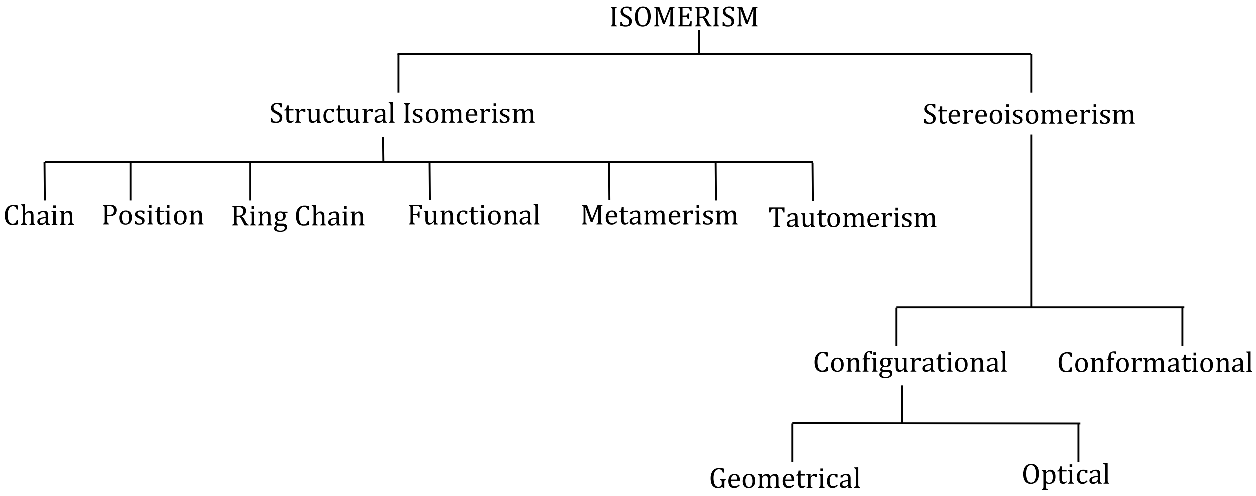
THE P-BLOCK ELEMENTS

ISOMERISM

- **Isomerism:**
  Two or more than two compounds having the same molecular formula but different physical/chemical or both properties are called isomers and the phenomenon is called isomerism.

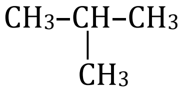


Structural Isomerism

Chain Isomerism (C.I.)

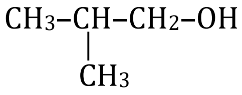
The compounds which have same molecular formula, same functional group but different arrangement of carbon chain (Parental or side chain) show chain isomerism.

Ex. (Butane (4C)


$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_3$

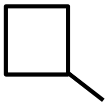
2-Methyl propane (3C)

Ex. 1-Butanol (4C)

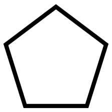

$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-OH$

2-Methyl-1-propanol (3C)

Ex.



Methylcyclobutane



Cyclopentane

Position Isomerism (P.I.)

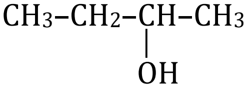
The compounds which have same molecular formula. Same functional group, same parent carbon chain but different position of functional group or multiple bond or substituents, show position isomerism.

Ex. $CH_2{=}CH-CH_2-CH_3$ $CH_3-CH{=}CH-CH_2$

But-1-ene But-2-ene

Ex. $CH_3-CH_2-CH_2-CH_2-OH$

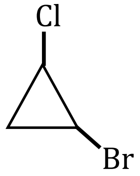
1-Butanol



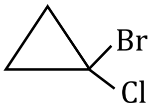
$CH_3-CH_2-\underset{\underset{OH}{|}}{CH}-CH_3$

2-Butanol

Ex.



1-Bromo-2-chlorocyclopropane



1-Bromo-1-chlorocyclopropane

Example of Cl and PI:

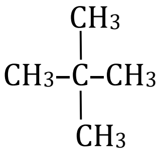
(i) C_5H_{12} has three structural isomers:

$CH_3-CH_2-CH_2-CH_2-CH_3$

Pentane

$CH_3-CH_2-CH-CH_3$

2-Methyl butane



$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$

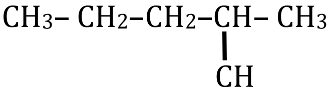
2,2-Dunethylpropane

(ii) C_6H_{14} has 5 structural isomers

(a) $CH_3CH_2CH_2CH_2CH_2CH_3$

Hexane

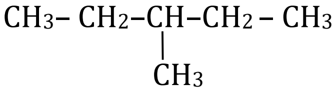
(b)



$CH_3-CH_2-CH_2-\underset{\underset{CH}{|}}{CH}-CH_3$

2-Methyl pentane

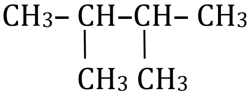
(c)



$CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_3$

Hexane

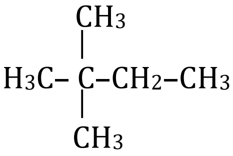
(d)



$CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-CH_3$

2-Methyl pentane

(e)



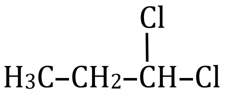
$H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-CH_3$

2,2-Dimethyl butane

- (a–b),(a–c),(a–d),(a–e)→ Chain Isomers (b–d),(b–e),(c–d),(c–e)
- b–c, d–e ⟶ Position Is b–c, d–e

(iii) **$C_3H_6Cl_2$ has 4 isomers:** Position of chlorine atom is different in all the structure, so these are position isomers.

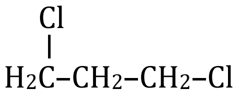
(a)



$$H_3C-CH_2-\overset{\overset{Cl}{|}}{C}H-Cl$$

1,1-Dichloropropane

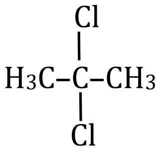
(b)



$$H_2\overset{\overset{Cl}{|}}{C}-CH_2-CH_2-Cl$$

1,3-Dichloropropane

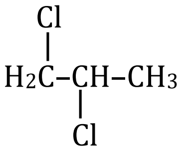
(c)



$$H_3C-\overset{\overset{Cl}{|}}{\underset{\underset{Cl}{|}}{C}}-CH_3$$

2,2-Dichloropropane

(d)



$$H_2\overset{\overset{Cl}{|}}{C}-\underset{\underset{Cl}{|}}{C}H-CH_3$$

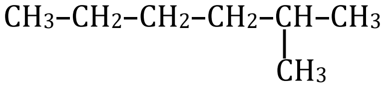
1,2-Dichloropropane

Ex. How many structural isomers of C_7H_{16} are possible?

Ans. (9)

1. $CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$ Heptane

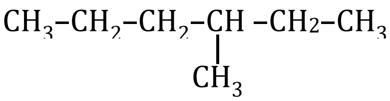
2.



$$CH_3-CH_2-CH_2-CH_2-\underset{\underset{CH_3}{|}}{C}H-CH_3$$

2–Methyl hexane

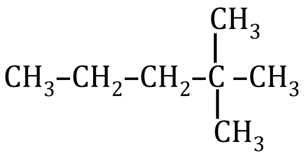
3.



$$CH_3-CH_2-CH_2-\underset{\underset{CH_3}{|}}{C}H-CH_2-CH_3$$

3–Methyl hexane

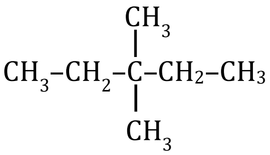
4.



$$CH_3-CH_2-CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$$

2,2–Dimethyl pentane

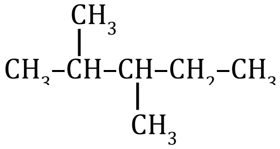
5.



$$CH_3-CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-CH_3$$

3,3–Dimethyl pentane

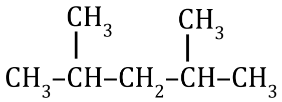
6.



$$CH_3-\overset{\overset{CH_3}{|}}{C}H-\underset{\underset{CH_3}{|}}{C}H-CH_2-CH_3$$

2,3–Dimethyl pentane

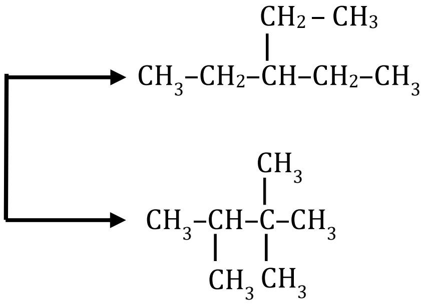
7.



$$CH_3-\overset{\overset{CH_3}{|}}{C}H-CH_2-\overset{\overset{CH_3}{|}}{C}H-CH_3$$

2,4–Dimethyl pentane

8. 9

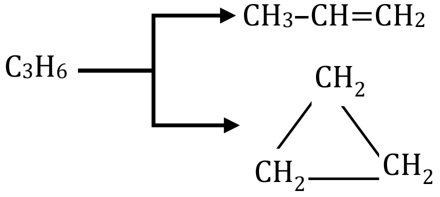


8. $CH_3-CH_2-CH(CH_2-CH_3)-CH_2-CH_3$ 3–Ethyl pentane

9. $CH_3-CH(CH_3)-C(CH_3)_2-CH_3$ 2,2,3–Trimethyl butane (Triptane)

Ring chain isomerism (RCI)

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



C_3H_6 → $CH_3-CH=CH_2$ **[Open Chain]**

[closed Chain or ring]

- Alkenes with cycloalkane and alkynes and alkatrienes with cycloalkenes show Ring-chain Isomerism.
- Ring-chain Isomers are also Functional Isomers but priority must be given to Ring-chain Isomers.

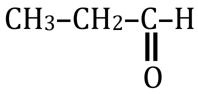
Functional Isomerism

Same molecular formula but different functional groups.

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

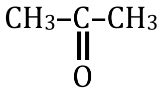
(i) Alcohol and Ether ⟶ CH_3-CH_2-OH and CH_3-O-CH_3

(ii) Aldehydes and Ketones ⟶



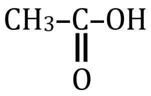
$CH_3-CH_2-\underset{\underset{O}{\|}}{C}-H$

and



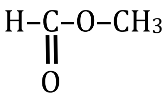
$CH_3-\underset{\underset{O}{\|}}{C}-CH_3$

(iii) Acids and Ester ⟶



$CH_3-\underset{\underset{O}{\|}}{C}-OH$

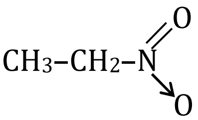
and



$H-\underset{\underset{O}{\|}}{C}-O-CH_3$

(iv) Cyanide and Isocyanide ⟶ $CH_3-CH_2-CH_2-CN$ and $CH_3-CH_2-CH_2-NC$

(v) Nitro and Nitrite ⟶

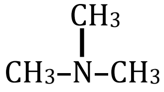


$CH_3-CH_2-N(=O)\rightarrow O$

and $CH_3-CH_2-O-N=O$

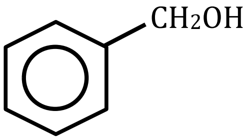
(vi) 1º,2º,3º Amines

(a) $CH_3-CH_2-CH_2-NH_2$ (b) $CH_3-NH-CH_2-CH_3$ (c)

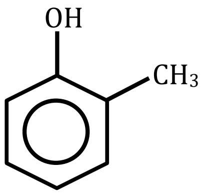


$CH_3-\overset{\overset{CH_3}{|}}{N}-CH_3$

(vii) Alcoholic and Phenolic compounds:



and



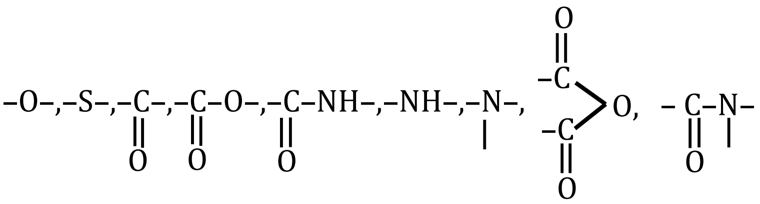
(viii) Alkyl halides do not show Functional isomerism.

(ix) $CH_3-C\equiv CH$ propyne and $CH_2=CH=CH_2$

Metamerism

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

Polyvalent Functional group [Which have more than one valency] are:



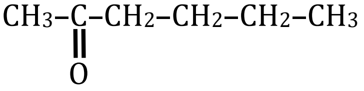
$-O-,-S-,-\underset{\overset{\|}{O}}{C}-,-\underset{\overset{\|}{O}}{C}-O-,-\underset{\overset{\|}{O}}{C}-NH-,-NH-,-\underset{|}{N}-,\ \begin{matrix}-\overset{\overset{O}{\|}}{C}\\ -\underset{\underset{O}{\|}}{C}\end{matrix}\Big\rangle O,\ -\underset{\overset{\|}{O}}{C}-\underset{|}{N}-$

Ex. $CH_3-O-CH_2-CH_2-CH_3$ $H_3C-CH_2-O-CH_2-CH_3$

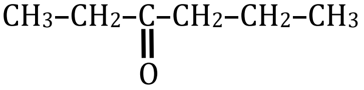
Ex. $CH_3-CH_2-NH-CH_2-CH_3$ $CH_3-NH-CH_2-CH_2-CH_3$

Ex. $CH_3-NH-CH_2-CH_2-CH_2-CH_3$ $H_3C-CH_2-NH-CH_2-CH_2-CH_3$

Ex.



$CH_3-\underset{\overset{\|}{O}}{C}-CH_2-CH_2-CH_2-CH_3$

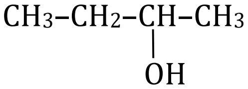


$CH_3-CH_2-\underset{\overset{\|}{O}}{C}-CH_2-CH_2-CH_3$

Examples Based on Structural Isomerism: -

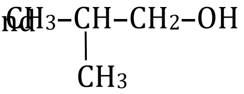
Ex.-1 $C_4H_{10}O$ Structural isomers ⇒ 7 [4 alcohol and 3 ethers] total 7 structural isomers are possible.

Alcohol: $CH_3-CH_2-CH_2-CH_2-OH$

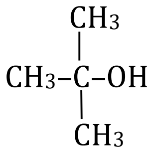


$CH_3-CH_2-\underset{\underset{OH}{|}}{CH}-CH_3$

and

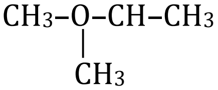


$$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-OH$$



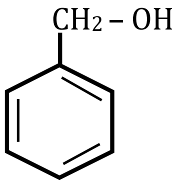
$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH$$

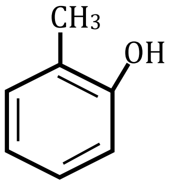
Ethers: $CH_3-O-CH_2-CH_2-CH_3$, $C_2H_5-O-C_2H_5$,

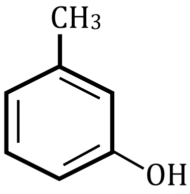


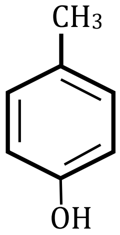
$$CH_3-O-\underset{\underset{CH_3}{|}}{CH}-CH_3$$

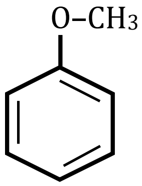
Ex. 2 Aromatic isomers of C_7H_8O.

(a) 

(b) 

(C) 

(d) 

(e) 

- a, b - Functional isomers
- b, c - Position isomers
- c, d - Position isomers
- a, d - Functional isomers
- a, e - Functional isomers
- a, c - Functional isomers

Note: Alcoholic and phenolic groups are Functional isomers.

Stereo Isomerism

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

(A) **Configurational Isomerism:** Stereo isomers which have following characteristics.

(a) Stereo isomer which cannot interconvert at room temperature due to restricted rotation known as Geometrical isomerism.

(b) Stereo isomers which have different behavior towards plane polarized light are known as optical isomers.

(B) **Conformational Isomerism**

Geometrical isomerism (G.I):

(i) Alkenes (>C=C<), oximes (>C=N–OH) and azo compounds [–N=N–] ets., show G.I. due to restricted rotation about double bond

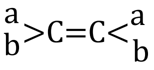
(ii) cycloalkanes show G.I. due to restricted rotation about single bond in ring.

G.I. IN ALKENES:

Reason: Restricted rotation about double bond:

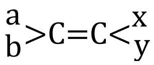
Condition for Geometrical isomerism:

Only those alkenes show G. I. in which "Each sp^2 carbon individually have different atoms or groups"



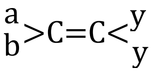
$\begin{matrix}a\\b\end{matrix}\!>C=C<\!\begin{matrix}a\\b\end{matrix}$

Geometrical isomerism possible



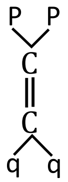
$\begin{matrix}a\\b\end{matrix}\!>C=C<\!\begin{matrix}x\\y\end{matrix}$

Geometrical isomerism possible



$\begin{matrix}a\\b\end{matrix}\!>C=C<\!\begin{matrix}y\\y\end{matrix}$

Geometrical isomerism not possible

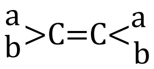


Geometrical isomerism not possible

Nomenclature Systems of Geometrical isomers

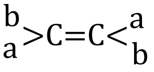
(a) Cis-Trans System

If same groups are at same side, then cis and if same groups are at different side, then trans.



$\begin{matrix}a\\b\end{matrix}\!>C=C<\!\begin{matrix}a\\b\end{matrix}$

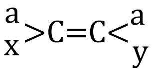
[Same groups, same side cis]



$\begin{matrix}b\\a\end{matrix}\!>C=C<\!\begin{matrix}a\\b\end{matrix}$

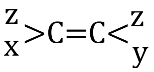
[Same groups different side cis]

Ex.



$\begin{matrix}a\\x\end{matrix}\!>C=C<\!\begin{matrix}a\\y\end{matrix}$

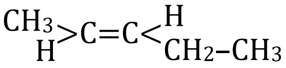
cis



$\begin{matrix}z\\x\end{matrix}\!>C=C<\!\begin{matrix}z\\y\end{matrix}$

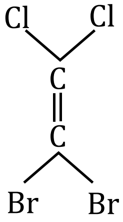
cis

Ex.



$\begin{matrix}CH_3\\H\end{matrix}\!>C=C<\!\begin{matrix}H\\CH_2-CH_3\end{matrix}$

Trans-2-pentene



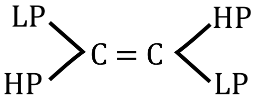
It does not show Geometrical isomers

So, no cis-trans

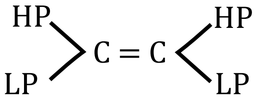
(b) E-Z System:

E (Ent Gegen): When high priority groups are at opposite side.

Z (Zu Samman): When high priority groups are at same side.



'E'

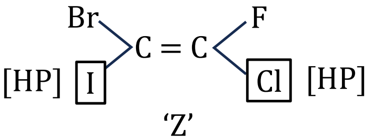


'Z'

HP-High priority and LP-Low priority

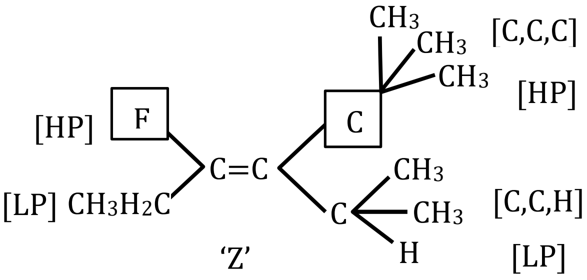
Priority Rules [CIP Sequence Rule):

Rule I: Priority is proportional to atomic number of atoms which is directly attached to sp^2 carbon.



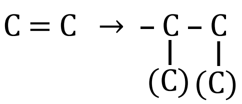
'Z'

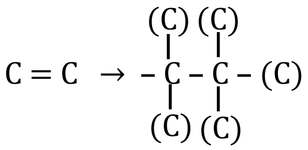
Rule II: If rule-I is failed then consider the atomic number of next atom and so on.

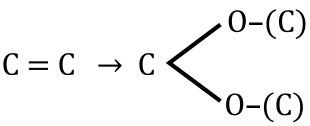


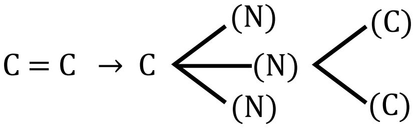
'Z'

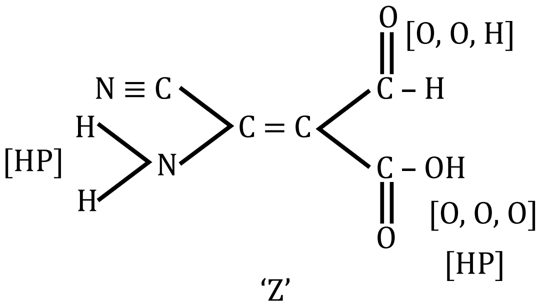
Rule III: - If multiple bonds is present then consider them as: -





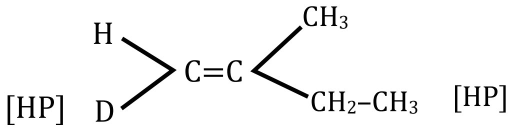






‘Z’

Rule IV: If isotopes are present then consider atomic weight.



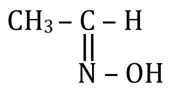
‘Z’

GEOMETRICAL IOSMERS IN OXIMES [>C=N–OH]:

- Oximes show G.I. due to restricted rotation about double bond.
- Only those oximes show Geometrical isomerism in which sp^2 carbon have two different groups.

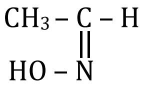
$$CH_3{-}CH{=}\boxed{{=}O + H_2}N{-}OH \longrightarrow CH_3{-}CH{=}N{-}OH \text{ (oxime)}$$

Ex. Acetaldoximes has two Geometrical isomers-



$$\begin{matrix} CH_3 - & C & - H \\ & \| & \\ & N & - OH \end{matrix}$$

syn



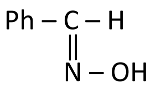
$$\begin{matrix} CH_3 - & C & - H \\ & \| & \\ HO - & N & \end{matrix}$$

anti

When H and OH are on the same side.

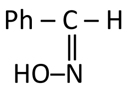
When H and OH are on the opposite side

Ex. Benz aldoxime



$$\begin{matrix} Ph - & C & - H \\ & \| & \\ & N & - OH \end{matrix}$$

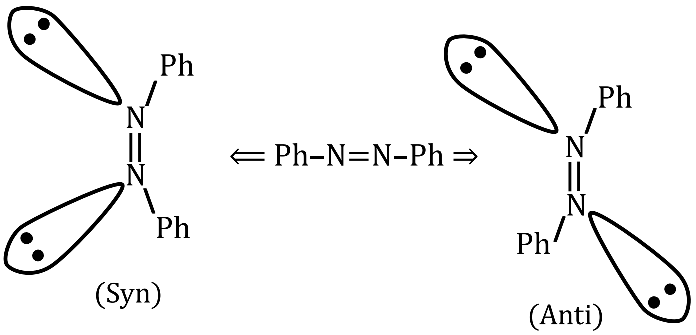
[syn.]



$$\begin{matrix} Ph - & C & - H \\ & \| & \\ HO{-} & N & \end{matrix}$$

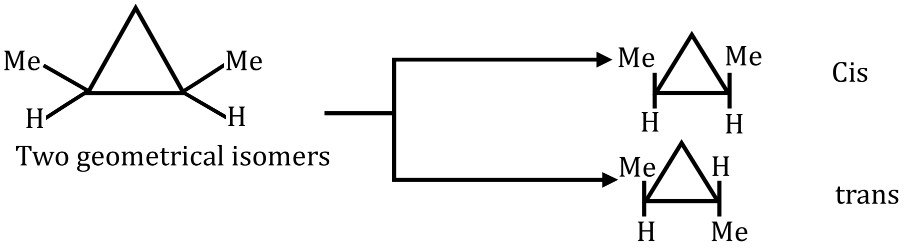
[Anti]

GEOMETRICAL ISOMERS IN AZO COMPOUNDS: ($-\ddot{N}=\ddot{N}-$)



(Syn) (Anti)

GEOMETRICAL ISOMERS IN CYCLOALKANES: Cycloalkanes show Geometrical isomerism due to restricted rotation about single bond. Only those cycle alkanes show Geometrical isomers in which at least two different carbons have two different groups.



NUMBER OF GEOMETRICAL ISOMERS IN POLYENES:

$R_1-CH=CH-CH=CH$ .... $CH=CH-R_2$

(a) If $R_1 \neq R_2$ then number of Geometrical isomers $= 2^n$

[n = number of double bonds which show G.I.]

Ex. $CH_3-CH=CH-CH=CH-CH=CH-CH_2CH_3$

As $n = 3$, number of Geometrical isomers $= 2^3 = 8$

(b) If $R_1 = R_2$ then number of Geometrical isomers $= 2^{n-1} + 2^{p-1}$

Where $p = \frac{n}{2}$ (when n is even) and $p = \frac{n+1}{2}$ (n is odd)

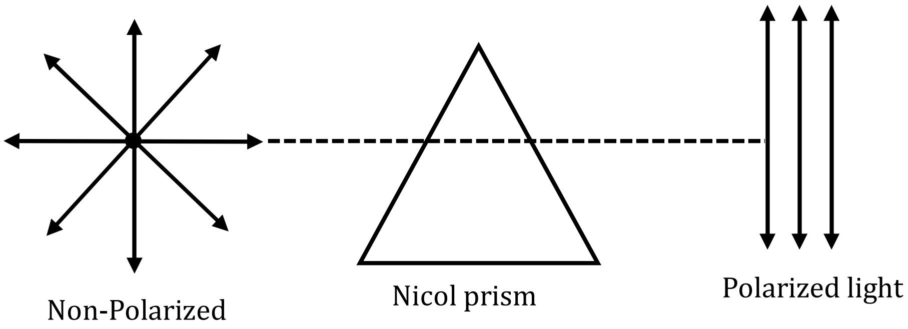
Ex. $CH_3-CH=CH-CH=CH-CH=CH-CH_3$ [n = 3]

Number of Geometrical isomers $= 2^2 + 2^1$

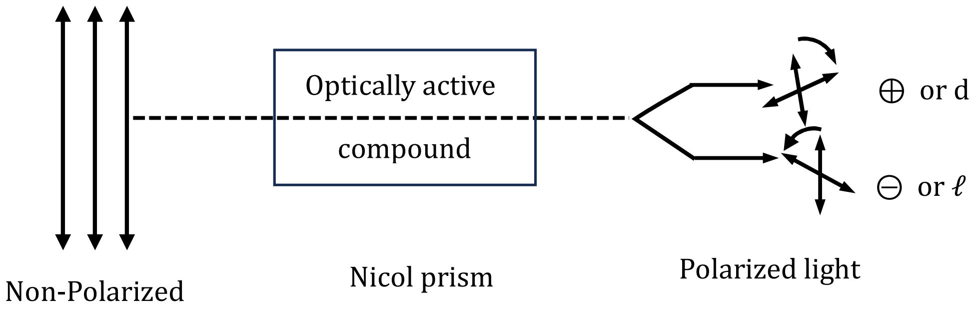
$= 4 + 2 = 6$

OPTICAL ISOMERISM:

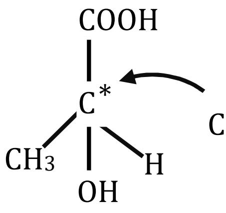
Optical isomers: Two or more than two compound have same molecular formula, same structural formula but different behaviour towards PPL (plane polarized light).



Optical activity: Tendency to rotate plane of PPL in a particular direction. If a compound rotates plane of PPL in clockwise direction, then it will be dextrorotatory or d or (+) and if a compound rotates plane of PPL in anticlockwise direction, then it will be levorotatory or λ or (–).



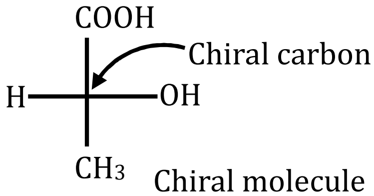
Chiral carbon: Carbon which is bonded to four different atoms or groups.



Chiral carbon or asymmetric carbon.

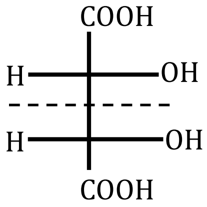
Chiral molecule:

(i) A molecule having only one chiral centre then it will be always chiral. Except flipping

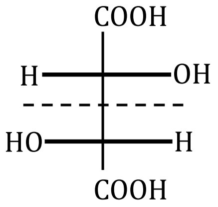


Chiral molecule

(ii) A molecule having at least two chiral carbons and no symmetry then it will be chiral molecule.



Plane of symmetry
(Achiral molecular)



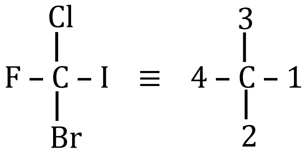
No symmetry
(Chiral molecular)

Essential and sufficient condition for optical activity is:
"Molecule should be **chiral**" or "Molecule should be **unsymmetrical**" or "**Nonsuperimposable** mirror images"

Absolute Configuration (R, S configuration):
The actual three-dimensional arrangement of groups in a molecule containing asymmetric carbon is termed as **absolute configuration.**
(R) (S) nomenclature is assigned as follows:

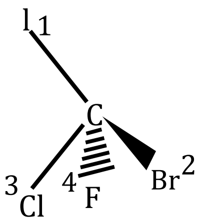
1. Each group attached to stereocenter is assigned a priority on the basis of CIP sequence rule.

Example:



$$F-\underset{\displaystyle Br}{\overset{\displaystyle Cl}{\underset{|}{\overset{|}{C}}}}-I \equiv 4-\underset{\displaystyle 2}{\overset{\displaystyle 3}{\underset{|}{\overset{|}{C}}}}-1$$

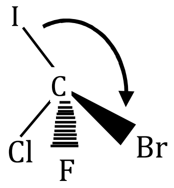
2. After assigning priorities, the least priority group is written at remotest valency (going away).



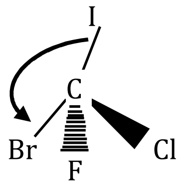
Note that priority order is: I>Br>Cl>F

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

For example.

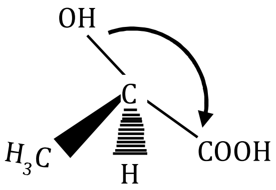


R–Configuration
(Clockwise from top priority)

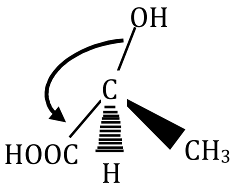


S–Configuration

(Anti clockwise from top priority)



R–Configuration
(Clockwise from top priority)

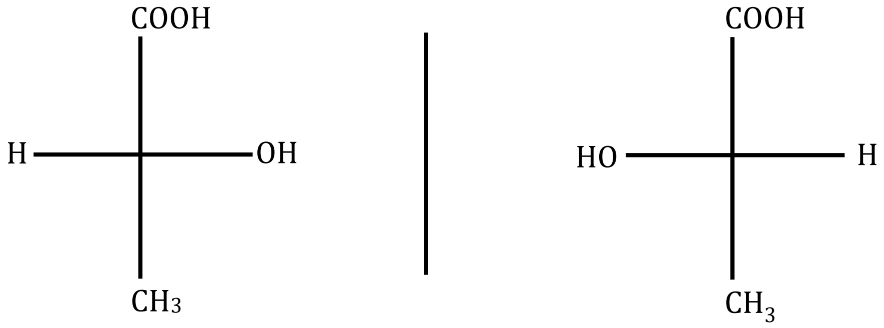


S–Configuration
(Anti clockwise from top priority)

Enantiomers:

Stereoisomers which are mirror images to each other and not superimpose to each other.

Nonsuperimposable mirror images are called as enantiomers.



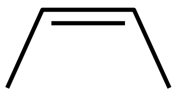
Object (I) mirror Image (II)

I and II are nonsuperimposable mirror images, so I and II are enantiomers.

(i) Enantiomers have chiral structures.

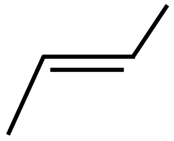
(ii) Enantiomers are optically active substance. They rotate the plane polarized light in opposite directions but to the equal extent.

Diastereomers: Stereoisomers which are not mirror images of each other's.



Cis–2 butene

(I)



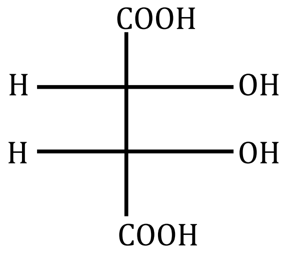
Cis–2 butene

(II)

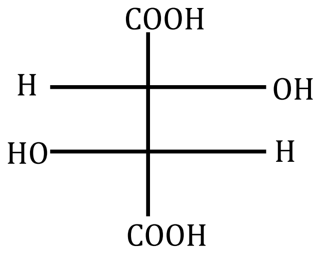
I and II are not mirror images, so I and II are diastereomers.

EXAMPLES OF OPTICAL ISOMERISM

Example: 1.

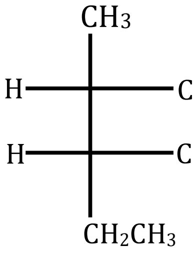


2.

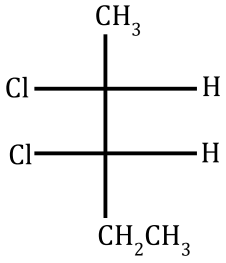


(1) and (2) are diastereomers

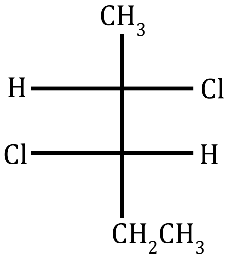
Example:



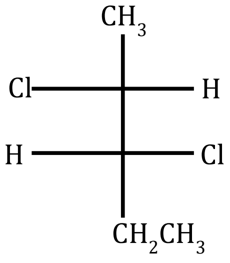
(I)



(II)



(III)



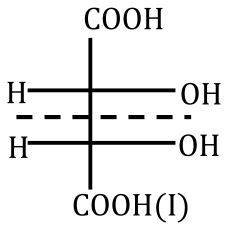
(IV)

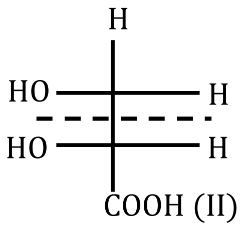
I, II = Enantiomers, III, IV = Enantiomers

I, III = Diastereomers, II, IV = Diastereomers

II, III = Diastereomers, I, IV = Diastereomers

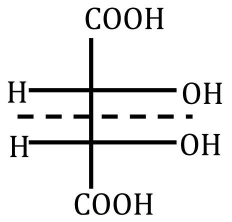
Example:





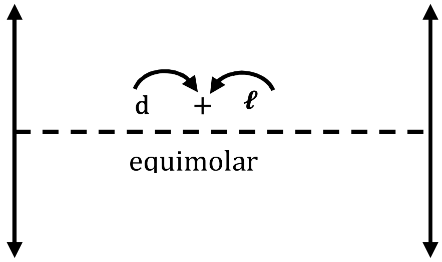
Achiral I and II are identical

Meso compounds: Compounds having at least two chiral carbons and plane of symmetry is called meso compounds. It is optically inactive due to internal compensation.



Plane of symmetry
(Achiral molecule
optically inactive)

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



Net rotation zero
[External compensation]

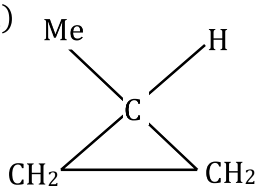
“Racemic mixture is optically inactive due to external compensation.

Number of Stereoisomers: -

S.N.	Nature of compounds	No. of optically Active isomers (a)	No. of meso compound (m)	Total no. of Stereoisomer (a+m)
1.	Compounds having dissimilar ends	2^n N = No. of chiral centre	0	$(2^n + 0)$
2.	Compounds having similar ends with even chiral centres	2^{n-1}	$2^{\frac{n}{2}-1}$	$(2^{n-1} + 2^{\frac{n}{2}-1})$
3.	Compounds having similar ends with odd chiral centres	$2^{n-1} - 2^{\frac{n-1}{2}}$	$2^{\frac{n-1}{2}}$	2^{n-1}

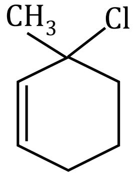
Optical Isomerism in cyclic compounds:

(i)



No Chiral carbon, Molecule is achiral Molecule is optical Inactive

(ii)

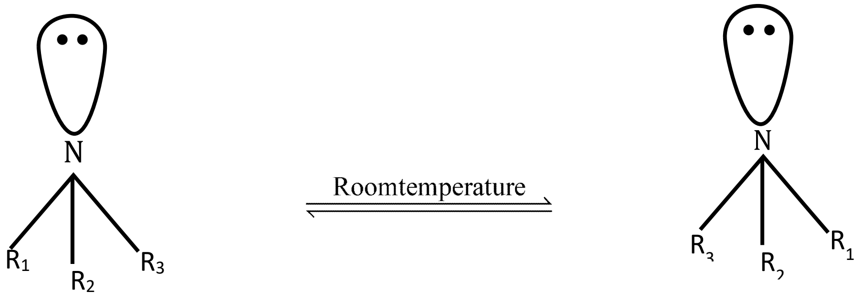


Chiral carbon, Chiral Molecule, optically active

Special Point:

1. Chiral nitrogen containing/tertiary/open chain amine does not show optical isomerism.

   Reason: - Rapid umbrella inversion.

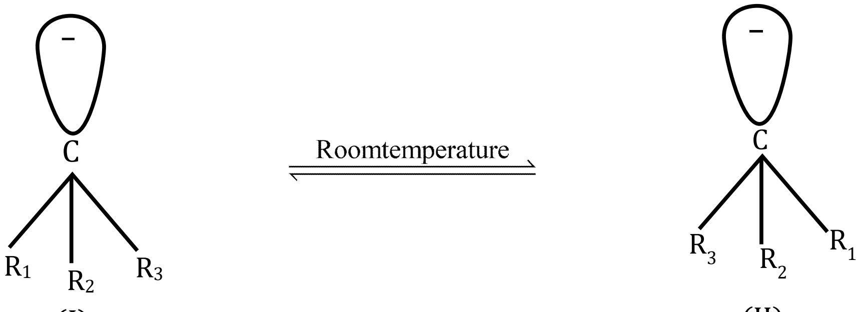


(I) (II)

Energy required for this interconversion is available at room temperature. So, I and II are interconvertible.

2. Chiral C containing carbanion does not show optical isomerism.

   Reason: - Rapid umbrella inversion.

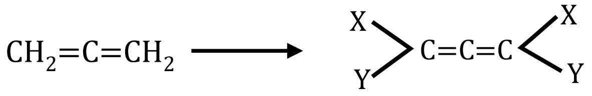


(I) (II)

Energy required for this interconversion is available at room temperature. So, I and II are interconvertible.

Note: - Only 2nd period elements show flipping.

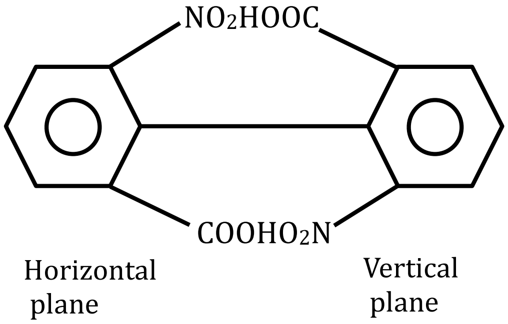
3. Substituted Allenes do not have chiral carbons but molecule is chiral, so show optical isomerism.



$$CH_2=C=CH_2 \longrightarrow \begin{matrix}X\\Y\end{matrix}\!>C=C=C<\!\begin{matrix}X\\Y\end{matrix}$$

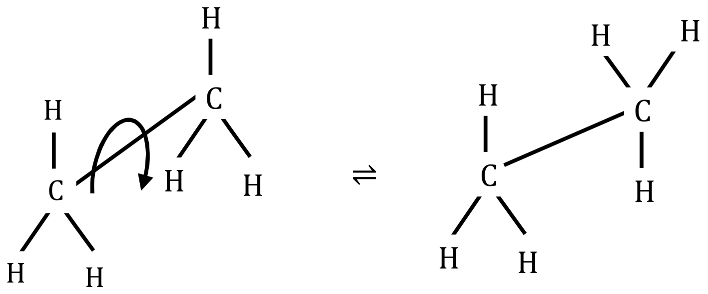
Only those substituted allenes will be optically active in which "each sp^2 C have different atoms or group".

4. Ortho substituted biphenyl compounds do not have any chiral carbon but due to chiral molecule, they are optically active.

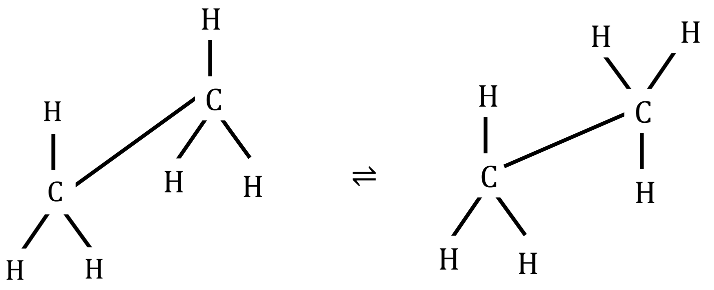


Conformational Isomerism

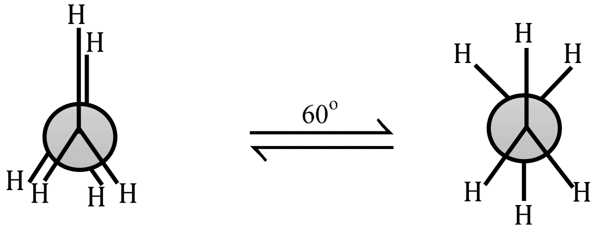
The different arrangement of atoms in space that result from the free rotation around single bond, are called conformations. The phenomenon is called conformational isomerism



Conformation of ethane [CH_3–CH_3]



(Saw horse projection)



(III) (IV)

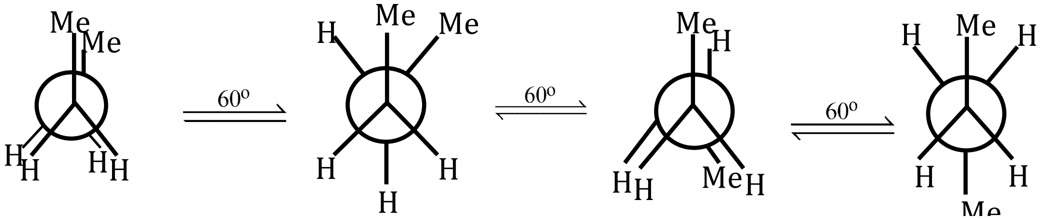
(Newman projection)

[Stability order: Staggered > Eclipsed]

Dihedral Angle: Dihedral angle in eclipsed form of ethane is 0º.
Dihedral angle in staggered form of ethane is 60º.

Conformation of Butane

[$CH_3–CH_2–CH_2–CH_3$]



(i) (ii) (iii) (iv)

I (Fully eclipsed form): In this form distance between 2 methyl groups is minimum so maximum repulsion or minimum stable.
IV (Anti or staggered): In this form distance between 2 methyl groups is maximum so minimum repulsion or maximum stable.

Stability order: IV > II > III > I