

Unit - II

* Geometrical Isomerism *

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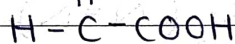
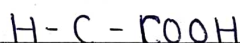
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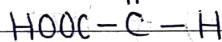
* GI →

The isomers which have the same M.F & structural formula but different arrangement of atoms about the double bond are called as Geometrical Isomerism or Cis-trans isomerism. e.g...

Maleic acid is the cis isomer as the two carboxylic groups lie on the same side of the molecule while fumaric acid is the trans isomer as carboxylic groups lie on opposite sides.



Maleic acid



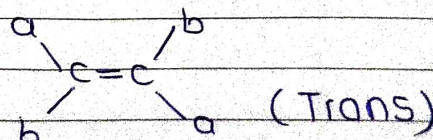
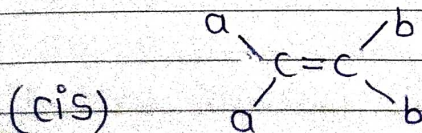
fumaric acid

* Nomenclature of Geometrical Isomers :-

① Cis-Trans nomenclature →

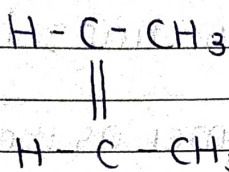
• Isomers in which similar atoms or groups lie on the same side of double bond is called as cis isomer.

• Isomers in which similar atoms or groups lie on the opposite side of the double bond is called as trans isomer.

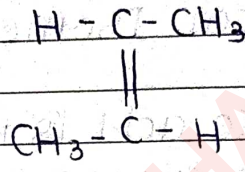


Example :-

① 2 butene



cis-2 butene



Trans-2-butane

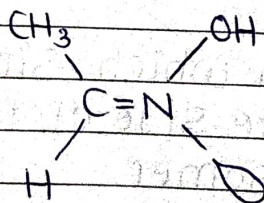
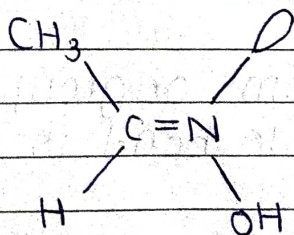
② Syn - Anti System →

Geometrical isomerism occurs in oximes ($\text{C}=\text{N}-\text{OH}$) & Azo compounds ($\text{N}=\text{N}$) Such compounds gives Syn-Anti isomerism Syn means Cis & Anti means trans.

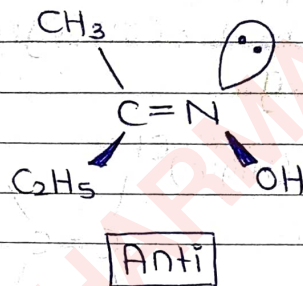
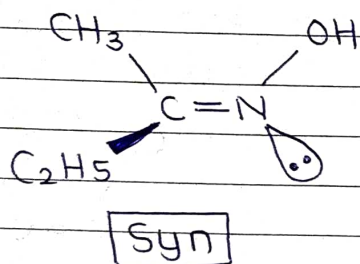
In the Syn-oxime, the hydroxyl group on nitrogen & hydrogen on Carbon atom are on the same side while, In the anti isomer this are on opposite sides

e.g....

① Acetaldoxime

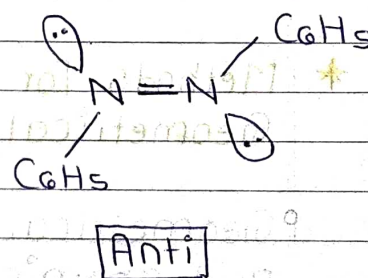
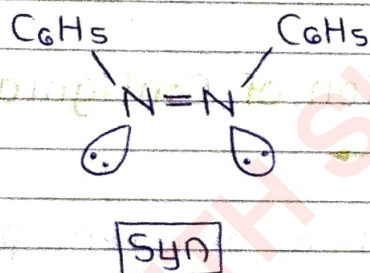


② Butanexime



③ Azobenzene

(nitrogen)



③ E-Z Nomenclature →

° E-Z has derived from German word

E = Entgegen (opposite side)

Z = Zusammen (together)

° E-Z nomenclature is applied to the molecule where all the four substituents are different

° Isomers in which two groups of higher priority are on the same side of double bond is called as Z Configuration

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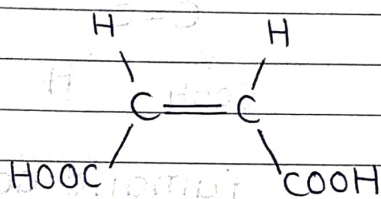
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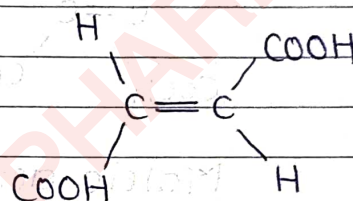
On the opposite side of double bond & pack well in the crystal lattice.

Hence, inter molecular force of attraction of trans isomer is stronger than cis-isomer.

e.g.....



Maleic acid

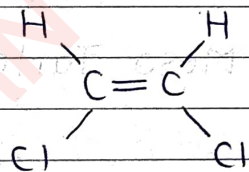


Fumaric acid

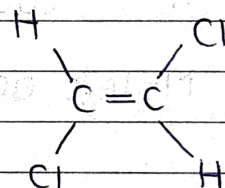
② B. Point →

B. Point of cis-isomer is higher than the trans isomer. It is due to more polar nature of cis-isomer than the trans isomer which results in stronger inter-molecular attraction.

e.g...



cis-dichloroethene
(B.P = 60°)



trans-dichloroethene
(B.P = 48°)

② Solubility →

Molecules of cis-isomer are less closely pack & have weak inter molecular force of attraction

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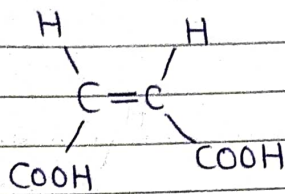
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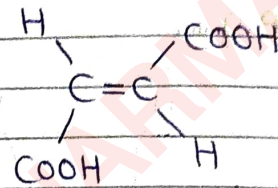
than the trans isomer. Hence, cis isomer have higher solubility than trans isomer.

e.g.,



Maleic acid

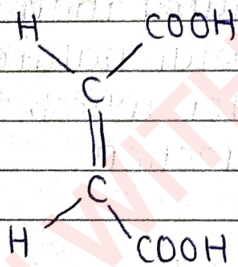
(79 gm/100 ml)



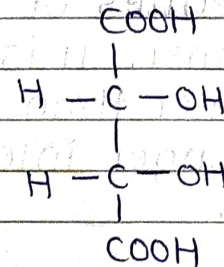
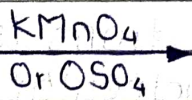
Fumaric acid

(0.7 gm/100 ml)

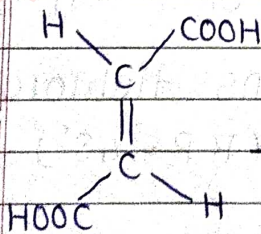
④ From the type of optical isomer formed →



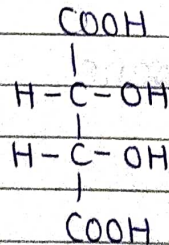
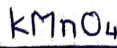
Maleic acid



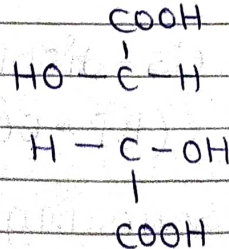
Meso. Tartaric acid.



Fumaric acid



(+) Tartaric acid



(-) Tartaric acid

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Maleic acid & fumaric acid on hydroxylation gives optically inactive tartaric acid, maleic acid cis isomer on hydroxylation gives meso tartaric acid. While fumaric acid (trans) gives a racemic (\pm) tartaric acid.

Difference

Conformation	Configuration
<p>① Conformation are 3 dimensional arrangement in space of the atoms or groups in a molecule which can be converted to another form by rotation around <u>single bond</u>.</p>	<p>Configuration are 3 dimensional arrangement in space of atoms or groups in a molecule which can not be converted to another form by rotation around a single bond.</p>
<p>② This interconversion by rotation around single bond does not require breaking & making of bond.</p>	<p>They can show interconversion by making & breaking of bonds.</p>
<p>③ Conformational isomer cannot be separated by any physical & chemical methods.</p>	<p>Configurational isomers can be separated by suitable physical & chemical methods.</p>

④ The phenomenon of existence of conformation is known as conformational isomerism.

The phenomenon of existence of Configuration is known as C.I. e.g... geometrical isomerism, optical isomerism.

* Stereospecific & Stereoselective Reactions →

• A stereospecific reaction is a reaction in which a starting material react differently to give different products.

* In the stereospecific reactions, the stereoisomers

① React at different rate i.e. diff. rate of reaction

② They give different stereoisomers as products.

③ They have different paths to give different types of compounds as products.

e.g.,

2-butene occurs in two forms, i.e.

① Cis-2-butene ② trans-2-butene

Cis-2-butene on bromination gives enantiomers A & B that is racemic 2,3-dibromobutane as follows :-

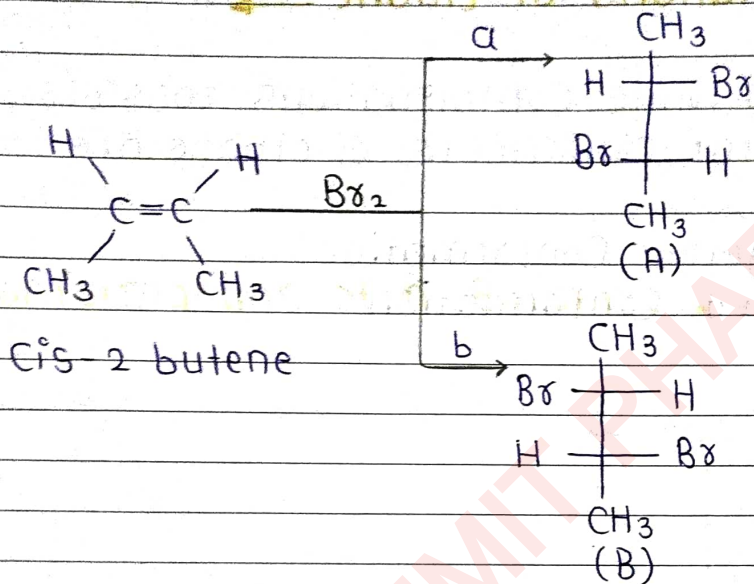
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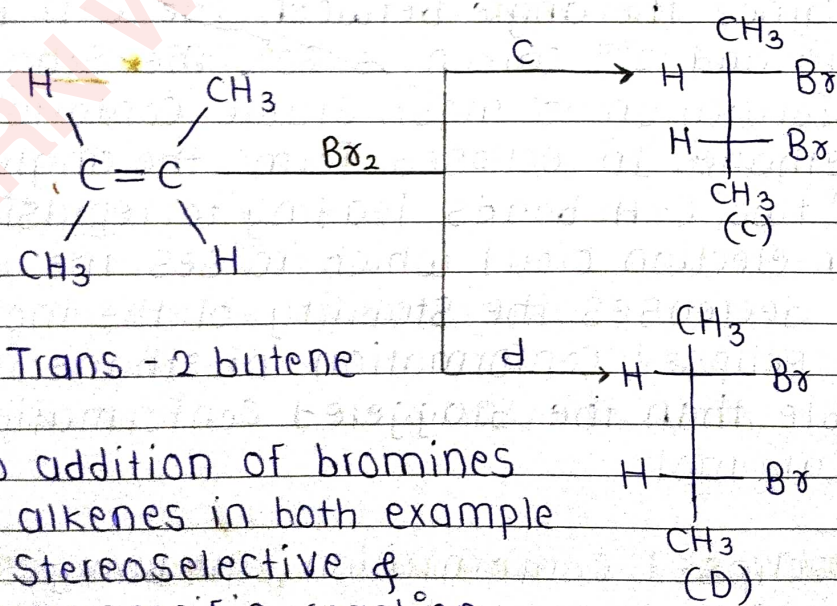
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A & B are enantiomers

trans-2-butene on the other hand involves anti-addition of bromine & give C and D



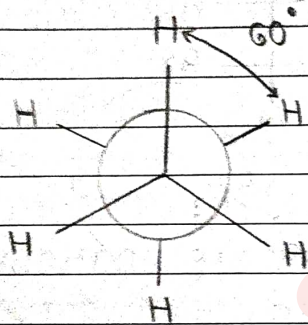
So addition of bromines to alkenes in both example of stereoselective & stereospecific reaction

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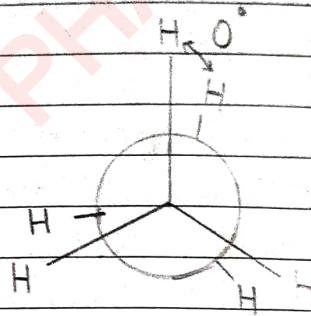
* Conformations of Ethane →

Out of infinite conformations possible, most important conformers of ethane are

- (i) Staggered Conformation
- (ii) Eclipsed Conformation



Staggered



Eclipsed

Since the angle between the C-H bonds of 1st and 2nd carbon is 60° , the Staggered Conformation is most stable Conformation of ethane. In eclipsed form, the angle is 0° betⁿ two C-H bonds leading to repulsion in their electron cloud which raises the energy and decreases the stability of the molecule. The eclipsed Conformation of ethane is less stable than the Staggered Conformation by 3 kcal/mol.

In eclipsed Conformation, the bulky substituents of the molecule are brought closer leading

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Dihedral Angle → It is angle created by two intersecting planes

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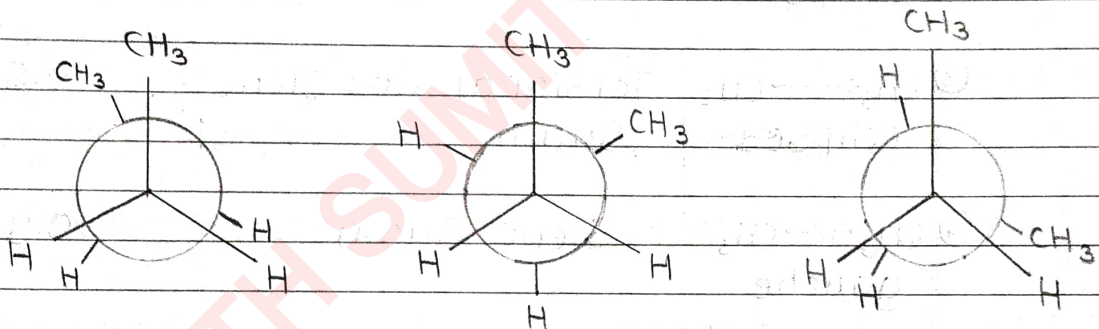
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to repulsion amongst them. This hindrance cause resistance to rotation.

It is not possible to isolate either of ethane conformations due to their interconversion at room temperature.

* Conformations of n-Butane

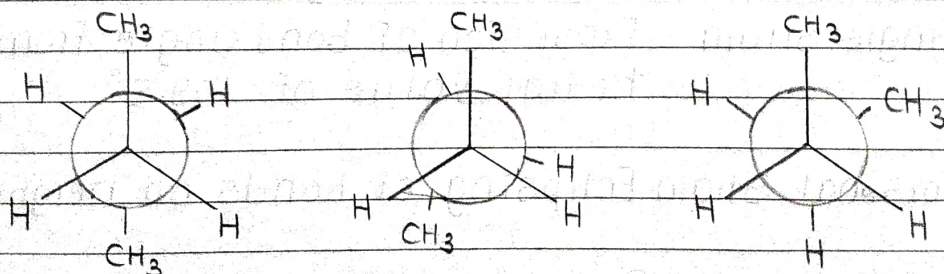
* Various conformations of n-butane include



• Syn (Eclipsed E_2) Gauche (Staggered) Eclipsed E_1

• Dihedral angle 0° 120°

• Maximum energy Energy = 0.88 lower Energy



• Anti (Staggered) Eclipsed Gauche (Staggered)

• 180° 240° 300°

• least energy lower energy Energy = 0.88

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* Types of interactions in conformers of n-butane

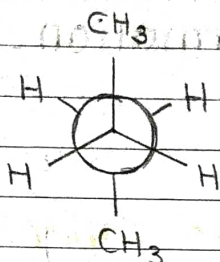
Interaction	Cause	Energy Cost kcal/mole
① $H \longleftrightarrow H$ eclipsed	Torsional Strain	1.0
② $H \longleftrightarrow CH_3$ eclipsed	Torsional Strain	1.4
③ $CH_3 \longleftrightarrow CH_3$ eclipsed	Torsional and Steric Strain	2.6
④ $CH_3 \longleftrightarrow CH_3$ gauche	Steric Strain	0.9

* Various strains contributing to rotational energy barrier

Name	Cause
① Angle Strain	Expansion of bond angle from tetrahedral value of 109.5°
② Torsional Strain	Eclipsing of bonds on neighbouring atoms
③ Steric strain	Repulsive interaction bet ⁿ non-bonded atoms in close proximity
④ Ring Strain	Combint ⁿ of angle Strain & torsional

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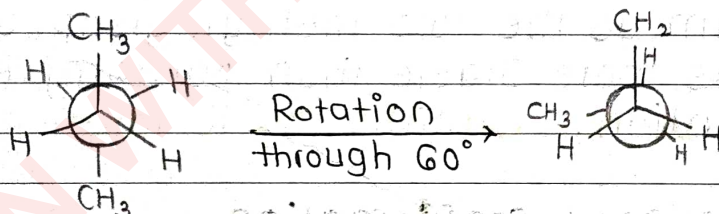
① Anti Conformation →



In this conformation, methyl groups and a hydrogen linked to C_2 & C_3 are at a max distance apart.

Hence force of repulsion is minimum which makes it more stable conformation.

② Partially eclipsed (shadow) Conformation →



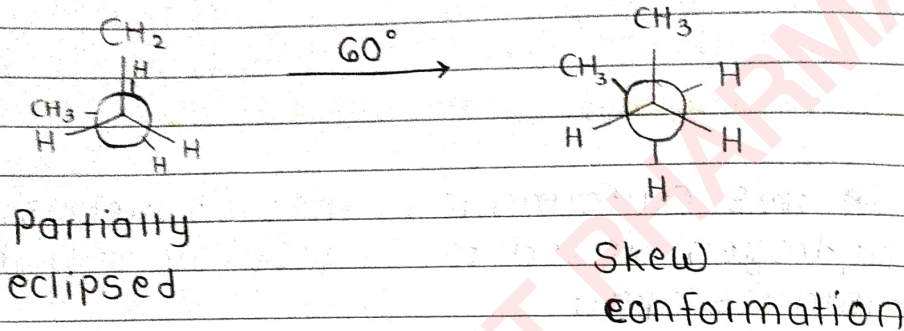
In this conformation, if we rotate C_2-C_3 bond through 60° we get partially eclipsed form.

In this, CH_3 attached to one carbon atom is at the back of hydrogen atom.

The repulsive interaction betⁿ methyl groups and bonding electrons are less than fully eclipsed conformation. Thus, partially eclipsed conformation is more stable than fully

eclipsed Confirmation

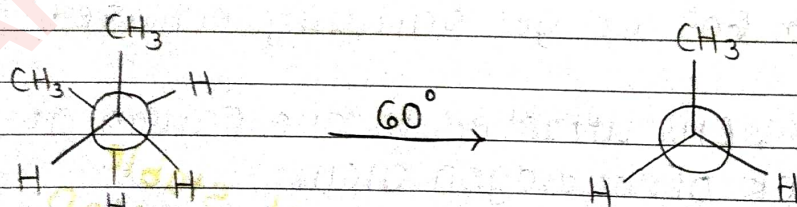
③ Gauche or skew Confirmation →



On rotating C₂-C₃ bond by 60° we get Gauche or Skew Confirmation.

In this Conformation, the Force of repulsion is minimum as the two methyl group are apart thus it is more stable than partially eclipsed Confirmation.

④ Fully eclipsed conformation →



The rotation of C₂-C₃ Sigma bond by 60° gives Fully eclipsed Confirmation in which the methyl grps & hydrogen atom completely

eclipse each other.

The repulsion betⁿ methyl grp & bonding e⁻ is maximum which requires max. energy which makes it minimum stable.

From the above Confirmation, it is proved that anti Confirmation is more stable than skew Confirmation which is more stable than partially eclipsed which is more than fully eclipsed.

Anti > Skew > Partially eclipsed > Fully eclipsed.

* Confirmations of Cyclohexane →



The important Confirmation of cyclohexane are as follows :-

① Chair Confirmation.

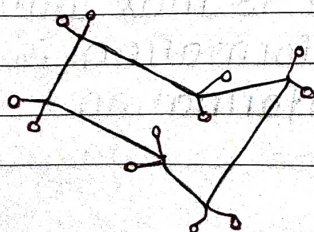
② Boat " "

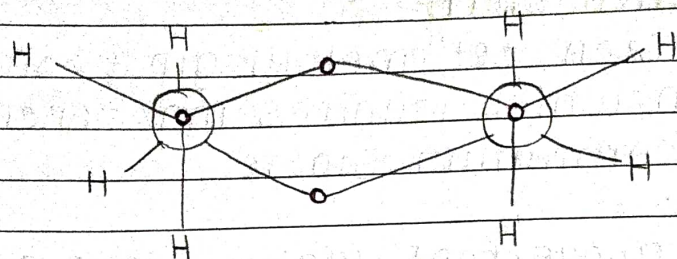
③ Twist " "

④ Half chair " "

① Chair Confirmation →

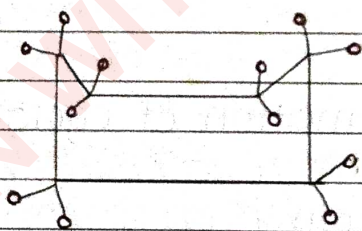
most stable
Confirmation.



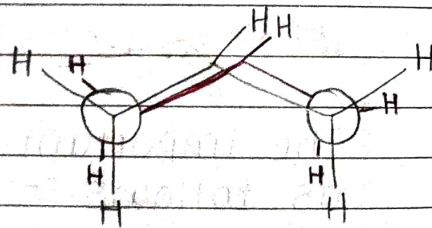


This is the most stable confirmation of cyclohexane. There is no angle strain and torsional strain in this confirmation. There is no steric interaction betⁿ the non-bonding atoms. Thus this confirmation is free on strain & has minimum energy and maximum stability.

② Boat Conformation →



Boat conformation

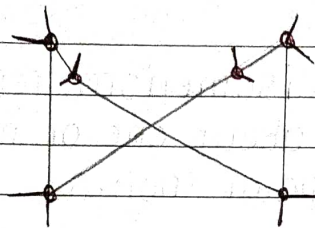


Newman projection

In this boat conformation, there is no angle strain. The hydrogen atoms are eclipsed, so there is torsional strain.

The force of repulsion is max which requires energy and boat conformation is less stable than chair conformation.

③ Twist boat Conformation →



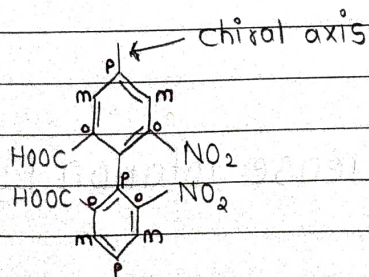
In this Conformation there is no angle Strain
The torsional Strain betⁿ the hydrogen atom
is minimum thus the twist Conformation
Stable than boat Conformation but it is less
Stable than Chair Conformation.

④ Half chair Conformation →

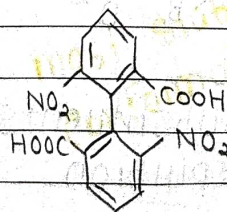


In this Conformation, angle Strain & torsional
Strain are present, Hence this Conformation is
less Stable than Chair Conformation.

* Atropisomerism →



6,6-dinitro-2,2'-diphenic acid
(I)



(III)

Atropisomerism is stereochemistry arising from restricted bond rotation that creates a chiral axis.

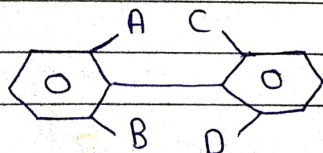
Atropisomers are stereoisomerism resulting from hindered rotation about one or more single bonds betⁿ two polar moities.

The bulkier groups on ortho position of the biphenyl ring restrict the rotation through C-C bond gives two enantiomers & resolvable at room temp^e.

Atropisomers have different pharmacokinetic, biological, toxicology profile. Atrop isomerism is also called as axial chirality. Only biphenyls having different substituents at ortho position contains a chiral axis.

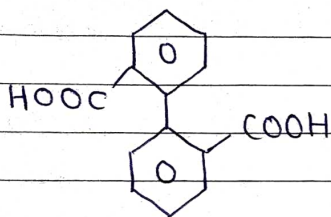
imp * Conditions For optical Activity in Biphenyl Compound →

- ① Biphenyl compounds must contain bulkier groups at ortho position



- ② ortho substituents increase rotation by these steric repulsion.
- ③ Mono-ortho substituted biphenyl compounds

do not show atropisomerism at room temp^e
e.g...



Mono-ortho substituted biphenyl

- ④ The bulkier group adjacent to the ortho substituent increase stability of the Atropisomerism.