 - C - CH_3$$
 (II)  $CD_3 - C - CH_3$   
(III)  $CD_3 - C - CD_3$ 

Sol. As we know C – D > C – H (Bond strength)
⇒ C – D will not break easily.
⇒ Compound will have less tendency to come into in enol form as C – D bond breaking is one

of the step for conversion of keto into end.

- $\Rightarrow$  Enol percent will be less.
- $\Rightarrow$  (I) > (II) > (III) (Enol content)

## **DEUTERIUM EXCHANGE REACTION** (Deuterium Exchange Tautomerism)



To get the product directly replace all  $\alpha$ -hydrogen w.r.t. carbonyl group by D (Deuterium).

E.g.,



## **RING-CHAIN ISOMERISM**

If one isomer has open chain structure and the other has cyclic structure then isomers are known as ring-chain isomers and isomerism between them is known as ring-chain isomerism.

## For examples :

1. Alkene and cycloalkane,  $(C_nH_{2n})$  $CH_3 - CH = CH_2$   $CH_2 - CH_2$ 

2. Alkyne and cycloalkene, 
$$(C_n H_{2n-2})$$
  
 $C_4 H_6$ :  $CH_3 - CH_2 - C \equiv CH$   
 $CH - CH_2$   
 $H - CH_2$   
 $CH - CH_2$ 

Alkenols and cyclic ethers, 
$$(C_n H_{2n} O)$$
  
 $C_3 H_6 O$ :  $CH_2 = CH - CH_2 OH$   
 $CH_2 - CH_2$   
 $|$   
 $CH_2 - O$ 

Note

Ring-chain isomers are always functional isomers.

## **GEOMETRICAL ISOMERISM** Definition

Isomers which possess the same molecular and structural formula but differ in the arrangement of atoms or groups in space due to restricted rotation are known as geometrical isomers and the phenomenon is known as geometrical isomerism.

## **Conditions of geometrical Isomerism**

1. Geometrical isomerism arises due to the presence of a double bond or a ring structure.

(i.e. 
$$\supset C = C \subset$$
,  $\supset C = N - , -N = N - or ring structure)$ 

3.

4.

Due to the rigidity of double bond or the ring structure to rotate at the room temperature the molecules exist in two or more orientations. This rigidity to rotation is described as restricted rotation *l* hindered rotation *l* no rotation.

## E.g.,



2. Different groups should be attached at each doubly bonded atom. For example,



are identical but not geometrical isomers. On the other hand, following types of compounds can exist as geometrical isomers :



#### **Examples of Geometrical isomers**







Along - N = N - bond



Along  $\sigma$  bond of cycloalkane



and

and

and









Me Me

Н

Н



Motion Education | 394 - Rajeev Gandhi Nagar | ©: 1800-212-1799 | url : www.motion.ac.in | Page No. #18 5. Along  $\supset C = C \subset$  in ring structures :

Usually in cycloalkenes double bond has its configuration. Their trans isomers do not exist due to large angle strain. But if the ring is large enough a trans stereoisomer is also possible. The smallest trans cycloalkene that is stable enough to be isolated & stored is trans-cyclooctene.



## Configurational nomenclature in geometrical Isomerism

Time	Criterla	Remarks
		If the two similar groups
cis / trans	Similarity of groups	are on same side of
		restricted bond the
		configuration is cis
		otherwise trans.
E/Z	Seniority of groups	If the two senior groups are
		on same side of restricted
		bond the configuration is Z
		(Z = zusammen = together)
		otherwise $E(E = entgegen$
		= opposite).

Sequence rules : (Cahn - Ingold - Prelog sequence rules)

For deciding the seniority of groups following rules are applied :

**Rule I :** The group with the first atom having higher atomic number is senior. According to this rule the seniority of atom is :

$$I > Br > Cl > S > F > O > N > C > H$$

Rule II : The higher mass isotope is senior. Thus (A) - T > -D > -H.  $(B) - C^{14}H_2 > -C^{12}H_2$ 

**Rule III :** If the first atom of group is identical then second atom is observed for seniority.

**E.g.** (A) 
$$- \operatorname{CH}_2\operatorname{Cl} > - \operatorname{CH}_2\operatorname{OH} > - \operatorname{CH}_2\operatorname{NH}_2 > - \operatorname{CH}_2\operatorname{CH}_3 > - \operatorname{CH}_3$$
  
(B)  $- \operatorname{C}_2\operatorname{Cl} > - \operatorname{C}_2\operatorname{Cl} - \operatorname{Cl}_3$   
(B)  $- \operatorname{C}_2\operatorname{Cl} > - \operatorname{C}_2\operatorname{Cl}_3$ 

**Rule IV :** Groups containing double or triple bonds are assigned seniority as if both atoms were duplicated or triplicated.

> C = Y as if it were 
$$\begin{array}{c} \begin{array}{c} C - Y \\ | \\ (Y) \\ (C) \end{array}$$
 & (Y) (C)  $\begin{array}{c} (C) \\ - C = Y \\ | \\ (Y) \\ (C) \end{array}$ 

**E.g.,** For deciding seniority among  $- C = CH, - CH = CH_2$ , their hypothetical equivalents are compared.

$$\begin{array}{cccc} C & C & & & C & C \\ | & | & & & \\ -C - C - H & > & & | & | \\ -C - C - H & > & & | & | \\ H & C & & & \\ C & C & & & (for - CH = CH_2) \end{array}$$

Rule V : Bond pair gets priority over lone pair.

**Rule VI :** Z > E & R > S.

## Number of Geometrical Isomers :

Number of geometrical isomers can be found by calculating the number of stereocentres in the compound. (Stereocentre is defined as an atom or bond bearing groups of such nature that on interchange of any two group will produce a new stereoisomer).

	Nature of Compound	No. of G.I. (n = no. of Stereocentres)	Example	No. of Isomers	Isomers
(I)	Compound with dissimilar ends	2n	$CH_3-CH=CH-CH=CH-C_2H_5$	4	I : (cis, cis) II : (trans, trans) III : (cis, trans) IV : (trans, cis)
(II)	Compound with similar ends with even stereocentres	$2^{n-1} + 2^{\frac{n}{2}-1}$	CH <sub>3</sub> -CH=CH-CH=CH-CH <sub>3</sub>	3	I : (cis, cis) II : (trans, trans) III : (cis, trans)(trans, cis)
(III)	Compound with similar ends with odd stereocentre	$2^{n-1} + 2^{\frac{n-1}{2}}$	CH <sub>3</sub> -CH=CH-CH=CH-CH=CH-CH <sub>3</sub>	6	I : (cis, cis, cis) II : (cis, cis, trans) (trans, cis, cis) III : (cis, trans, trans) (trans, trans, cis) IV : (trans, trans, trans) V :(cis, trans, cis) VI : (trans, cis, trans)

## **Physical Properties of Geometrical Isomers :**

Physical Properties	Br = C = C = C = H $H = H$ $H = H$ $H = H$	Remarks
Dipole moment	I > II	cis-isomer has resultant of dipoles while in trans ison dipole.
Boiling point	I > II	Molecules havig higher dipole moment have higher boiling point dur to large intermolecular force of attraction.
Solubility (in H <sub>2</sub> O)	I > II	More polar molecules are more soluble in $H_2O$ .
Melting point	II > I	More symmetric isomers have higher melting points to better packing in crystalline lattice and trans isome are more symmetric than cis.
Stability	II > I	The molecule having more vander waal's strain are less stable. In cis isomer the bulky groups are closer they larger Vander Waals strain.

Physical Properties	$H_{3}C_{X} = C = C H H_{3}C_{X} = C H H_{3}C_{X} = C H H_{3}C_{X} = C H H_{3}C_{X} = C H_{3}C_{1} = C H_{3}C_$
Dipole moment	I > II
Boiling point	I > II
Solubility (in H <sub>2</sub> O)	I > II
Melting point	I > II
Stability	I > II

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**Unsolved problem :** Find the number of geometrical isomers in

(A) 
$$CH_3 - CH = C - CH = CH - CH = N - OH$$
  
|  
 $CH_3$ 

$$(B) \underbrace{CH = CH - CH_3}_{CH_3}$$

**Unsolved problem :** Compare the physical properties (dipole moment, boiling point, melting point, solubility & stability) in the geometrical. isomers of  $CH_3 - CH = CH - CN$ .

## **OPTICAL ISOMERISM**



If there is no rotation of light then substance is called optically inactive.

## **CHIRAL CARBON**

If all the four valencies of carbon are satisfied by four different atom or four different group atom then carbon is known as chiral carbon.





Motion Education | 394 - Rajeev Gandhi Nagar | 1800-212-1799 | url : www.motion.ac.in | Page No. # 21

- ⇒ After 180° rotation, mirror image and object are identical.(mirror image of meso compound will be identical)
- If the compound have only one chiral carbon then it will be certainly optically active.



Object and its non-superimposable mirror image are called enantiomer to each other

## Example 32

A and B are enantiomer to each other. If specific rotation of A is  $+ 20^{\circ}$  and rotation of mix of A and B is  $-10^{\circ}$  then find the percentage of A and B in the mixture?

#### Sol.

Let x mol A (1-x) mol of B total rotational of A = x × 20 total rotational of B = (1-x)(-20)Total rotation of the mixture = -10 x × 20 + (1-x)(-20) = -10 20 x - 20 + 20x = -10  $40 x = 10 \Rightarrow x = \frac{10}{40} = 0.25$   $\Rightarrow \% A = 25\%$  $\therefore \% B = 75\%$ 

## FISCHER PROJECTION

By fischer projection three dimensional structure is converted into 2D.

## Example 33

Write the Fischer projection of CH<sub>3</sub>CH(OH)COOH.



- ( Maximum carbon must be in vertical line.
- Place higher priority carbon containing functional group on top of vertical line.

#### Example 34

Write Fischer projection of



Sol.

**1.** Place higher priority carbon containing functional group on top of vertical line.

**2.** Arrange other group according to its clock wise or anticlock wise position w.r.t. group on the top.



## WEDGE DASH STRUCTURE



Fourth priority order can be eliminated during checking of clockwise and anticlockwise. To draw Fisher projection of such structure:

- **1.** Dotted group is placed below
- 2. The group attached by dark line is placed on the top.

**3.** Remaining group are placed according to their clock wise or anticlockwise position w.r.t. group in dark line.





## **R AND S FORM**

 $\begin{array}{c} & \bigcap \quad R \rightarrow Rectus \quad \rightarrow Right \rightarrow Clockwise. \\ & \bigcap \quad S \rightarrow Sinister \quad \rightarrow Left \rightarrow Anticlockwise. \end{array}$ 

## **PRIORITY ORDER**

Higher the atomic number of the element, greater will be its priority.













Mirror image of R is S If lowest priority element is in horizontal then exact order is obtained by reversing the form (i.e. it comes R then exact form will be S and vice versa).





 $\Rightarrow$  It comes as R but will be S form,



If lowest priority element is not in dotted then we bring it in dotted by doing even number of inter changes (2,4 or 6) as by even no. of inter change, the configuration does not change.

After odd number of change the configuration changes (If R then goes into S and vice versa).

## For Example:





All the carbons are placed in vertical.

Group attached to the chiral carbons are placed on any side. After that they are adjusted whether they are R or S form with respect to chiral carbons.

## Example 37 Draw the Fischer projection of the following.



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## **RACEMIC MIXTURE**

It is an equimolar mixture of R and S or d and l. Racemic mixture is optically inactive.

- A compound is optically active due to
- 1. Absence of plane of symmetry (POS)
- 2. Absence of centre of symmetry (COS)



- Plane of symmetry is an imaginary plane where if we place a mirror, mirror image will exactly overlap the other half.
- For meso form, there must be at least two identical chiral carbon.

Identical carbon  $\Rightarrow$  Chiral carbons having identical group attached.

- If compound has Plane of symmetry then it will be certainly optically inactive and will be called meso form.
- After finding two identical carbons. We assign them as R or S. If first part is R and other is S then they will rotate the light in opposite direction but to equal extent the compound will be optically inactive (meso form).



If a compound have 'n' different chiral carbon then total no. of optically active isomers = 2<sup>n</sup> No. of meso form = 0

E.g.,

(i)

(ii)



No. of different chiral carbon = 4 Total optical isomer  $= 2^n = 2^4 = 16$ 

There will be no meso as the compound does not have identical chiral carbon.

G If a compound has n identical chiral centre (symmetrical) ⇒ There must be symmetry from some where.

If n is even optical isomer (a) =  $2^{n-1}$ mesoform (m) =  $2^{n/2-1}$ total optical isomer = a + m If n is odd

$$a = 2^{n-1} - 2^{\frac{n-1}{2}}$$
$$m = 2^{\frac{n-1}{2}}$$

Total optical isomer =  $2^{n-1} - 2^{\frac{n-1}{2}} + 2^{\frac{n-1}{2}} = 2^{n-1}$ 



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- When there is odd no. of identical carbon atom (i.e. symmetrical) then this compound will certainly contain pseudo chiral w.r.t. to which compound is symmetrical (i.e. POS).
- Other meso compound of the above compound will form by changing the place Br and H around Pseudo chiral carbon.



Total meso = 2









 $m = 2^{\frac{n}{2}-1} = 2^{\frac{4}{2}-1} = 2^{2-1} = 2^{1} = 2$ Total isomer = 8 + 2 = 10

## DIASTEREOISOMERS



For single chiral centre, there is no diastereoisomer. The stereoisomer which are not related as object and mirror image. They may be optically active or optically inactive.



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For compound having 3 chiral carbon to get diastereoisomer, fix two chiral carbon and one interchange with left carbon or fix one chiral carbon and interchange with other two,



 $\begin{array}{c|cccc}
OH & OH & OH \\
Br + H & H + Br \\
H + Br & Br & Br + H \\
H + Br & Br & Br + H \\
COOH & COOH \\
(III) & (IV)
\end{array}$ 

(I) and (III), I and (IV), (II) and (III), (II) and (IV) are diastereoisomers.

## Example 38



What are the relation among the above compounds?

#### Sol.

I and II are identical III and IV are identical II and III are diastereoisomer I and IV are diastereoisomer

## Example 39

Find total isomers obtained by dichlorination of cyctopentane

Sol.



Total isomers = 3 + 3 + 1 = 7Optically isomers = 6, Optically active isomers = 4

#### Example 40

Find the total isomers obtained by trichlorination of propane.

Sol.



## Example 41

Find total isomers obtained by dichlorination of n-Butane

Sol.

(3) (2 optically + 1 meso ) Total isomers = 10 (6 optically active + 1 meso + 3 structural)

#### Example 42

How many stereoisomers of 1,2,3-Cyclohexantriol?

Sol.

OH OH OH OHSymmetrical)

a = 
$$2^{n-1} - 2^{\frac{n-1}{2}} = 2^{3-1} - 2^{\frac{3-1}{2}} = 4 - 2$$
  
m =  $2^{\frac{n-1}{2}} = 2^{\frac{3-1}{2}} = 2$   
Total stereoisomers =  $2 + 2 = 4$ 



Mesoform is optically inactive due to internal compensation and racemic mixture is optically inactive due to external compensation.

## Example 43

A and B are enantiomer of each other. Specific rotation of A is 20 °. Rotation of mixture of A and  $B = -5^{\circ}$  what is the percentage of racemic part?

#### Sol.

x mol A, 1-x mol B  
x × 20 + (1-x) (-20) = -5  
20 x - 20 + 20x = -5  
40 x = 15 
$$\Rightarrow$$
 x =  $\frac{3}{8}$  = 0.375  
moles of A =  $\frac{3}{8}$   
moles of B =  $1 - \frac{3}{8} = \frac{5}{8}$   
 $\frac{3}{8}$  moles of A and  $\frac{3}{8}$  moles of B will form  
racemic mixture.  
Enantiomer excess or optical purity  
=  $\frac{5}{8} - \frac{3}{8} = \frac{2}{8} = \frac{1}{4}$ 



They are non superimposable mirror image



## **SPIRO COMPOUNDS**



Planer compound Always have POS ∴ Optically inactive

## **BIPHENYLS**



If biphenyl contains bulky group at its ortho position (only) then due to repulsion the planarity of compound disappears and its mirror image is non superimposable.

(P

In the biphenyls none of the two ring must have





In 2° Amines.



Optically inactive due to formation of racemic mixture.

 $\bigcirc$  Order of flipping in amines  $1^{\circ} > 2^{\circ} > 3^{\circ}$ 

## **D-Form**

For compound having one chiral carbon

- **1.** If OH is right side  $\rightarrow$  D
- **2.** If OH is left side  $\rightarrow$  L

#### Note

All the carbon must be in vertical position having highest O.N.



CONVERSION OF FISHER PROJECTION IN SAW HORSE STRUCTURE



First write first chiral carbon (as given in molecule).

After it, change the position of second chiral carbon (if both group are on the same side) otherwise write as it is.

The above fischer projection can also written in sawhorse form as follows



(P





## CONFORMATIONAL ISOMERS

## **Conformational Isomerism in Alkanes**

Different spatial arrangements of the atoms that result from **restricted** rotation about a single bond are called conformations. Different conformations are also called conformational isomers.

When an ethane molecule rotates about its carbon-carbon single bond, two extreme conformations can result : the staggered conformation and the eclipsed conformation. An infinite number of conformations between these two extreme conformation is also possible. There are several ways to represent on paper the three dimensional conformation that, occur as a result of rotation about a single bond. Wedgeand -dash structures, Saw horse projections and Newmann projections are all commonly used methods. But here we will use only Newmann projections. In a Newmann projection you will look down the length of a particular carbon-carbon single bond. The carbon that is in the front, is represented by the point at which three bonds intersect and the carbon that is in the back is represented by a circle. The three lines emanating from each of the carbons represent the carbon's other three bonds.



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#### **Staggered conformations**

A conformation with a 60° dihedral angle is known as staggered conformation.

## **Eclipsed conformation**

A conformation with a 0° dihedral angle is known as eclipsed conformation.

The electrons in a carbon-hydrogen bond will repel the electrons in another carbon-hydrogen bond if the bonds get too close to each other. The staggered conformation, therefore, is the most stable conformation because the carbonhydrogen bond are as far away from each other as possible. The eclipsed conformation is the least stable conformation, because in no other conformation are the carbon-hydrogen bond closer to one another. In staggered conformation the distance between the hydrogen nuclei is 2.55 Å. but, they are only 2.29 Å apart in the eclipsed conformation. The rotational barrier in ethane is 2.9 kcal/mol. This rotational barrier can be described in terms of the change in potential energy of the molecule as a function of the change in dihedral angle. The extra energy of the eclipsed conformation is called **torsional strain**. Torsional strain is the name given to the repulsion felt by bonding electrons of one substituent as they pass close the bonding electrons of another substituent. The energy barrier between staggered and eclipsed conformation in ethane molecule is 2.9 kcal/mol (12 kJ/mole). This barrier is more than RT (  $\approx 0.6$  kcal/mol) at room temperature (energy for free rotation) and less than 16-20 kcal/mol (energy barrier for frozen rotation). Hence the rotation about carbon-carbon single bond is neither completely free nor frozen but only restricted.

## Note

1. Fpr free rptation, energy barrier is 0.6 kcal/ mol.

2. For restricted rotation, energy barrier is in between > 0.06 and < 16 kcal/mol.

3. For frozen rotation, energy barrier is  $\geq 16$  kcal/mol/

Similarly propane has also two conformations.



Staggered

Eclipsed

In this case, out of six substituents on two C's (carbon -1 and carbon-2) five, are hydrogens and one is CH<sub>3</sub> group.

Butane has three carbon-carbon single bonds and the molecule can rotate about each of them.

If rotation will be about C - 2 and C - 3 bond then conformation will be symmetrical.

$$CH_3 - CH_2 - CH_2 - CH_3$$

For conformational analysis treat butane as the derivative of ethane. Out of six substituents four are hydrogens and two are methyl groups Different conformations of butane are obtained by rotation.



Butane has three staggered conformers (I, III and  $\mbox{V})$  .

Conformer -(III), in which the two methyl groups are as far apart as possible, is more stable than other two staggered conformers (I and the V). The most stable of the staggered conformers is called the anti **conformer** ( in anti conformation the angle between two methyl groups is 180°) and the other two staggered conformers are called gauche conformers. (anti in Greek for "opposite of gauche in French for " left"). In gauche conformation the angle between two methyl groups is 60°.

In the anti conformer, the largest substituents  $(CH_3 \text{ and } CH_3)$  are opposite to each other; in the gauche conformer, they are adjacent. Two gauche conformers have the same energy but each is 0.9 kcal/mol less stable than the anti conformer.

Anti and gauche conformers do not have the same energy because of the steric strain. **Steric strain** or **steric hindrance** is the strain put on a molecule when atoms or groups are large in size and due to this they are too close to each other, which causes repulsion between the electrons of atoms or groups. There is more steric strain in the gauche conformer than in the anti because the two methyl groups are closer together in the gauche conformer. Steric strain in gauche conformer is called gauche interaction.

The eclipsed conformer in which the two methyl groups are closest to each other (VI) is less stable than the other eclipsed conformers (II and IV). All these eclipsed conformers have both torsional and steric strain. Torsional strain is due to bondbond repulsion and steric strain is due to the closeness of the eclipsing groups.

In general steric strain in the molecule is directly proportional to the size of the eclipsing groups. Eclipsed conformer (VI) is called the fully eclipsed conformer (angle between two methyl groups is zero) whereas (II) and (IV) are called eclipsed conformers. The energy diagram for rotation about the C-2–C-3 bond of butane is shown in the **Fig.** 



Thus the relative stabilities of the six conformers of n-butane in decreasing order is as follows: Anti > gauche > eclipsed > fully eclipsed (III) (I) and (II) and (VI) Thus molecules with carbon-carbon single bonds have many interconvertible conformers. Conformers cannot be separated because they rapidly interconvert.

Although anti conformation is more stable than the gauche conformation but in some cases gauche conformation is more stable than the anti because of the intramolecular hydrogen bonding which is geometrically possible only in the gauche conformation.



In Ethylene chlorohydrin also gauche conformation is more stable than the anti conformation due to the dipole-dipole attraction between OH and Cl which is geometrically possible only in the gauche conformation.





Dipole -dipole attraction between OH and Cl (more stable)

#### Example 46

Write Gauche conformation of the compound CH<sub>2</sub>Cl – CH<sub>2</sub>Cl ?

#### Sol.

Gauche conformation of the given compound



1. Mole fraction of anti and gauch form : Mole fraction of stable conformers (i. e., mole fraction of anti and gauche can be calculated if dipole moment of anti and gauche form is known.

 $\mu_{ob} = \mu(anti) \times x_a + \mu(gauche) \times x_g$ 

where  $x_a =$  mole fraction of anti form and

 $x_b =$  mole fraction of gauche form. Suppose

$$\mu_{ob} = 1.00 \qquad \qquad \mu_g = 5.55$$
  
Then x<sub>a</sub> can be calculated as follows :

$$\mu_{ob} = \mu_a \times x_a + \mu_g \times x_g$$
$$1 = 0 \times x_a + 5.55 x_g$$
$$\therefore \qquad x_g = \frac{1}{5.55} = 0.18$$

Sum of mole fraction of  $x_a + x_g = 1$  $x_a = 1 - x_g = 1 - 0.18 = 0.82$ 

## 2. Relative amounts of anti and gauche conformers

The anti conformer of n-butane is more stable than the gauche may about 900 kcal/mol (i.e., 0.9 kcal/mol). This is energy barrier between anti and gauche.

Thus gauche  $\implies$  anti,  $\Delta H = -900$  cal/mol. Suppose at room temp  $\Delta G$  is negligible.

So 
$$\Delta G = -RT \ln K_{eq}$$

$$K_{_{eq}} = \frac{\left[\text{anti}\right]}{\left[\text{gauche}\right]}$$

and  $\ln K_{eq} = \frac{-\Delta G}{RT} = \frac{-900 \text{ cal / mole}}{1.99 \text{ cal / mole K} \times 298 \text{ K}} =$ 

1.52

The ratio of  $K_{eq}$  is 4.57  $\approx$  4.6, which means that

about 82% mole  $\left(\frac{4.6 \times 100}{5.6}\right)$  of the molecule are

in the anti conformation and 18% in the gauche conformation at any one time.

## **STABILITY OF CYCLOALKANES**

Compounds with three and four membered rings are not as stable as compounds with five or six membered rings.

The German chemist Baeyer was the first to suggest that the instability of these small ring compounds was due to angle strain. This theory is known as Baeyer-Strain theory.

Baeyer strain theory was based upon the assumption that when an open chain organic compound having the normal bond angle 109.5° is converted into a cyclic compound, a definite distortion of this normal angle takes place leading to the development of a strain in the molecule.

Baeyer assumed that cyclic rings are planar. Assuming that the rings are planar, the amount of strain in various cycloalkanes can be expressed in terms of angle of deviation (d).



1.

3.

Sol.

$$d = \frac{1}{2} \left[ 109.5 - \frac{2(n-2)}{n} \times 30 \right] \text{ or } d = \frac{1}{2} \left[ 109.5 - \alpha \right]$$
  
where

n = number of carbon-carbon bonds in cycloalkane ring

 $\alpha$  = inner bond angle in the cycloalkane ring.

Angle strain 
$$\propto d \propto \frac{1}{\text{inner angle}}$$

Stability 
$$\propto \frac{1}{d} \propto \text{ inner angle } (\alpha)$$

Now let us take the case of three to eight membered cyclic compounds.



The positive and negative values of (d) indicate whether the inner angle is less than or more than the normal tetrahedral value.

Baeyer thus predicted that a five membered ring compound would be the most stable. He predicted that six membered ring compounds would be less stable and as cyclic compound became larger than five membered ring they would become less and less stable.

Contrary to what Baeyer predicted, cyclohexane is more stable than cyclopentane. Furthermore, cyclic compounds do not become less and less stable as the number of side increase. Thus Baeyer strain theory is applicable only to **cyclopropane**, **cyclobutane and cyclopentane**.

The mistake that Baeyer made was to assume that all cyclic compounds are planar. In real sense only cyclopropane is planar and other cycloalkanes are not planar. Cyclic compounds **twist** and **bend** in order to achieve a final structure that minimises the three different kinds of strain that can destabilise a cyclic compound.

- Angle strain is the strain that results when the bond angle is different from desired tetrahedral bond angle of 109.5°.
- 2. Torsional strain is caused by repulsion of the bonding electrons of one substituent with bonding electrons a nearby substituent.

**Steric strain** is caused by atoms or groups of atoms approaching each other too closely.

## Example 47

According baeyer-st	rain theory which				
compound has minimum angle strain?					
(A) n-Butane	(B) Cyclopentane				
(C) Cyclopropane	(D) Cyclohexane				
<b>(B)</b>					
Cyclopentane has minimum angle strain.					

#### Example 48

Which form of cis 1,4-Cyclohexane diol is most stable?



 $\Rightarrow$ 

(i)

(ii)

## **CONFORMATION OF CYCLOHEXANE**

Despite Baeyer's prediction that give-membered cyclic compound would be the most stable, the six membered cyclic compound is the most stable. Six membered cyclic compound are most stable because they can exist in a conformation that is almost completely free of strain. This conformation is called the **chair conformation**. In a chair conformation of cyclohexane all bond angles are 111° which is very close to the 109.5° and all the adjacent carbon-hydrogen bonds are staggered.



- $\Rightarrow$  Each carbon in chair conformation has an axial bond and an equatorial bond.
- $\Rightarrow$  Axial bonds are perpendicular to the plane of the ring and equatorial bonds are in the plane of the ring.
- $\Rightarrow$  If axial bond on carbon-1 is above the plane of the ring then axial bond on carbon-2 will be below the plane of the ring. Thus

C -1 , C - 3 and C - 5 axial bonds are above C -1 , C - 4 and C - 6 axial bonds are below



⇒ Thus C -1 axial and C - 2 axial are trans to each other. Similarly C - 1 and C - 5 axials are cis to each other.

It axial bond on carbon - I will be above the plane then equatorial bond on this carbon will be below the plane.



Thus C - 1 equatorial and C -5 equatorial will be cis.

C - 1 axial and C-2 equatorial will be cis.

As a result of rotation about carbon-carbon single bonds cyclohexane rapidly intercoverts between two stable chair conformations. This interconversion is known as ring-flip. When the two chair forms interconvert, axial bonds become equatorial and equatorial bonds become axial.



Cyclohexane can also exist in a boat conformation. Like the chair conformation, the boat conformation is free of angle strain. However, the conformation is less stable than the chair conformation by 11 Kcal/mole. Boat conformation is less stable because some of the carbon-hydrogen bonds in boat conformation are eclipsed.



The boat conformation is further destabilised by the close proximity of the flagpole hydrogens. These hydrogens are 1.8 Å apart but the vander Waal's radii is 2.4 Å. The flagpole hydrogens are also known as trans nuclear hydrogens.

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When one hydrogen of cyclohexane is placed by a larger atom or group, crowding occurs. The most sever crowding is among atoms held by the three axial bonds on the same side of the molecule; the resulting respulsive interaction is called 1,3-diaxial interaction. This causes steric strain in the molecule.

Thus, monosubstituted cyclohexane will assume chair conformation in which the substituent occupies an equatorial position. Similarly in disubstituted cyclohexanes the chair conformation containing both the substituents in equatorial positions will be the preferred conformation. In general, the conformation with bulkier substituent in an equatorial position will be the preferred conformation. For examples:



cis 1,3-cyclohexanediol has shown to have diaxial rather than the diequatorial orientation. This is because of the stabilisation orientation. This is because of the stabilisation of the diaxial form by intramolecular hydrogen bonding which is not possible in the diequatorial form.



The preferred conformation of the cyclohexane ring is the chair form, but when intromolecular hydrogen bonding is possible between groups in 1 and 4 positions the molecule assumes a boat conformation rather than the chair conformation in which this hydrogen bonding is not possible.



## SOME IMPORTANT TERMINOLOGY

- **Asymmetric carbon :** The carbon which is attached with four different groups of atoms is called asymmetric carbon.
- Asymmetric molecule : If all the four substituents attached to carbon are different, the resulting molecule will lack symmetry. Such a molecule is called asymmetric molecule. Asymmetry of molecule is responsible for optical activity in such organic compounds.
  - Achiral molecule : A molecule that is superimposable on its mirror image. Achiral molecules lack handedness and are incapable of existing as a pair of enantiomers.
- **Axial bond :** The six bonds of a cyclohexane ring (below) that are perpendicular to the general plane of the ring, and that alternate up and down around the ring.
- **Boat conformation :** A conformation of cyclohexane that resembles a boat and that has eclipsed bonds along its two sides.
- **Chair conformation :** The all-staggered conformation of cyclohexane that has no angle strain or torsional strain and is therefore, the lowest energy conformation.

- Chiral molecule : A molecule that is not superimposable on its mirror image. Chiral molecules have handedness and are capable of existing as a pair of enantiomers.
- **Chirality :** The property of having handedness.
- **Configuration :** The particular arrangement of atoms (or groups) in space that is characteristic of a given stereoisomer.
- **Conformation :** A particular temporary orientation of a molecule that results from rotations about its single bonds.
- **Conformational analysis :** An analysis of the energy changes that a molecule undergoes as its groups undergo rotation (sometimes only partial) about the single bonds that join them.
- **Conformer** : A particular staggered conformation of a molecule.
- **Connectivity :** The sequence, or order, in which the atoms of a molecule are attached to each other.
- **Diastereomers :** Stereoisomers that are not mirror images of each other.
- **Dextrorotatory :** Those substances which rotate the plane of polarisation of light towards right are called dextrorotatory. Currently, dextro and laevo rotations are represented by algebraic signs of (+) and (-) respectively.
- Eclipsed conformation : A temporary orientation of groups around two atoms joined by a single bond such that the groups directly oppose each other.
- Enantiomers : Stereoisomers that are mirror images of each other. enantiomers rotate the plane of polarised light to the same extent but in opposite direction.
- Equatorial bond : The six bonds of a cyclohexane ring that lie generally around the "equator" of the molecule.

- **Leavoratatory :** A compound that rotates plane polarised light in a counterclockwise direction.
- **Meso compound :** An optically inactive compound whose molecules are achiral even though they contain tetrahedral atoms with four different attached groups. A meso-compound is optically inactive due to internal compensation.
- **Optically active substances :** Those substances which rotate the plane of polarisation of plane-polarised light when it is passed through their solution are called optically active substances. This phenomenon is called optical activity.
- **Plane of symmetry :** An imaginary plane that bisects a molecule in a way such that the two halves of the molecule are mirror images of each other. Any molecule with a plane of symmetry will be achiral.
- **Plane-polarized light :** Ordinary light in which the oscillations of the electrical field occur only in one plane. It is obtained by passing a monochromatic light (light of single wavelength) through a Nicol prism.
- **Polarimeter :** A device used for measuring optical activity.
- **(R-S)** System : A method for designating the configuration of tetrahedral stereogenic centres.
- **Racemic form (racemate or racemic mixture) :** An equimolar mixture of enantiomers. A racemic mixture is optically inactive due to external compensation. **Racemisation :** The process of conversion of an enantiomer into racemic mixture is known as an racemisation.
- **Retention :** If in an optically active molecule the relative configuration of the atomic groups around a chiral centre remains the same before and after the reaction, the reaction is said to proceed with retention of configuration.

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- **Relative configuration :** The relationship between the configuration of two chiral molecules. Molecules are said to have the same relative configuration when similar or identical groups in each occupy the same position in space. The configuration of molecules can be related to each other through reactions of known stereochemistry, for example through reactions that cause no bonds to a stereogenic center to be broken.
- **Resolution :** The process by which the enantiomers of a racemic form are separated.
- **Ring flip :** The change in a cyclohexane ring (resulting from partial bond rotations) that converts one ring conformation to another. A chair-chair ring flip converts any equatorial substitutent to an axial substituent and vice versa.
- **Ring strain :** The increased potential energy of the cyclic form of a molecule (usually measured by heats of combustion) When compared to its acyclic form.

- **Specific rotation :** Specific rotation is defined as the number of degrees of rotation observed when the concentration of optically active substance is 1 g cm<sup>-3</sup> and length of polarimeter tube is 1 decimetre (dm) for D-line of sodium vapour lamp at  $25^{\circ}$ C.
- **Stereogenic center :** An atom bearing group of such nature that an interchange of any two groups will produce a stereoisomer.
  - **Steric hindrance :** An effect on relative reaction rates caused when the spatial arrangement of atoms or groups at or near the reacting site hinders or retards a reaction.
- **Torsional strain :** The strain associated with an eclipsed conformation of a molecule; it is caused by repulsions between the aligned electron pairs of the eclipsed bonds.

## **Exercise 1 (Level-A)**

#### Structural Isomers

1. Which of the following pairs of compounds are not metamers ?



(A) CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> and CH<sub>3</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>3</sub> (B) CH<sub>3</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>3</sub> and CH<sub>3</sub>OCH(CH<sub>3</sub>)<sub>2</sub> (C) CH<sub>3</sub>NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> and CH<sub>3</sub>CH<sub>2</sub>NHCH<sub>2</sub>CH<sub>3</sub> (D) CH<sub>3</sub>NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> and  $CH_3$ CH<sub>3</sub>-N-CH<sub>2</sub>-CH<sub>3</sub>

[ C. 57.79%, I.C. 29.32%, U.A. 12.89% ]

**2.**  $CH_3 - CH_2 - CHO \& CH_2 = CH - CHO & CHO$ CH<sub>2</sub> -OH are -



(A) functional (B) tautomers (C) position

(D) metamers [ C. 56.70%, I.C. 28.19%, U.A. 15.11% ]

Functional isomer of CH<sub>3</sub>COOCH<sub>3</sub> is 3.



- (A) CH<sub>3</sub>CH<sub>2</sub>COOH
- (B) HOCH<sub>2</sub>—CH<sub>2</sub>CHO
- (C) Both of the above
- (D) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>COOH

[ C. 52.72%, I.C. 32.47%, U.A. 14.81% ]

Given compound show which type of 4. isomerism?





- (A) Chain isomerism
- (B) Positional isomerism
- (C) Metamerism
- (D) Functional group isomerism

[ C. 52.47%, I.C. 33.05%, U.A. 14.48% ]

Metamerism is shown by-5.



- (A) Diethyl ether and n-propyl methyl ether
- (B) Ethyl alcohol and diethyl ether
- (C) Acetone and propionaldehyde
- (D) Propionic acid and acetic acid

[ C. 51.07%, I.C. 34.10%, U.A. 14.83% ]



- (A) Tautomers (C) Position
- (D) All the above

**(B)** Functional

JEE Main Level

[ C. 49.87%, I.C. 38.44%, U.A. 11.69% ]

- Shows which type of isomerism : 7. H and °CH₂
  - (A) Functional group isomerism
  - (B) Geometrical isomerism
  - (C) metamerism **(D)** Position isomerism
    - [ C. 49.34%, I.C. 32.12%, U.A. 18.54% ]
- **8.**  $CH_3CONH_2$  & HCONHCH<sub>3</sub> are called -



- (A) Position
- (C) Tautomers
- **(B)** Chain (D) Functional
- [ C. 49.06%, I.C. 36.05%, U.A. 14.89% ]
- 9. Which one of the following pairs are called position isomers -



(A) CH<sub>2</sub> (OH) CH<sub>2</sub>COOH & CH<sub>3</sub> CH (OH) COOH

- **(B)** C<sub>2</sub>H<sub>5</sub>OH & CH<sub>3</sub>OH
- (C) (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>CO & CH<sub>3</sub>COCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>
- **(D)** All the above

[ C. 47.82%, I.C. 37.06%, U.A. 15.12% ]
						Isomer	ism
10.	The repres	number sented by	of the fo	ether ormula	metamers C <sub>4</sub> H <sub>10</sub> O is		
	<b>(A)</b> 4			<b>(B)</b>	3		
	<b>(C)</b> 2			<b>(D)</b>	1		
				[ C. 47.0	7%, I.C. 37.81%, U	J.A. 15.12% ]	
11.	Pheno	and ben	zyl a	lcohol a	are		

(A) functional isomers (B) Homologous

(D) not isomer (C) position isomers

[ C. 44.68%, I.C. 44.92%, U.A. 10.40% ]

- **12.** Possible number of disubstituted benzene isomers is –
  - **(A)** 1 **(B)** 2
  - **(C)** 3

[ C. 44.61%, I.C. 43.07%, U.A. 12.32% ]

**(D)** 4

**13.** Methyl propyl thioether and isopropyl methyl thioether are -



- (A) Metamers
- **(B)** Position isomers
- (C) Chain isomers
- (D) Chain and position both

#### [ C. 40.18%, I.C. 47.29%, U.A. 12.53% ]



- (A) chain isomers
- (B) positional isomers
- (C) both
- (D) metamers

#### [C. 39.13%, I.C. 39.13%, U.A. 21.74%]

**15.** Number of structural isomers of compound having molecular formula C<sub>4</sub>H<sub>7</sub>Cl.



(A) 4 **(B)** 8 **(C)** 12 **(D)** 16 [ C. 35.21%, I.C. 46.15%, U.A. 18.64% ]

# Tautomerism

- **16.** The phenomenon involving the migration of a proton to give two structural isomers in equilibrium with each other is known is -
  - (A) Metamerism (B) Tautomerism
  - (C) Cis trans isomerism
  - (D) Stereo isomerism

#### [ C. 70.17%, I.C. 24.31%, U.A. 5.52% ]

17. Ethyl acetoacetate shows -



- (A) Enantiomorphism
- (B) Geometrical isomerism
- (C) Diastereoisomerism
- (D) Keto-enol Tautomerism

#### [ C. 67.33%, I.C. 29.32%, U.A. 3.35% ]

18. Tautomerism is exhibited by -





#### [ C. 67.11%, I.C. 28.50%, U.A. 4.39% ]

**19.** Which of the following compounds can exhibit tautomerism





**20.** Which of the following will show tautomerism



(A) Ph - CHO(C)  $CH_3 - C \equiv N$ 

**(D)**  $\cap$ 

(B) CH<sub>3</sub>CHO

**(B)** 

[ C. 58.12%, I.C. 35.04%, U.A. 6.84% ]

-Ph

-CHO

**21.** Which of the following does not show tautomerism?



(A)  $C_6H_5COCH_3$ (C) CH<sub>3</sub>COCH<sub>3</sub>

(D)  $C_6H_5COC(CH_3)_3$ [ C. 46.16%, I.C. 39.97%, U.A. 13.87% ]

**22.** Identify the compound that exhibits tautomerism-



- (A) 2-Butene
- (C) 2-Pentanone

(D) Cyclobutane [ C. 42.62%, I.C. 47.54%, U.A. 9.84% ]

23. Which of the following compound will be undergo Tautomerism?











[ C. 25.33%, I.C. 38.67%, U.A. 36.00% ]

[ C. 38.94%, I.C. 23.01%, U.A. 38.05% ]

27. Keto-enol tautomerism is observed in



[ C. 25.00%, I.C. 41.67%, U.A. 33.33% ]

28. Tautomerism is observed in-



**29.** Tautomer in following is Diad system



(A) CH<sub>3</sub>COCH<sub>3</sub> **(C)** 



**(D)** 

[ C. 10.00%, I.C. 40.00%, U.A. 50.00% ]

[ C. 9.09%, I.C. 44.70%, U.A. 46.21% ]

**30.** Which of the given compound gives least enol content?









**31.** Which can show the cis-trans isomerism :



(A) ClCH<sub>2</sub>CH<sub>2</sub>Cl (C)  $Cl_2C = CCl_2$ 

**32.** Geometrical isomerism is due to -



- (A) The restricted rotation about a double bond
- (B) The presence of keto group
- (C) The presence of CH(OH) group
- (D) The presence of an asymmetric carbon

[ C. 69.58%, I.C. 16.88%, U.A. 13.54% ]

**(B)**  $Cl_2C = CH_2$ 

(D) ClCH = CHCl[ C. 71.69%, I.C. 23.49%, U.A. 4.82% ]

**33.** Which of the following will exhibit geometrical isomerism?



- (A) 1-phenyl-2-butene
- (B) 3-phenyl-1-butene
- (C) 2-phenyl-1-butene
- (D) 1,1-diphenyl-1-propene

[ C. 67.87%, I.C. 22.99%, U.A. 9.14% ]

**34.** The geometrical isomerism is shown by -





[ C. 62.98%, I.C. 28.24%, U.A. 8.78% ]



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- **47.** Which of the following compounds will show geometrical isomerism -

  - (A) 2-Butyne
     (B) 2-Pentene
     (C) 2-Methylpropene
     (D) 2-Methyl-2-Butene
     [C. 49.82%, I.C. 37.05%, U.A. 13.13%]

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and

(A) conformers

(C) optical

CH<sub>3</sub>

(B) position

(D) geometrical

[ C. 65.36%, I.C. 22.19%, U.A. 12.45% ]

**53.** At room temperature the eclipsed and the staggered forms of ethane cannot be isolated because -



(A) both the conformers are equally stable

(B) They inter convert rapidly

(C) there is a large energy barrier of rotation about the  $\sigma$ -bond

**(D)** the energy difference between the conformers is large

[ C. 64.18%, I.C. 26.18%, U.A. 9.64% ]

**54.** How many conformations does ethane have



- (A) 1 (B) 2 (C) 3 (D) Infinite
- **55.** In 2-Fluoroethanol which conformer will be most stable ?
  - (A) Eclipsed (B) Skew
  - (C) Gauche Staggered (D) Anti Staggered [C. 60.57%, I.C. 35.43%, U.A. 4.00%]
- **56.** Isomers which can be interconverted through rotation around a single bond are –



(B) Diastereomers (D) Positional isomers [C. 60.48%, I.C. 32.16%, U.A. 7.36%]

**57.** Which is incorrect statement :-



- **58.** Which conformer of cyclohexane is chiral?
  - (A) Chair
  - (C) Twisted boat

[ C. 47.62%, I.C. 46.19%, U.A. 6.19% ]

(D) None of these

**(B)** Boat

(B) Chair

**59.** The least stable conformation of cyclohexane is



(A) Boat(C) Twist boat

**(D)** Half chair

[ C. 47.26%, I.C. 38.36%, U.A. 14.38% ]

**60.** Chair form of cyclohexane is more stable than boat form because :



(A) In chair form carbons are in staggered form and in baot form carbons are in eclipsed from(B) In chair form carbons are in eclipsed from and in boat form all the carbons are in staggered form

(C) Bond angle in chair form is 111° and bond angle in boat form is 109.5°

**(D)** Bond angle in chair form is 109.5° and in boat form 111°

#### [ C. 46.82%, I.C. 42.32%, U.A. 10.86% ]

**61.** The most stable form of trans-1,4-dimethylcyclohexane is represented as









[ C. 45.77%, I.C. 45.42%, U.A. 8.81% ]

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62. Which conformation of butane will have the minimum energy?



(A) Gauche

(C) Eclipsed

(D) partially ecliped [ C. 44.70%, I.C. 50.00%, U.A. 5.30% ]

**(B)** Staggered

**63.** Flagpole interaction is present in :



- (A) Boat form of cyclohexane
- (B) Chair form of cyclohexane
- (C) Anit form of n-butane
- (D) Fully eclipsed form on n-butane

#### [ C. 43.28%, I.C. 46.89%, U.A. 9.83% ]

64. The correct statement regarding the comparison staggered and eslipsed conformations of ethane,

(A) The staggered conformation of ethane is low stable than eclipsed conformation, because staggered conformation has torsional strain

(B) The esclipsed conformation of ethane is more stable than staggered conformation, because eclipsed conformation has no torsional strain

(C) The eclipsed conformation of ethen is more stable than staggered conformation even though the eclipsed conformation has torsional strain.

(D) The staggered conformation of ethane is more stable than eclipsed conformation,

because staggered conformation has no torsion strain.

#### [ C. 40.43%, I.C. 49.65%, U.A. 9.92% ]



## **Optical Isomerism**

66. The process of separation of racemic modifications into d and l enantiomer ; is called-



- (A) Resolution
- (B) Dehydration
- (C) Revolution
- (D) Dehydrohalogenation

[ C. 57.07%, I.C. 30.77%, U.A. 12.16% ]

**67.** How many asymmetric carbon atoms are present in -



- (i) 1,2-dimethyl cyclohexane
- (ii) 3-methyl cyclopentene
- (iii) 3-methyl cyclohexene
- (A) two, one, one
- (B) one, one one
- (C) two, none, two
- (D) two, none, one

#### [ C. 56.59%, I.C. 33.64%, U.A. 9.77%]

**68.** The molecule (s) that exist as meso structure(s)







- (B) both K and L
- (C) only L

(A) only M

(D) only K

[ C. 54.91%, I.C. 27.89%, U.A. 17.20% ]





[ C. 50.61%, I.C. 36.20%, U.A. 13.19% ]

**74.** Which of the following compounds can not exist as enantiomers –

(A)  $CH_3 CH(OH) COOH CH_3-CH_2-CH-CH_2OH$ (B)  $| CH_3$ (C)  $C_6H_5CH_2 CH_3$ (D)  $C_6H_5CHClCH_3$ 

[ C. 48.82%, I.C. 40.99%, U.A. 10.19% ]

**75.** Meso form of tartaric acid is –



- (A) Dextorotatory
- (B) Laevorotatory

(C) Neither Leave nor dextro rotatory due to internal compensation

**(D)** A mixture of equal quantities of dextro and leave rotatory forms

#### [ C. 47.74%, I.C. 34.73%, U.A. 17.53% ]

**76.** Which species exhibits a plane of symmetry ?





<sup>[</sup> C. 47.40%, I.C. 32.45%, U.A. 20.15% ]

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77. A Fischer projection of (2R, 3S)-2,3butanediol is : -



Which of the following heptanols are chiral: 1-heptanol, 2-heptanol, 3-heptanol, 4-heptanol. 81.



- (A) All are chiral
- (B) 2-heptanol and 3-heptanol
- (C) 2-heptanol, 3-heptanol & 4-heptanol
- (D) 3-heptanol and 4-heptanol

#### [ C. 45.14%, I.C. 38.30%, U.A. 16.56% ]

- **82.** The structures shown here are related as being С Н СН<sub>3</sub> Н<sub>3</sub>С (B) enantiomers
  - (A) conformers
  - (C) geometrical isomers (D) diastereoisomers

[ C. 43.57%, I.C. 43.34%, U.A. 13.09%]

Which of the following is properly 83. classified as a meso compound?









this compound is

- (A) it shows geometrical isomerism
- (B) it posses centre of symmetry
- (C) it posses plane of symmetry
- (D) it shows optical isomerism

[ C. 43.08%, I.C. 42.05%, U.A. 14.87% ]



#### [ C. 47.36%, I.C. 39.92%, U.A. 12.72% ]

**78.** 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 a above solution dilute

e	
ngle of rotation if	
ed to 1 Litre.	

(A) 16° & 36°	<b>(B)</b> 6° & 30°
( <b>C</b> ) 3° & 30°	<b>(D)</b> 60 & 36°
	[ C. 46.16%, I.C. 35.05%, U.A. 18.79% ]

**79.** The priority of groups OH, COOH, CHO, OCH<sub>3</sub> attached to a chiral carbon is in order -



(A)  $OH > COOH > CHO > OCH_3$ (B)  $OCH_3 > OH > CHO > COOH$ (C)  $OCH_3 > OH > COOH > CHO$ (D)  $OCH_3 > COOH > CHO > OH$ 

[ C. 45.86%, I.C. 38.55%, U.A. 15.59% ]

80. Molecular formula of an optically active organic compound is  $C_4H_{10}O$ . Its structure is



(A)  $C_2H_5OC_2H_5$ (B) CH<sub>3</sub>OC<sub>3</sub>H<sub>7</sub> (C) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH (D) CH<sub>3</sub>CHOHCH<sub>2</sub>CH<sub>3</sub> [ C. 45.75%, I.C. 37.28%, U.A. 16.97% ]



[ C. 38.73%, I.C. 48.55%, U.A. 12.72% ]

**89.** 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 become 87.5% d-form and 12.5% l-form, then what will be the observed rotation for the mixture.

(A) 
$$-22.50$$
 (B)  $+22.5^{\circ}$   
(C)  $+7.5^{\circ}$  (D)  $-7.5^{\circ}$   
(C  $37.18\%$ , LC  $34.44\%$ , U.A.  $28.38\%$  [

•



# Calculation Of Isomers



Number of geometrical isomer o given compound will be :

(A) 2	<b>(B)</b> 3
<b>(C)</b> 4	<b>(D)</b> 5
	IC 51 44% IC 41

[ C. 51.44%, I.C. 41.13%, U.A. 7.43% ]





# **Exercise 1 (Level-B)**

#### **Structural Isomers**

1. Find DU of following compound



2. Draw all structurally isomeric 2° alkyl chlorides with molecular formula  $C_5H_{11}Cl$ .

(b)

(I)

- **3.** Draw all structurally isomeric benzene containing isomers with molecular formula  $C_7H_8O$ .
- 4. Draw all structurally isomeric cyclic bromides with molecular formula  $C_4H_7Br$ .
- 6. The ring chain functional isomer of compound But-2-ene are

**5.** The general formula  $C_nH_{2n}O_2$ 

#### Tautomerism

represents

**7.** Keto and enol form of a compound are related to each other as configurational isomers or constitutional isomers explain.



8. Which has greater enol content





9. Out of the following give structure which can form enol content. Give reason to your answer.



**Basic Learning** 





How many hydrogen can be replaced by 'D' when it reacts with in the presence  $D_2O/OD^-$ . Explain

**11.** How many compounds can show tautomerism.Explain it.









## **Geometrical Isomerism**

- **12.** Indicate whether each of the following compound is 'E' or 'Z'. (i)  $\stackrel{CH_3}{\xrightarrow{H}} C = C \stackrel{Cl}{\xrightarrow{Br}}$  (ii)  $\stackrel{I}{\xrightarrow{H}} C = C \stackrel{CH_3}{\xrightarrow{C_{H_2Cl}}}$ (iii)  $\stackrel{D}{\xrightarrow{H}} C = C \stackrel{H}{\xrightarrow{D}}$  (iv)  $\stackrel{H}{\xrightarrow{CH_3}} C = C \stackrel{CH_2Cl}{\xrightarrow{Cl}}$
- **13.** (a) BrHC = CHBr exists as two diastereomers draw them and compare their dipole moment. If Ist is trans and IInd is cis



(b) Trans-Butenedioic acid has higher melting point then cis-butenedioic acid. Why ?

(c) Draw the cis and trans structures of hex-2-ene. Which isomer will have higher b.p. and why ?

- 14. Number of groups or atoms which have higher priority than OCH<sub>3</sub> according to CIP rule.
  -CH<sub>3</sub>, -CH<sub>2</sub>-CH<sub>3</sub>, -OH, , CH<sub>2</sub>-I, -OH, -OC H<sub>3</sub>, -SH, -NMe<sub>2</sub>, -O-CH=CH<sub>2</sub>, -CCl<sub>3</sub>, -F
- **15.** Which of the following can show geometrical isomerism.







**16.** Define restricted rotation and give one example each of acyclic and cyclic compound, which can show geometrical isomersm.



#### **Conformational Isomerism**

**17.** 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

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









# projection formulas for tartaric acid.



(3)(4)(a) Which represent the same compound ? (b) Which represent enantiomers ?

- (c) Which represent a meso compound
- (d) Which are diastereomers?
- 20. Which conformational state of nbutane lies in higher energy state when rotated along C2–C3 bond?



**21.** What, if anything, can be said about the magnitude of the equilibrium following constant for the Κ equilibrium?



# **Optical Isomerism**

22. Mark each chiral center in the following molecules with an asterisk. How many stereoisomers are possible for each molecule?





**23.** Which of the following compounds are chiral? Which, if any, are meso?





24. How many stereoisomers exist for (a) 3-methylcyclopentanol? (b) 1,3-Cyclohexanediol?



**25.** Among the following How many compounds are chiral ?



**26.** Are the formulas within each set identical, enantiomers, or diastereomers ?





- **27.** How many compounds among the following have a stereoisomer that is achiral ?
  - (a) (i) 2,3-Dichlorobutane
    - (ii) 2,3-Dichloropentane
    - (iii) 2,3-Dichloro-2,3-

# dimethylbutane

- (b) (i) 1,2-Dimethylcyclobutane
  - (ii) 1,3-Dibromocyclobutane
  - (iii) 1,3-Dichlorocyclopentane
  - (iv) 1,2-Dimethylcyclopentane
- (c) (i) 2,4-Dibromopentane
  - (ii) 2,3-Dibromopentane
  - (iii) 1,4-Dimethylcyclohexane
- **28.** Following are stereo representations for the three stereoisomers of 2,3-Butanediol. The carbons are numbered beginning from the left, as shown in (1).





(a) Assign an R or S configuration to each chiral center.

- (b) Which are enantiomers ?
- (c) Which is the meso compound?
- (d) Which are diastereomers ?

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- **29.** Classify each of the following pairs of
  - structure as
  - I. Identical
  - E. Enantiomers.



**30.** (18) Now for some questions about stereochemical relationships. **Column A** 



Circle the word (s) in this column that describe the molecules in column A.



Circle one word in this column that best describes the relationship of the molecules in columns A and B



enantiomers diastereomers identical none of these



enantiomers diastereomers identical none of these



enantiomers diastereomers identical none of these



enantiomers diastereomers identical none of these







**32.** Select chiral molecule out of the following list compound



# **Calculation Of Isomers**

**33.** Calculate the number of aromatic 1°amine isomers possible of Toluidine



**34.** How many alkyl groups are possible from alkane C<sub>5</sub>H<sub>12</sub>.



- **35.** Calculate the number of isomeric ethers (only benzenoid) possible of OH
- **36.** The total number of isomers possible with the molecular formula  $C_4H_6$  is :





# **Exercise 2**

# **JEE Advanced Level**

#### Structural Isomers (Single Correct)

**1.** Total isomers of  $C_8H_{18}$  in which each isomer must have at least one Quaternary carbon



**(B)** 6 **(A)** 4

**(C)** 7 **(D)** 8

[ C. 70.51%, I.C. 20.36%, U.A. 9.13% ]

#### (Multiple Correct)

Me

Me

2. Which of the following is not the correct relationship







(A) II & IV are metamer

- (B) I & II are functional isomer
- (C) I & III are chain isomer
- (D) I and IV are positional isomer

**4.** Total Primary, secondary & tertiary amine of  $C_4H_{11}N$  are x, y & z. The value of x + y - 3z are (Only consider chiral carbon)



<b>(A)</b> 4	<b>(B)</b> 5
<b>(C)</b> 6	<b>(D)</b> 7

[C. 43.30%, I.C. 28.87%, U.A. 27.83%]

#### Tautomerism (Single Correct)

Order of enolic content 5.



[ C. 46.55%, I.C. 46.55%, U.A. 6.90% ]



# **Paragraph:**

The compound having same molecular formula and different physical or chemical or both properties are known as isomers. There are two types of isomerism.

- (1) Structural & (2) Stereo
- 3. The total carboxylic acid & total esters of  $C_5H_{10}O_2$  are x & y respectively. Find (x + y)

<b>(A)</b> 12	<b>(B)</b> 13
<b>(C)</b> 14	<b>(D)</b> 15

[ C. 66.82%, I.C. 23.09%, U.A. 10.09%]

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[ C. 68.49%, I.C. 24.20%, U.A. 7.31% ]

6. Which of the following is not a pair of tautomers ?



#### (Multiple Correct)

**7.** Tautomers of the compound



#### Question No. 8 & 9

#### **Paragraph:**

#### Tautomerism :

Structural Isomers that undergo rapid interconversions and exist in dynamic equilibrium are known as Tautomers and relationship between them is known as Tautomerism. Tautomers generally have different functional groups.

At equilibrium more stable tautomer is present in higher amount but the ratio remains same until and unless change is made externally. Tautomerism actually arises due to rapid oscillation of an atom between two polyvalent atoms in a molecule.

$$CH_2 - CH \rightleftharpoons CH_2 = CH$$

<sup>H</sup> Keto form enol form

Above is an example of Keto-enol tautomerism. Condition for this type of keto enol tautomerism is presence of  $\alpha$ -H. Amount of enol at equilibrium is known as enolic content. It is more if enol is more stable and less if keto is more stable.

8. Tautomer of which of the following can show geometrical isomerism



(A)  $CH_3 - CHO$ (B)  $CH_3 CH_2 - CHO$ (C)  $(CH_3)_2 CH - CH = O$ (D)

[ C. 65.00%, I.C. 10.00%, U.A. 25.00% ]





Me

[ C. 91.30%, I.C. 8.70% ]

(A) I & II are conformational isomers while II & III are functional isomers

ĊH₃

**(B)** I & II are functional isomers while II & III are conformational isomers

(C) I & II are functional isomers while I & III are not isomers

**(D)** I & II are isomers while I & II are conformational isomers

ĊH:

H<sub>2</sub>C

(III)

CH<sub>3</sub>

 $C_2H_5$ 

[ C. 32.00%, I.C. 54.91%, U.A. 13.09% ]

# (Multiple Correct)

**15.** The Fischer projection of the molecule as represented in the wedge





**16.** 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) -

(A) 
$$\stackrel{H}{\underset{H_2C}{\overset{H}{\longrightarrow}}} c - c \stackrel{H}{\underset{CH_2}{\overset{H}{\longrightarrow}}} (B) H - c \equiv c - c \stackrel{H}{\underset{CH_2}{\overset{H}{\longrightarrow}}} (C) H_2C = C = O (D) H_2C = C = CH_2 (C.43.30\% LC)$$

17. In the Newman projection for 2,2dimethylbutane Х Y and can respectively be



- (A) H and H **(B)** H and  $C_2H_5$
- (C)  $C_2H_5$  and H
- (D) CH<sub>3</sub> and CH<sub>3</sub>



28.87%, U.A. 27.83% [

[ C. 28.24%, I.C. 41.57%, U.A. 30.19% ]

# **Optical Isomerism (Single Correct)**

- **18.** Dextorotatory  $\alpha$ -pinene has a specific rotation  $[\alpha]_{\rm D}^{20}$  = +51.3°. A sample of  $\alpha$ pinene containing both the enantiomers was found to have a specific rotations value  $\left[\alpha\right]_{\rm D}^{20} = +30.8^{\circ}$ . The percentages of the (+) and (-)enantiomers present in the sample are, respectively.
  - (A) 70% and 30%
  - **(B)** 80% and 20%
  - (C) 20% and 80%
  - **(D)** 60% and 40%

#### [C. 43.79%, I.C. 38.58%, U.A. 17.63%]

**19.** Which of following pair is Diastereomers:







# (Multiple Correct)

**20.** Which of the following compounds is optically active ?





#### [ C. 48.72%, I.C. 33.08%, U.A. 18.20% ]

**21.** In which of the following molecule show chirality.





- (A) I is trans & chiral
- (B) II is trans & chiral
- (C) I is cis & chiral
- **(D)** II is trans & achiral

[ C. 40.50%, I.C. 38.63%, U.A. 20.87% ]

#### Question No. 22 - 24

#### **Paragraph:**

If a molecule contains one carbon atom carrying four different groups it will not have a plane of symmetry and must therefore be chiral. A carbon atom carrying four different groups is a steregoenic or chiral centre.

A structure with a plane of symmetry is achiral and superimposable on its mirror image and cannot exist as two enantiomer. A structure without a plane of symmetry is chiral and not superimposable on its mirror image and can exist as two enantiomer.





Relation between (a) & (b) is

- (A) Enantiomer (B) Diastereomer
- (C) Identical

**(D)** Structural isomer

- [ C. 65.61%, I.C. 26.11%, U.A. 8.28% ]
- **23.** Compound has both center of symmetry and P.O.S



[ C. 64.67%, I.C. 24.55%, U.A. 10.78% ]



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# **Exercise 3**

1. How many structures of  $2^{\circ}$  amines are possible by C<sub>5</sub>H<sub>13</sub>N (without counting stereoisomers)?



2. Number of cyclic structural isomers of  $C_5 H_{10}$ . (x) Double bond equivalent



\_<u>сно</u>. (у) Ph

Find the value of x + y

How many of the following pair 3. of compounds are position isomers (x) & chain isomers (y). Find value of



Total number of stereoisomer of 4. compound is :  $CH_3 - CH = CH - CH - CH = CH - C_2H_5$ Ċ1



How many of the following 5. compounds can show tautomerism?



Structural isomers possible for 6. C<sub>4</sub>H<sub>8</sub>Br<sub>2</sub> are -



**Numerical Type** 

In given compounds how many can 7. show geometrical isomerism-



- CH<sub>3</sub> (i) (ii) CH, (iv) (111) он
- 8. How many Hydrogen atoms are replaced by D in the following tautomerization.





In given compounds how many have 9 Z configuration along double bond?



Me<sub>3</sub>C ∕Ph (i) •NMe<sub>2</sub> H  $CH = CH_2$ Me (ii) Η Ft 12 (iii) 'NH<sub>2</sub> (iv)



**10.** Find how many geometrical isomers are possible for following comounds





Find w + x + y + z?



compounds Total compound if they are E (a) if they are Z (b) Find the value of a × b ?

- How many geometrical isomer are possible for this compound? CH<sub>3</sub>-CH=C-C=CH-CH<sub>3</sub> I Br Cl
- **13.** How many pair(s) of geometrical isomers are possible with  $C_5H_{10}$ (only in open chain structues)?
- **14.** Total number of compounds with molecular formula C<sub>5</sub>H<sub>10</sub> which can show geometrical isomerism are (only cyclic)?



- **15.** Calculate the total number of open chain isomeric compounds of molecular formula C<sub>4</sub>H<sub>8</sub>O which can show geometrical isomerism.
- **16.** How many of the following compounds represent 2-methyl pentane :





**17.** How many of the following are (configurational) enantiomers of (A) ?





**18.** Number of diastereomer of given compound :





19. Calculate total number stereocentre, prochiral carbon and theoretical stereoisomer in following compound.



of

the



Number of stereocentre = x; Number of plrochiral carbon = y and number of stereoisomer = z. Represent your answer as vxyz. Find x + y + z

**20.** How many of the following will rotate the plane polarized light at room temperature?



**21.** How many of the following statements are correct?



(1) The most stable conformer of cis-1,3-cyclohexanediol is chair form.

(2) Cis 1,3-cyclohexanediol is more

stable than trans-1 3-cyclohexanediol

(3) In cis-1,3-cyclohexanediol both the OH groups occupy equatorial positions.

(4) The most stable conformer of trans-1,4-cyclohexanediol is chair form

(5) The most stable conformer of cis-1,4-cyclohexanediol is boat conformer.

**22.** How many of the following alkynes which can exhibit optical isomerism are



- 4—methyl—1—pentyne
- 3—methyl—1—butyne
- 3—methyl—1—pentyne
- 4-methyl-2-pentyne

23. Draw all the possible stereoisomers of 3-pentene-2-ol.



24. How many total number of structural isomers of  $C_4H_6$   $Cl_2$  are possible having cyclic structures.

**25.** How many isomers are possible for

Nitrophenol?



26. The total number of cyclic isomers possible for a hydrocarbon with the molecular formula C<sub>4</sub>H<sub>6</sub> is / are :



- **27.** Find out the total number of cyclic isomers of  $C_5H_{10}$  which are optically active?
- **28.** Are the following structures chiral as drawn? When placed in a solution at 298 K, which structure will show an optical rotation? Explain.





**29**. How many compounds are theoretically possible for formula C<sub>3</sub>H<sub>6</sub>O (excluding stereoisomers)?



**30.** Total number of optically active stereoisomers of  $CH_3 - CH - CH = CH - CH - CH_3$ CI CI are :



# **Exercise 4 (Level-A)**

**1.** Among the following compounds, geometrical isomerism is exhibited by





2. Which one of the following pairs of isomers is an example of metamerism ?





# JEE Main (Previous Year Questions)

**3.** Choose the correct name for compound given below :



- (A) (4E)–5–Bromo-hex–4–en–2–yne
- **(B)** (2E)–2–Bromo-hex–4–en–2–yne
- (C) (4E)–5–Bromo-hex–2–en–2–yne
- (D) (2E)-2-Bromo-hex-2-en-4-yne [C. 39.22%, I.C. 33.92%, U.A. 26.86%] (JEE Main 2021)
- **4.** Staggered and eclipsed conformers of ethane are:



- (A) Enantiomers (B) Rotamers
- (C) Mirror images (D) Polymers

```
[ C. 37.43%, I.C. 42.11%, U.A. 20.46% ] (JEE Main 2021)
```

5. Compound with molecular formula  $C_3H_6O$  can show :



- (A) Both positional isomerism and metamerism
- (B) Metamerism
- (C) Positional isomerism
- (D) Functional group isomerism

[C. 36.40%, I.C. 43.58%, U.A. 20.02%] (JEE Main 2021)

6. Which of the following compounds shows geometrical isomerism ?



- (A) 2-methylpent-1-ene(B) 4-methylpent-2-ene
- (C) 2-methylpent-2-ene(D) 4-methylpent-1-ene [C. 36.30%, I.C. 53.70%, U.A. 10.00%] (JEE Main 2020)
- 7.  $H_3C + Br_2 \rightarrow Product "P"$



Consider the above chemical reaction. The total number of stereoisomers possible for product 'P' is

[ C. 32.99%, I.C. 56.85%, U.A. 10.16% ] (JEE Main 2021)

8. The number of chiral carbons present in the molecule given below is

Η

HO

H<sub>3</sub>C



[C. 31.40%, I.C. 52.09%, U.A. 16.51%] (JEE Main 2020)

9. The number of stereoisomers possible for 1,2-dimethyl cyclopropane is :



- (A) One (B) Four
- (C) Two (D) Three

[ C. 30.82%, I.C. 60.69%, U.A. 8.49% ] (JEE Main 2021)

**10.** Arrange the following conformational isomers of n-butane in order of their increasing potential energy:





(A) II < III < IV < I</li>
(B) I < III < IV < II</li>
(C) I < IV < III < II</li>
(D) II < IV < III < I</li>
(C. 27.10%, I.C. 46.27%, U.A. 26.63% (JEE Main 2021)



image of above compound A. In the light of the above statement, choose the most appropriate answer from the options given below.

(A) Both Statement I and Statement II are correct

**(B)** Both Statement I and Statement II are incorrect

(C) Statement I is correct but Statement II is incorrect

(D) Statement I is incorrect but Statement II is correct

[ C. 24.33%, I.C. 65.67%, U.A. 10.00% ] (JEE Main 2022)

12. Number of isomeric compounds with molecular formula  $C_9H_{10}O$  which (i) do not dissolve in NaOH (ii) do not dissolve in HCl. (iii) do not give orange precipitate with 2, 4– DNP (iv) on hydrogenation give identical compound with molecular formula  $C_9H_{12}O$  is :-



[ C. 23.01%, I.C. 45.81%, U.A. 31.18% ] (JEE Main 2023)

**13.** Which one of the following molecules does not show stereoisomerism ?



- (A) 3, 4-dimethylhex-3-ene
- **(B)** 4-Methylhex-1-ene
- (C) 3-Methylhex-1-ene
- **(D)** 3-Ethylhex-3-ene

[C. 21.78%, I.C. 54.15%, U.A. 24.07%] (JEE Main 2021)

**14.** Optical activity of an enantiomeric mixture is  $+12.6^{\circ}$  and the specific rotation of (+) isomer is  $+30^{\circ}$ . The optical purity is %

[C. 21.15%, I.C. 58.33%, U.A. 20.52%] (JEE Main 2022)

**15**. The dihedral angle in staggered form of Newman projection of 1,1,1-Trichloro ethane is degree. (Round off to the nearest integer)

[C. 19.35%, I.C. 28.47%, U.A. 52.18%] (JEE Main 2021)

**16.** L-isomer of a compound 'A'  $(C_4H_8O_4)$  gives a positive test with  $[Ag(NH_3)_2]^+$ . Treatment of 'A' with acetic anhydride yields triacetate derivative. Compound 'A' produces an optically active compound (B) and an optically inactive compound (C) on treatment with bromine water and HNO<sub>3</sub> respectively. Compound (A) is:



**17**. The total number of chiral compound/s from the following is



<sup>[</sup>C. 17.29%, I.C. 34.30%, U.A. 48.41%] (JEE Main 2023)

**18.** The number of acyclic structural isomers (including geometrical isomers) for pentene are



[ C. 13.91%, I.C. 39.57%, U.A. 46.52% ] (JEE Main 2021)

**19** The number of stereoisomers formed in a reaction of

 $(\pm) \operatorname{Ph}(C = O)C(OH)(CN)\operatorname{Ph}$  with HCN

is

Where Ph is 
$$-C_6H_5$$
]

#### [C. 13.31%, I.C. 61.98%, U.A. 24.71%] (JEE Main 2022)

**20.** Which of the following conformations will be the most stable?





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# 21. Match List I with List II

L	ist I (Isomeric pairs)	) List II (Type of isomers)		
A.	Propanamine and N- Methylethanamine	I.	Metamers	
B.	Hexan-2-one and Hexan-3-one	II.	Positional isomers	
C.	Ethanamide and Hydroxyethanimine	III.	Functional isomers	
D.	o-nitrophenol and p- nitrophenol	IV.	Tautomers	

Choose the correct answer from the options given below :-

- (A) A-II, B-III, C-I, D-IV
- (B) A-III, B-I, C-IV, D-II
- (C) A-III, B-IV, C-I, D-II
- (D) A-IV, B-III, C-I, D-II
  - [ C. 10.46%, I.C. 70.46%, U.A. 19.08% ] (JEE Main 2023)

**22.** The isomeric deuterated bromide with molecular formula  $C_4H_8DBr$  having two chiral

carbon atoms

is

- (A) 2–Bromo–2–deuterobutane
- (B) 2–Bromo–1–deuterobutane
- (C) 2–Bromo–1–deutero–2–methylpropane
- (D) 2–Bromo–3–deuterobutane

[C. 9.22%, I.C. 71.27%, U.A. 19.51%] (JEE Main 2023)

**23.** Total number of possible stereoisomers of dimethyl cyclopentane is



[C. 6.35%, I.C. 67.99%, U.A. 25.66%] (JEE Main 2022)

**24.** Smallest optically active alkene  $\xrightarrow{\text{Hydrogenation}} \xrightarrow{\text{Cl}_2/\text{h}\nu} \xrightarrow{}$ 



```
How many monochloro products [including stereoisomer] are formed ?
```

[ C. 5.79%, I.C. 70.25%, U.A. 23.96% ] (JEE Main 2020)

**25.** Total number of isomers (including stereoisomers) obtained on monochlorination of methyl cyclohexane is



[C. 4.35%, I.C. 72.67%, U.A. 22.98%] (JEE Main 2022)

# **Exercise 4 (Level-B)**

1. Newman projections P, Q, R and S are shown below:





Q



Which one of the following options represents identical molecules?

(A) P and	Q	<b>(B)</b> Q	and S	
(C) Q and	R	<b>(D)</b> R	and <b>S</b>	
	10 21 500/ 10	16 000/ XX 4	22 (10) 1 (TEE 11	

[C. 31.50%, I.C. 46.09%, U.A. 22.41%] (JEE Adv. 2020)

- **JEE Advanced (Previous Year Questions)** 
  - 2. The Fischer projection of D-erythrose is shown below.
    - СНО
    - н—он н—он
    - CH<sub>2</sub>OH

D-Erythrose and its isomers are listed as P, Q, R, and S in Column-I. Choose the correct relationship of P, Q, R, and S with D-erythrose from Column II.



- (A)  $P \rightarrow 2$ ,  $Q \rightarrow 3$ ,  $R \rightarrow 2$ ,  $S \rightarrow 2$ (B)  $P \rightarrow 3$ ,  $Q \rightarrow 1$ ,  $R \rightarrow 1$ ,  $S \rightarrow 2$
- (C)  $P \rightarrow 2$ ,  $Q \rightarrow 1$ ,  $R \rightarrow 1$ ,  $S \rightarrow 3$
- (**b**)  $\mathbf{P} \rightarrow 2$ ,  $\mathbf{Q} \rightarrow 3$ ,  $\mathbf{R} \rightarrow 3$ ,  $\mathbf{S} \rightarrow 1$

[C. 29.55%, I.C. 44.89%, U.A. 25.56%] (JEE Adv. 2020)

**3.** The total number(s) of stable conformers with nonzero dipole moment for the following compound is (are).





[C. 27.47%, I.C. 61.80%, U.A. 10.73%] (JEE Adv. 2014)



 Total number of isomers, considering both structural and stereoisomers, of cyclic ethers with the molecular formula C<sub>4</sub>H<sub>8</sub>O is ...... [Divide your answer by 5]



[C. 24.59%, I.C. 39.04%, U.A. 36.37%] (JEE Adv. 2019)

 The total number of stereoisomers that can exist for M is H<sub>3</sub>C<sub>5</sub> CH<sub>3</sub>





[C. 24.53%, I.C. 54.67%, U.A. 20.80%] (JEE Adv. 2015)

6. Among the following, the conformation that corresponds to the most stable conformation of meso-butane-2,3-diol is



[C. 21.98%, I.C. 55.68%, U.A. 22.34%] (JEE Adv. 2021)

**7.** For the given compound X, the total number of optically active stereoisomers is



OH OH н OH òн

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

(**••••**) This type of bond indicates that he configuration at the specific carbon and the geometry of the double bond is NOT fixed.

#### [C. 13.77%, I.C. 76.92%, U.A. 9.31%] (JEE Adv. 2018)

8. An organic compound  $(C_8H_{10}O_2)$ rotates plane-polarized light. It produces pink color with neutral FeCl<sub>3</sub> solution. What is the total number of all the possible isomers for this compound?



[C. 7.49%, I.C. 71.58%, U.A. 20.93%] (JEE Adv. 2020)

	Isomerism								
	Answer Key								
Exe	ercise 1 (Level-A)						JEE Main Level		
1.	D 2. A	<b>3.</b> C	<b>4.</b> C	5. A	<b>6.</b> B	<b>7.</b> C	8. D		
9.	A 10. B	11. D	<b>12.</b> C	<b>13.</b> B	<b>14.</b> A	<b>15.</b> C	<b>16.</b> B		
17.	D 18. D	<b>19.</b> B	<b>20.</b> C	<b>21.</b> D	<b>22.</b> C	<b>23.</b> D	<b>24.</b> C		
25.	D 26. B	<b>27.</b> C	<b>28.</b> B	<b>29.</b> D	<b>30.</b> C	<b>31.</b> D	<b>32.</b> A		
33.	A 34. D	<b>35.</b> B	<b>36.</b> A	<b>37.</b> D	<b>38.</b> C	<b>39.</b> D	<b>40.</b> B		
41.	C 42. D	<b>43.</b> D	<b>44.</b> D	<b>45.</b> D	<b>46.</b> C	<b>47.</b> B	<b>48.</b> C		
49.	A 50. D	<b>51.</b> A	<b>52.</b> A	<b>53.</b> B	<b>54.</b> D	<b>55.</b> C	<b>56.</b> A		
57.	A 58. C	<b>59.</b> D	<b>60.</b> A	<b>61.</b> C	<b>62.</b> B	<b>63.</b> A	<b>64.</b> D		
65.	B 66. A	<b>67.</b> A	<b>68.</b> B	<b>69.</b> B	<b>70.</b> D	<b>71.</b> B	72. B		
73.	D 74. C	<b>75.</b> C	<b>76.</b> D	77. A	7 <b>8.</b> B	<b>79.</b> C	80. D		
81.	B 82. D	<b>83.</b> A	<b>84.</b> B	<b>85.</b> C	<b>86.</b> C	<b>87.</b> A	<b>88.</b> A		
89.	B 90. D	<b>91.</b> C	<b>92.</b> C	<b>93.</b> C	<b>94.</b> A	<b>95.</b> D	96. D		
97. E	C 98. C						Desis Lesuria -		
Exe	ercise I (Level-B)						Basic Learning		
1.	(a) = 1, (b) = 5			2.	, CI	CI,	CI		
3.	OCH3 CH3 OH	CH <sub>3</sub>	CH <sub>2</sub> OH	4.	Br, $M$ , $M$	Br			
		- υп,	νπ ,	6.	CH <sub>3</sub> or				
8.	В			<b>9.</b> A,	B & C				
10.	6			11. A,	B, D, E				

#### Isomerism 14. 5

- 13. (a) II > I
  - (b) Good packing
  - (c) Cis

- 18. (a) Cis (b) Cis (c) Cis(d) Trans (e) Trans (f) Trans
- 20. Fully Eclipsed
- 22. (a) S.I. =  $2^2 = 4$  (b) S.I. =  $2^2 = 4$  (c) S.I. =  $2^1 = 2$ (d) S.I. =  $2^3 = 8$  (e) S.I. =  $2^2 = 4$  (f) S.I. =  $2^2 = 4$ (g) S.I. =  $2^2 = 4$
- 25. 2
- 27. (a) (i) -Achiral (ii)-Chiral (iii)- Achiral (b) (i)- Achiral (ii)-Achiral (iii) Achiral (iv) Achiral (iv) Achiral (c) (i) -Achiral (ii)-Chiral (iii)- Achiral (iii)-Achiral (ii)-Achiral (iii)-Achiral (iii)-Achiral (iii)-Achiral (iii)-Achiral (ii)-Achiral (ii)-Achiral (iii)-Achiral (ii)-Achiral (ii)-A
- 29. (a)Enantiomers.(b)Diastereomers(c)Identical
- 31. (a) = 16 (b) = 4
- **33.** 4
- **35.** 5

- **15.** (iii), (iv), (vi), (vii) and (viii)
- 17.  $H_{3}^{1}C \overset{2}{C}H \overset{3}{C}H_{2} \overset{4}{C}H_{2} \overset{5}{C}H_{2} \overset{6}{C}H_{3}$

(a)Most stable conformer (b)Least stable conformer



**19.** a. Same Compound  $\rightarrow$  3 & 4

b. Enantiomer  $\rightarrow 1 \& 3, 1 \& 4$ 

- C. Meso  $\rightarrow 2$
- D. Diastereomers  $\rightarrow$  (2,3)(2,4)(1,2)
- **21.** K < 1
- 23. (a) chiral (b) chiral(c) meso (d) Achiral
- **24.** (a) =4 (b) =3
- 26. (A) Enantiomers(B) Diastereomers(C) Diastereomers
- (a) 1. (2R,3R) 2. (2R,3S) 3. (2S,3S)
  (b)Enantiomer → 1 & 3
  (c) Meso → (ii)
  (d) Diastereomers → i, ii & ii, iii
- 30. Column -A Column -B
  (A)-Chiral (a)- Enantiomer
  (B)-Chiral (b)-Enantiomer
  (C)-Meso (c)-Diastereomer
  (D)-Chiral (d)- Diastereomer
- 32. (i) achiral (ii) achiral (iii) chiral (iv) chiral (v) achiral (v) achiral
- **34.** 8

Exercise 2	2					JEE Adv	anced Level
1. D	<b>2.</b> A,D	3. D	<b>4.</b> B	5. C	<b>6.</b> C	7. A,B,C,D	8. B
9. D	<b>10.</b> B	11. A,B,D	<b>12.</b> A	13. D	<b>14.</b> C	<b>15.</b> A,C	16. B,C
17. B,D	<b>18.</b> B	<b>19.</b> B	<b>20.</b> B,C	<b>21.</b> A,D	<b>22.</b> B	<b>23.</b> D	<b>24.</b> B
25. <sub>A-R</sub> , B	-P, C-S, D-S	26. A-PQR, E QRS, D-F	3-QRS, C- PQR				
Exercise 3	}					Nui	nerical Type
1. 6	<b>2.</b> 14	<b>3.</b> 1	<b>4.</b> 8	<b>5.</b> 2	<b>6.</b> 9	7. 4	<b>8.</b> 4
<b>9.</b> 1	<b>10.</b> 6	11. 4	<b>12.</b> 4	<b>13.</b> 1	<b>14.</b> 2	15. 4	<b>16.</b> 1
17.4	<b>18.</b> 3	<b>19.</b> 78	<b>20.</b> 1	<b>21.</b> 4	<b>22.</b> 1	23. 4	<b>24.</b> 9
<b>25.</b> 3	<b>26.</b> 5	<b>27.</b> 2	<b>28.</b> 2	<b>29.</b> 9	<b>30.</b> 4		
Exercise 4	(Level-A)				JEE Ma	in (Previous Yea	r Questions)
1. A,B	<b>2.</b> B	3. D	<b>4.</b> B	5. D	<b>6.</b> B	7. 2	<b>8.</b> 5
9. D	<b>10.</b> B	<b>11.</b> C	<b>12.</b> 2	13. D	<b>14.</b> 42	<b>15.</b> 60	16. A
17. 2	<b>18.</b> 6	<b>19.</b> 3	<b>20.</b> B	<b>21.</b> B	<b>22.</b> D	<b>23.</b> 6	<b>24.</b> 8
<b>25.</b> 12							
Exercise 4	(Level-B)				JEE Advance	ed (Previous Yea	r Questions)
1. C	<b>2</b> . C	3. 3	4. 2	5. 2	6. B	<b>7</b> . 7	<b>8.</b> 6
