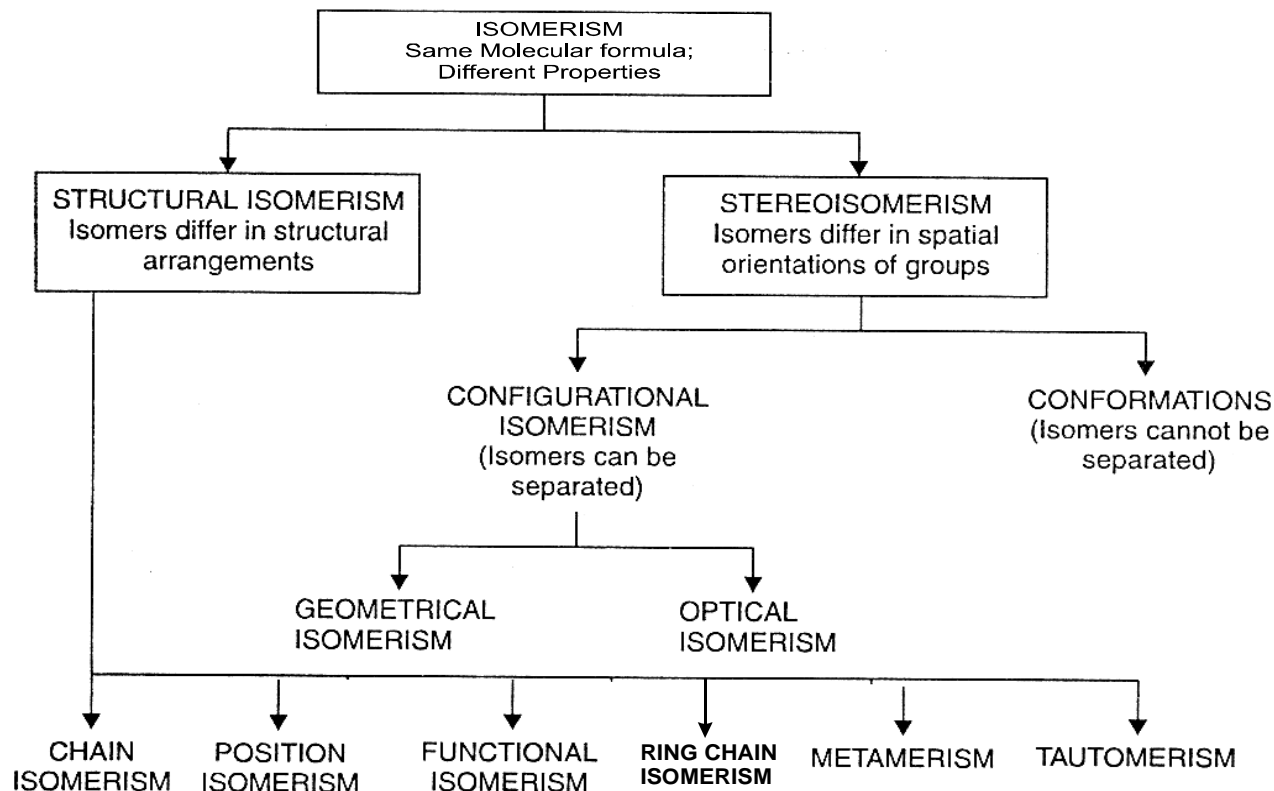


# Iso**mer**ism

## 1 ISOMERISM

The compounds which differ in their properties but have same molecular formula are called **isomers** and the



### TYPES OF ISOMERISM

There are two types of isomerism :

(1) Structural isomerism

(2) Stereoisomerism

### 1.1 STRUCTURAL ISOMERISM :

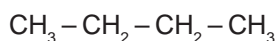
In this type of isomerism, the compounds possessing same molecular formula but differ in their properties due to the difference in the linkages of atoms inside the molecule, i.e., due to the difference in their structure.

**Structural isomerism is of the following types**

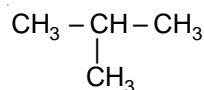
#### 1.1.1 CHAIN ISOMERISM :

In this type of isomerism, the compounds possessing same molecular formula differ in their properties due to the difference in the arrangement of carbon chain present in them.

E.g.

(i)  $C_4H_{10}$ 

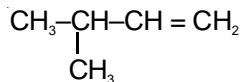
n-butane



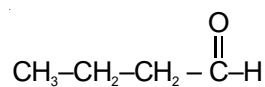
isobutane

(ii)  $C_5H_{10}$ 

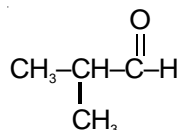
Pent-1-ene



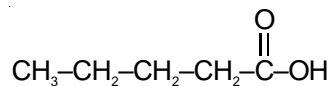
3-Methyl but-1-ene

(iii)  $C_4H_8O$ 

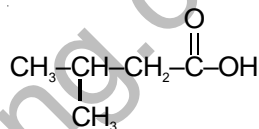
Butanal



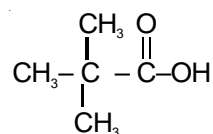
2-Methyl propanal

(iv)  $C_5H_{10}O_2$ 

Pentanoic acid



3-Methyl butanoic acid

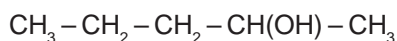


2, 2- Dimethyl propanoic acid

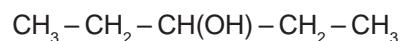
**1.1.2 POSITION ISOMERISM :**

In this type of isomerism, the compounds possessing same molecular formula differ in their properties due to the difference in the position of either the functional group or the multiple bond or the branched chain attached to the main carbon chain.

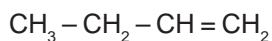
E.g.

(i)  $C_5H_{12}O$ 

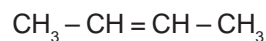
2-Pentanol



3-pentanol

(ii)  $C_4H_8$ 

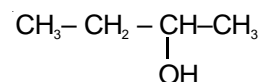
1-butene



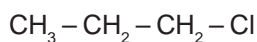
2-butene

(iii)  $C_4H_{10}O$ 

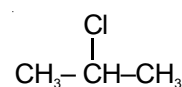
Butan-1-ol



Butan-2-ol

(iv)  $C_3H_7Cl$ 

1-Chloro propane



2-chloro propane

**Note :**

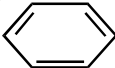

1. Aldehyde, carboxylic acids (and their derivatives) and cyanides do not exhibit position isomerism.
2. Mono substituted alicyclic compounds and aromatic compounds do not exhibit position isomerism.

**1.1.3 FUNCTIONAL ISOMERISM :**

In this type of isomerism the compounds possessing same molecular formula differ in their properties due to the difference in their functional group, i.e. the functional isomers differ in the functional group present in them.

**E.g.**

**(i) Alcohols and ethers, (C<sub>n</sub>H<sub>2n+2</sub>O)**

- $C_2H_6O$   $CH_3CH_2OH$   $H_3C-O-CH_3$   
Ethanol Methoxy methane
- $C_7H_8O$    $CH_2OH$    $OCH_3$   
Benzyl alcohol Anisole (Methyl phenyl Ether)

**(ii) Aldehyde and ketone (C<sub>n</sub>H<sub>2n</sub>O)**

- $C_3H_6O$   $CH_3CH_2CHO$   $CH_3COCH_3$   
Propanal Propanone

**(iii) Acid and ester (C<sub>n</sub>H<sub>2n</sub>O<sub>2</sub>)**

- $C_3H_6O_2$   $CH_3CH_2COOH$   $CH_3COOCH_3$   
Propanoic acid Methyl ethanoate

**(iv) Cyanide and Isocyanides**

- $R-C \equiv N$   $R-N \equiv C$   
Alkyl cyanide Alkyl isocyanide

**(v) Nitro and nitrite**

-   $R-O-N=O$   
Nitroalkanes Alkyl nitrites

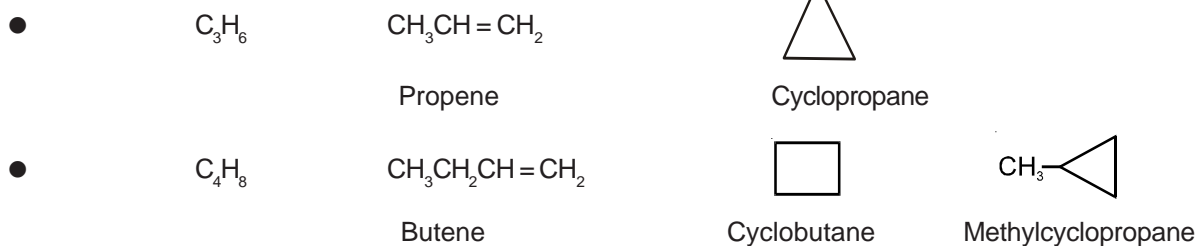
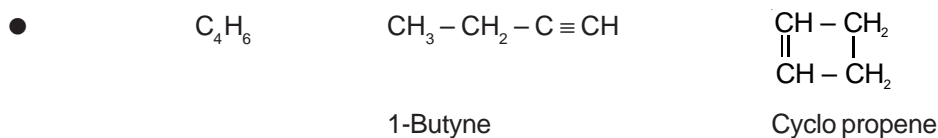
**(vi) Alkyne and alkadiene**

- $CH_3-CH_2-C \equiv CH$   $H_2C=CH-CH=CH_2$   
1-Butyne 1,3-Butadiene

**1.1.4 RING CHAIN ISOMERISM :**

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

E.g.

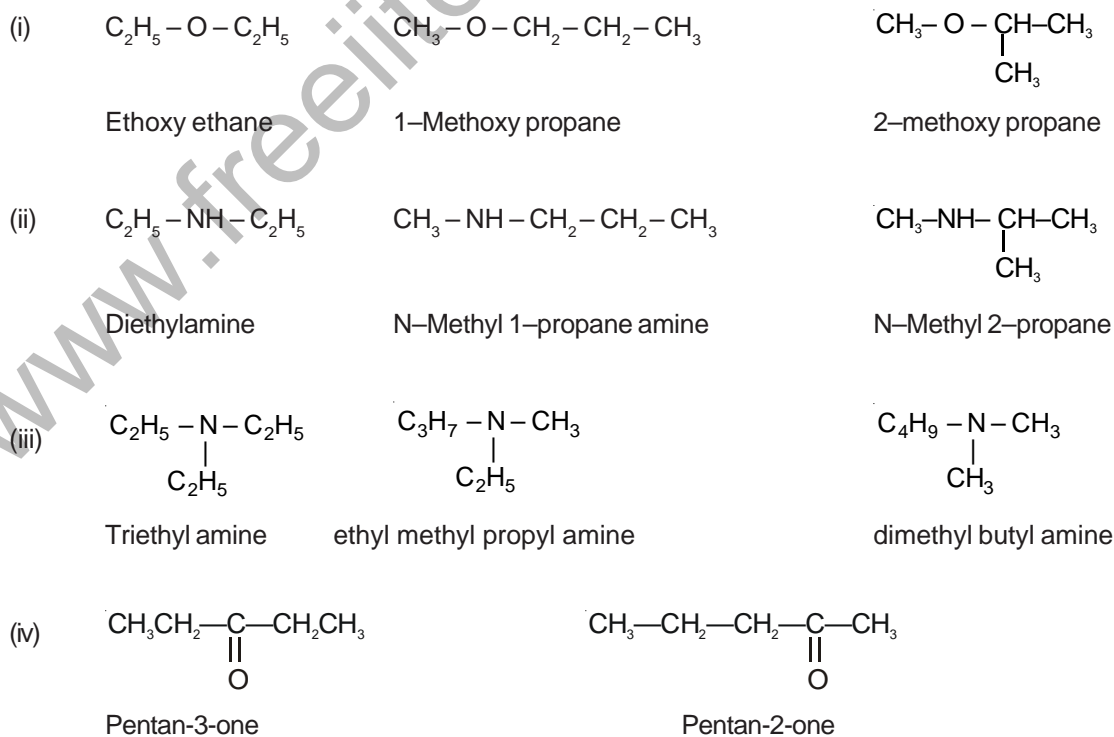
(i) Alkene and cycloalkane ( $C_nH_{2n}$ )(ii) Alkyne and cyclo alkene ( $C_nH_{2n-2}$ )

**Note :** Ring chain isomers are always function isomers.

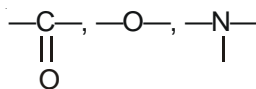
## 1.1.5 METAMERISM :

It is exhibited by compounds having R-A-R formula where 'A' is functional group. In this type of isomerism the compounds possessing same molecular formula differ in their properties due to the difference in alkyl groups bounded to functional group.

E.g.



**Note :** 1. Polyvalent functional groups are those functional groups which have more than one free valency e.g.,



2. Metamers include same class of compounds.

3. If two molecules contain same functional group (Polyvalent) never write chain or position isomerism it will always be metamerism.

4. Metamerism is never shown by alkenes or alkynes.

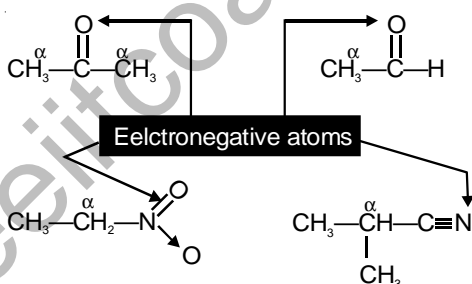
### 1.1.6 TAUTOMERISM :

Tautomerism is a special type of functional isomerism which is defined as “when the molecules have same molecular formula but different structural formula due to wandering nature of hydrogen atom in between two polyvalent atoms, the isomers are called **tautomers**.”

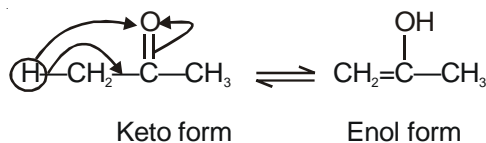
● The tautomerism is also called **kryptomerism or allotropism or desmotropism or dynamic isomerism**.

● **Structural requirements for tautomerism**

1. The compound should have at least one highly electronegative atom (e.g. F, O and N) bonded with a multiple bond.
2. Compound should have at least 1 acidic hydrogen present on  $\alpha$ -carbon atom of the molecule e.g.



● **Cause of tautomerism :** The migration of acidic hydrogen from  $\alpha$  carbon to multiple bonded electronegative atom, E.g.

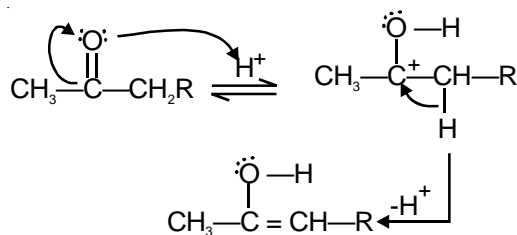


● **The characteristics of tautomerism :**

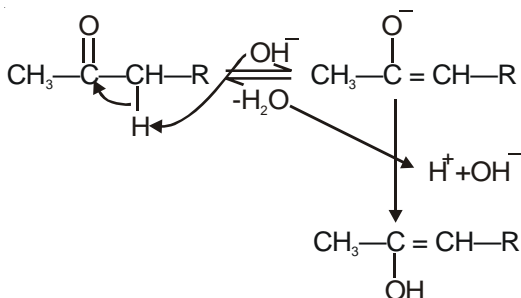
1. Tautomers always exist in dynamic equilibrium.
2. Number of electrons and lone pairs in both tautomers always remain the same.
3. It is a chemical phenomenon which takes place only in liquids and gaseous phase only. It never takes place in solid state.
4. The process can be catalyzed by the acid as well a bases.

The procedure for most common type of isomerism i.e. keto enol tautomerism include the following steps.

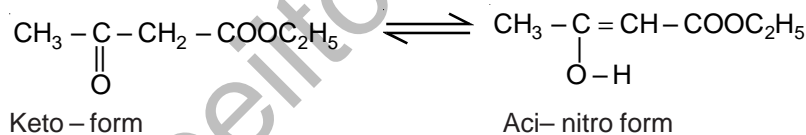
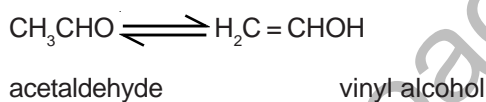
(a) Acid catalyzed conversion :



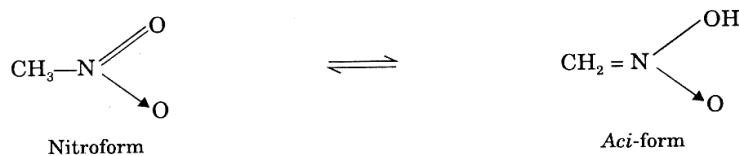
(b) base catalyzed conversion :



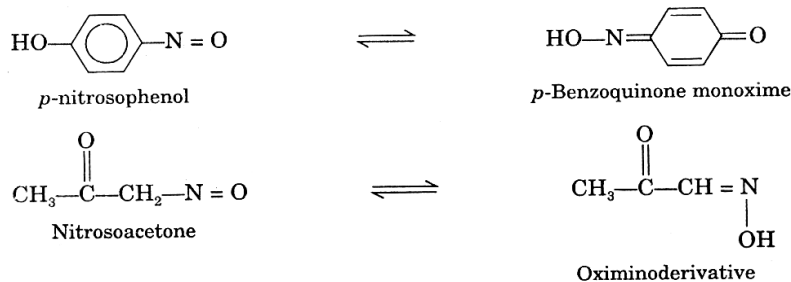
In this type of isomerism two functional isomers exist together in equilibrium. The two forms existing in equilibrium are called as **tautomers**.



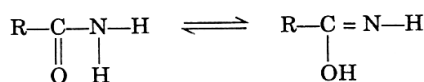
• **Nitro-Aci tautomerism**



• **Nitro-oximino tautomerism**



• **Amido-imidol tautomerism**

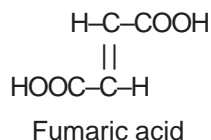
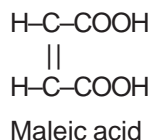


## 1.2 STEREOISOMERISM

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

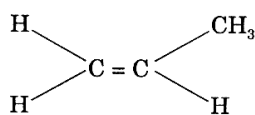
### 1.2.1 GEOMETRICAL ISOMERISM :

In this type of isomerism the compounds possessing same molecular formula differ in their properties due to the difference in their geometry, i.e., due to the difference in the direction of attachment of some atoms or groups in their molecule.

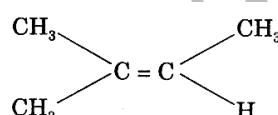


### ➤ CONDITIONS FOR GEOMETRICAL ISOMERISM

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



Propene

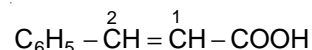
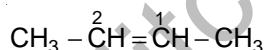


2-methyl-but-2-ene

No geometrical isomerism

### ➤ Examples :

- Alkenes**

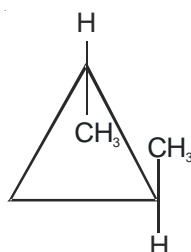


In these cases both substituents on carbon-1 and carbon-2- are different hence they will show geometrical isomerism.

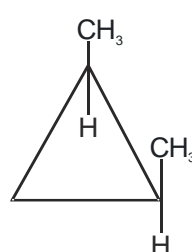
- Cycloalkanes**

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

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



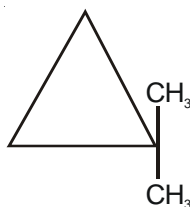
trans form



cis form

1, 2-dimethyl cyclopropane

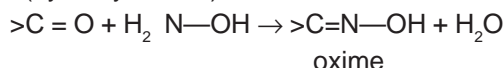
**A requirement for geometrical isomerism in cyclic compounds :** There must be at least 2 other groups besides hydrogen on the ring and these must be on different ring C-atom. for example no geometrical isomers are possible for 1, 1-dimethyl cyclopropane.



1, 1-dimethyl cyclopropane (No isomers possible)

● **Oximes and Azo compounds**

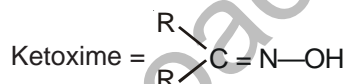
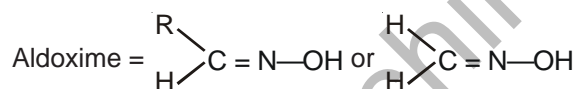
The oximes are formed by the reaction of carbonyl compounds ( $>C=O$  compounds i.e., aldehydes and ketones) with  $NH_2OH$  (hydroxyl amine) as :



If  $\begin{array}{c} \text{---C---} \\ || \\ \text{O} \end{array}$  = aldehyde then oxime = aldoxime

If  $\begin{array}{c} \text{---C---} \\ || \\ \text{O} \end{array}$  = ketone then oxime = ketoxime

Hence,

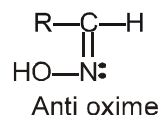
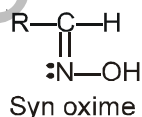


**Note:**

In nitrogen compounds the steric repulsion occurs between the lone pair of nitrogen with bond pair of larger group (i.e., in oximes and imines) or between the two lone pairs of two nitrogens (i.e. in azo compounds) resulting to syn (corresponding to cis) and anti (corresponding to trans) forms, e.g.,

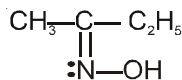
**(a) IN OXIMES :**

**(i) IN ALDOXIMES :**



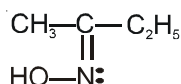
The first member of aldoximes does not show any geometrical isomer.

**(ii) in ketoximes :**



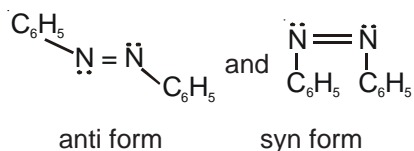
This compound is syn for ethyl group and anti for methyl group or this can be called anti compound.

Similarly,



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

**(b) In azo compounds i.e.,**





## ➤ E, Z SYSTEM FOR GEOMETRICAL ISOMERS :

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

### Cahn-Ingold-Prelog Rules

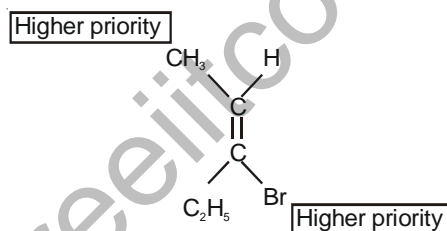
1. The higher the atomic number of the atom bonded directly to the stereocentre, the higher is the priority of the substituent. Among isotopes, the one with higher mass number gets the higher priority.
2. If two identical atoms are attached to the stereocentre, the relative priority of the two groups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



**Priority Order :-** -I, -Br, -Cl, -SO<sub>3</sub>H, -SH, -F, -OCOR, -OR, -OH, -NO<sub>2</sub>, -NR<sub>2</sub>, -NHCOR, NHR, -CO<sub>2</sub>R, -CO<sub>2</sub>H, -CONH<sub>2</sub>, COR, -CHO, -CH<sub>2</sub>OH, -CN, -CR<sub>3</sub>, -C<sub>6</sub>H<sub>5</sub>, -CHR<sub>2</sub>, CH<sub>3</sub>, D, H

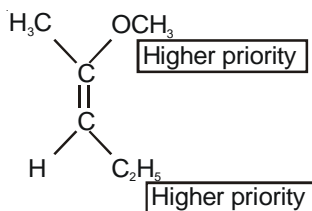
Some examples are being given below :

1.



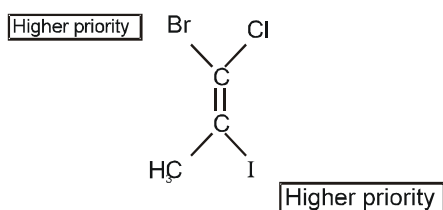
The groups of higher priorities are on opposite sides.  
Hence it is (E) - 3-Bromopent-2-ene

2.

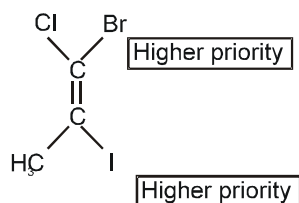


The groups of higher priorities are on same side.  
Hence it is (Z) - 2-Methoxypent-2-ene

3.

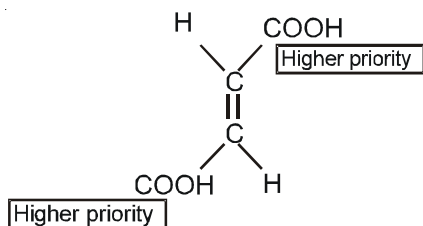


Groups of higher priority  
are on opposite sides  
(E) -1-bromo-1-chloro-2-iodo propene

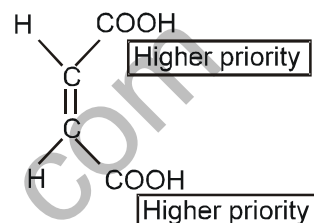


Groups of higher priority  
are on same sides  
(Z) -1-bromo-1-chloro-2-iodo propene

4.



(E)-But-2-ene-1, 4-dioic acid  
(Fumaric acid)

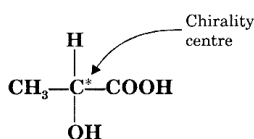


(Z)-But-2-ene-1, 4-dioic acid  
(Maleic acid)

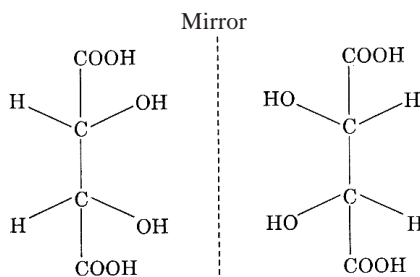
### 1.2.2 OPTICAL ISOMERISM

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

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



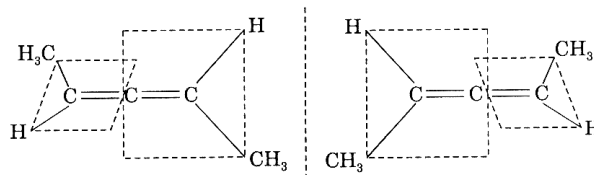
- Generally, the compounds containing an asymmetric carbon in their molecules are dissymmetric and hence show enantiomerism. But there are examples where in spite of the presence of asymmetric carbons the compound does not show enantiomerism because its molecules are non-dissymmetric. For example, meso-tartaric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



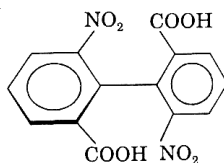
meso-Tartaric acid

Superimposable : does not show enantiomerism

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



Non-superimposable : shows enantiomerism

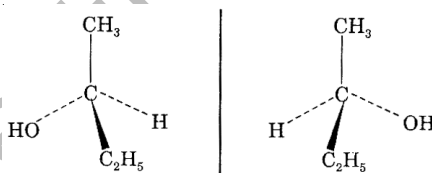


DISSYMMETRIC MOLECULE

(Shows enantiomerism)

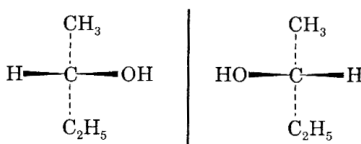
### ➤ Representation of Enantiomers

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



(Enantiomers of 2-butanol)

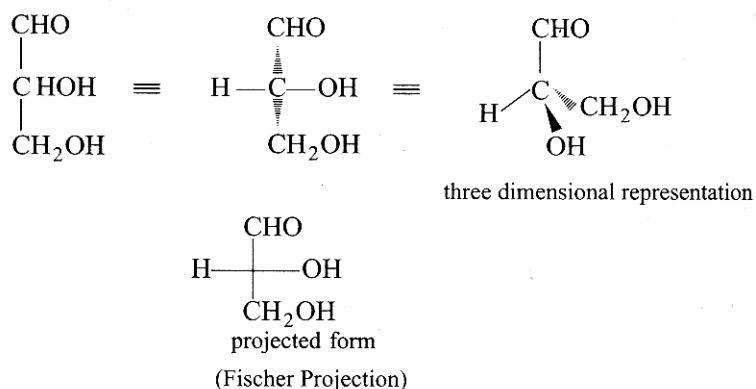
- Projection Formula :** Here the molecule is imagined to be held in such a way that two of the bonds coming towards the viewer are in the horizontal plane and are represented by solid wedges. The other two bonds going behind the plane of paper are in vertical plane which are represented by broken lines.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



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

the plane of the paper away from the viewer.

E.g.



### ➤ Characteristics of Enantiomers

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

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

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

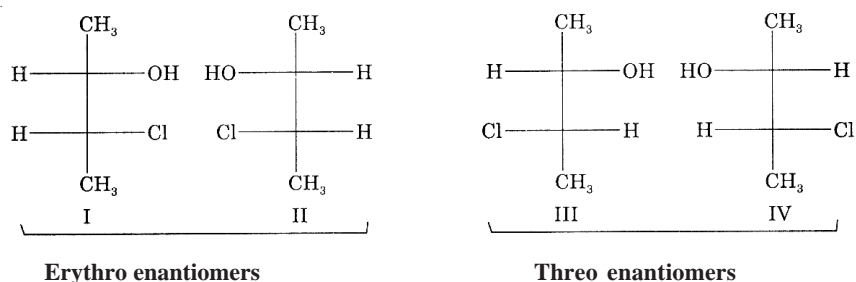
4. Enantiomers have **identical chemical properties**. This means that they form same products as a result of chemical combination. However, their reactivity, i.e. rates of reaction with other optically active substances are different.

### ➤ Stereoisomers with more than one chirality centres

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

### ➤ Diastereomers

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



- Stereoisomers I and II are non-superimposable mirror images. Hence, they are called **enantiomers**.
- Stereoisomers III and IV are also non-superimposable mirror images. They are also **enantiomers**.
- I and II also represent enantiomers in which similar groups (H atoms) are present on same side of carbon chain such enantiomers are called **erythro enantiomers**.
- In III and IV similar groups (H atoms) are present on opposite side of carbon chain. Such enantiomers are called **threo enantiomers**.
- Stereoisomers I and III are neither identical nor mirror images. Such stereoisomers are called **diastereomers**.
- In the similar way I and IV; II and III; II and IV also represent diastereoisomeric pairs.

Thus, diastereomers are configurational isomers which are not enantiomers (It may be noted that cis-trans geometrical isomers which are configurational isomers but not enantiomers can also be called diastereomers).

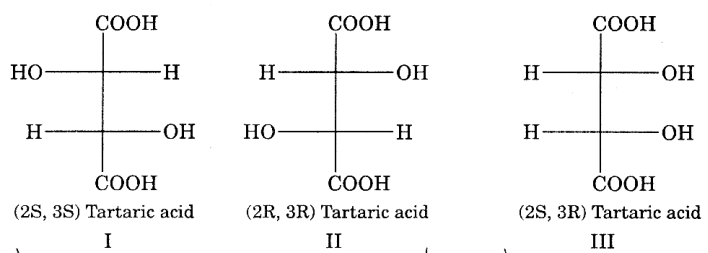
### Characteristics of Diastereomers

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



### Meso compounds

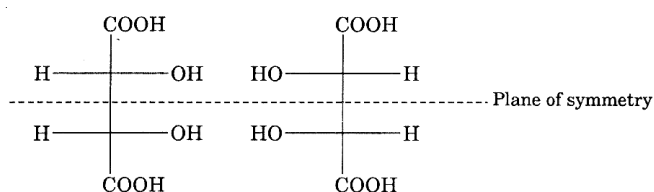
According to  $2^n$  rule each compound having two chirality centres should have ( $2^2 = 4$ ) four stereoisomers. However, there are some compounds with two chiral carbons which have only three stereoisomers. For example, tartaric acid molecule has two chirality centres but it has only three stereoisomers.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



Pair of enantiomers

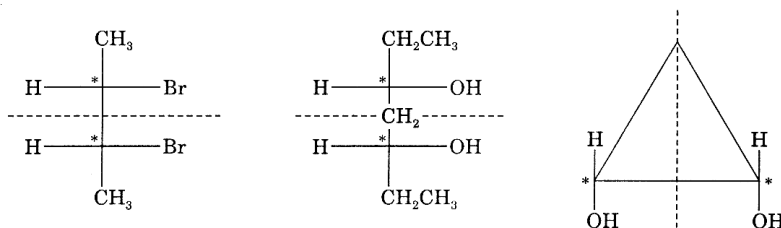
Optically inactive

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



(Identical Mirror Images)

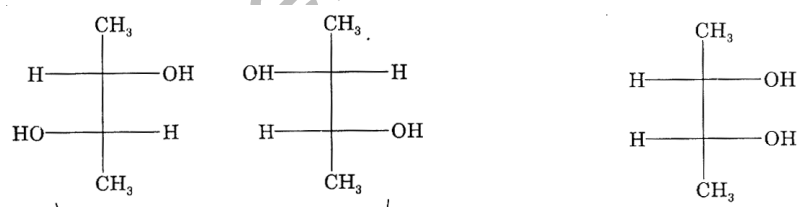
- Structure III or IV which are identical are called **meso compounds** (From Greek : meso means middle). Thus, the compounds containing two or more chirality centres but possessing a chiral molecular structure because of having plane of symmetry, are called **meso compound**.



MESO compounds

(Plane of symmetry is represented by dotted line .....

- Meso compounds are optically inactive**  
Meso compounds do not rotate the plane of polarized light in any direction i.e. they are **optically inactive**. This is because of achiral nature of their molecules. Because of the present of plane of symmetry the optical rotation caused by half of the molecule is compensated by the rotation caused by the other half. This cancellation of rotation within the molecule is referred to as internal compensation. In short, the **meso compounds are optically inactive due to internal compensation**. It may be noted that if a compound with two chirality centres has the same four groups bonded to each of the chiral carbon, than one of its stereoisomer will be a meso compound.

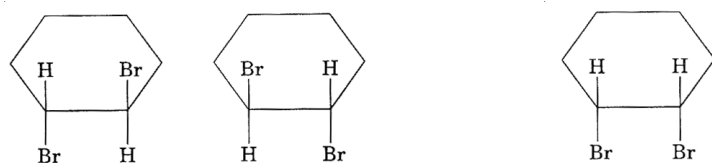


Pair of enantiomers

Meso Compound

## ➤ OPTICAL ISOMERISM IN CYCLIC COMPOUNDS

In case of **cyclic compounds**, the cis isomer will be meso compound and the trans isomer will exist as a pair of enantiomers.



Pair of enantiomers

Meso Compound

### ➤ RACEMIC MODIFICATION

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

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

### ➤ Calculation of d-, l-forms and meso forms

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

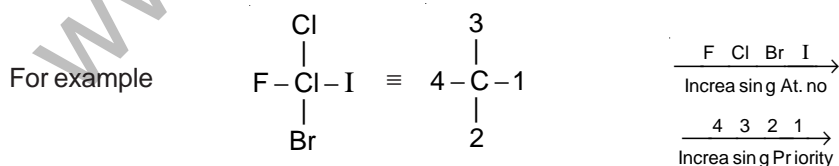
### ➤ Absolute Configuration (R, S configuration)

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

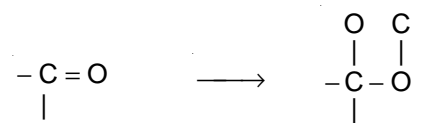
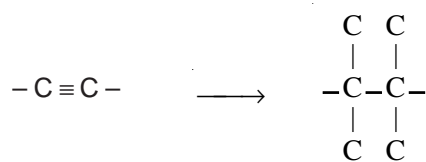
System which indicates the absolute configuration was given by three chemists R.S. Cahn, C.K. Ingold and V. Prelog. This system is known as (R) and (S) system or the Cahn–Ingold system. The letter (R) comes from the latin rectus (means right) while (S) comes from the latin sinister (means left).

It is better system because in many cases configuration to a compound cannot be assigned by D, L method. (R) (S) nomenclature is assigned as follows :

- Each group attached to stereocentre is assigned a priority on the basis of atomic number. The group with the directly attached atom with highest atomic number out of the four groups gets top priority while the group with the atom of least atomic number gets the least priority.



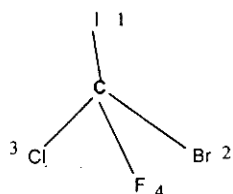
- If out of the four attached atoms in consideration, two are isotopic (like H and D), then priority goes to higher atomic mass i.e. D.
- If out of the four attached atoms in consideration, two or more are same, then priority is decided on the basis of the atom attached next to it in its group. e.g. out of  $\text{CH}_3$  and  $\text{COOH}$ ,  $\text{COOH}$  gets priority.
- While deciding the priority, if the atom in consideration is attached is further to an atom through a double bond then it is treated as if it is attached to two such atoms. For example :



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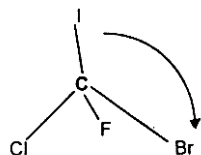




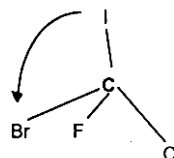
Note that priority order is :  $I > Br > Cl > F$

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

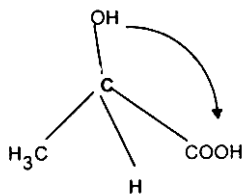
Eg. :



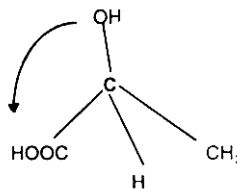
**R-configuration**  
(clockwise from top priority)



**S-configuration**  
(clockwise from top priority)

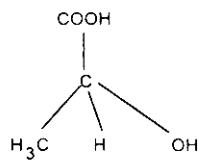
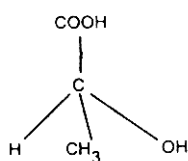


**R-configuration**  
(clockwise from top priority)

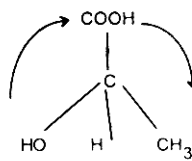


**S-configuration**  
(clockwise from top priority)

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



(single exchange)

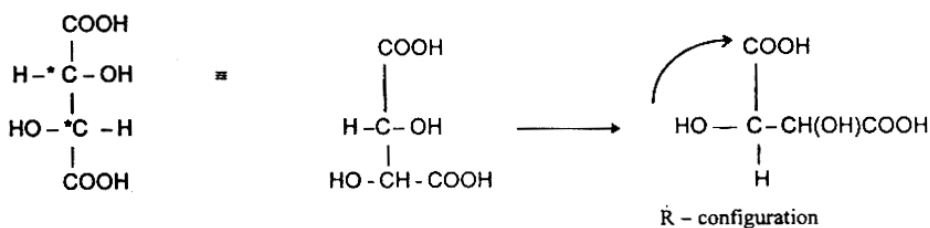


(double exchange) R-configuration

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

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

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



### 1.2.3 CONFORMATIONS

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

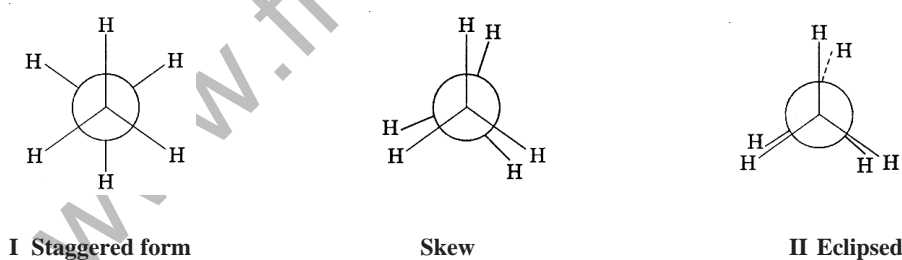
#### Conformation of Ethane

- Out of infinite number of possible conformations of ethane, the two extreme conformations are **staggered** conformation and **eclipsed** conformation. The infinite intermediate conformations are known as **skew** conformations.
- The **Sawhorse projection formula** of the two extreme conformations of ethane are shown in figure.



Staggered and Eclipsed conformations of ethane

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

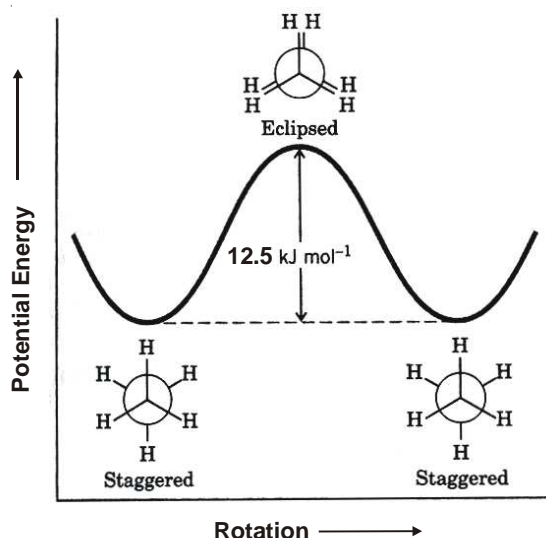


Newman's projection formulae of conformations of ethane

#### Relative Stabilities of the Conformations of Ethane

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

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



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

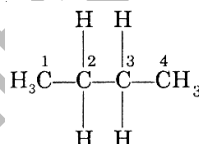
The difference in the energy of various conformers constitutes an energy barrier to rotation. The energy required to rotate the ethane molecule about carbon-carbon single bond is called **torsional energy**. But this energy barrier is not large enough to prevent the rotation. Even at ordinary temperature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

- Torsional energy :-**

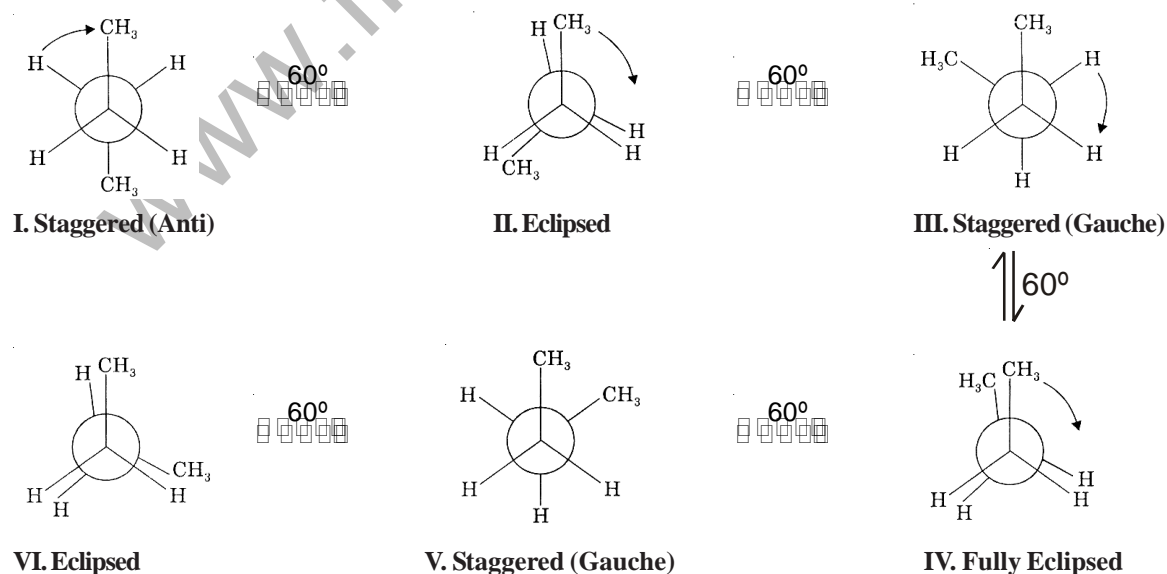
The energy required to rotate the ethane molecule about 'C-C' bond is called torsional energy

#### Conformations of Butane

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



Considering the rotation around single bond between C-2 and C-3 we get many conformations. Some of them have been given as Newman Projections in figure.



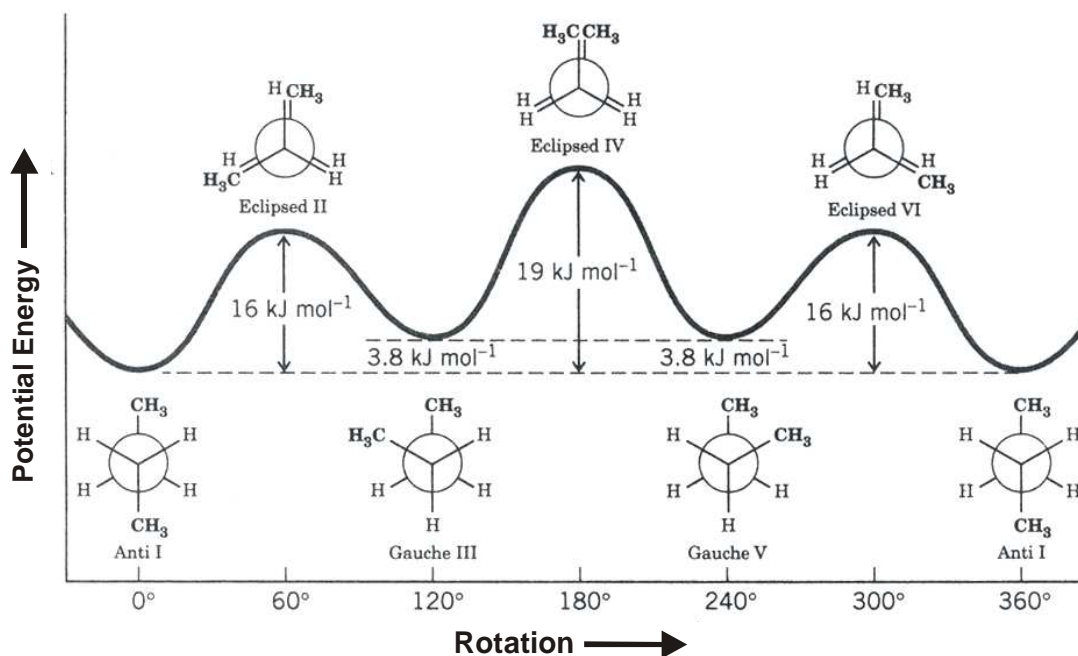
#### Conformations of Butane

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

Further rotation through  $60^\circ$  gives another staggered conformation (III). The conformation is also called **gauche** conformation. Gauche conformation on further rotation through  $60^\circ$  gives **fully eclipsed conformation (IV)**.

(IV) in which methyl groups on two carbons are just opposite each other. In this conformation steric strain is maximum hence this conformation is most unstable. Further rotation through  $60^\circ$  gives again gauche conformations (V) which is mirror image of gauche conformation (III). Conformation (V), on rotation through  $60^\circ$  gives conformation (VI) which is again eclipsed conformation.

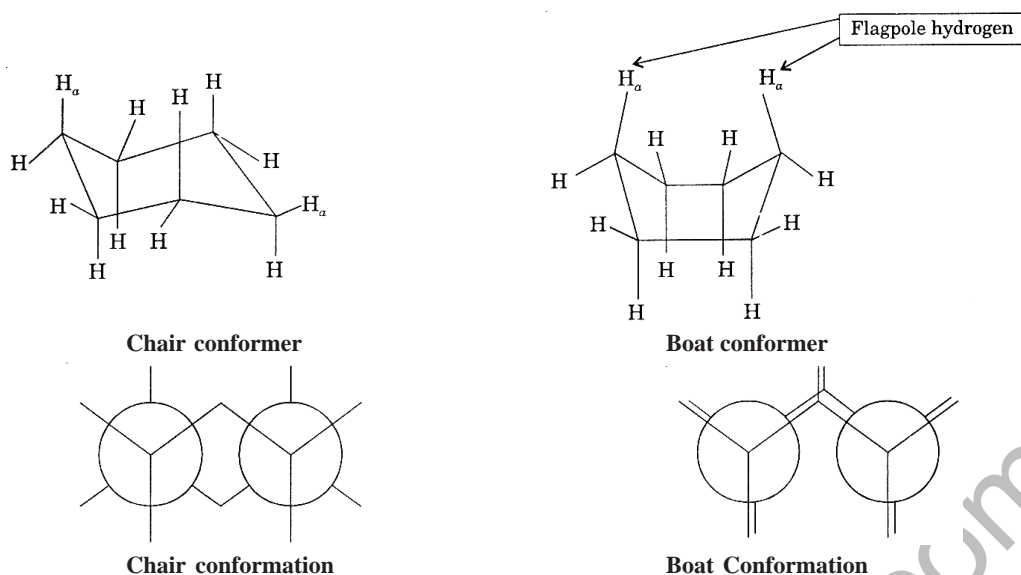
The energy profile diagram for the conformation of butane is given below along with the difference of energy between various conformation of butane.



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

### ● Conformations of Cyclohexane

If cyclohexane molecule were to be planar, the c-c-c angle would have been  $120^\circ$ . Therefore, ring would be highly strained. Cyclohexane avoids this strain by assuming conformations in which all bond angles between carbon atoms are close to tetrahedral angle,  $109^\circ 38'$ . The two most important conformations of cyclohexane are the **chair form** and the **boat form** as shown in figure. Of the two, the chair form is more stable than the boat form, the energy difference being about  $30 \text{ kJ mol}^{-1}$ . However, the energy barrier between the two conformations is of about  $44 \text{ kJ mol}^{-1}$ . This is because in the boat form, many hydrogens on adjacent carbons correspond to the unfavorable eclipsed conformation of ethane. Also the two hydrogens marked  $H_a$  also called **flagpole hydrogen** in the boat form are quite close and repel one another.



Chair and boat conformations of cyclohexane

● **Difference between conformation and configuration**

Conformation	Configuration
<ol style="list-style-type: none"> <li>1. It refers to different arrangement of atoms or groups relative to each other and raised due to free rotation round a sigma bond.</li> <li>2. The energy difference between two conformers is lower.</li> <li>3. Conformers are not isomers and they can not be separated from each other.</li> <li>4. These are easily inter converted to one another.</li> </ol>	<p>It refers to different arrangement of atoms or groups in space about a central atom.</p> <p>The energy difference between two configuration forms is large.</p> <p>These are optical isomers and can be separated from each other.</p> <p>These are not easily converted to one another.</p>