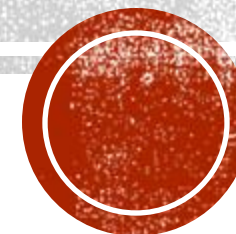


GEOMETRICAL ISOMERISM

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Geometrical Isomerism

Geometrical isomerism is a form of stereo merism describing the orientation of functional groups within a molecule.

In general such isomers contain double bonds which can not rotate but they can also arise from ring structures, wherein the rotation of bond is greatly restricted cis and trans both isomers occur inorganic molecules,

Nomenclature of geometrical isomers

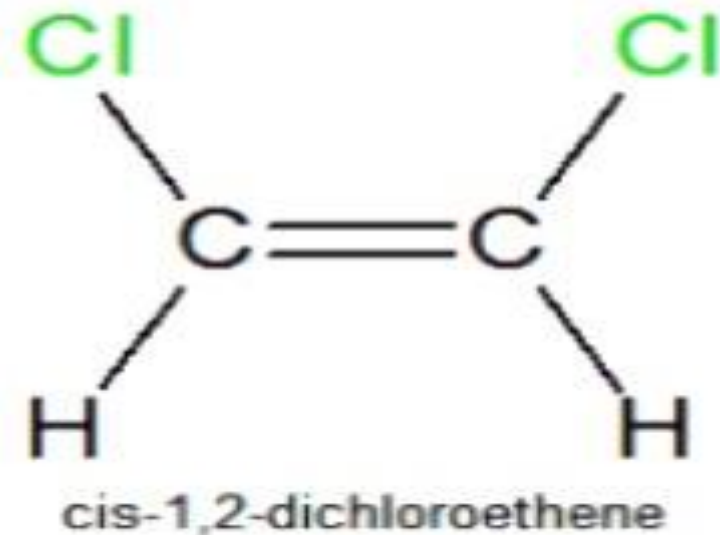
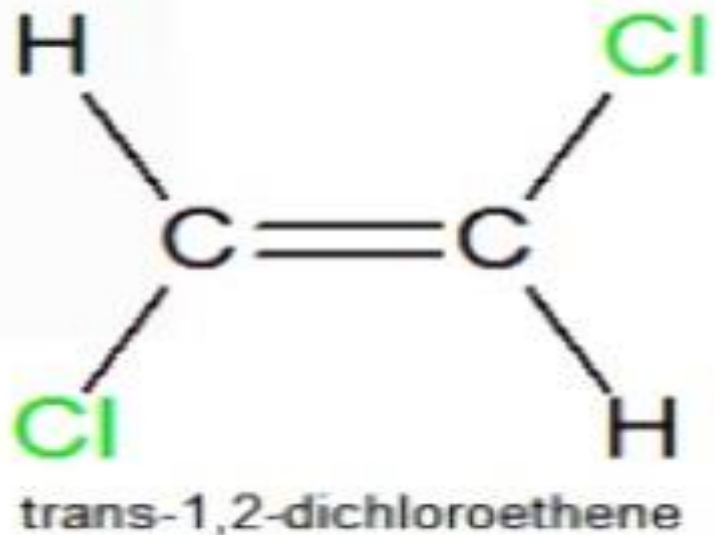
- i. Cis -Trans nomenclature
- ii. E-Z nomenclature
- iii. Syn -Anti system of nomenclature.

i.) Cis -Trans nomenclature

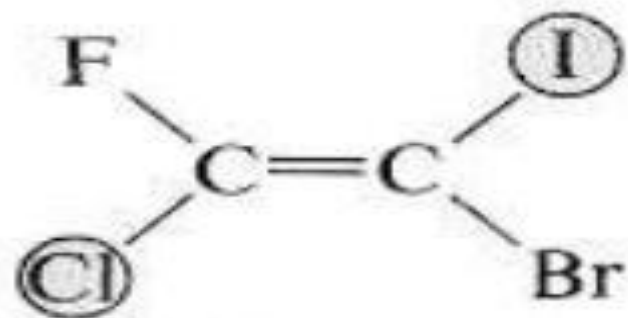


- In this, compound of the type $abc = cab$ can exist in the following two forms due to frozen rotation about carbon - carbon double bond. The isomers in which the identical groups are on the same side of the double bond is called cis which the group are on opposite side called as trans.

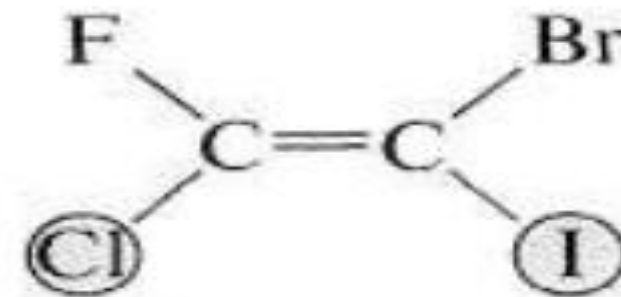
- For example : 1,2 dichloroethene exist as both i.e cis & trans form.



- When all the four substituents are different cis-trans type of isomerism cannot be applied. In this type E-Z system of nomenclature is applied based upon the sequence rules of Cahn Ingold and prelog for naming.
- Higher priority is assigned to atoms of higher atomic number.
- Z = Zusammen (same side)
- E = (opposite side)



priority groups
on opposite sides
E configuration

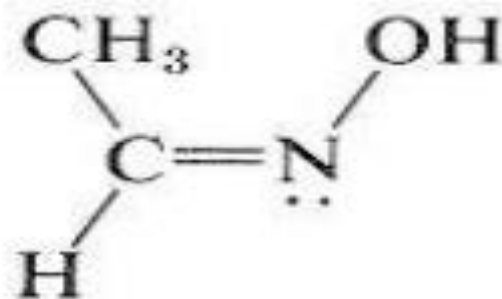


priority groups
on same side
Z configuration

- The above is an example of an alkene in which one of the bonded carbon atom has bromine and Iodine and the other has fluorine and chlorine.

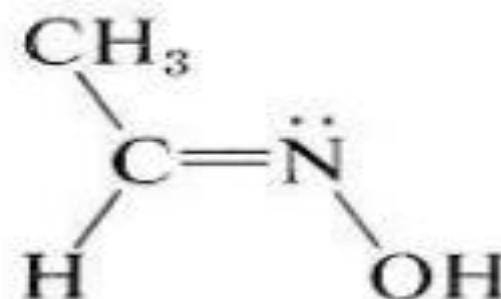
iii) Syn -Anti system of nomenclature

- When C=N is formed by reaction of aldehyde with NH₂-G then H on carbon and substituent's on nitrogen are on the same side then configuration is **Syn** and when on opposite sides and configuration is **anti** where G may be H,R,OH,NH,NHph and NHCONH₂.



11

Z (syn)



12

E (anti)

Methods of determination of configuration of geometrical isomers.

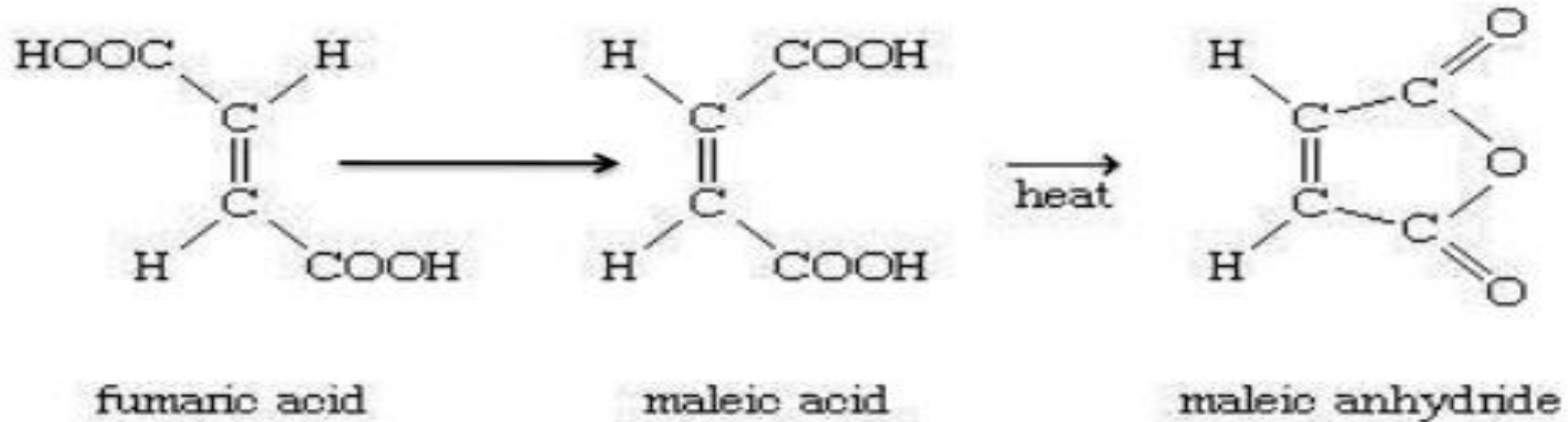
- Method of cyclization.
- By converting into the compound of known configuration.
- Optical activity.
- Method based on physical property.
- By stereoselective addition and elimination reaction.

Method of cyclization

- This method is applied in which either of the form capable of forming a ring.

This method is based on the principle that the intermolecular reaction occur easily when the reacting groups are closed together. For ex. Among two acids Malic and fumaric only the former give anhydride on gentle heating so in malic acid the two reactive groups (-COOH) are close together

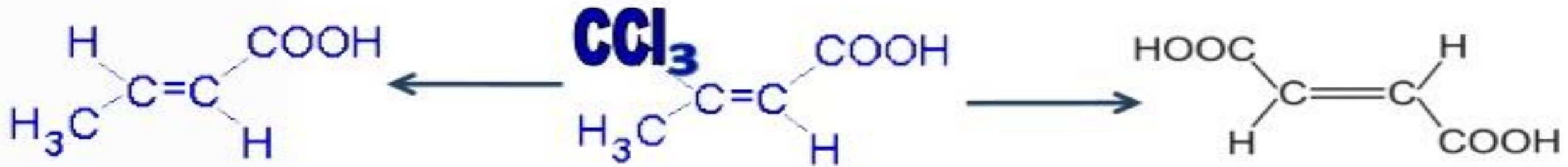
and hence it is the cis and fumaric acid is the trans.



By converting into the compound known configuration

- Geometrical isomers of pair can be converted into a compound of known configuration.
- For example: The conversion of one form of the trichlorocrotonic acid into fumaric acid on hydrolysis so the above trichlorocrotonic acid must be the trans-isomer moreover the same trichlorocrotonic acid gives crotonic acid (m.p=72 degree Celsius) on reduction. The other isomer of trichlorocrotonic acid does not give fumaric acid on hydrolysis and from isocrotonic acid (m.p 15.5 degree Celsius) on reduction.

Hence the isocrotonic acid and the corresponding trichlorocrotonic acid are cis-isomers.



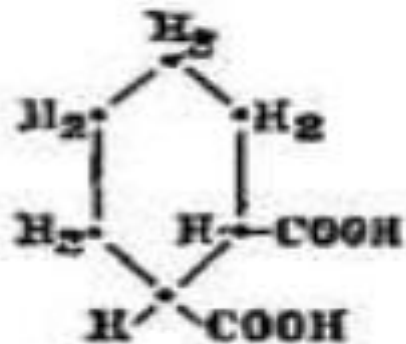
Crotonic acid
(trans)

Trichloro crotonic acid
(trans)

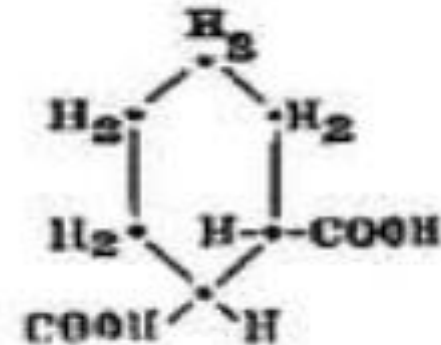
Fumaric acid
(trans)

Method of optical activity

- Among the two member of geometrical isomers only one form is optically active where as the other is optically inactive due to presence of an element of symmetry is optically active form can be resolved and may be used to establish its configuration
- Ex. Hexahydrophthalic acid the trans-form of which has been resolved



cis-Hexahydrophthalic acid.



trans-Hexahydrophthalic acid.

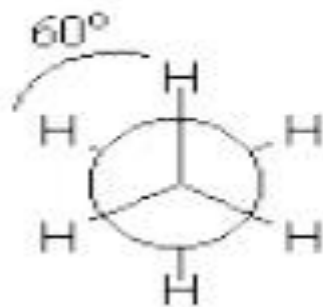
Cis = Optically inactive due to plane of symmetry
 Trans = Optically active and hence resolved

METHOD BASED ON PHYSICAL PROPERTIES

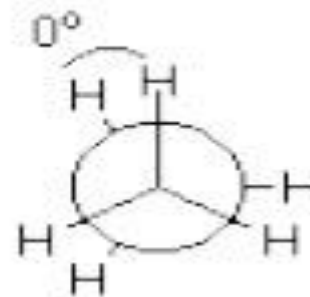
- Physical properties often be used for establishing the configuration of various physical properties which help in determining configuration are
- Dipole moment
- Melting point
- Boiling point
- Solubility
- Refractive index
- Acid strength
- X-ray
- Electron diffraction
- Spectroscopy

Conformational isomerism ethane

- When an ethane molecule rotates about its carbon-carbon single bond two extreme conformations can be result, the staggered and eclipsed conformation. Here we will use Newman projection to discuss the conformation of ethane even then it is chiral because it has plane of symmetry.

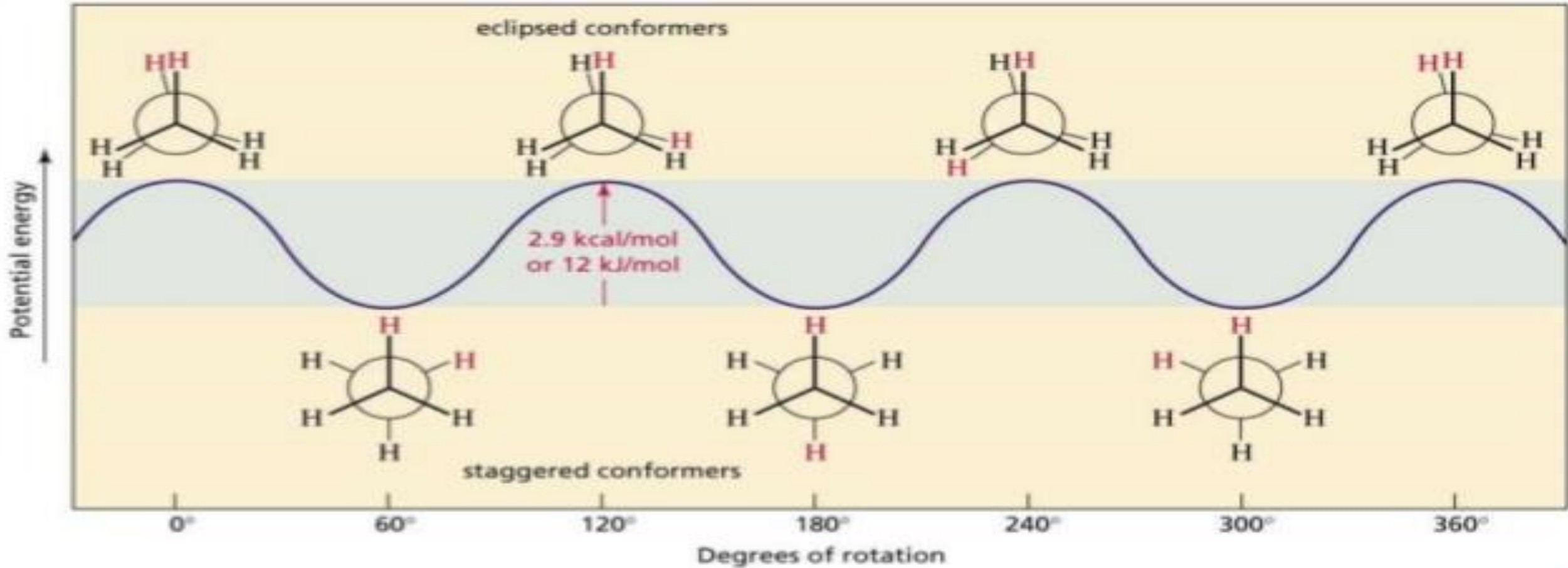


staggered



eclipsed

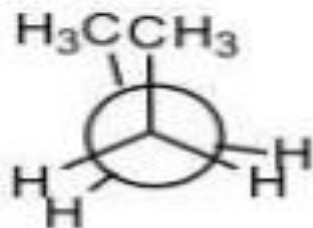
- Newman projection of Ethane various possible conformation of Ethane. If one of the methyl group is allowed to rotate keeping the rest of molecule undisturbed and number of possible arrangement can be obtained.
- By doing so six possible confirmation can be obtained out of which 3 are staggered and 3 are eclipsed form. Potential energy of 1,3,5 is less than that of 2,4,6.



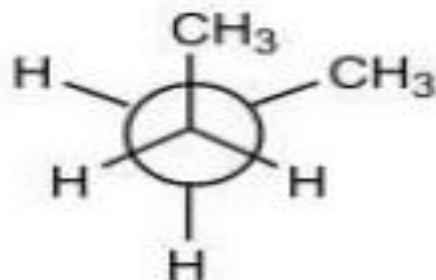
Conformational isomerism n- butane

- Butane has three carbon-carbon single bond and molecule can rotate about each of them .
- If the rotation will be about C2 and C3 bond then confirmation will be symmetrical. Different conformation of butane can be obtained by rotating about its middle carbon-carbon single bond.
- Butane has 3 staggered (i.ii.iii) conformer iii in which the two methyl group are as far apart as possible is more stable than the other two staggered form I and v ,iii is called as anti confirmation and (I,v) are called gauche conformers.

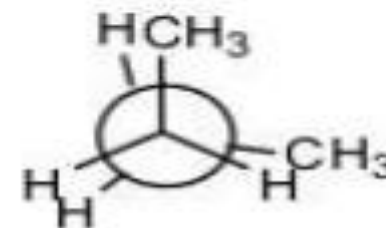
Conformation of n-butane



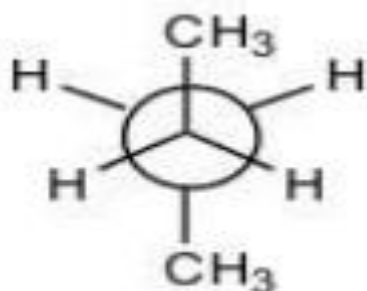
Eclipsed conformation (I)



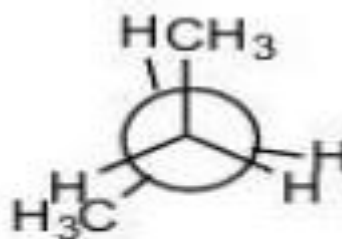
Gauche configuration (II)



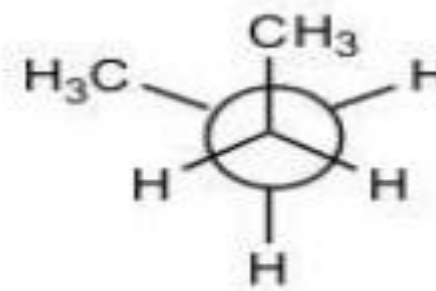
Eclipsed conformation (III)



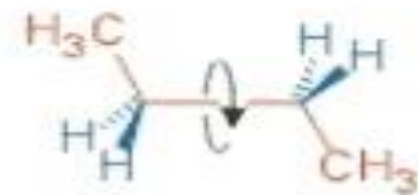
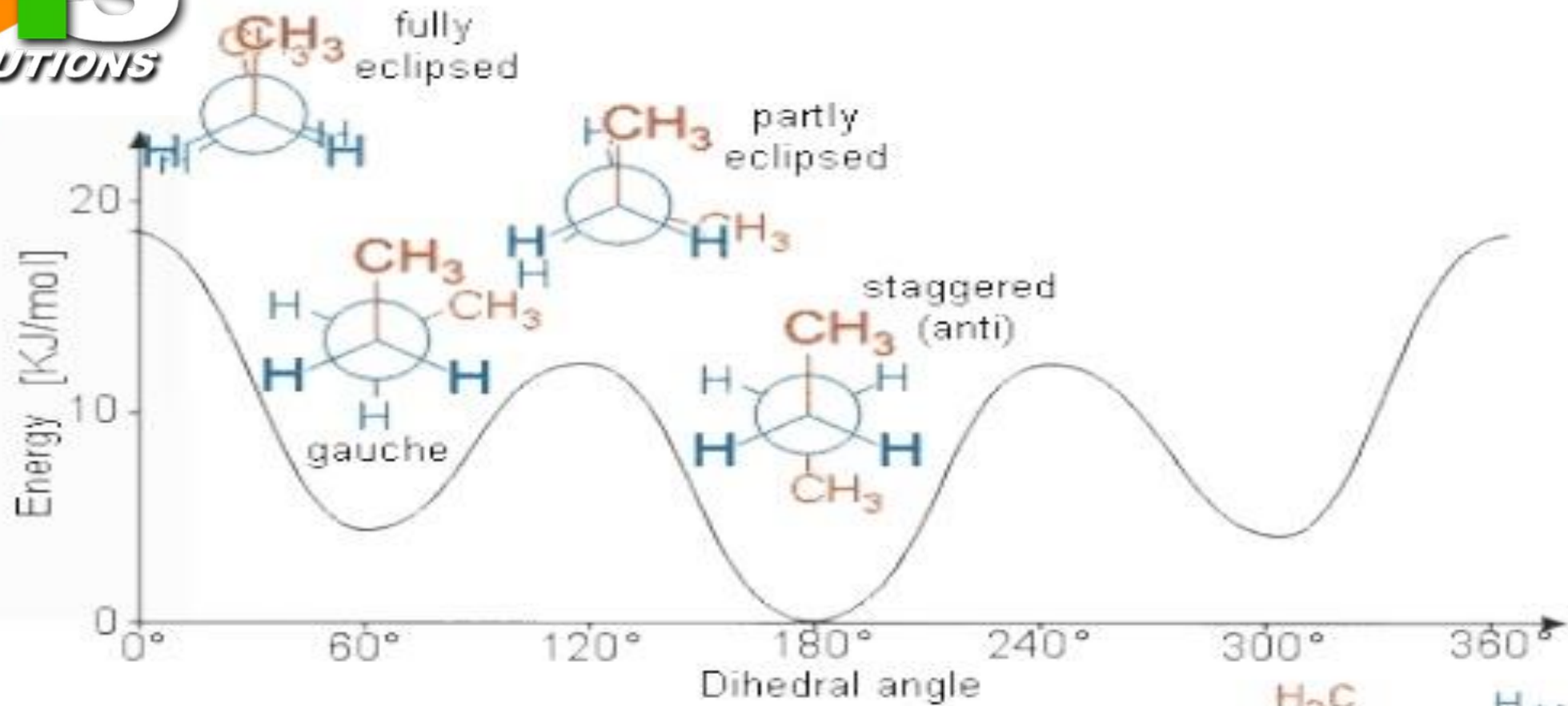
Anti conformation (IV)



Eclipsed conformation (V)



Gauche conformation (VI)



Conformational isomerism Cyclohexane

- Sachse (1890) proposed that cyclohexane and larger rings are not planar but they are puckered in which all the angles are tetrahedral and thus the rings are strainless.
- Thomas chair and boat conformations 1931 suggested the possibility of existence of interconversion by rotation about single bonds in the ring. In boat conformation the carbon-hydrogen bonds at C3 are eclipsed while in chair conformation the carbon-hydrogen bonds on adjacent carbons are staggered, further in boat conformation there is steric repulsion between two hydrogens.

Stereoisomerism in biphenyl compounds

- Biphenyl compounds are devoid of individual chiral carbon atom but the molecules are chiral due to restriction rotation around on the between the two benzene nuclei and hence they must exist in two forms which are non-superimposable mirror images of each other such type of steriomorphism which is due to restricted rotation about single bond is known as atropisomerism.
- ex. 6,6 dinitrophenic acid was the first diphenyl compound to show optical isomerism. acid.

- Kenner synthesized 6,6 dinitrophenic acid by means of ullmann reaction by ethyl ester of 2-chloro-3-nitrobenzoic

Stereospecific reaction

- A reaction in which a particular stereoisomers react to give one specific stereoisomer of the product is called a stereospecific reaction. Such a reaction is said to display stereospecificity .A stereospecific reaction gives a different stereoisomers of the starting material.
- For example: Addition of bromine to cis-2-butene gives racemic 2-3-dibromobutane while the trans isomer give meso 2-3-dibromobutane .This reaction is stereospecific because different stereoisomer gives different stereoisomer.

Stereoselective reaction



- A reaction in which one stereoisomer is formed predominantly or excessively out of several stereoisomers possibilities is called a stereoselective reaction. Such a reaction is said to display stereoselectivity. In this one stereoisomer is formed more rapidly thus resulting in a selective reaction.
- The stereoelectronic requirement of the mechanism of a stereoselective reaction offers alternatively paths so that the reaction proceeds either via the most favourable path or via the path which gives the most stable stereoisomers as the major product.

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THANK YOU

