OC Mega Revision

• Live at 8:00 PM

5th April - 24th April

eSaral

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Complete Chemistry Mega Revision Timetable

5 April	7 April	9 April	12 April
IUPAC + GOC	Structural + Stereo Isomerism	Hydrocarbon	Haloalkane & Haloarenes

14 April	16 April	19 April	21 April
Alcohol, Phenol & Ether	Carbonyl Compounds	Oxidation, Reduction, Carboxylic Acid & amines	**Polymer & Environmental Chem**

23 April
Biomolecule and CIEL

Organic Chemistry Mega Revision Imp Qs Timetable

6 April	8 April	10 April	13 April
IUPAC + GOC	Structural + Stereo Isomerism	Hydrocarbon	Haloalkane & Haloarenes

15 April	17 April	20 April	22 April
Alcohol, Phenol & Ether	Carbonyl Compounds	Oxidation, Reduction, Carboxylic Acid & amines	**Polymer & Environmental Chem**

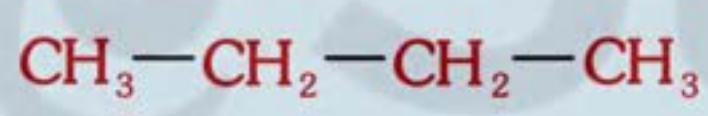
24 April
Biomolecule and CIEL

I Love Chemistry

OC → Magic

Isomers

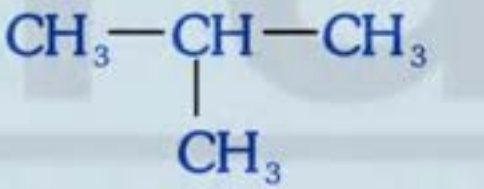
C_4H_{10}



Butane(4C)

-139.4°C

C_4H_{10}



2-Methyl propane (3C)

-159.6°C

Isomers

C_2H_6O

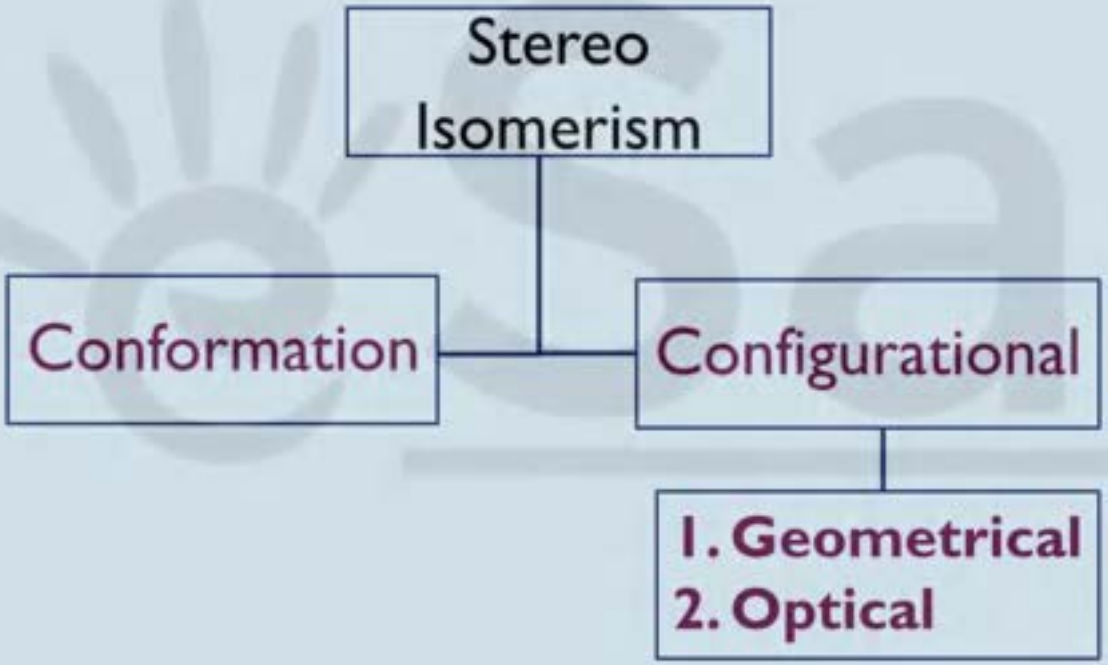
$CH_3—CH_2—OH$

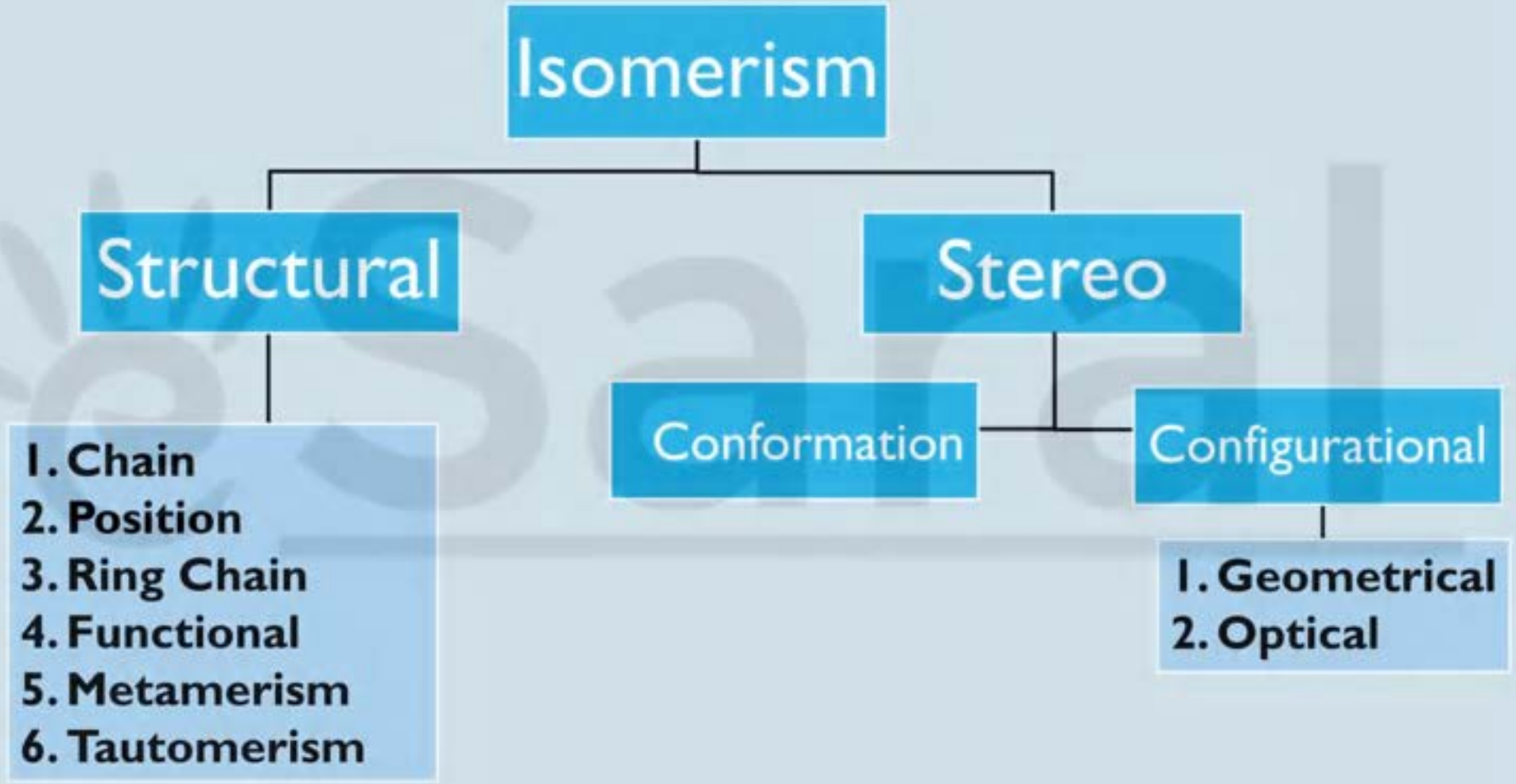
C_2H_6O

$CH_3—O—CH_3$

Structural Isomers

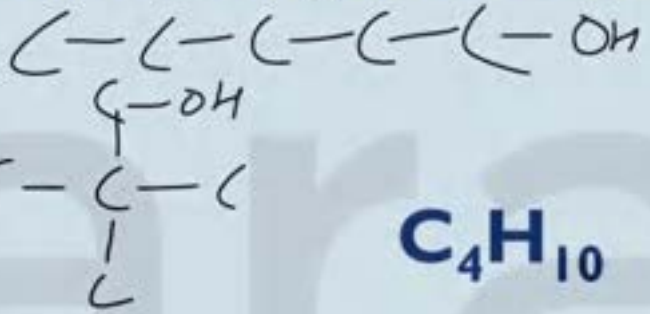
Stereo Isomers





1. Chain Isomerism (CI)

The compounds which have same molecular formula, same functional group, but difference in length of carbon chain (parent chain or side chain) show chain isomerism.



C_4H_{10}

$CH_3—CH_2—CH_2—CH_3$

Butane(4C)

-139.4°C

C_4H_{10}

$CH_3—CH(CH_3)—CH_3$

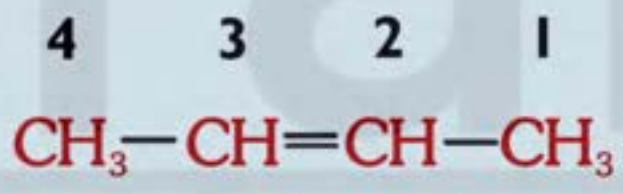
2-Methyl propane (3C)

-159.6°C

2. Position Isomerism

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.

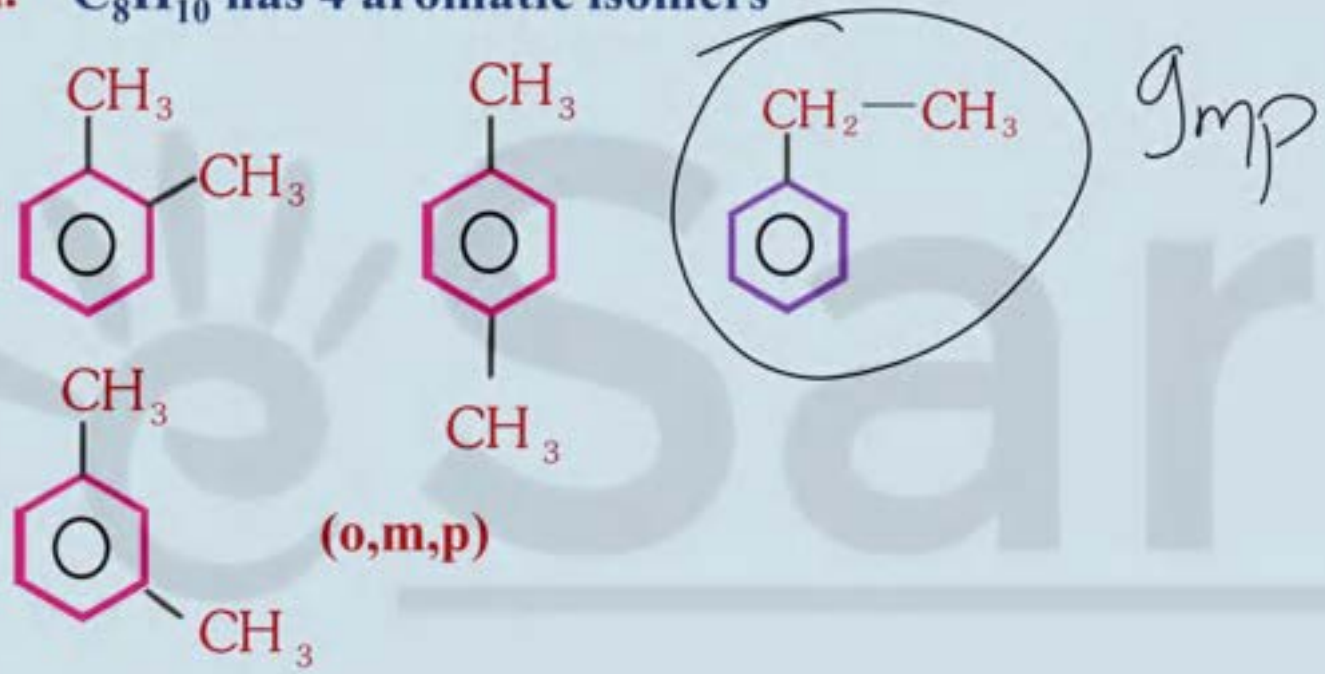
But–1–ene



But–2–ene

Q) How many benzenoid isomers are possible for molecular formula C_8H_{10} ?

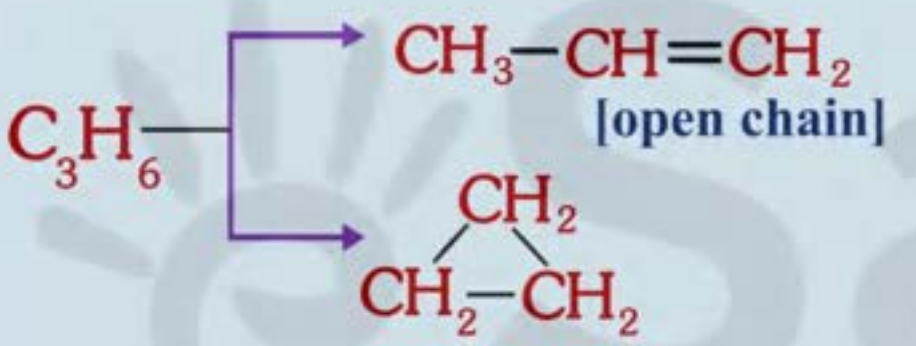
Sol. **C_8H_{10} has 4 aromatic isomers**



(o,m,p)

3. Ring Chain Isomerism (RCI)

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



DB, TB

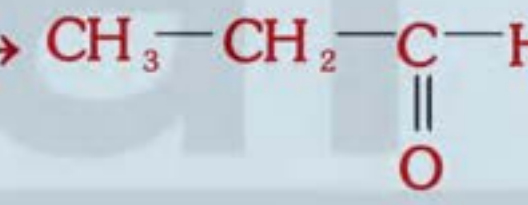
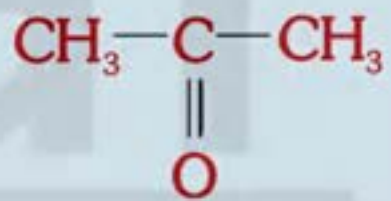
C-C=C-C C_4H_8

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

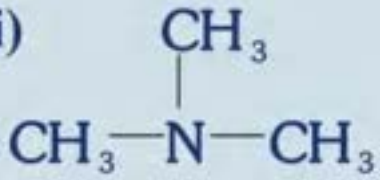
4. Functional Isomerism

Same molecular formula but different functional groups.

(i) Alcohol and ether $\longrightarrow$ $CH_3—CH_2—OH$ and $CH_3—O—CH_3$

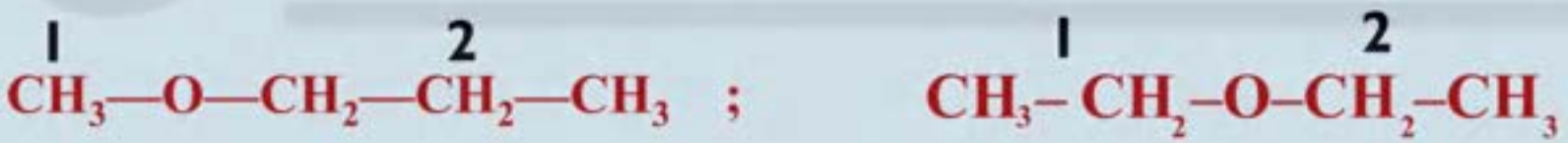
(ii) Aldehydes and ketones $\longrightarrow$  and 

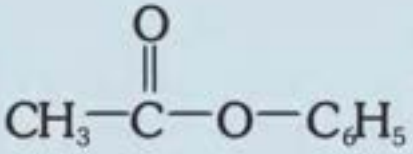
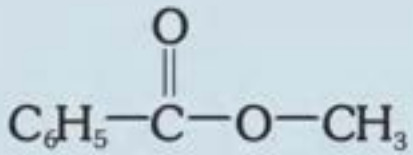
1°, 2°, 3° amines

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

Metamerism

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



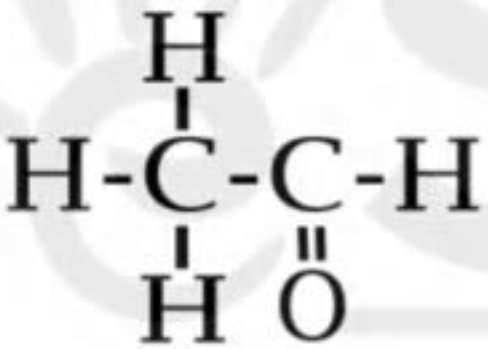
Q) **Structures**  **and**  **are?**

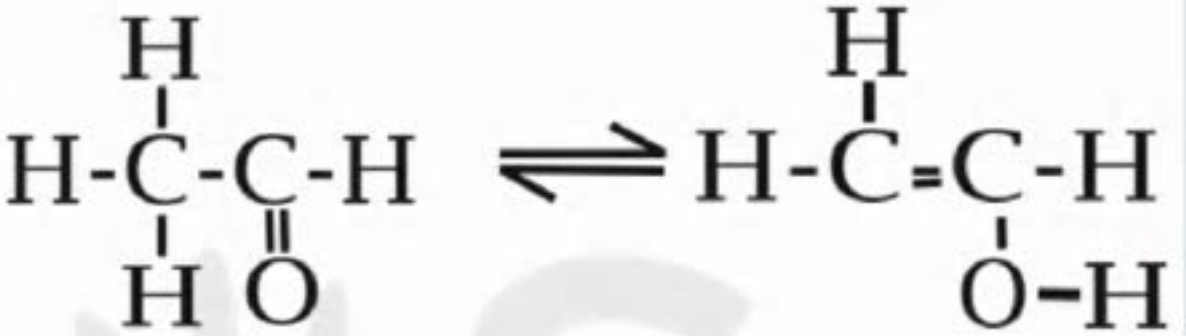
Sol. **Both are metamers.**

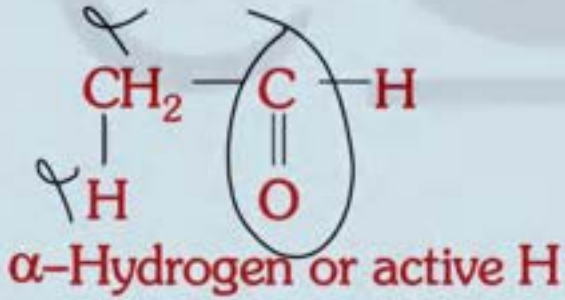
Tautomerism

gmp

It Arises due to rapid oscillation of an atom, usually hydrogen, between 2 polyvalent atoms in a molecule.







α–H attached to carbonyl compound is active H

→ Tautomers remain in dynamic equilibrium with each other

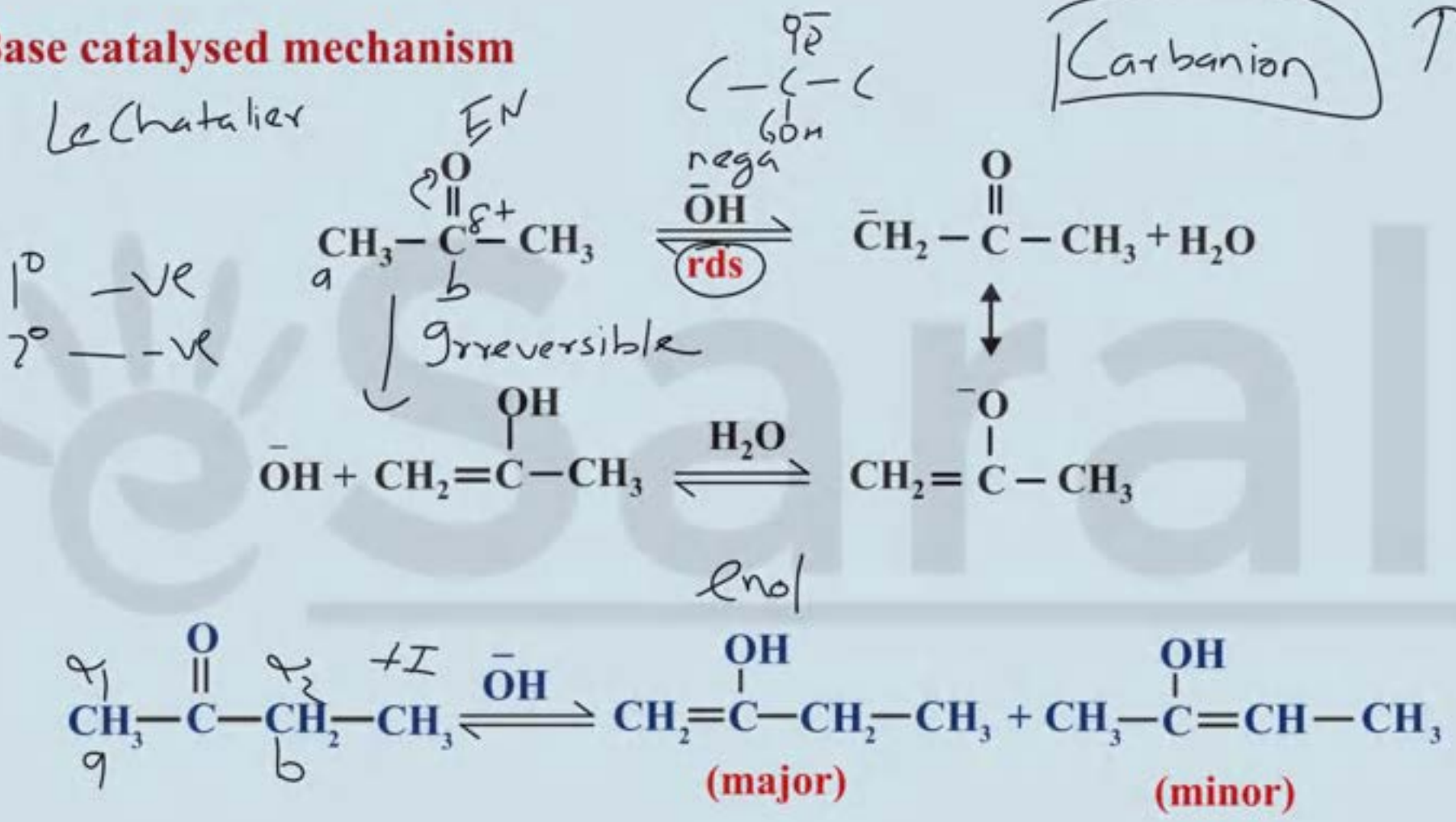
→ More stable isomer is present in higher concentration.

→ The process can be catalysed by acid as well as base

Base catalysed mechanism

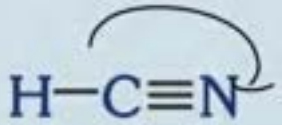
Le Chatalier

Carbanion

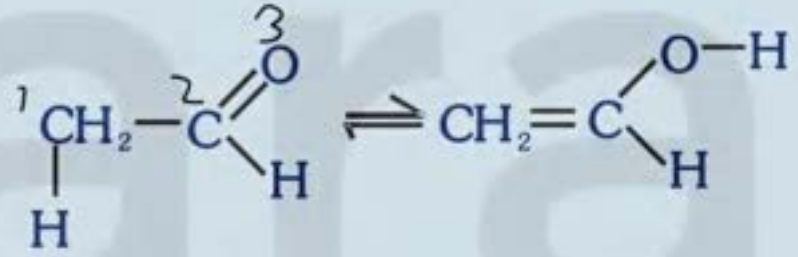


(a) For carbonyl compounds :- **Carbonyl compounds should have at least one α–H in order to show Tautomerism**

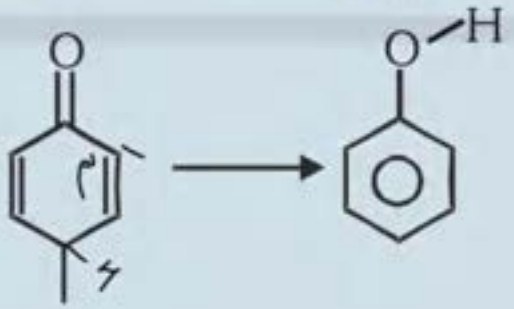
(1) Diad Tautomerism



(2) Triad Tautomerism



(3) Space Tautomerism



Generally keto form is more stable than enol form

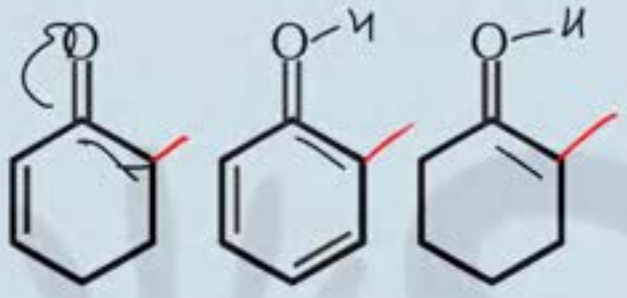
enol content ∝ stability of enol

enol content ∝ aromatization of enol

enol content ∝ stability of enolate ion

enol content ∝ Intramolecular H-bonding

Q) Arrange following in decreasing order of enol content?

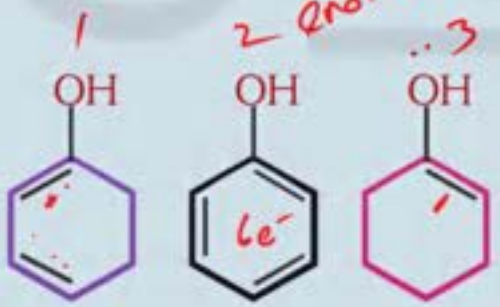


1 2 3

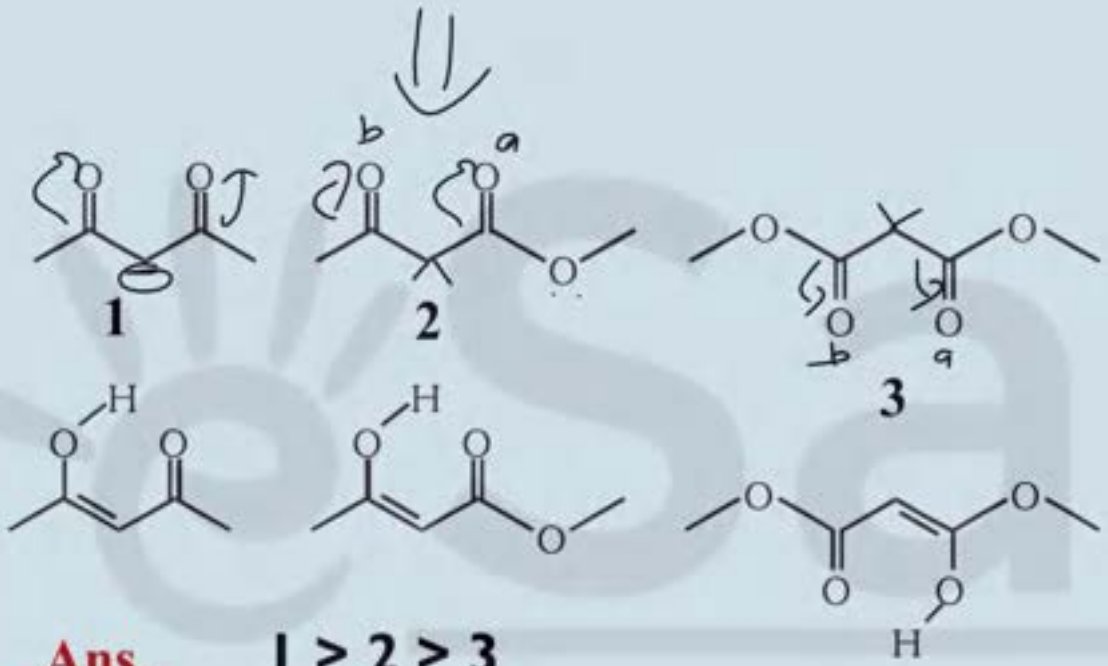
Aromatic

Ans. 2>1>3

Sol.

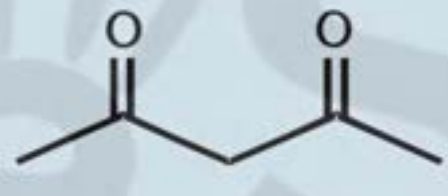


2 enol content ↑

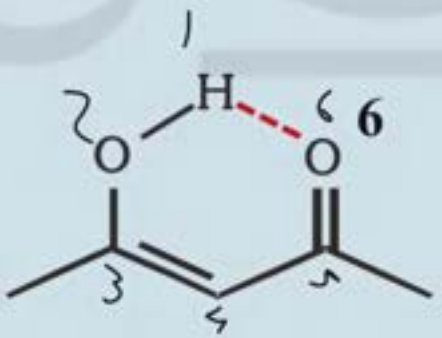


Ans. **I > 2 > 3**

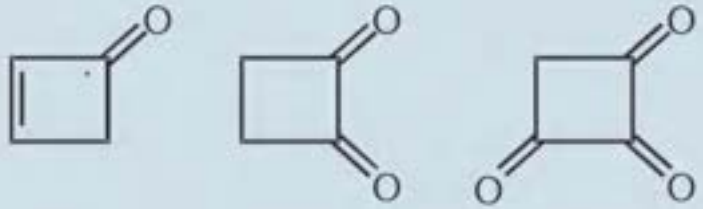
Due to + M of O group



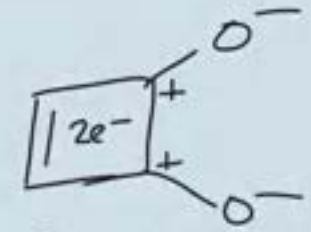
Keto



Enol



1 2 3



4n + 2

n = 0 2e⁻

Ans.

Aromatic

↑

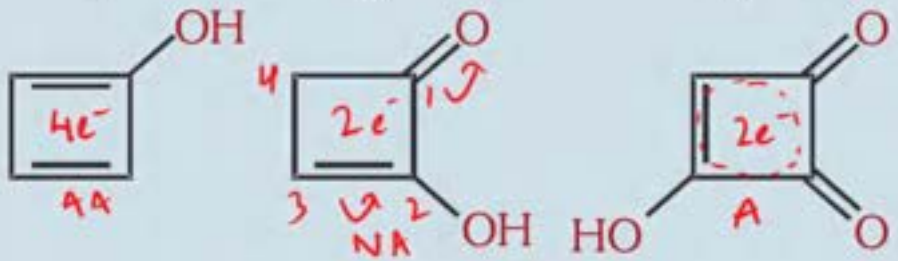
3 > 2 > 1 → Anti

↓

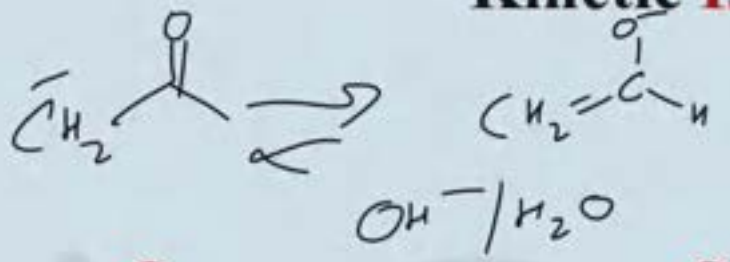
Non aromatic

Sol.

1 2 3

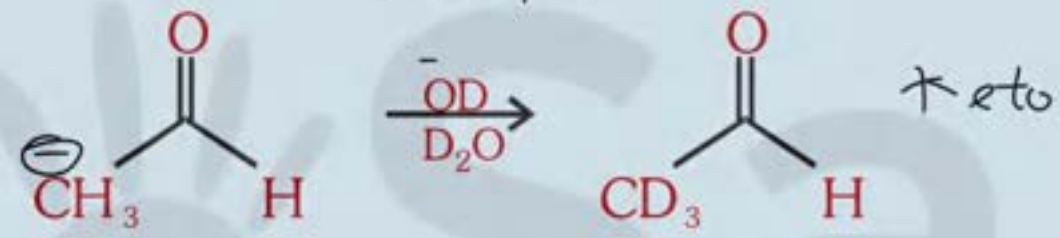


Kinetic Isotopic Exchange



OH^-/H_2O

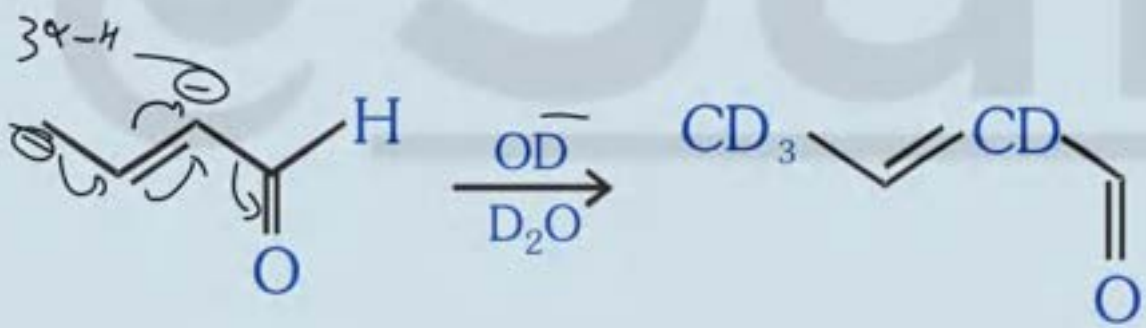
Find number of D exchanged

1. 

keto

all α-H/active

Replace with D

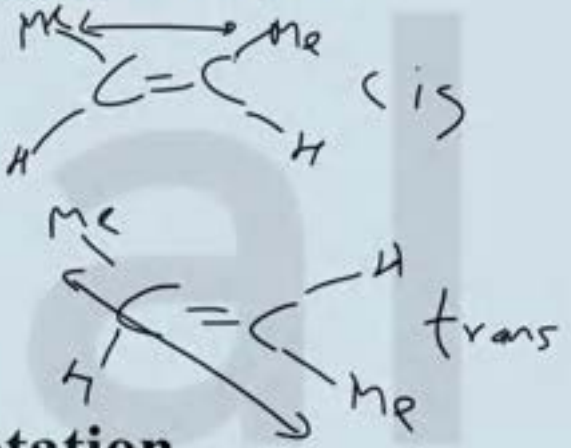
2. 

9

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.

Condition for G.I.



Conditon 1

Restricted rotation must be present.

Restricted Rotation

$CH_3-CH=CH-CH_3$

sp^2 sp^2

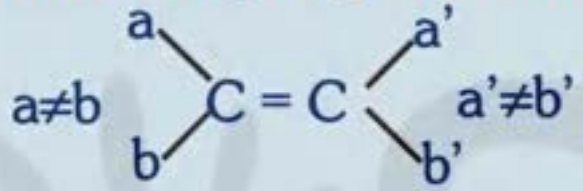
Free Rotation

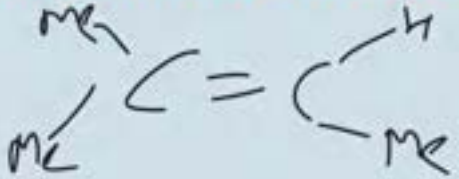
$CH_3-CH_2-CH_2-CH_3$

sp^3 sp^3

Condition 2

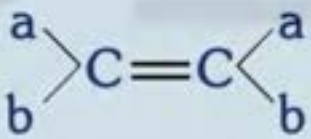
(i) The two groups at each end of restricted bond must be different.





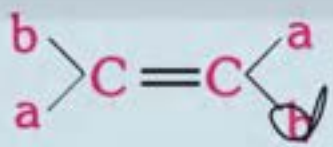
Condition 3

Terminal valency should be present in the same plane.



[Same groups, same side]

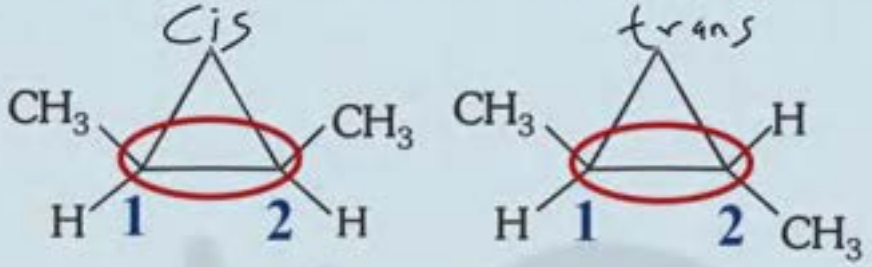
cis



[Same groups different side]

trans

Geometrical isomerism in cyclic compound

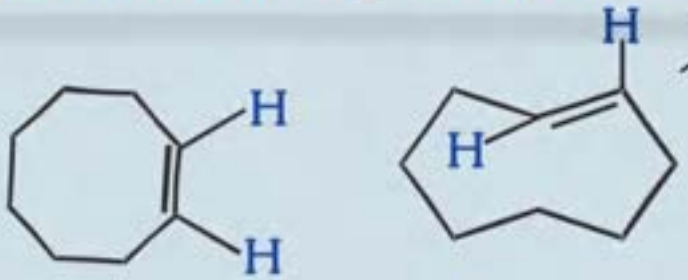


Cycloalkanes < 8

Restricted rotation

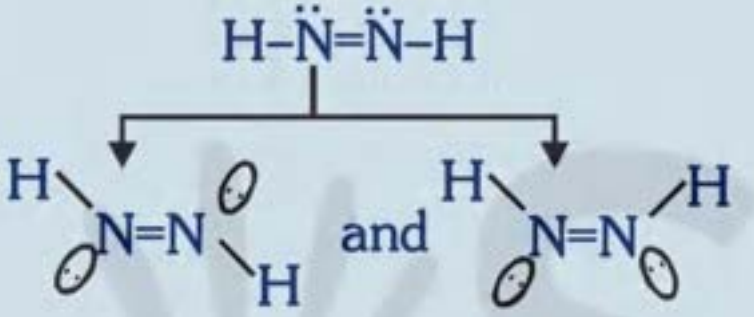
Geometrical isomerism in cycloalkenes(endocyclic π – bonds) with double bonds

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



> 8

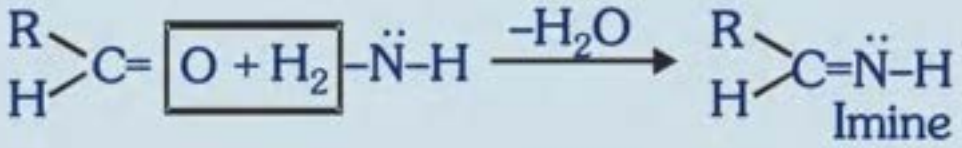
Geometrical isomerism in azo compounds (–N=N–)



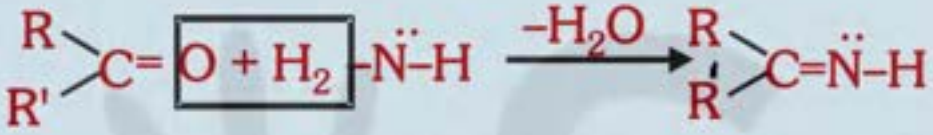
Geometrical isomerism in $>C=\ddot{N}-$

(a) Imine ($>C=\ddot{N}-H$ **)**

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

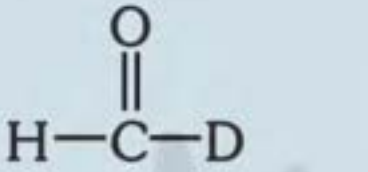


Condition R ≠ H
(aldehyde)

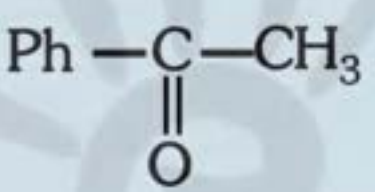


Condition R ≠ R'
(ketone)

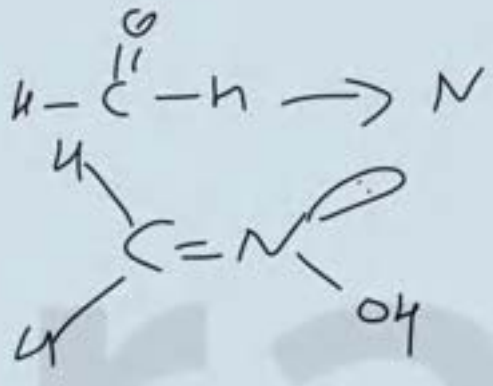
Q) Which of the following compounds show geometrical isomerism after reaction with NH_3.



✓

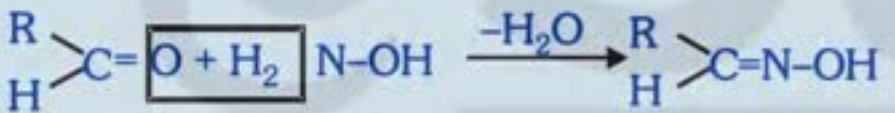


✓



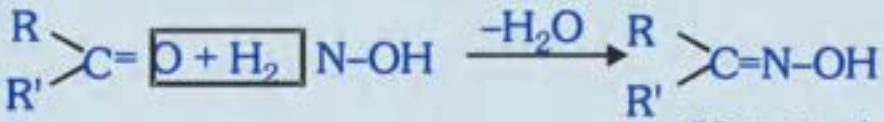
(b) Oximes ($>C=\ddot{N}-OH$)

They are prepared by reacting carbonyl compound with hydroxyl amine (NH_2–OH)



(Aldoxime)

R ≠ H



(Ketoxime)

R ≠ R'

(6) G.I. in spiro compounds

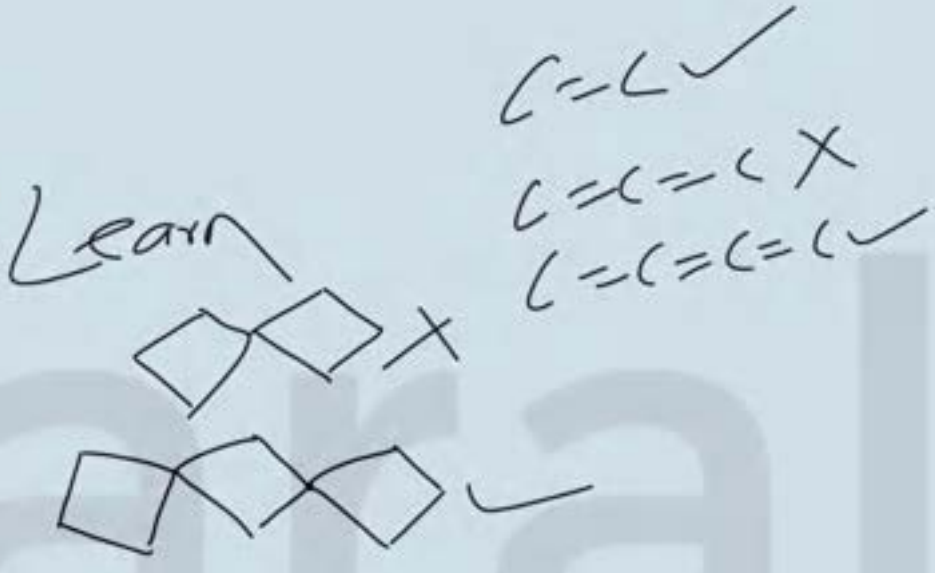
Even no of rings – no G.I

Odd no of rings - show G.I.

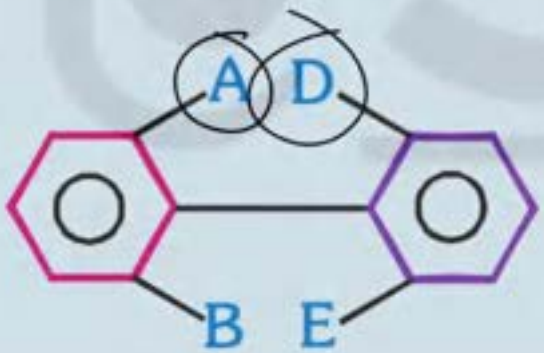
(7) G.I. in cummenes

Even π-bond – No G.I

Odd π-bond - show G.I.



(8) G.I. in Biphenyl Compound



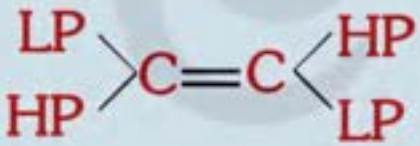
Even no of phenyl rings – don't show G.I

Odd no of phenyl rings - show G.I.

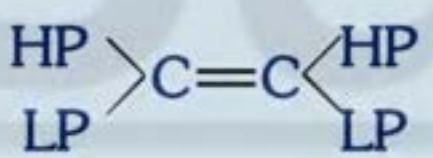
E – Z System

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

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



'E'



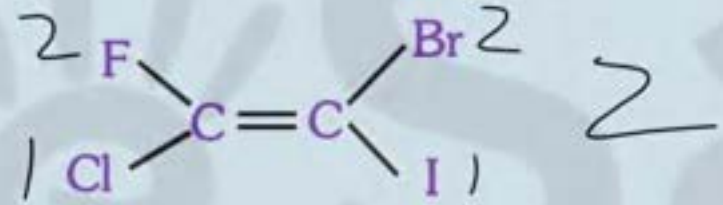
'Z'

HP – High priority and LP – Low priority

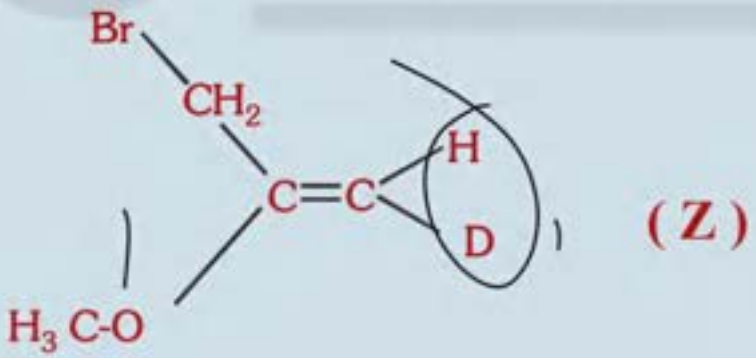
Priority Rules

Cahn, Ingold, Prelog (CIP Rule)

Rule 1. **Priority ∝ Atomic number of atom which is directly attached to restricted rotatory system.**



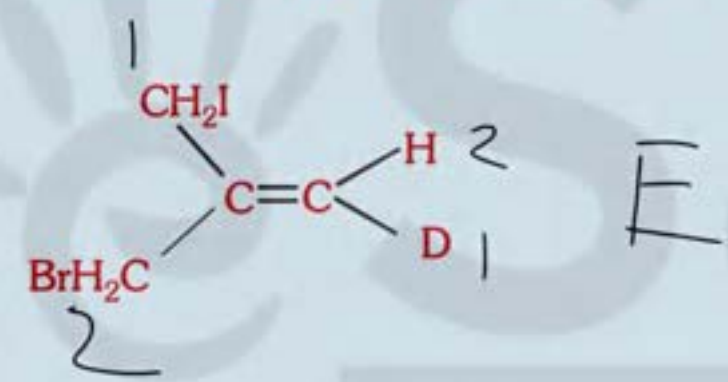
Rule 2. **Priority ∝ Atomic weight (in case of isotopes)**



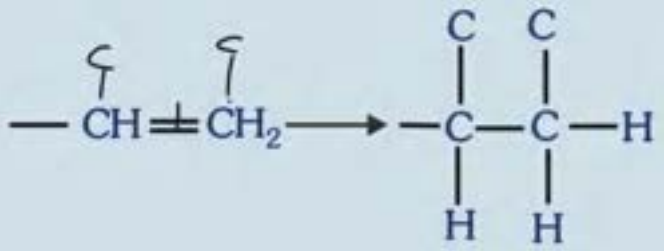
(Z)

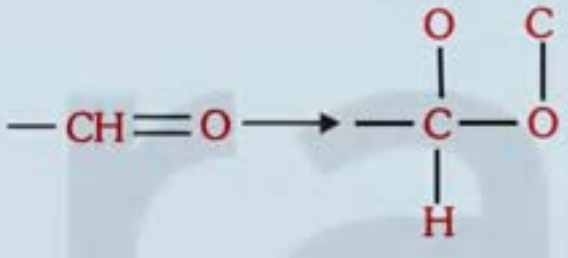
Rule 3. Lone pair is assigned Z = 0

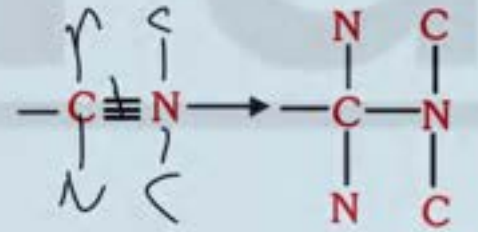
Rule 4. If at the first directly attached atom, Z is same on both sides (that is R–1 fails), move to next atom and atoms attached to it until you get a difference.



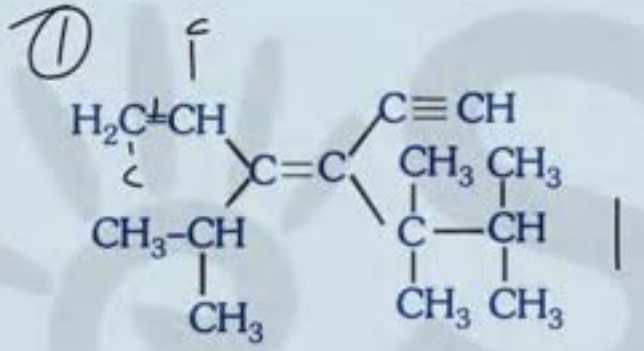
Rule 5. **If directly attached groups contain multiple bond then duplicate them by dummy atoms.**







Rule-6 **If after converting a multiple bond, it converts identical to a original, higher priority goes to original one.**



(E)

Rule-7

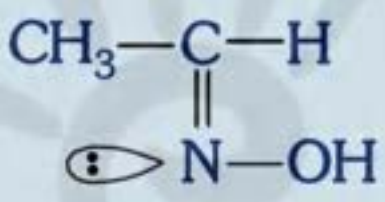
(Z)

cis/trans ⇒ cis

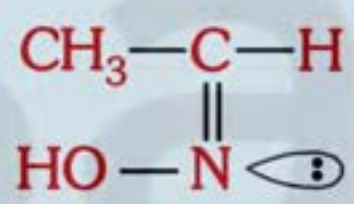
Z/E ⇒ Z

(c) Syn-Anti Nomenclature

Example : Acetaldoximes has two Geometrical isomers –



syn



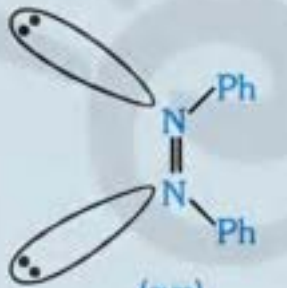
anti

When H and OH are on the same side

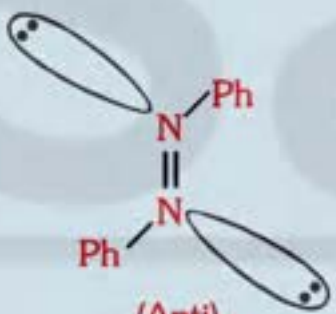
When H and OH are on the opposite side

lp opposite side → Anti

lp same side → Syn



(syn)



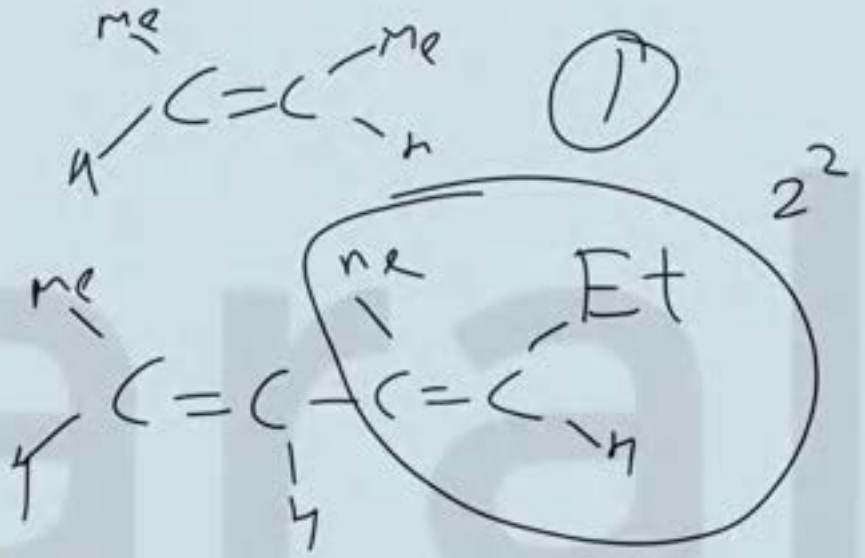
(Anti)

Ph—NN—Ph (Azo benzene)

Number of Geometrical isomers: (For compounds not showing OI)

Calculation of GI

n = no. of unit which can show GI



Case I : Compound is unsymmetrical: 2^n

n = 3 symmetrical

$2^{3-1} + 2^{\frac{3+1}{2}-1}$

$2^2 + 2^{2-1} = 6$

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)

BP

cis > trans

BP , MP

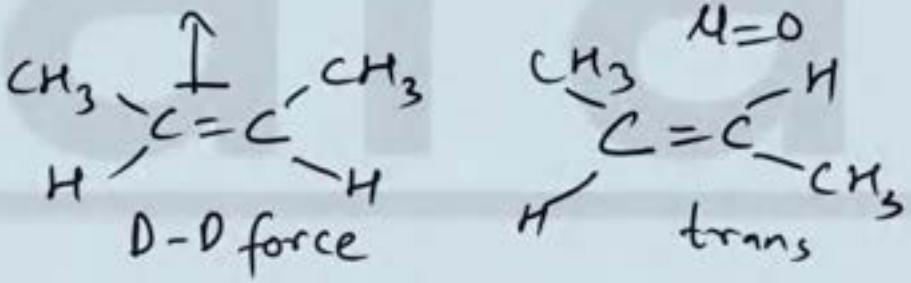
Boiling (Force of attraction)

$l \rightarrow g$

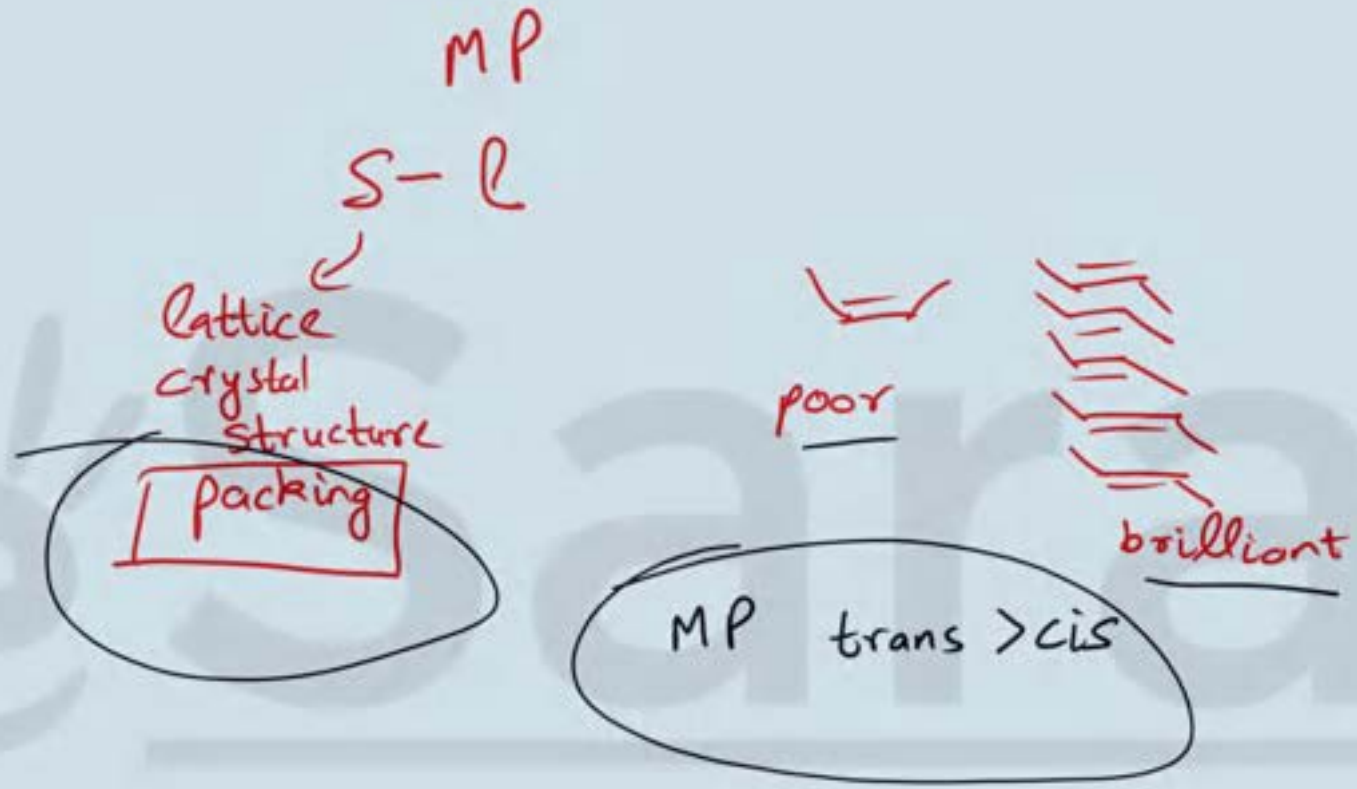
BP → M

cis (M) > trans (M)

Dipole - Dipole attraction

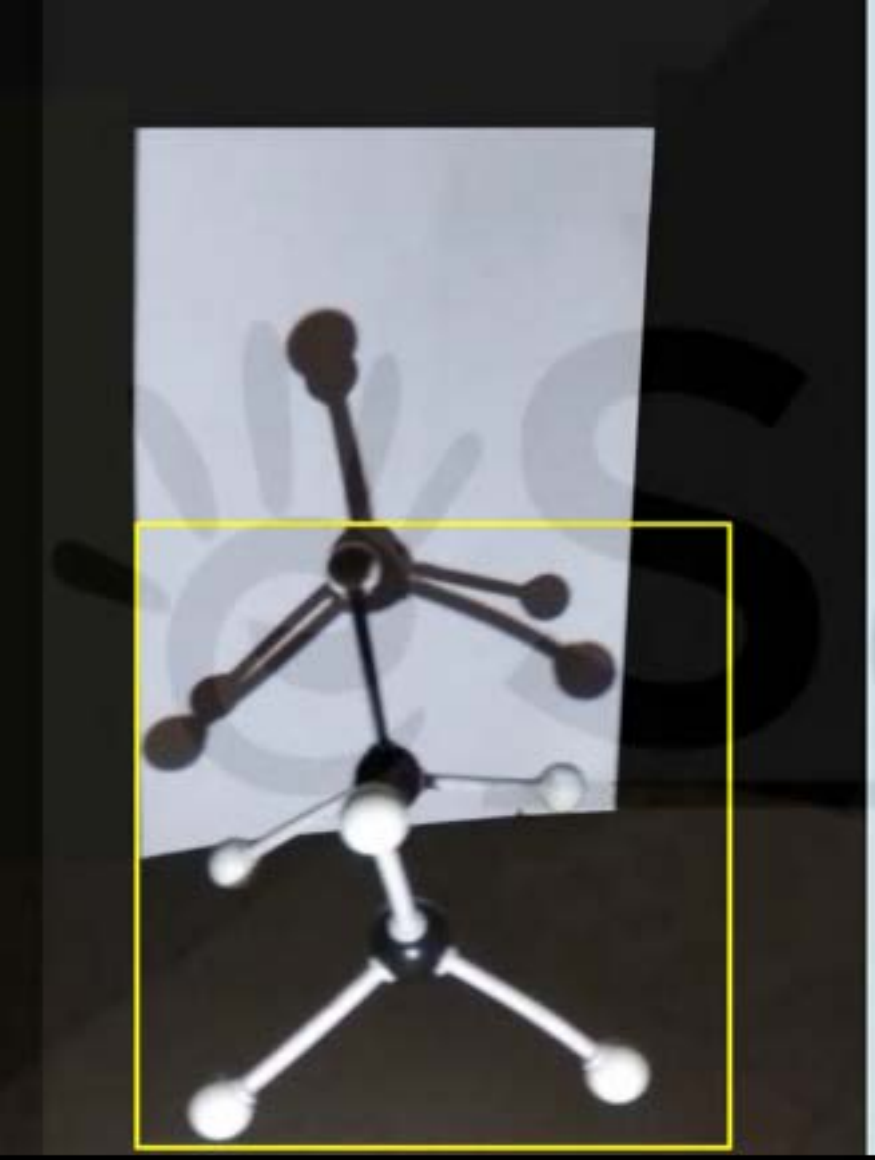


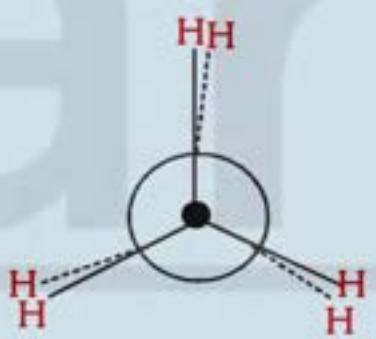
BP cis > trans



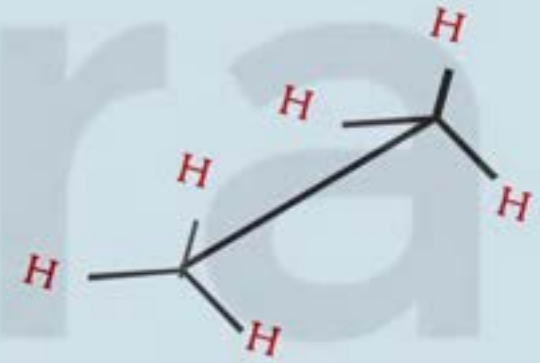
Conformational Isomerism

Conformational isomerism is a form of stereoisomerism in which the isomers can be interconverted just by rotations about single bonds.



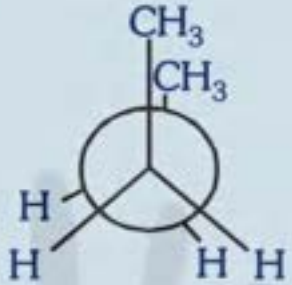


Newman Projection

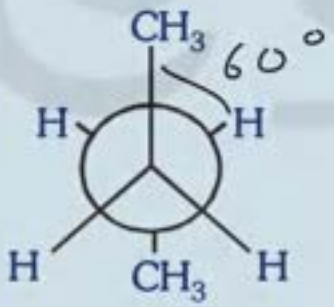


Sawhorse Projection

(i) Eclipsed Conformation:

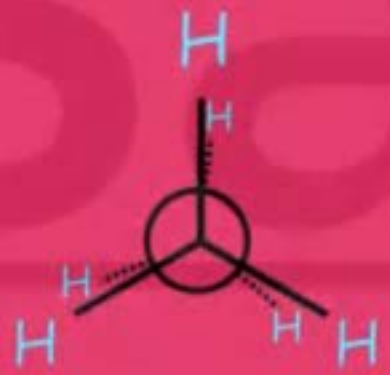


(ii) Staggered Conformation:



Conformers of ethane [CH_3—CH_3]

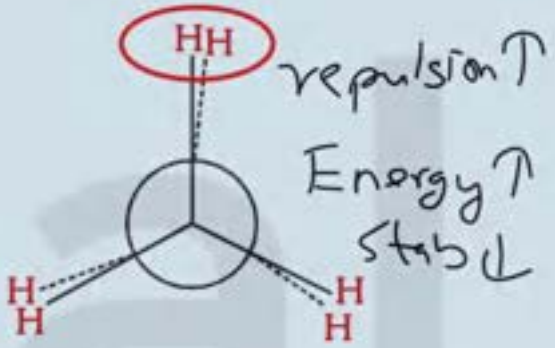
newman projection



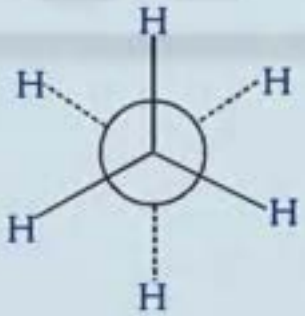
eclipse form

$\frac{KQ_1Q_2}{r^2}$ distance

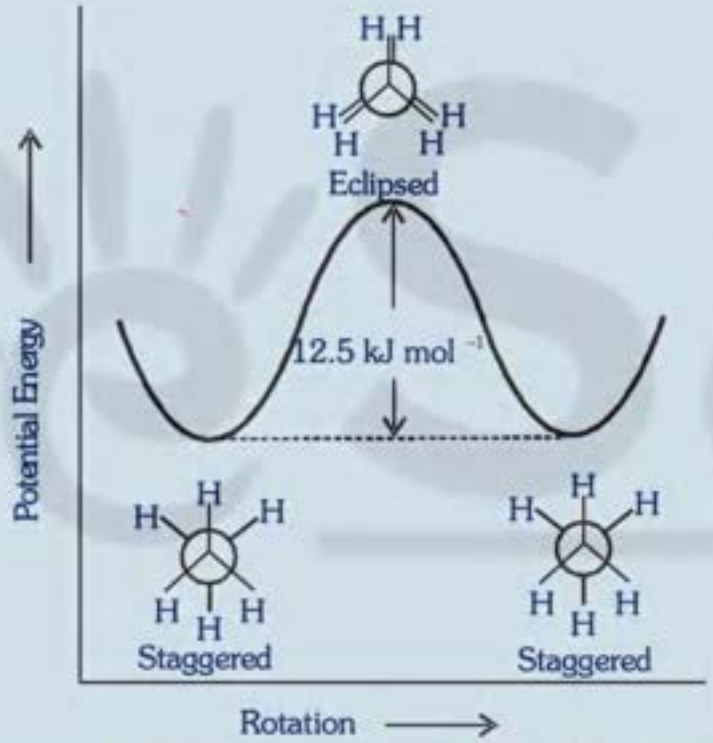
Eclipsed form - in this form distance between 2C–H bonds is minimum so maximum repulsion or minimum stable.



Staggered form - in this form distance between 2C–H bonds is maximum so minimum repulsion so maximum stable.



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

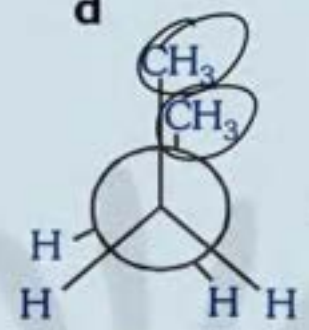
0° 0.1° 0.0000000

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

Stability order :Staggered > Skew > Eclipsed.

Propane

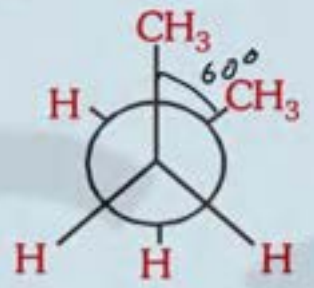
Eclipsed



(I)

60 →

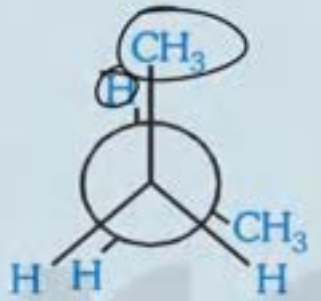
Gauche



(II)

60 →

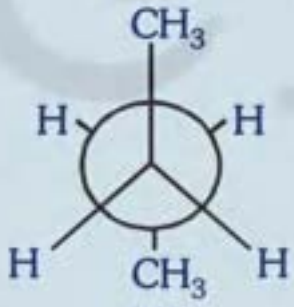
Partially Eclipsed



(III)

Anti/Staggered

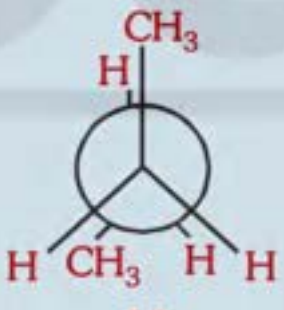
60 →



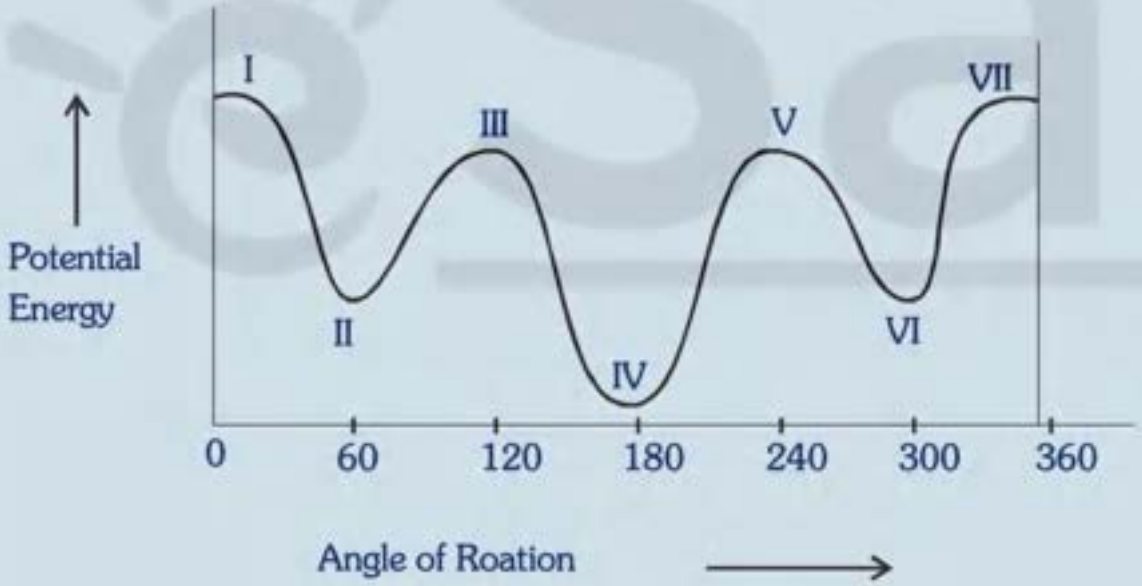
(IV)

60 →

Partially Eclipsed



(V)



I/VII = Fully eclipsed

II/VI = Gauche form

III/V = Partially eclipsed

IV = Anti form

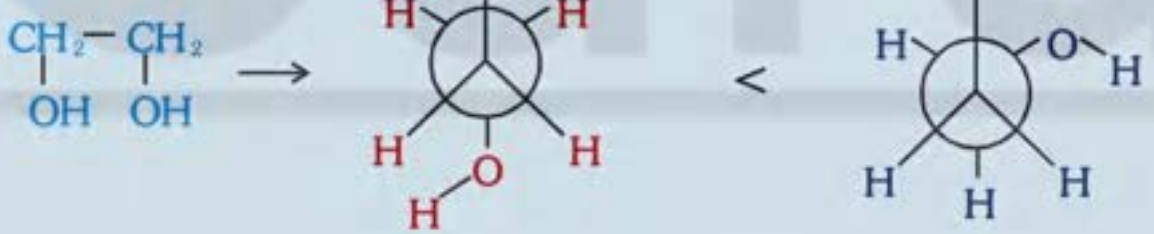
Stability Order IV > II > III > I

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

Q) Draw most stable conformation of following

H-bonding ⟶ Gauche

60°

(i) 

Due to H-bonding gauche is more stable than anti

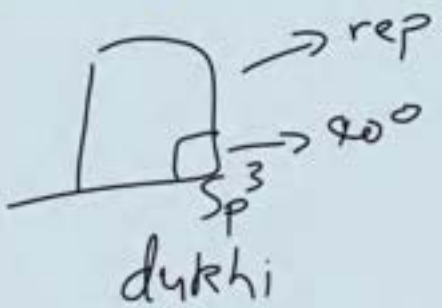
Conformational analysis of cycloalkane

$109.5^\circ - 60^\circ$

$= 10^\circ$

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

10.7°

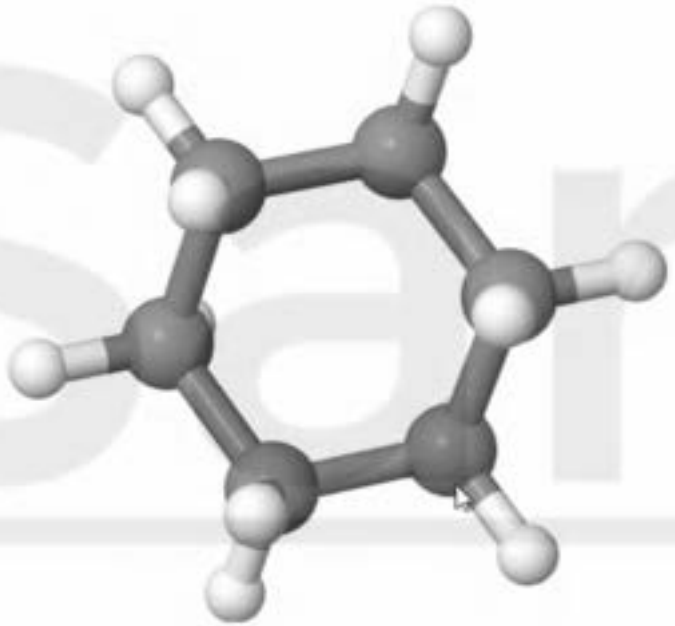


dukhi

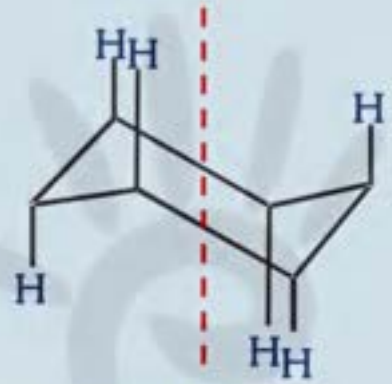
When size of ring increases then it becomes flexible and partial σ bond rotation is observed so larger ring acquires non-planar orientation to avoid eclipsing.

repulsion ↓

$e^- - e^-$ dist ↑



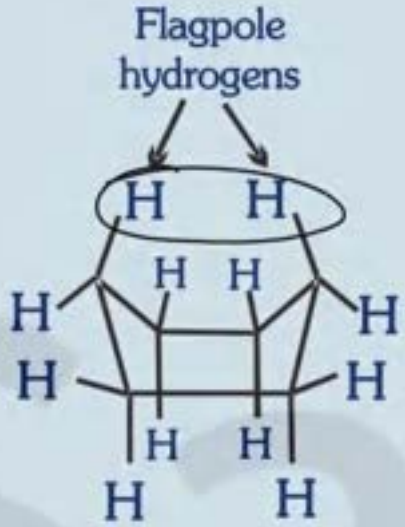
Conformational analysis of cyclohexane



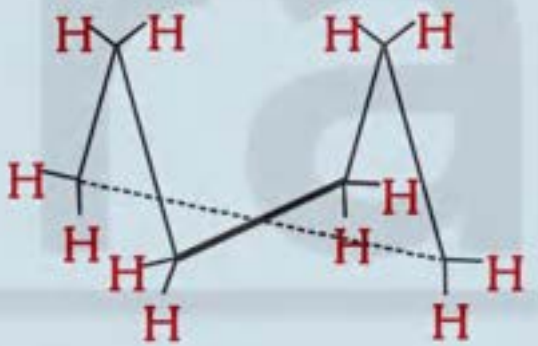
Axial C–H bonds

Equatorial C–H bonds

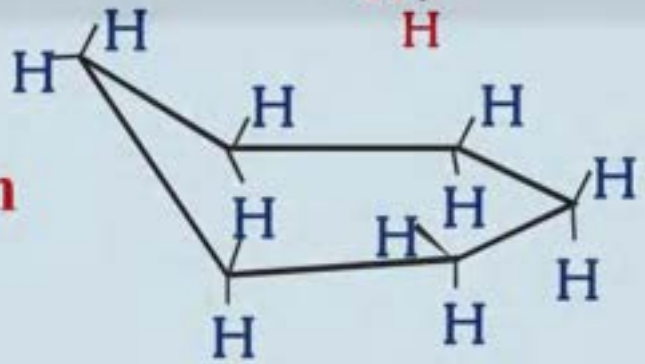
(ii) Boat Form



(iii) Twist Boat Conformation



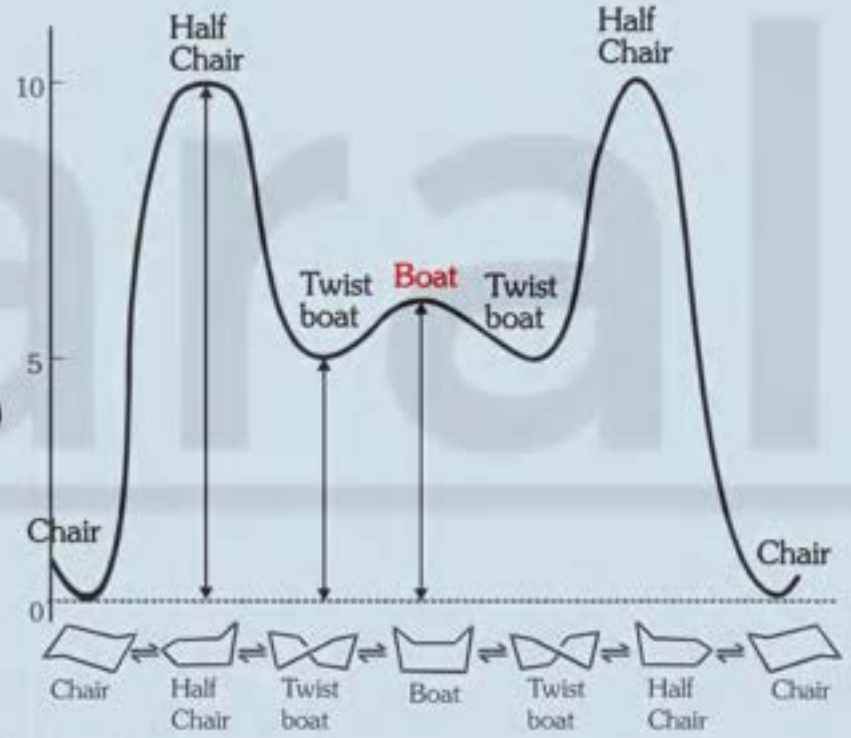
(iv) Half Chair Conformation



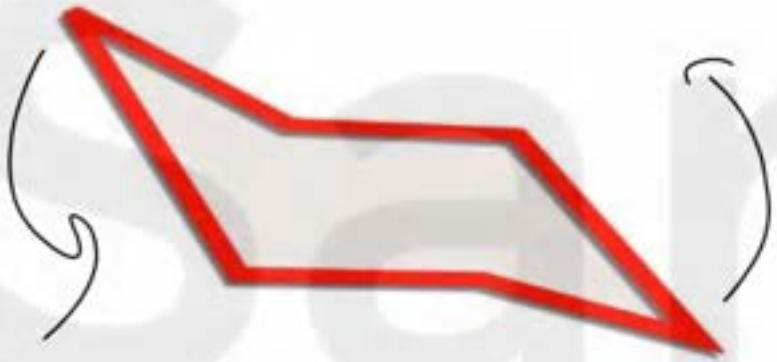
Stability Order

Stability

Chair > Twist boat > Boat > Half Chair

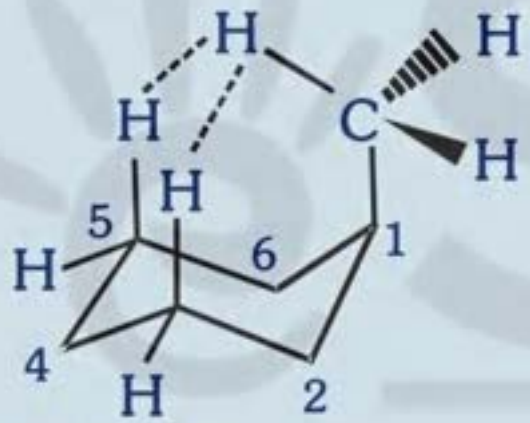


Conformational Inversion (Ring Flipping) In Cyclohexane



a → e
e → a

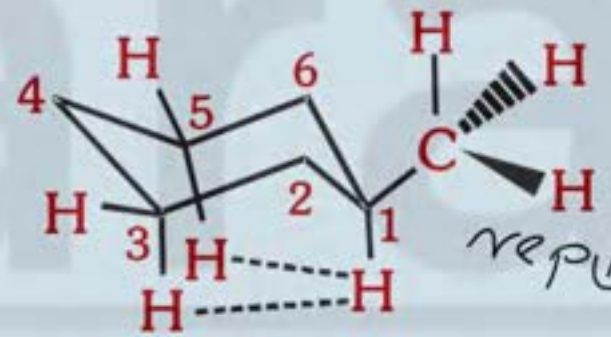
↓ repl ↑ E ↑ Stab



Repulsion between hydrogen of axial CH_3 and axial hydrogens at C-3 and C-5

Et, Pr

Bulky Groups prefer eqt position



repl Sta

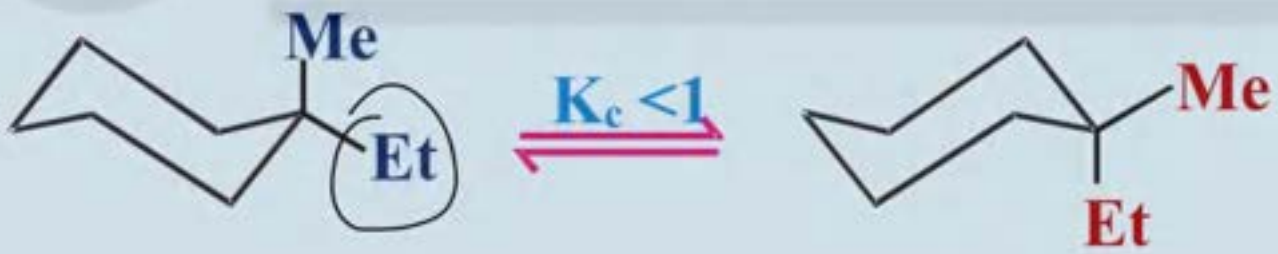
Repulsion between hydrogen at C-1 and axial hydrogens at C–3and C–5

Q) Give ring flipping equilibrium constant for following compunds.

(i)

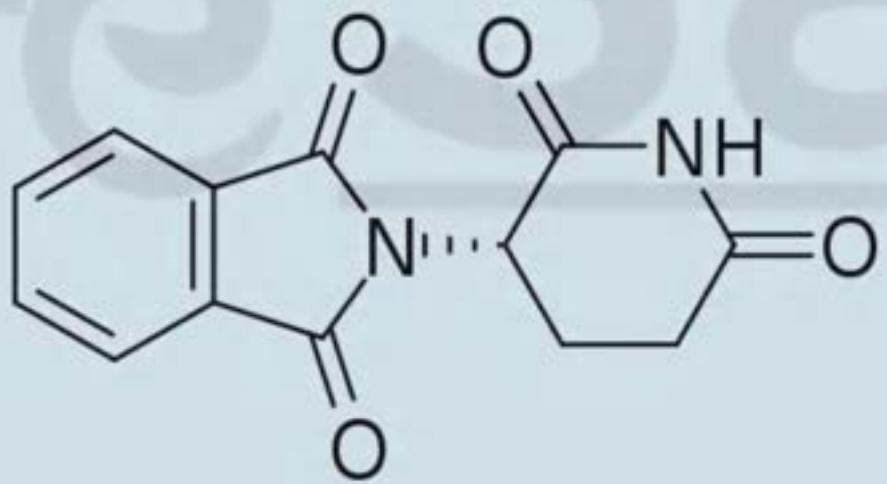
(ii)

(iii)

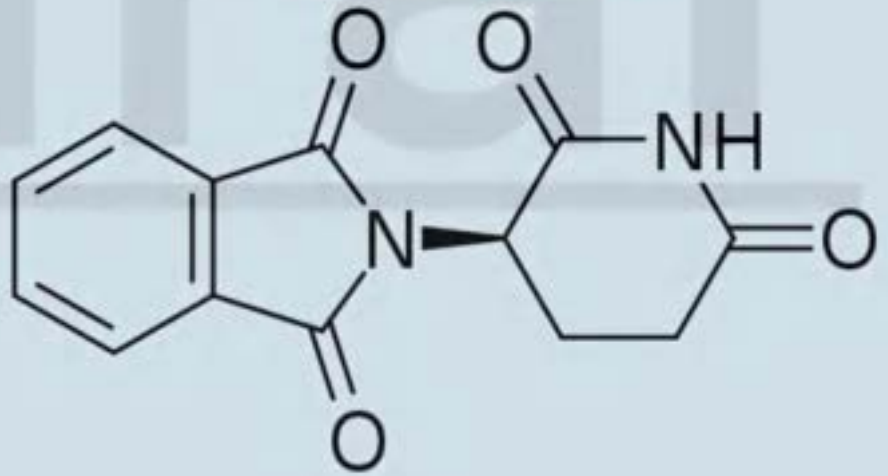


01

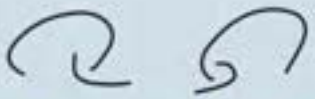
S-Thalidomide



R-Thalidomide



Optical Isomerism

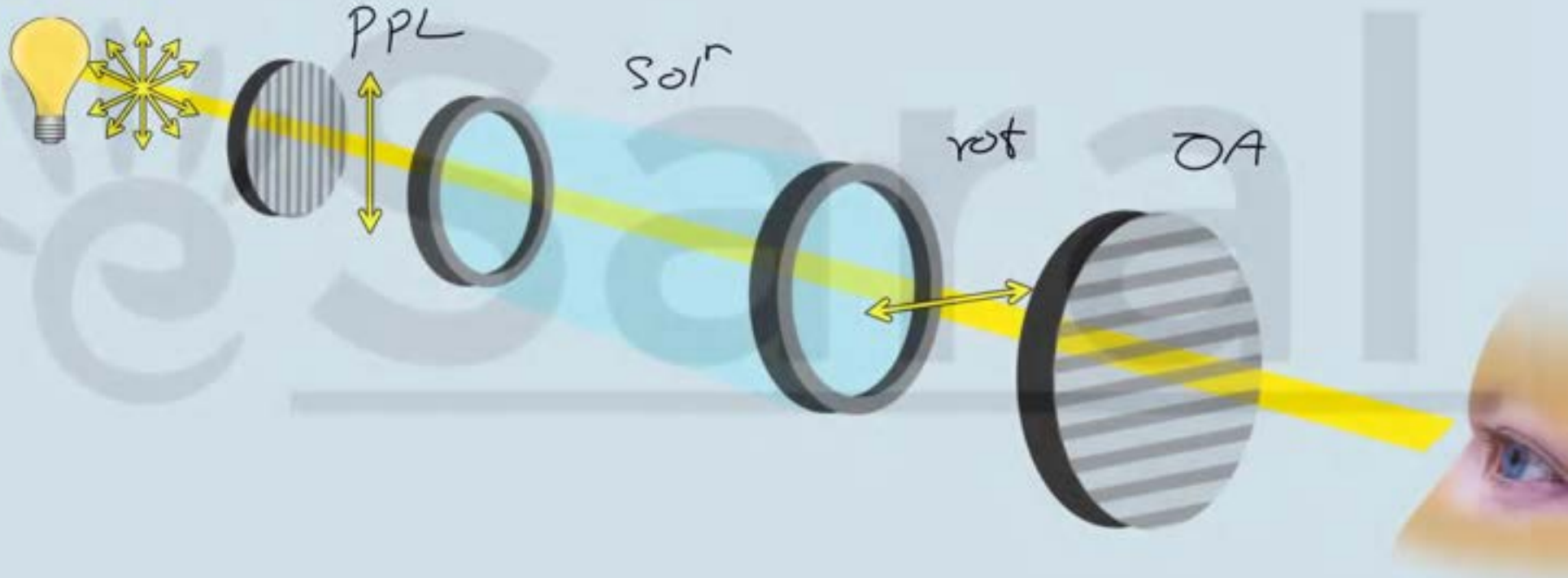


Compounds which have same molecular and structural formula but have different direction of rotation of PPL (Plane Polarized Light) are known as optical isomers.

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.



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 (–).

The observed rotation of the plane polarized light depends on four factors

The amount of the substance in tube

The length of the sample tube

The temperature of the experiment

The wavelength of the light used.

$$[\alpha]_D^t = \frac{\alpha_{obs}}{\ell \times C}$$

[where α = observed angle of rotation]

$[\alpha]_D^t$ = specific rotation determined at T°C per unit length at unit concentration, using D−line of sodium light.

ℓ = length of polarimeter tube in decimeters

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

Condition of Optical Activity

Compound must be asymmetrical or Compound should be Non Superimposable on its mirror image.

Unsymmetrical

Non-Superimposable Mirror image. Hence optically active.

Note

“Optically active compound is considered as chiral compound".
“Optically inactive compound is considered as achiral compound".

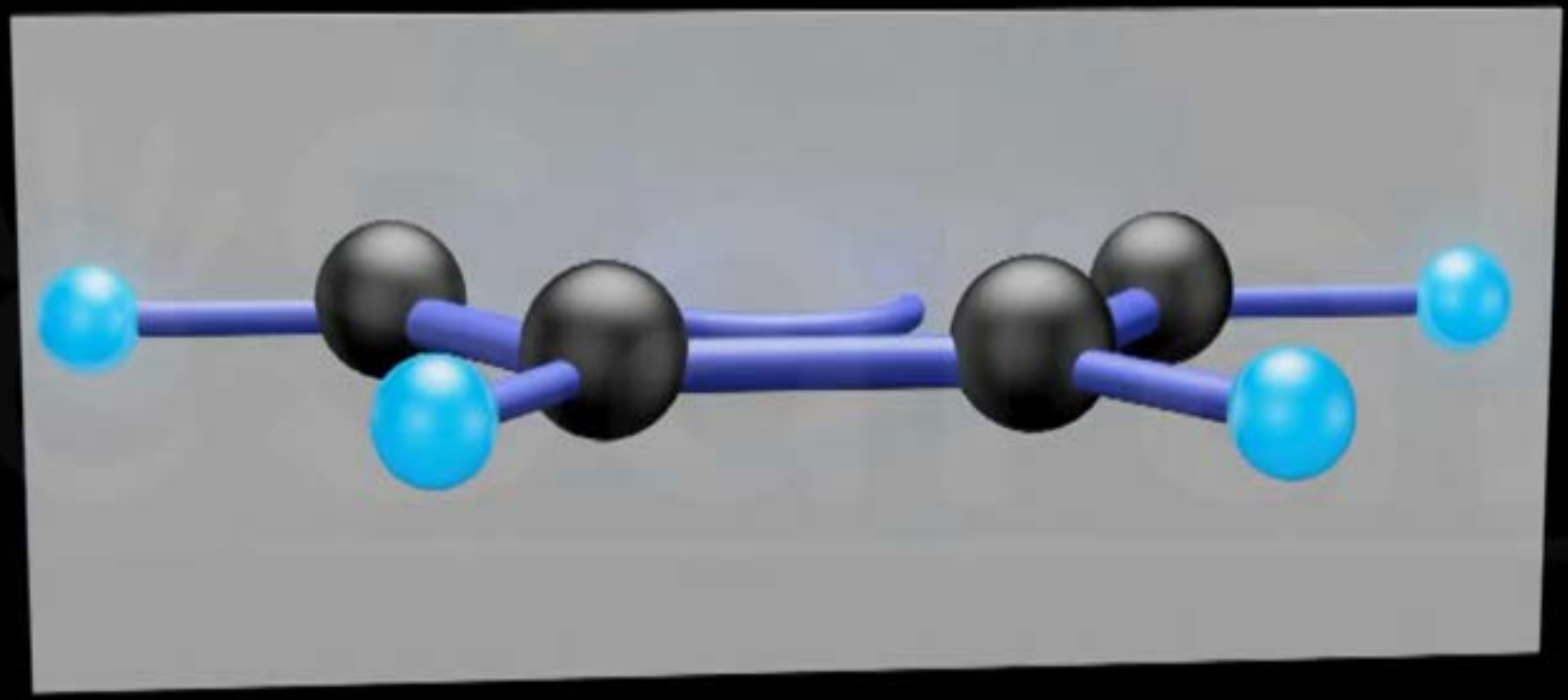
Types of Symmetry

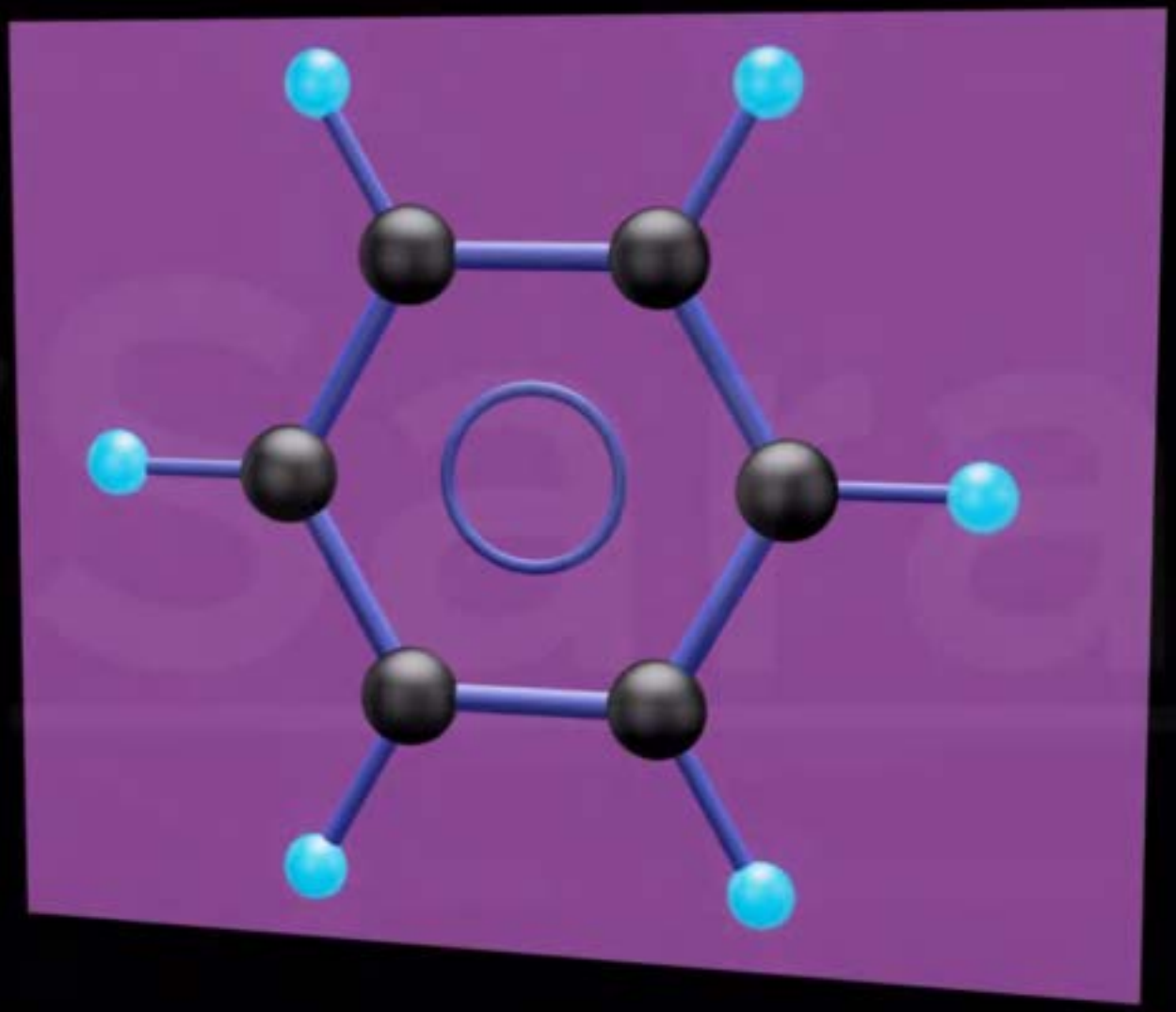
Plane of Symmetry (POS)

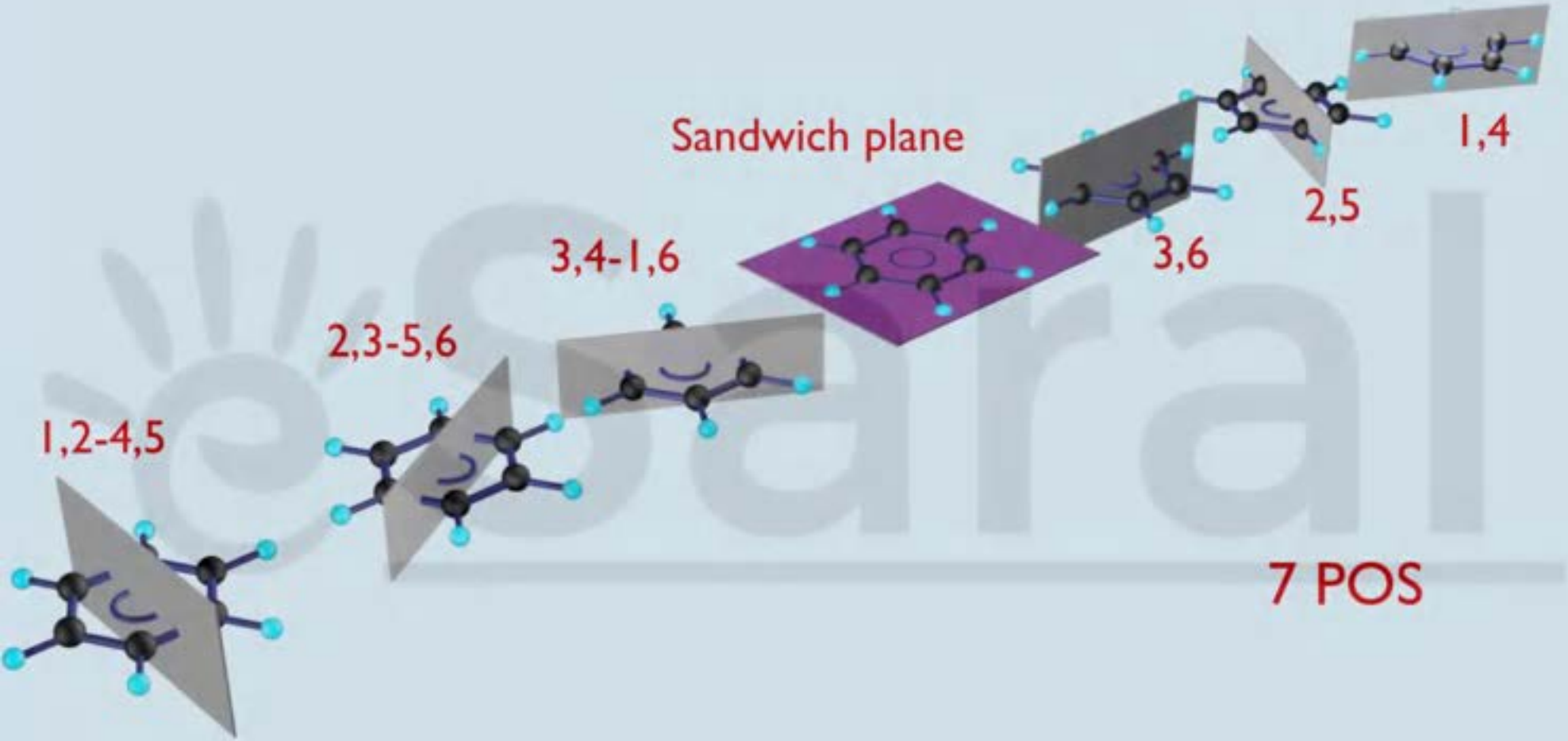
An imaginary plane which bisects any object or molecule into two equal parts which are mirror images of each other is known as Plane Of Symmetry.

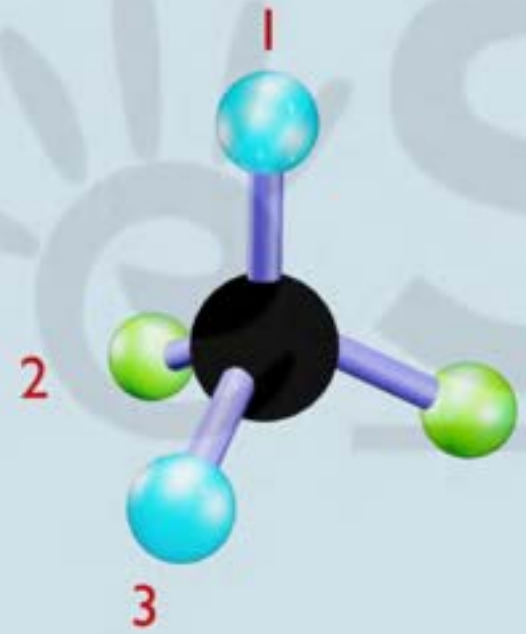
Plane of Symmetry

Q) Find number of POS in Benzene.



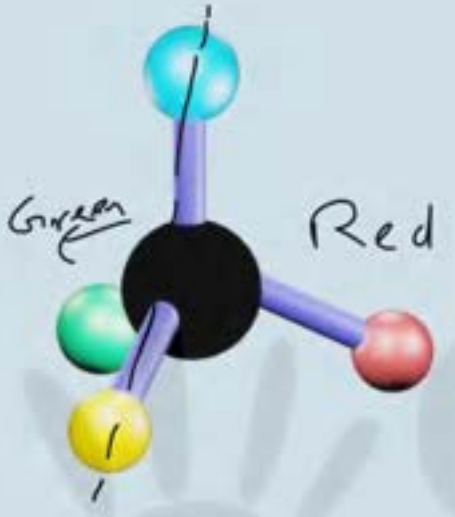




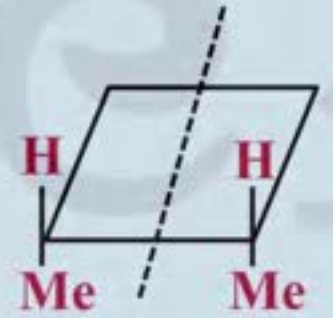


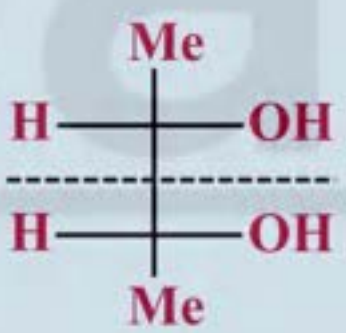
1,3

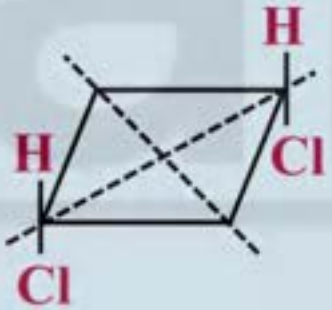
2,4



No POS

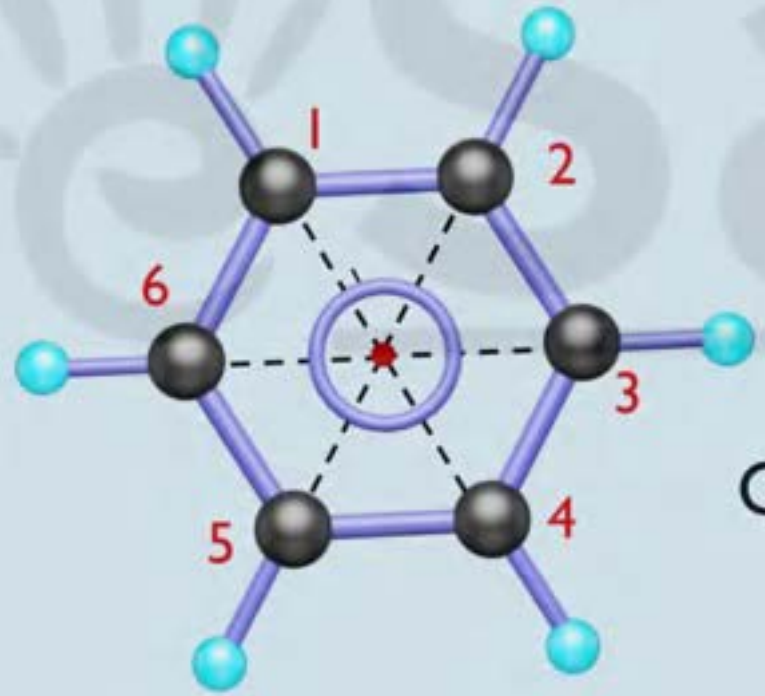






Center of Symmetry (COS)

It is a point at center of a molecule from which on travelling equal distance in opposite directions one meets the same group or atom.



1,4

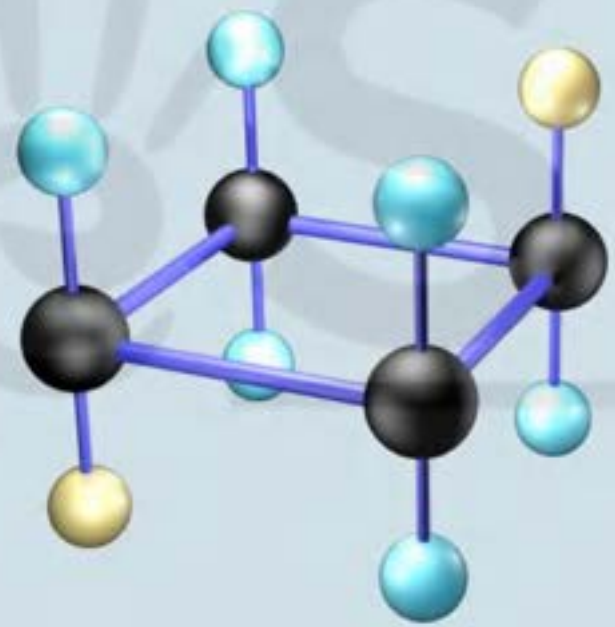
2,5

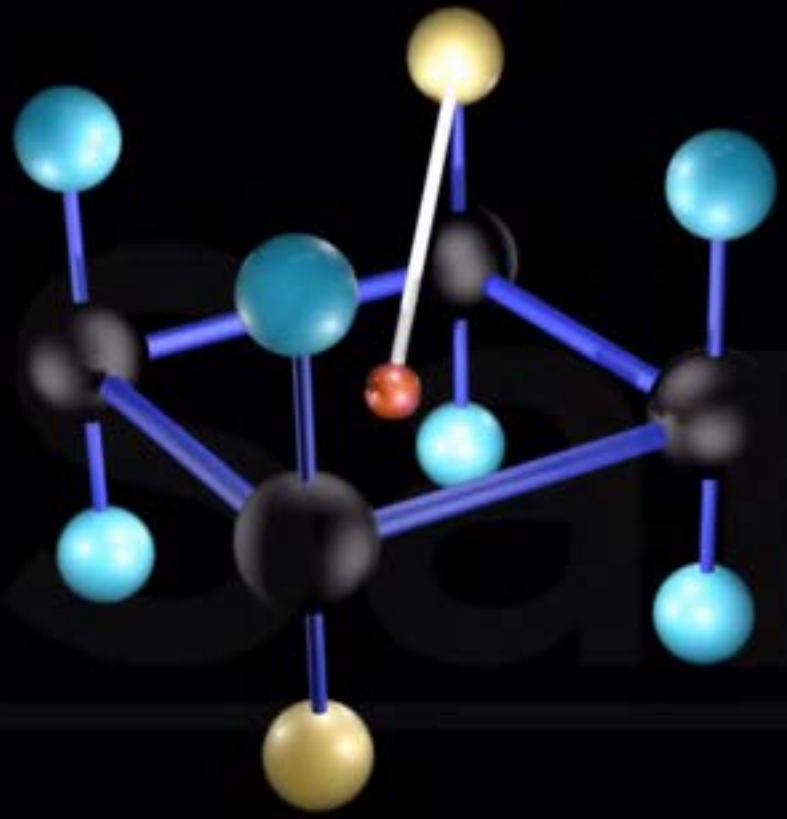
3,6

COS✓

Q) Does the following molecule has COS?

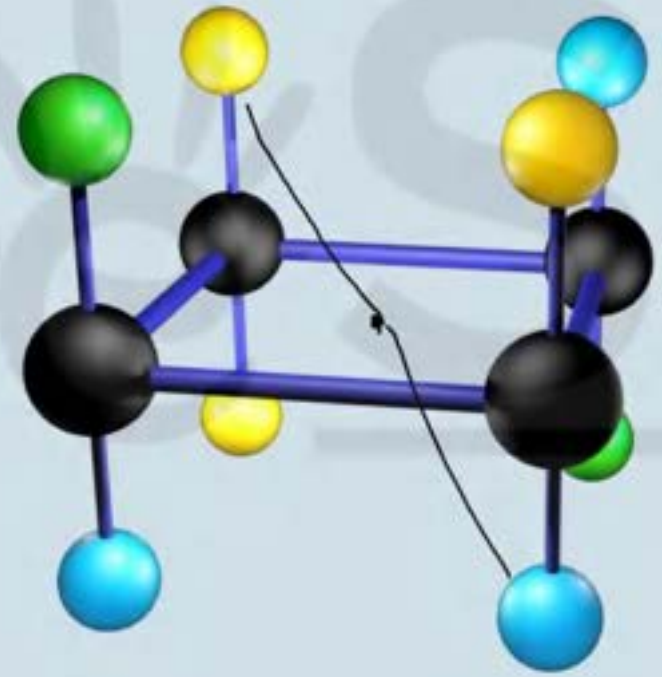
COS ✓





Q) Does the following molecule has COS?

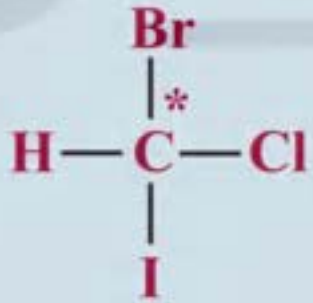
COS X



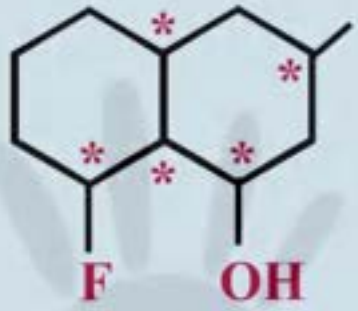
Asymmetric Carbon (or) Chiral Carbon

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

Example



Q) Count no. of chiral center/s present in following compounds ?



(3)-5

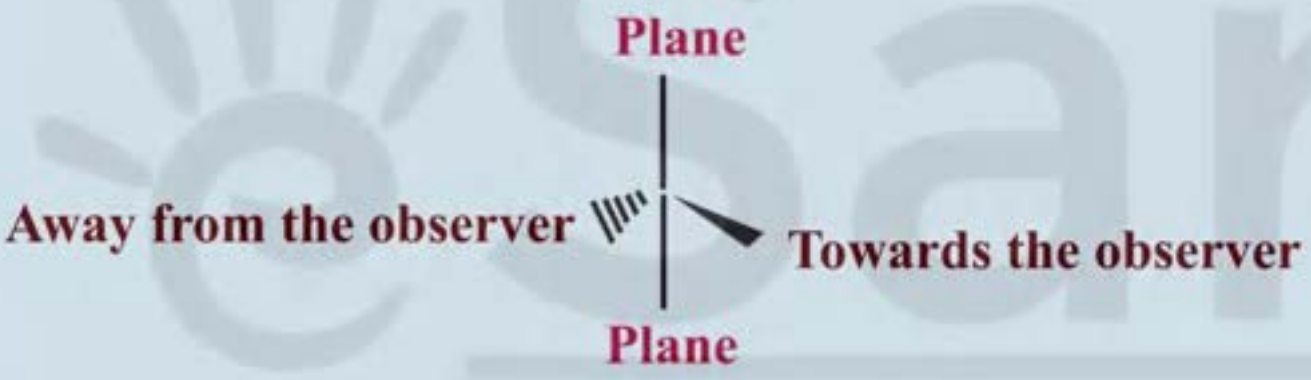
Optically Active Carbon Compounds

If a molecule contains either POS or COS or both then it is optically inactive.

If both POS AND COS are absent then only the molecule is optically active.

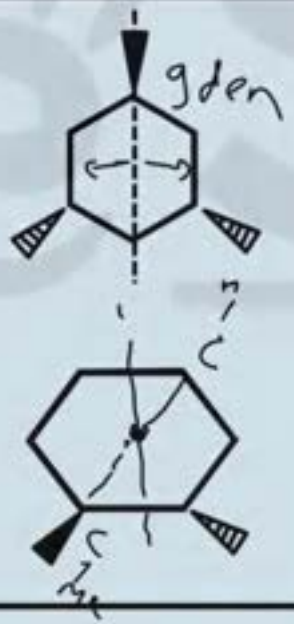
Projection Formula of Chiral Molecules

Wedge-dash Projection Formula

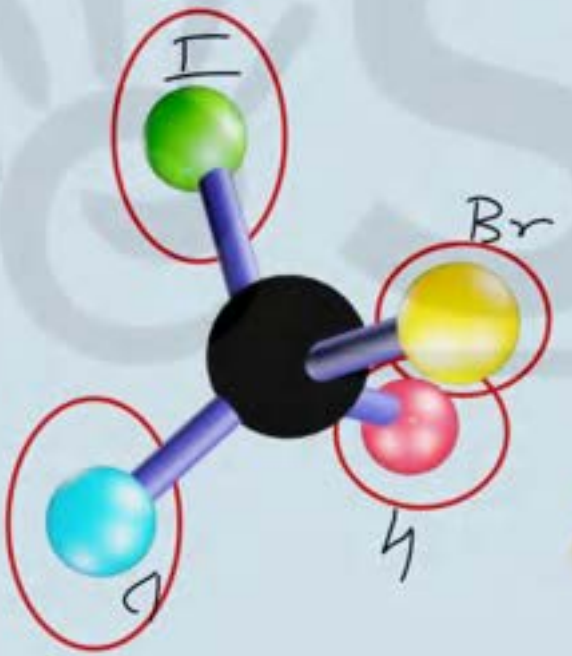


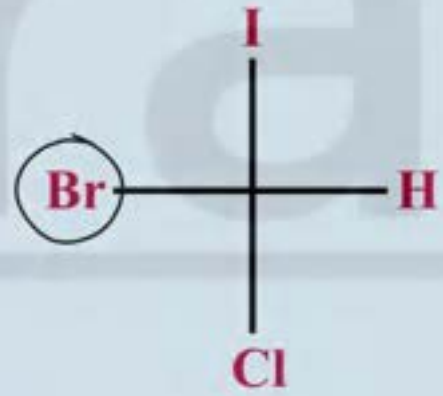
Two valency in same plane and rest two are in perpendicular plane.

Q)

Compound	POS	COS	Optical active / inactive
	Yes	No	Inactive
	No	No	Active

(II) Fischer Projection Formula(2-D representation of a 3-D molecule)



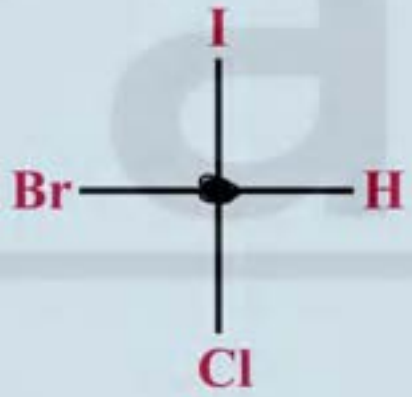


Rules for writing Fisher Projection Formula

a. Groups at Vertical line are away from observer.

b. Groups at Horizontal line are towards the observer.

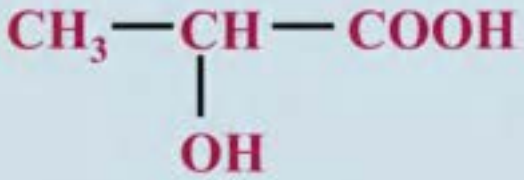
c. Central 'C' atom of the cross is chiral.



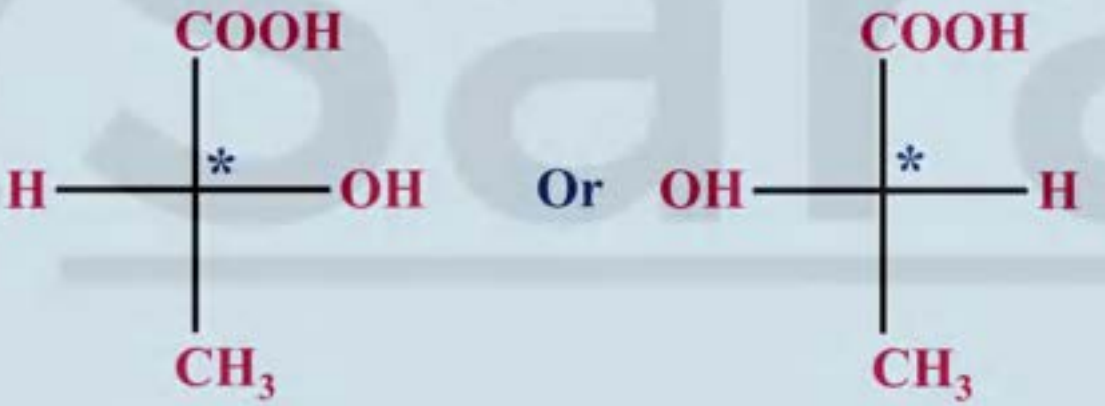
High priority group lie at the top of vertical line (Numbering starts from top according to IUPAC).

Maximum carbon atoms should be on the vertical line

Example

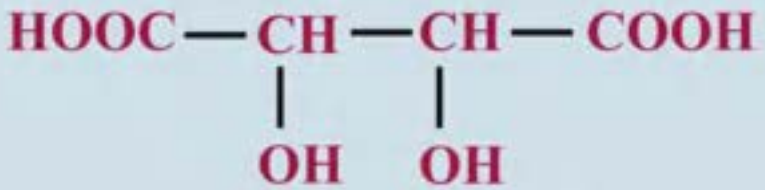


Lactic acid



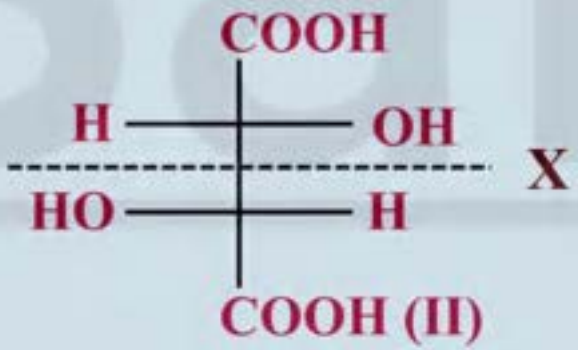
Fischer projection of Lactic acid

Example



Tartaric acid

Achiral

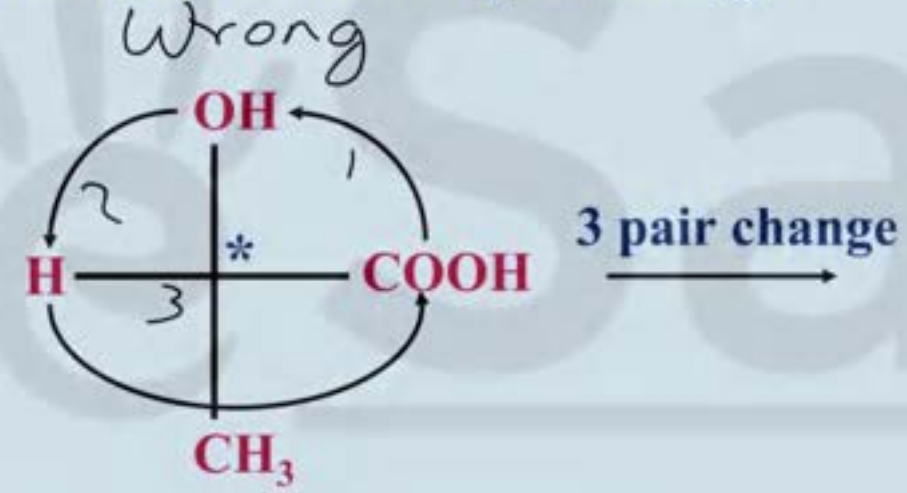


X

Chiral

How to correct wrong Fischer/ how to make perfect Fischer

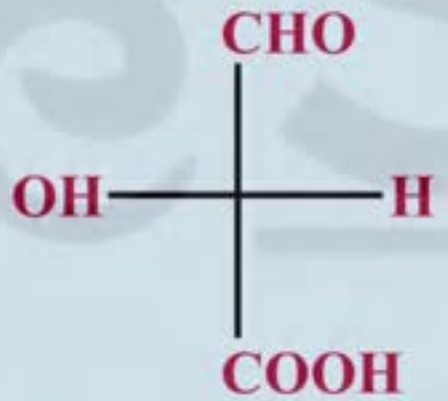
1) If carbon chain is on horizontal line then bring it on vertical line by simultaneous three pair change



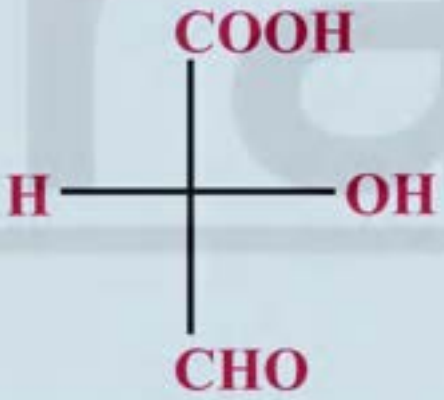
Wrong Fischer projection of Lactic acid

Perfect Fischer of Lactic acid

(2) High priority group lies at the top of vertical line (Numbering starts from top according to IUPAC). If not, rotate the complete molecule in the plane of screen by 180°



Wrong Fischer projection



Perfect Fischer projection

Optical Activity In Different Compounds

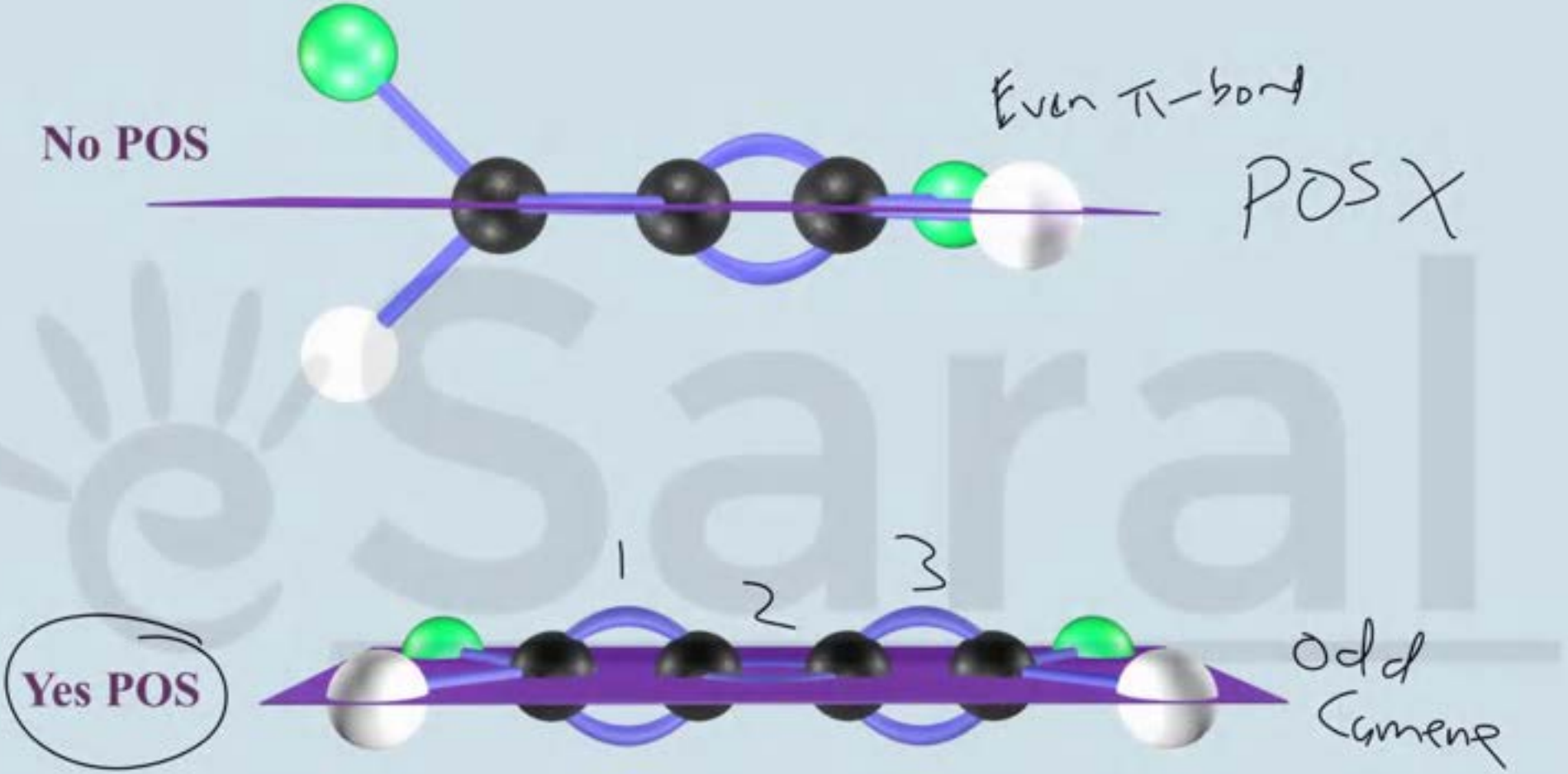
Condition(terminal valencies should be different)

For Cummene

C-C-C

1. Odd no. of π - Bond
   - G.I. Yes
   - Optical No

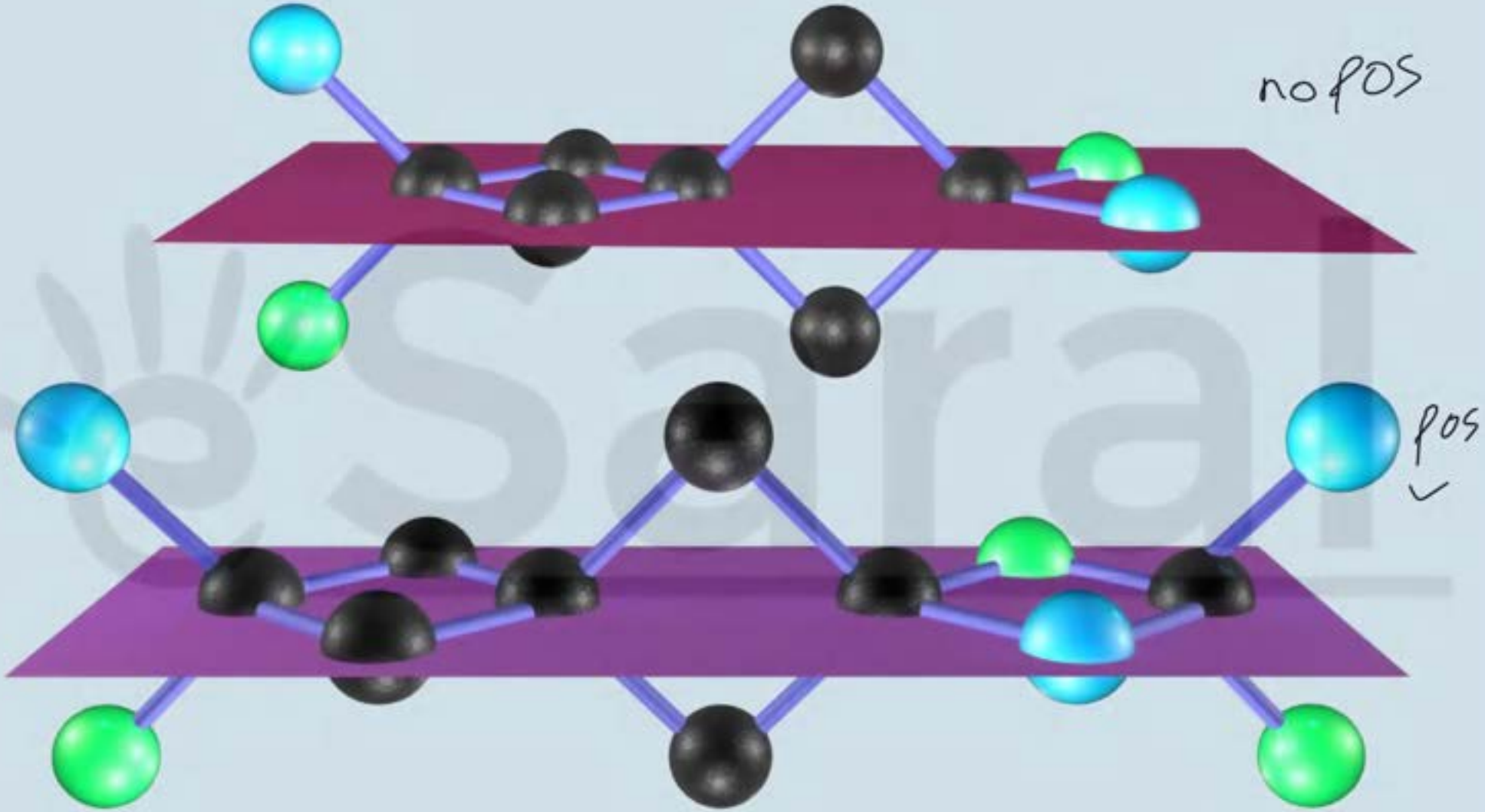
2. Even no. of π - Bond
   - G.I. No
   - Optical Yes



Condition for Spiro

1. Odd no. of rings
   - G.I. Yes
   - Optical No

2. Even no. of rings
   - G.I. No
   - Optical Yes



Ring + Bond

GI ✓

No. of ring + π bond = even

So Optical √ G.I. X

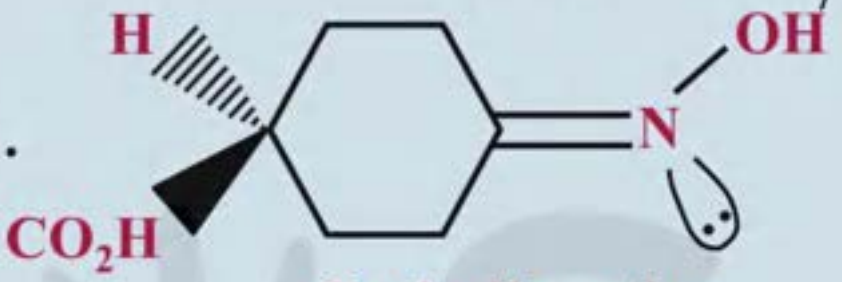
GI X

No. of ring + π bond = odd

So G.I √ Optical X

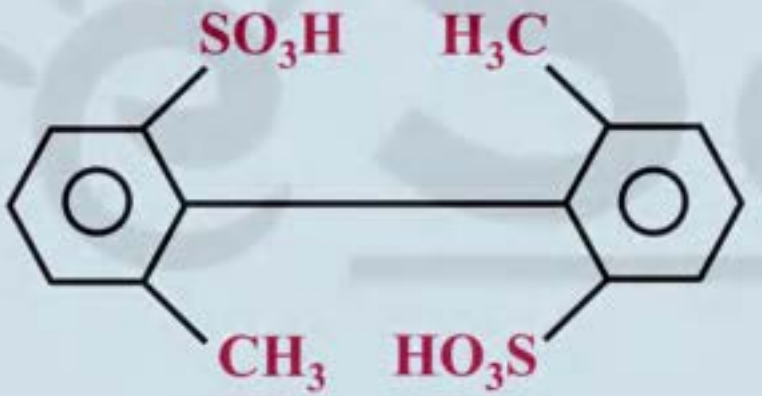
even no of ring + ↖

1.



Optically active

2.



even Biphenyl OA

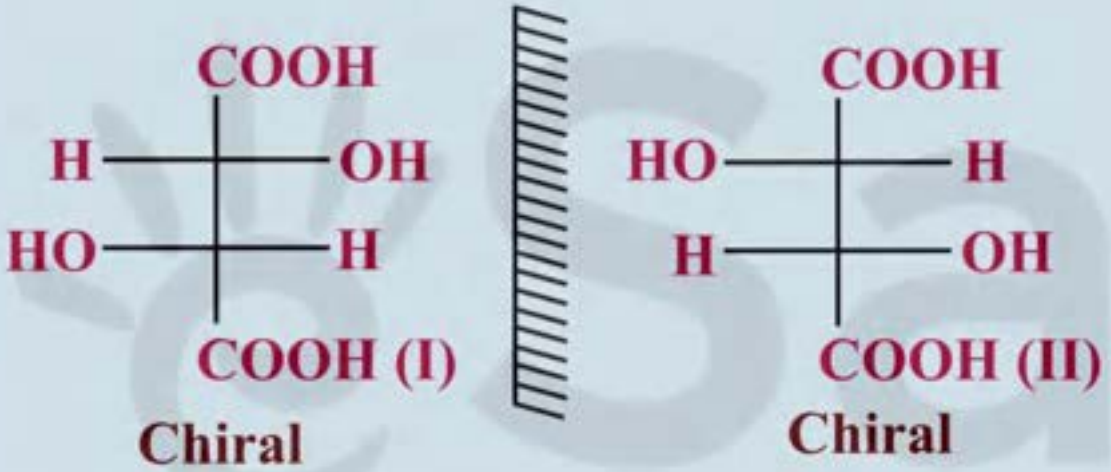
Optically active

Enantiomers

Optically active isomers which are non superimposable mirror-images of each other are called Enantiomers.

A B

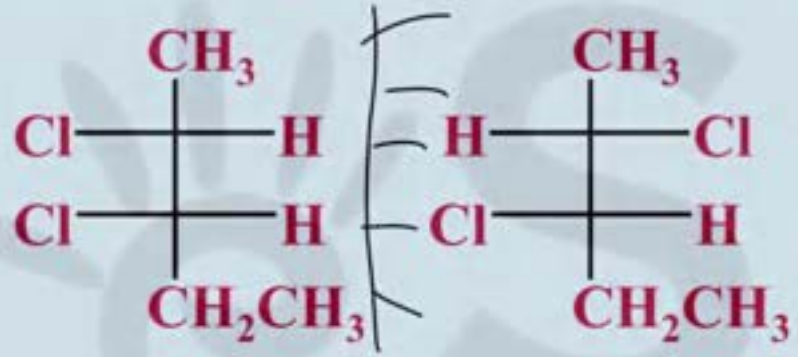
+70° −30°



All the physical and chemical properties of enantiomers are same except that they rotate PPL to the same extent but in opposite direction.

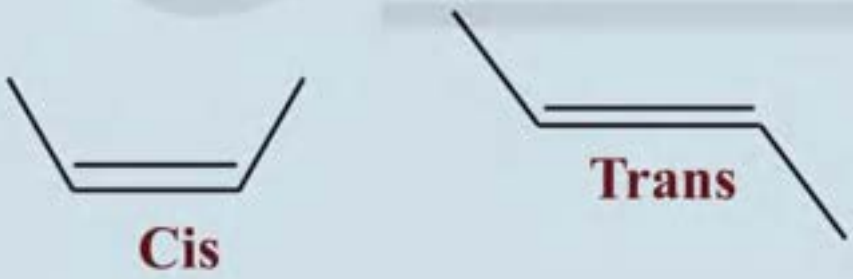
Diastereomerism

The stereoisomers (Geometrical and optical) which are not mirror images of each other are called diastereomers.

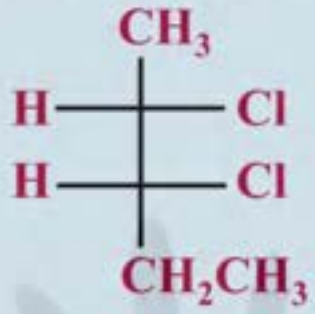


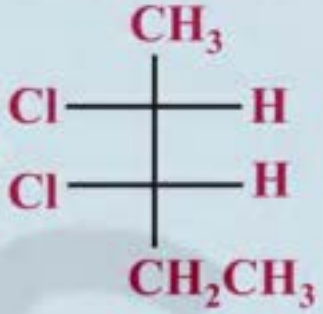
(I) (II)

All the physical and chemical properties of diastereomers are different.

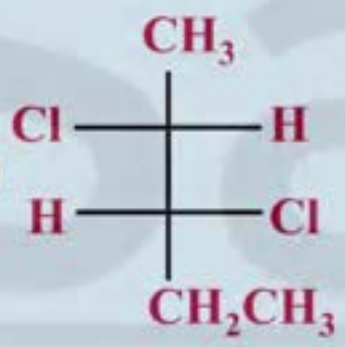


Q) Identify the relation between the following compounds

(I) 

(II) 

(III) 

(IV) 

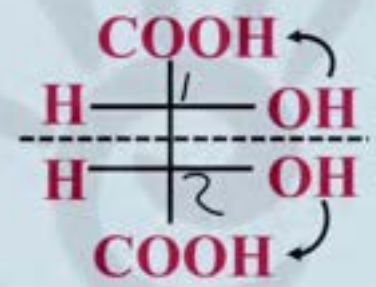
Sol. I, II = Enantiomers III, IV = Enantiomers

II, IV = Diastereomers II, III = Diastereomers

I, III = Diastereomers, I, IV = Diastereomers

Meso Compounds

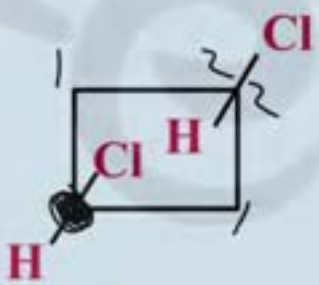
Compounds having at least two chiral carbons and have plane of symmetry or center of symmetry or both is called meso compounds.



Plane of symmetry

Q) Mark meso compounds among following

Meso



No Chiral center hence no meso

Racemic Mixture

10 mole
5 mole (+) 5 mole (−)
d ℓ

Equimolar mixture of d and ℓ enantiomers is called as racemic mixture (d,ℓ or ±).

+30° −30°

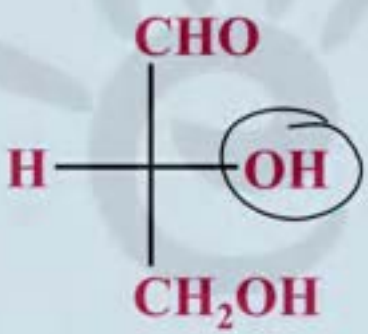
External Compensation

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.

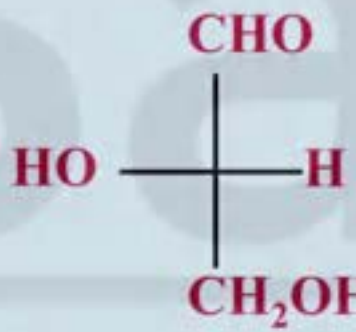
D – L System (Relative Configuration)

This method is used to relate the configuration of carbohydrates and amino acids.

In case of carbohydrates D-L configuration is decided relative to glyceraldehyde.

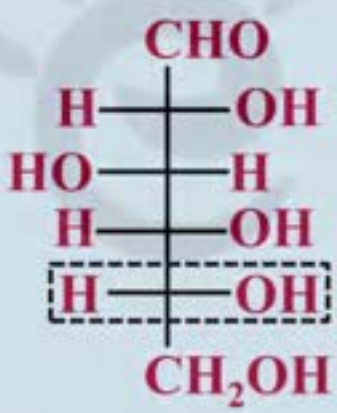


D – glyceraldehyde
– OH group on right side

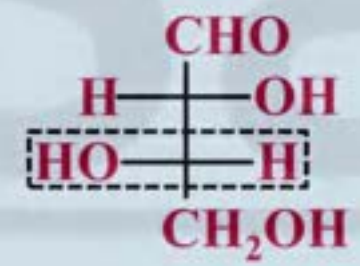


L – glyceraldehyde
– OH group on Left side

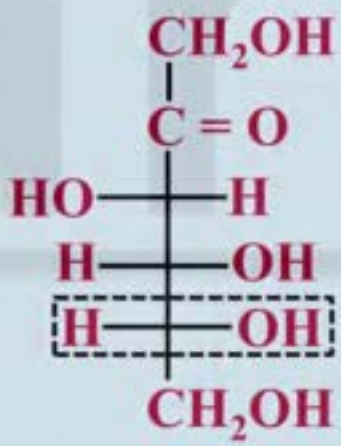
Examples



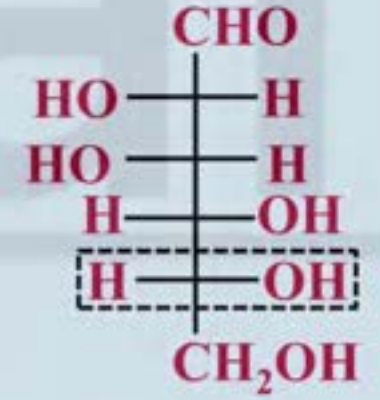
D – (+) – Glucose



L – (+) – Threose

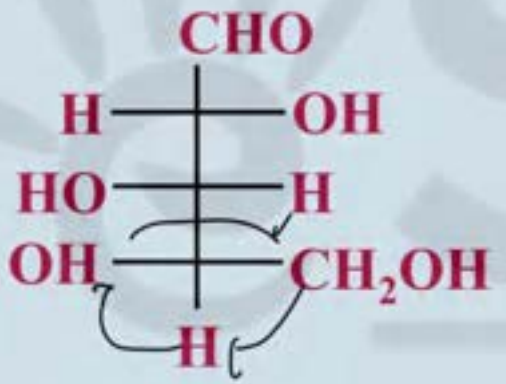


D – Fructose

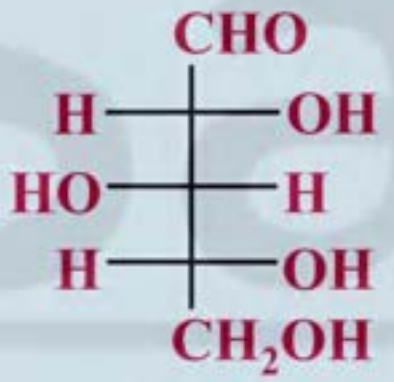


D – Mannose

Beware of
Incorrect Fischer



L-form



D-form

Absolute Configuration (R,S Configuration)

The letter (R) comes from the Latin word rectus (means right or clockwise).

The letter (S) comes from the Latin word sinister (means left or anticlockwise).

(R), (S) nomenclature is assigned as follows in Wedge -Dash System.

Step 1

Assign priority to the groups which are attached with chiral carbon on the basis of CIP rule.

Step 2

Lowest priority group should be on dash.

If not then 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.

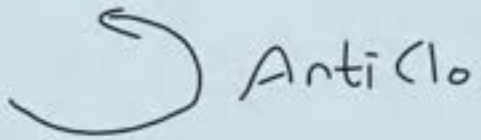
Step 4

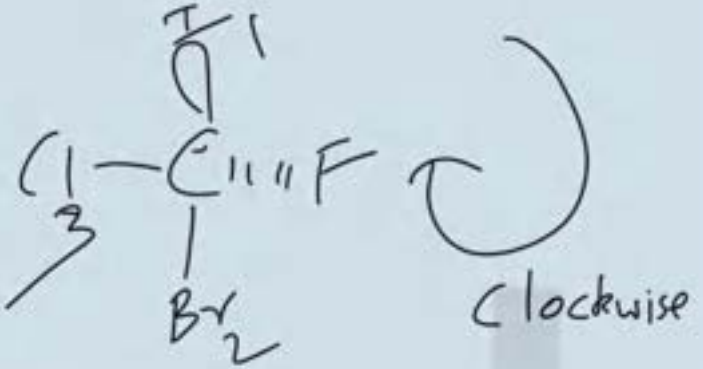
If the direction of arrow is clockwise the configuration is R and if anticlockwise then it is S.

Clockwise - R form

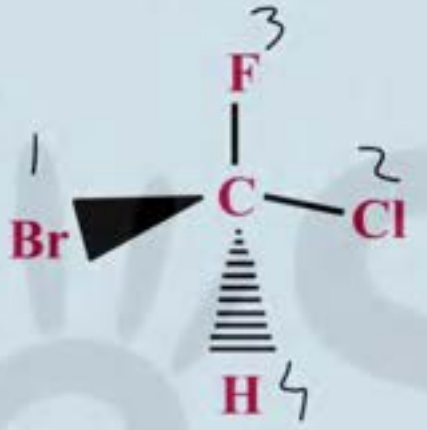
Anti clockwise - S form

Q)



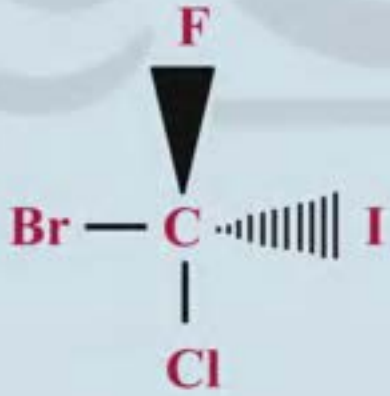


(1.)



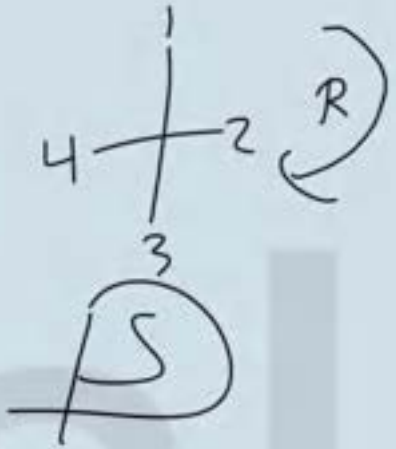
S - form

(2.)



R - form

RS Nomenclature in Fischer formula



Step 1

Assign priority to the groups which are attached with chiral carbon on the basis of atomic number.

Step 2

If lowest priority group is present on vertical line then observed configuration is same as real configuration.

Step 3

If lowest priority group is present on horizontal line then observed configuration is opposite to real configuration.

Step 4

Draw an arrow from first priority group to second priority group till third priority group.

Step 5

If the direction of arrow is clockwise the configuration is R and if anticlockwise it is S.

Clockwise - R form

Anti clockwise - S form

Important

R → ±

D → ±

Note that the designation of a compound as R or S has nothing to do with the sign of rotation, the CIP rule can be applied to any three dimensional representation of a chiral compound to determine whether it is R or S only.

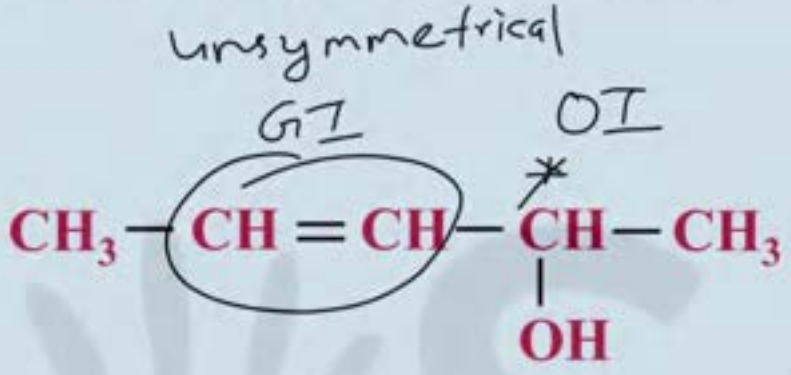
Calculation of Number of Optical Isomers / Stereo Isomers

Learnt

Molecule

- **Unsymmetrical**
  - Total no. of Stereoisomers = 2^n
- **Symmetrical**
  - **n = even**
    - Sns` k nm- ne Rsdqdnhrnl dqr
    - $= 2^{n-1} + 2^{\frac{n}{2}-1}$
    - Optically active + Meso (inactive)
  - **n = odd**
    - Sns` k nm- ne Rsdqdnhrnl dqr
    - $= 2^{n-1} + 2^{\frac{n-1}{2}}$
    - Optically active + Meso (inactive)

Q) Calculate total number of stereoisomers of following compunds.



$n = 2$

cis,R

cis,S

trans,R

trans,S

$\therefore 2^2 = 4$ Ans.

Resolvable and Non-Resolvable Compounds

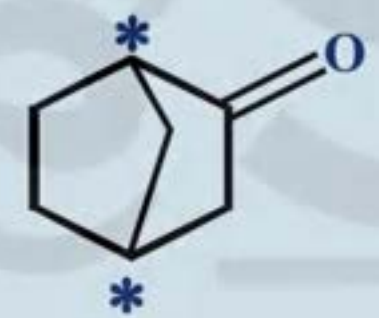
Optically active compounds are considered as resolvable.

Optically inactive compounds are considered as non–resolvable.

Rigid Body System

R → S

If chiral center is present at bridge head then inversion at that position is not possible, so only two stereo isomer are possible (one itself and another its mirror image).



2 + MI

Q). How many isomers are possible on monochlorination of isopentane ?

Total structural → 4

Total isomers → 6

Enantiomeric pair → 2

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*Results received so far

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Shreyansh Agarwal

AIR-379
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AIR-842
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