02 Geometrical Isomerism and Conformations

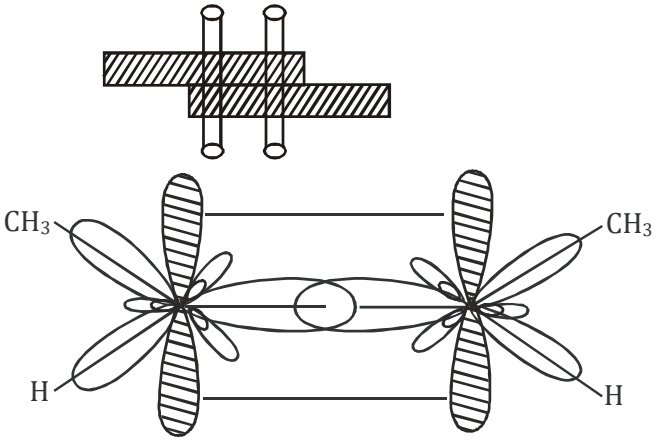
Geometrical isomerism :

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

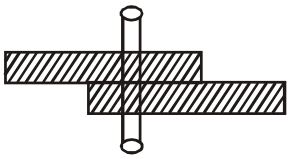
Condition for Geometrical isomerism :

Condition 1 : Restricted rotation must be present.

Restricted Rotation

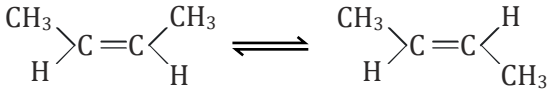


Free Rotation



$CH_3—\underset{\downarrow}{CH}=\underset{\downarrow}{CH}—CH_3$
$Sp^2 \quad Sp^2$

Example :



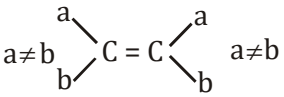
cis–2–butene ⇌ trans–2–butene

Note :

cis ⇌ trans is possible only when π bond break.

Condition 2

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

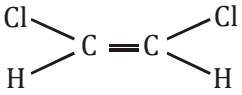
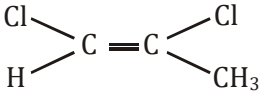
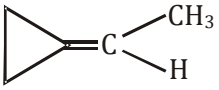
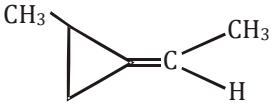


Example	G.I.
$C_{aa}=C_{aa}$	×
$C_{aa}=C_{bd}$	×
$C_{aa}=C_{bb}$	×
$C_{ab}=C_{ab}$	✓
$C_{ab}=C_{bd}$	✓
$C_{ab}=C_{de}$	✓

Condition 3

Terminal valency should be present in the same plane.

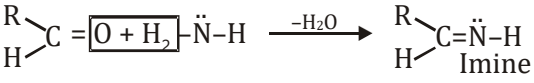
1. Geometrical isomerism in alkene $>C=C<$

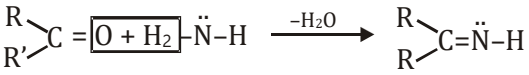
Example	G.I.
	Yes
	Yes
	Yes
	Yes

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

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

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

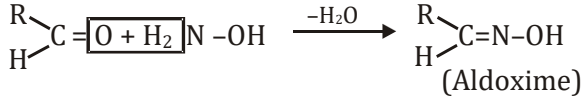


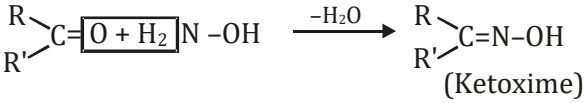


Imines prepared from unsymmetrical aldehydes and ketones, always show geometrical isomerism.

(b) Oximes ($>C=N-OH$ **)**

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

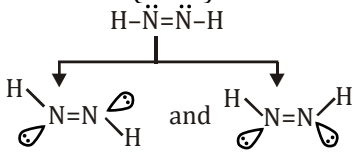




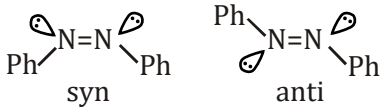
→ Unsymmetrical ketone forms two oximes.

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

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

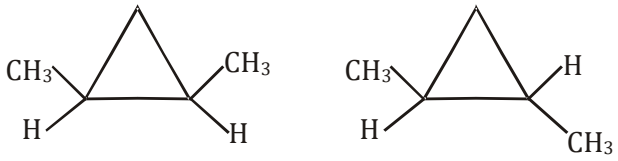


(ii) Ph_2N_2 (Azobenzene)



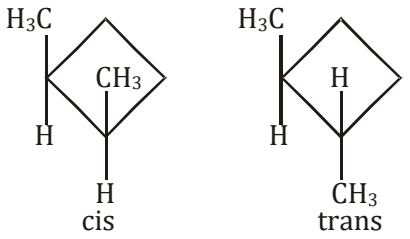
4. Geometrical isomerism in cyclic compound

(i)

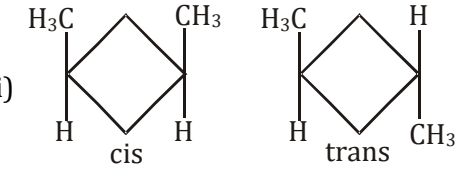


Restricted rotation

(ii)

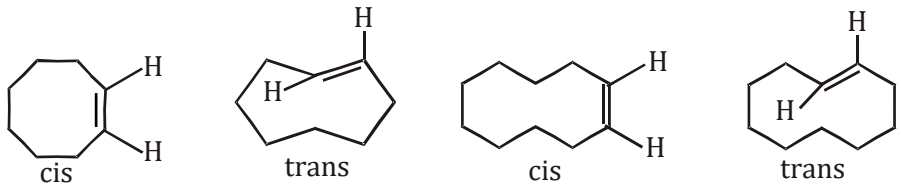


(iii)

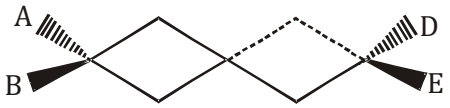
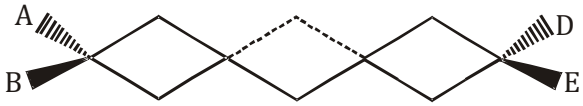


5. Geometrical isomerism in cycloalkenes in double bonds :

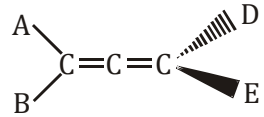
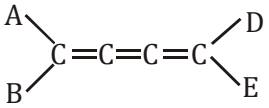
In cycloalkenes, G.I. exists across double bonds with ring size equal to or greater then 8 carbon atoms (due to ring strain)



6. G.I. in spiro compounds :

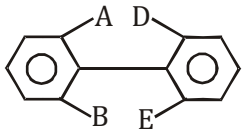
Example	G.I.
	NO
	Yes

7. G.I. in cumulenes

Example	G.I.
	NO
	Yes

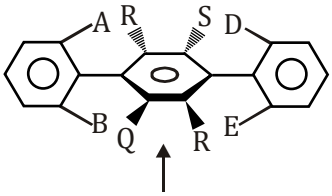
Note :
Even π-bond – don't show G.I.
Odd π-bond - show G.I.

8. G.I. in Biphenyl Compound

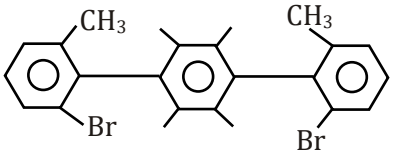


A,B,D & E : small ⇒ Conformation (Not show G.I.)
large ⇒ due to SIR (Not show G.I.)
⇒ no. G.I.

→ **Triphenyl Compound**



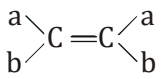
Not in plane ⇒ as due to most stable.

Example.  Show G.I.

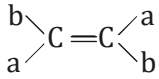
Nomenclature systems of Geometrical isomers:

(a) Cis–Trans System :

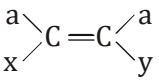
If similar groups at same side then cis and if same groups at different side then trans.



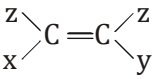
[Same groups, same side]
cis



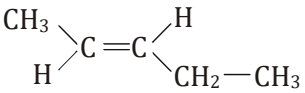
[Same groups different side]
trans

Example : 

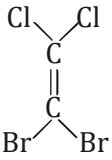
cis



cis

Example : 

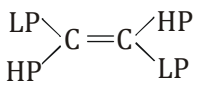
trans-2–pentene



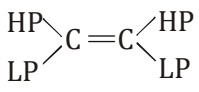
no cis–trans

(b) E – Z System :

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



'E'



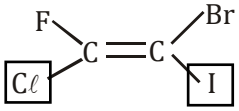
'Z'

HP – High priority and LP – Low priority

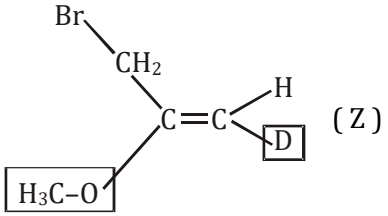
Priority Rules:

Cahn, Ingold, Prelog (CIP Rule)

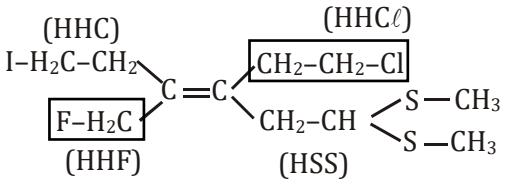
Rule 1. Priority α Atomic no. of atom which is directly attached to restrided rotatory system.



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

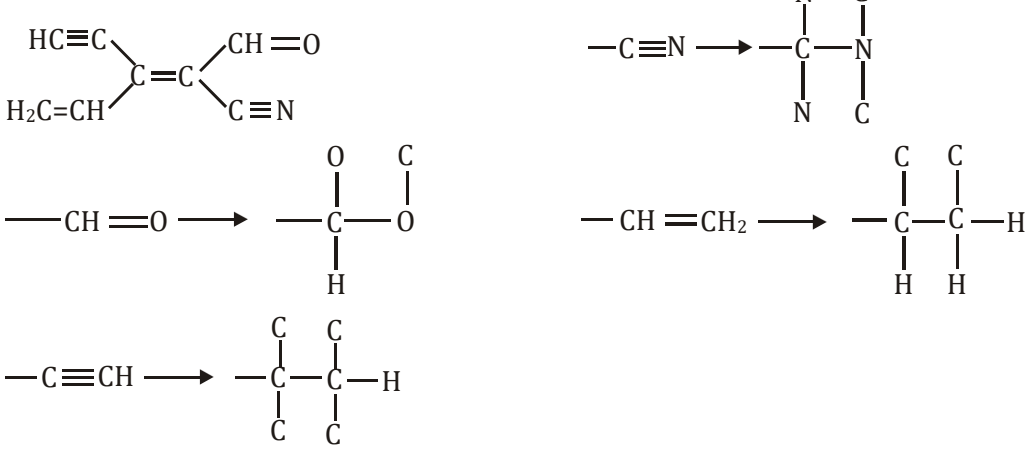


Rule 3. If at the first directly attached, R–1 fails move to next atom and atoms attached to it.

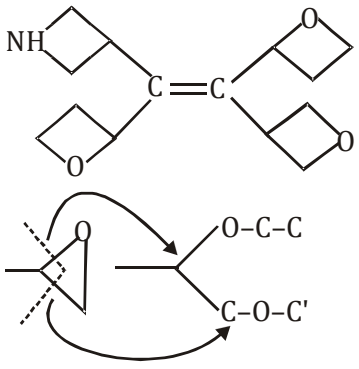


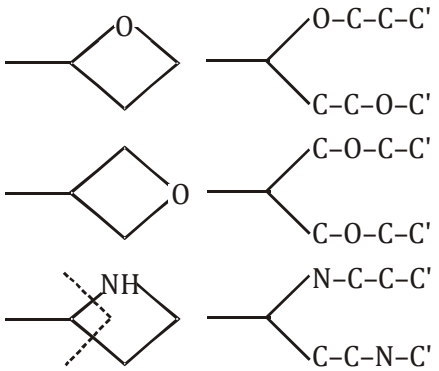
Rule 4. If directly attached groups contain double bond then duplicate them by dummy atoms.

Example :

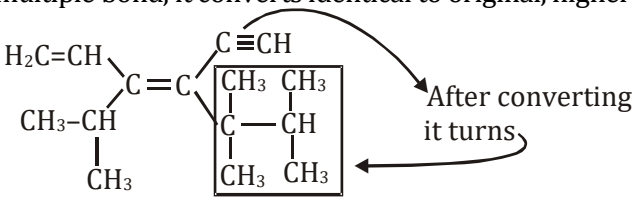


Example :

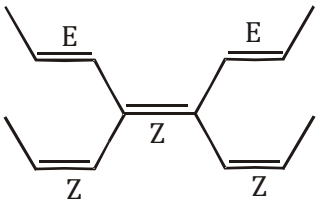




Rule 5. If after converting a multiple bond, it converts identical to original, higher priority to original one.



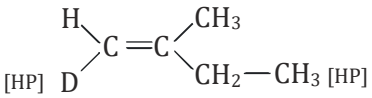
Rule 6.



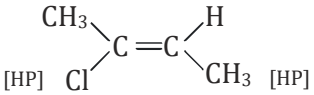
(Z)

cis/trans ⇒ cis
Z/E ⇒ Z
R/S ⇒ R

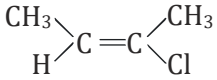
Example : Assign E-Z nomenclature

(i) 

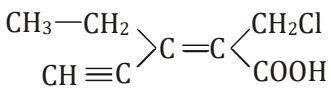
'Z'

(ii) 

'Z'

(iii) 

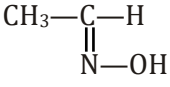
'E'

(iv) 

[Cl, H, H] [HP] ; [O, O, O] [LP]
'E'

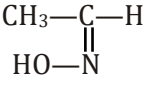
Syn-Anti Nomenclature :

Example : Acetaldoximes has two Geometrical isomers –



syn

When H and OH are on the same side

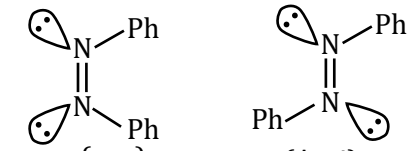


anti

When H and OH are on the opposite side

Example : Ph—CH=N—OH → Ph—C(=N—OH)—H [syn.] ; Ph—C(=HO—N)—H [Anti]

Benzaldoxime



(syn) (Anti)

Ph—N=N—Ph (Azo benzene)

Number of Geometrical isomers : (For compounds not showing optical isomerism)

Calculation of GI :

n = no. of unit which can show GI

Case I : Compound is unsymmetrical–2^n

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

Physical properties of Geometrical isomers :

Physical Properties of Cis–Trans Isomers :

S.No.	Physical properties	Comparison	Remarks
1	Dipole moment	cis > trans	cis-isomer has resultant of dipoles while in trans isomer dipole moments cancel out
2	Boiling point	cis > trans	Molecules having higher dipole moment have higher boiling point due to larger intermolecular force of attraction
3	Solubility (in H_2O)	cis > trans	More polar molecules are more soluble in H_2O
4	Melting point	trans > cis	More symmetric isomers have higher melting points due to better packing in crystalline lattice & trans isomers are more symmetric than cis.
5	Stability	trans > cis	The molecule having more Vander Waal strain are less stable. In cis isomer the bulky group are closer they have larger Vander Waal strain.

Dipole moment [μ] :

Example : $\overrightarrow{CH_3}—C(=)—H$; $\overrightarrow{CH_3}—C(=)—H$ cis μ≠0

H—C(=)—$\overleftarrow{CH_3}$; $\overrightarrow{CH_3}—C(=)—H$ trans μ=Zero

Example : $\overrightarrow{CH_3}—C(=)—H$; H—C(=)—$\overleftarrow{CH_2}—CH_3$ trans μ≠0

$\overrightarrow{CH_3}—C(=)—H$; $\overrightarrow{CH_3}—C(=)—H$ cis μ≠0

Example : $\overrightarrow{CH_3}—C(=)—H$; H—C(=)—$\overrightarrow{Cl}$ trans μ≠0

KEY POINTS

1. Cyclo heptene and lower cyclalkenes cannot exist in trans form. So they cannot show G.I.
2. Allenes which have odd number of double bonds can show G.I.
3. Double bond is not ncecssary condition for G.I. Restricted rotation is necesary condition for G.I.

Conformational Isomerism

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

Some Important Terms :

(i) Dihedral or Torsional angle : Angle between bonds of two adjacent atoms is knows as dihedral or Torsional angle.

(ii) Staggered Conformation: Conformations in which valency triangle are opposite and most priority group are also opposite then known as staggered/anti conformation.

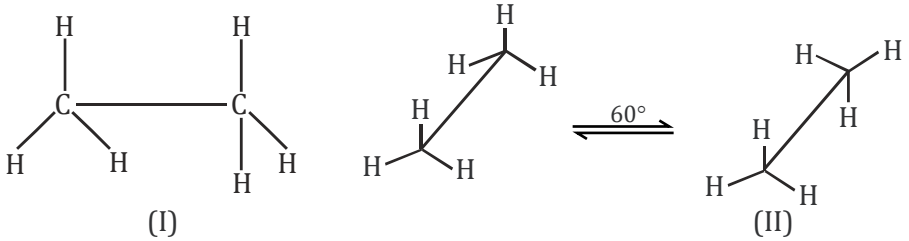
(iii) Eclipsed Conformation: In which two valency triangle as well as most priority group (according to CIP) are superimpose then known as Eclipsed conformation.

(iv) Skew Conformation : All other conformations are known as Skew Conformations.

(v) Torsional Strain : Is the name given to the repulsion felt by the bonded electron of front carbon atom with the bonded electrons of back carbon atom.

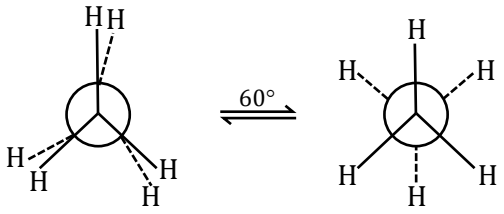
(vi) Steric Strain :- Strain felt by the repulsion of atoms or groups of atoms of front carbon atom with back carbon atom. In most circumstances torsional strain dominates over steric strain.

Conformers of ethane [CH_3—CH_3]



(I) (II)

(Saw horse projection)



(III) (IV)

(Newman projection)

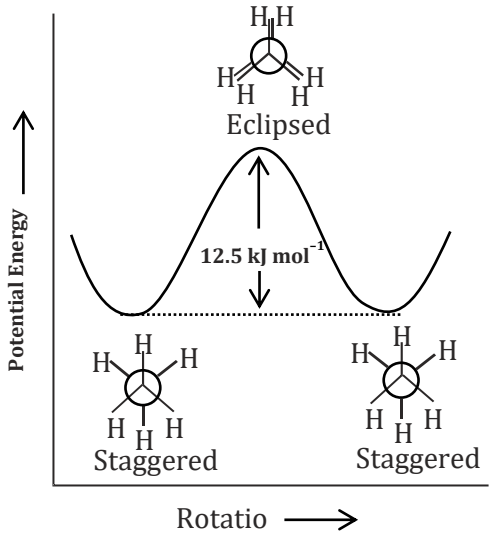
I = III (Eclipsed form) in this form distance between 2C–H bonds is minimum so maximum repulsion or minimum stable.

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

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

Stability order : Staggered > Skew > Eclipsed

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

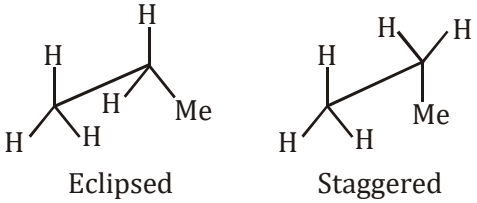


Changes in energy during rotation about C–C bond in

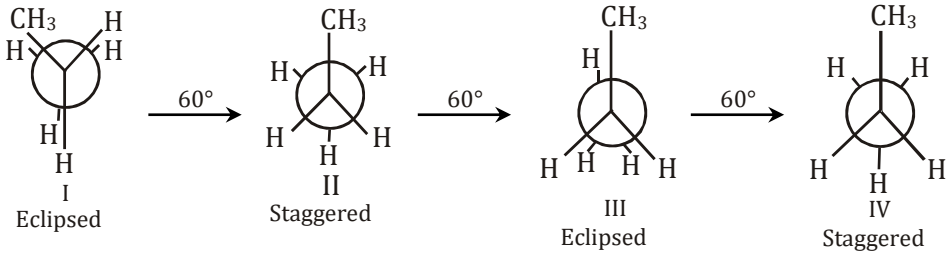
Conformation of propane :

Ex. $CH_3-CH_2-CH_3$

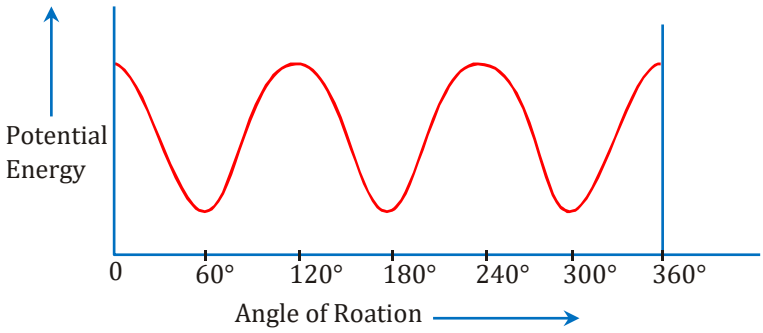
Saw horse projection Formula :



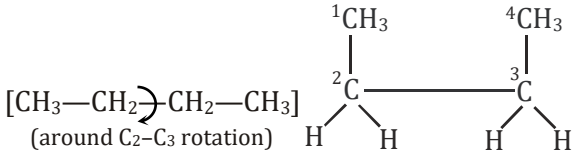
Newman Projection Formula :

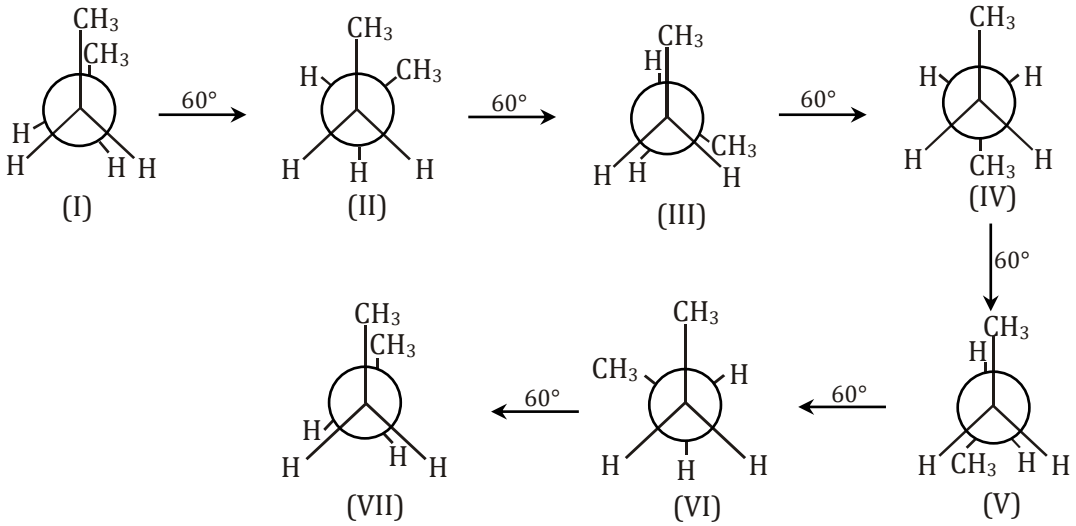


Propane :



Conformation of Butane :





I/VII = Fully eclipsed

II/VI = Gauche form

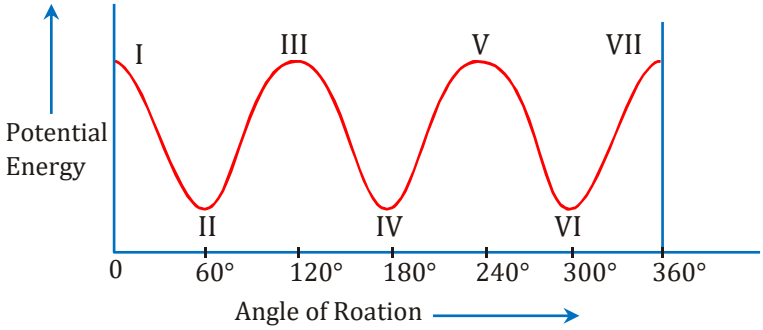
III/V = Partially eclipsed

IV = Anti form

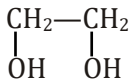
Stability Order IV > II > III > I

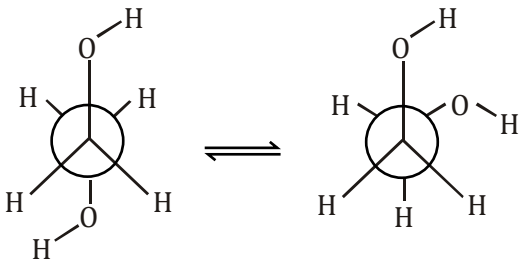
P.E. Order IV < II < III < I

Potential Energy Diagram :

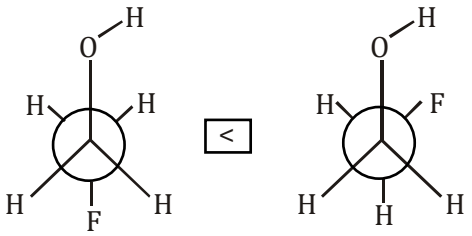


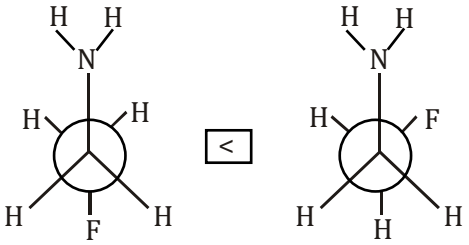
1. Draw most stable conformation of following :

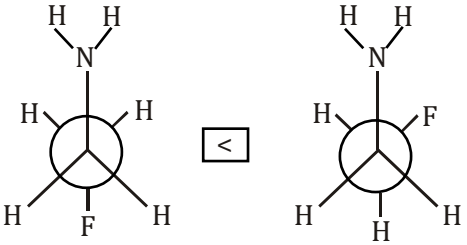
(i) 

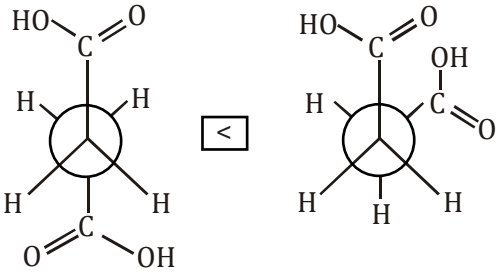


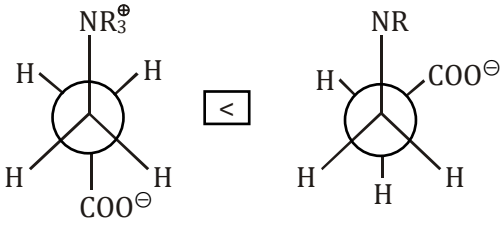
Due to H-bonding gauche is more stable than anti

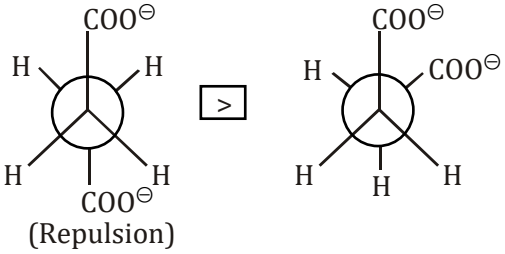
(ii) $CH_2(OH)-CH_2F$ 

(iii) $CH_2(NH_2)-CH_2F$ 

(iv) $CH_2(NH_2)-CH_2F$ 

(v) $CH_2(COOH)-CH_2COOH$ 

(vi) $CH_2(NR_3^{\oplus})-CH_2COO^{\ominus}$ 

(vii) $CH_2(NaOOC)-CH_2COONa$ 
(Repulsion)

Dipole moment in Conformational analysis :

Dipole moment (μ) :

$\mu_{net} = \sum \mu_i x_i$

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

$x_a + x_g = 1$

$\therefore$ Only stable conformers are considered.

a $\Rightarrow$ anti

g $\Rightarrow$ gauche

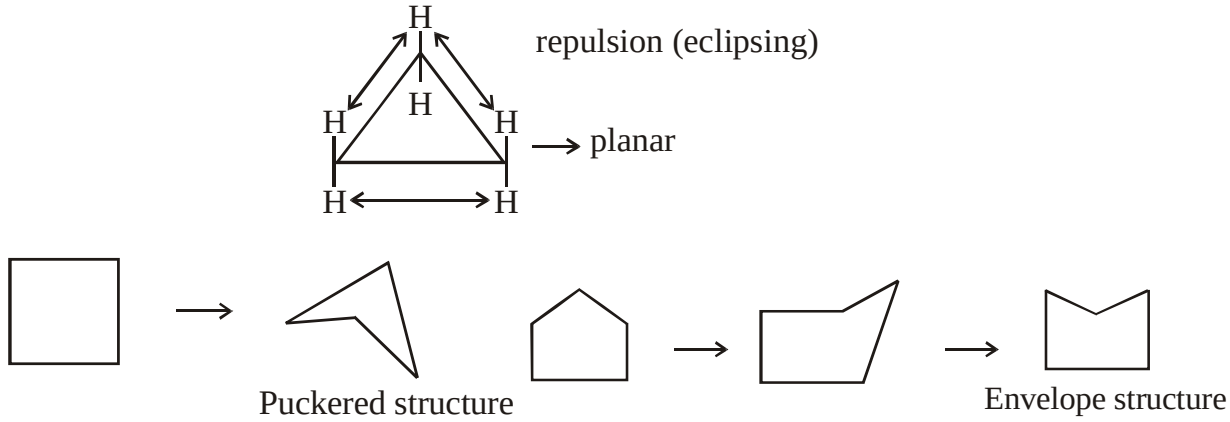
Conformational analysis of cycloalkane

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

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

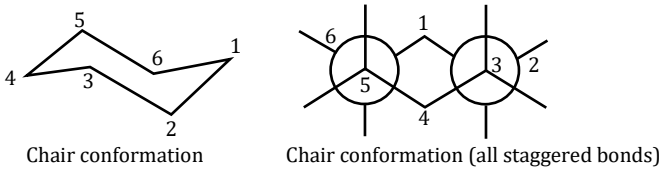
When size of ring increases then it becomes flexible and partial σ bond rotation is observed so larger ring acquire non-planar orientation to avoid eclipsing.

Eclipsing :



Conformational analysis of cyclohexane

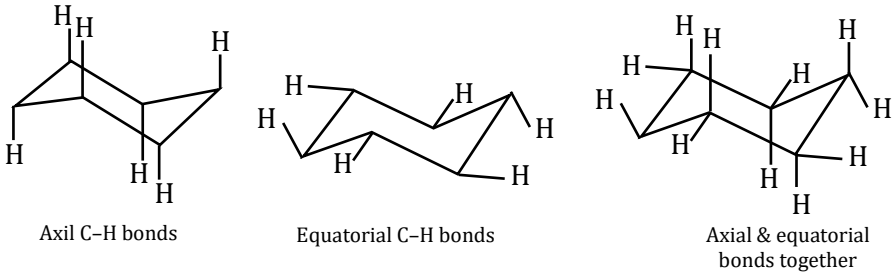
(i) Chair form : Experimental evidences show that cyclohexane is non-planar. If we look to the models of the different conformations that are free of angle strain first there is chair conformation. If we sight along each of the carbon-carbon bonds in turn we see in every case perfectly staggered bonds.



Chair conformation Chair conformation (all staggered bonds)

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

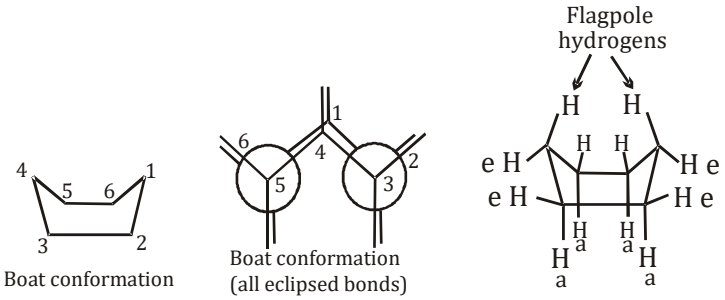
Axial and equatorial bonds in chair form of cyclohexane :



Axil C–H bonds | Equatorial C–H bonds | Axial & equatorial bonds together

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

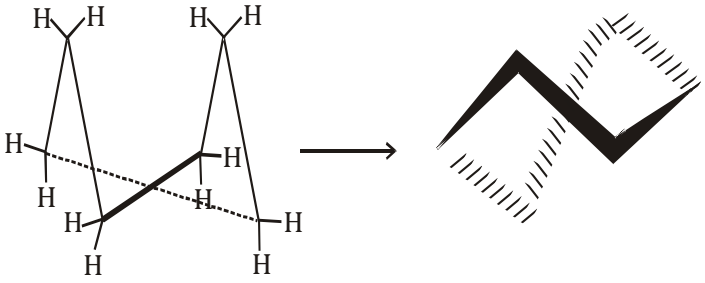
(ii) Boat form: Another conformation which is known as boat conformation has exactly eclipsed conformations.



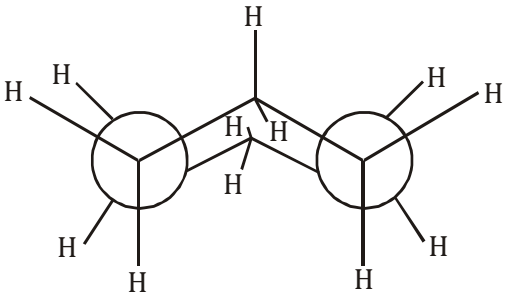
Boat conformation | Boat conformation (all eclipsed bonds)

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

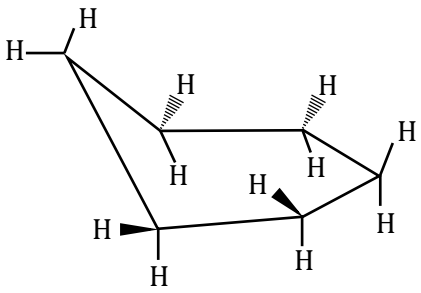
(iii) Twist Boat conformation



Newmann :

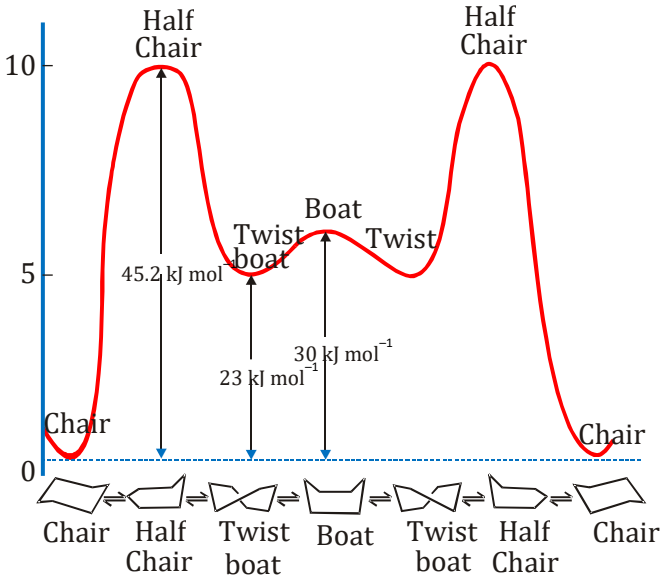


(iv) Half Chair Conformation



Stability order :

Chair > Twist boat > Boat > Half Chair

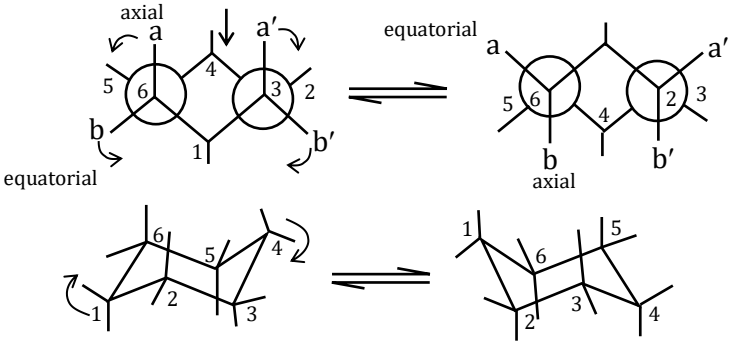


The relative energies of the various conformations of cyclohexane.

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

Conformational inversion (Ring flipping) in cyclohexane

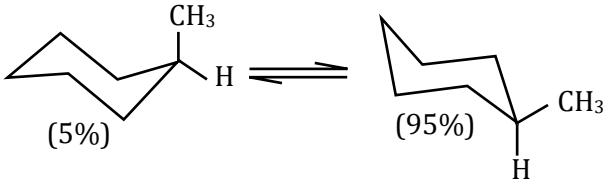
Like alkanes cyclohexane too is conformationally mobile. Through a process known as ring inversion, Chair-chair interconversion, or more simple ring flipping one chair conformation is converted to another chair.



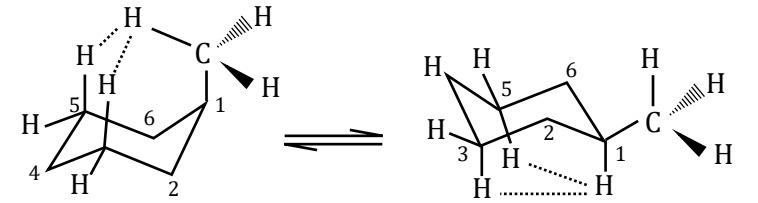
By ring flipping all axial bonds convert to equatorial and vice-versa. The activation energy for cyclohexane ring inversion is 45 kJ/mol. It is a very rapid process with a half-life of about 10^{-5} sec at 25°C.

Conformational analysis of monosubstituted cyclohexanes

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



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



Vander Waals strain between hydrogen of axial CH3and axial hydrogens at C-3 and C-5

No vander Waals strain between hydrogen at C-1 and axial hydrogens at C-3and C-5