Isomerism

Isomerism name was given by Berzilius. Two or more than two organic compounds having the same molecular formula and molecular weight but different physical and chemical properties are called isomers and the phenomenon is called isomerism.

Isomers

C_4H_{10}

$CH_3—CH_2—CH_2—CH_3$

Butane(4C)

-139.4°C

C_4H_{10}

$CH_3—CH(CH_3)—CH_3$

2-Methyl propane (3C)

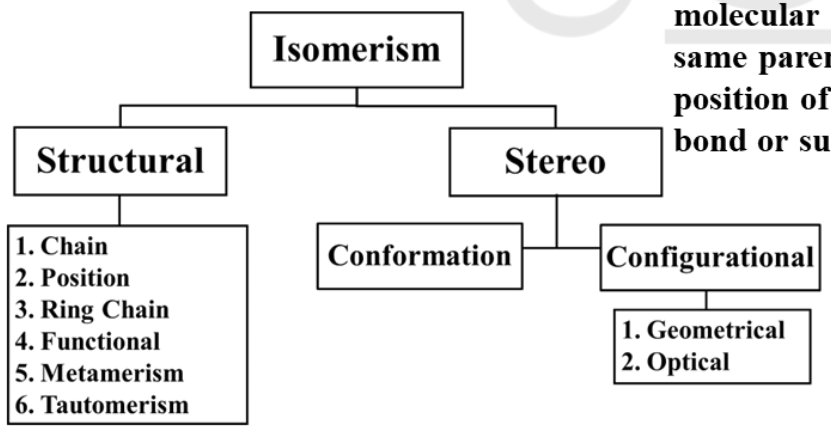
-159.6°C

C_2H_6O

$CH_3—CH_2—OH$

C_2H_6O

$CH_3—O—CH_3$



MIND MAP

Structural Isomerism

Structural Isomerism

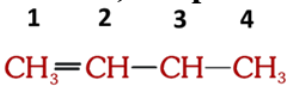
When two or more number of organic compounds have same molecular formula but different structural formula these are called structural isomers.

1. Chain Isomerism (CI)

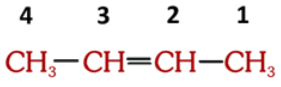
The compounds which have same molecular formula, same functional group, but difference in length of carbon chain (parent chain or side chain) show chain isomerism.

2. Position Isomerism

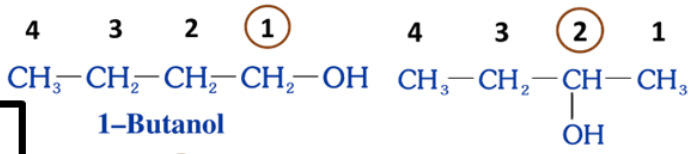
The compounds which have same molecular formula, same functional group, same parent carbon chain but different position of functional group or multiple bond or substituents, are position isomers.



But–1–ene

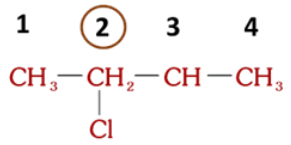


But–2–ene

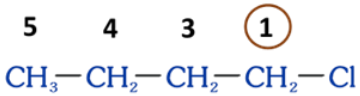


1–Butanol

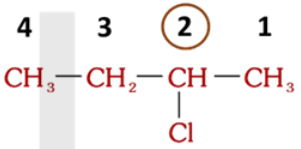
2–Butanol



2–Chlorobutane



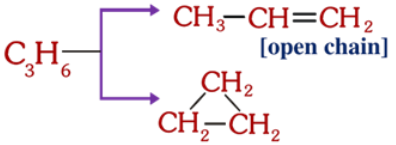
1–Chlorobutane



2–Chlorobutane

3. Ring Chain Isomerism (RCI)

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



They have same molecular formula so they are Ring chain isomers.

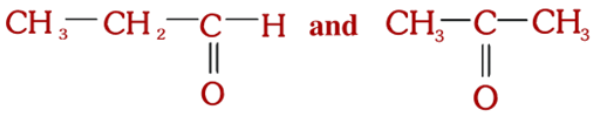
MIND MAP

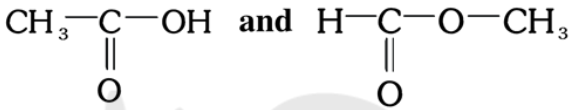
Structural Isomerism

Functional Isomers

Same molecular formula but different functional groups.

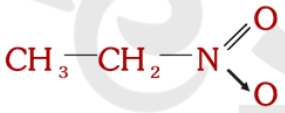
(i) Alcohol and ether ⟶ $CH_3—CH_2—OH$ and $CH_3—O—CH_3$

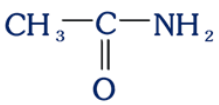
(ii) Aldehydes and ketones ⟶  and

(iii) Acids and ester ⟶ 

Cyanide — isocyanide

(iv) $CH_3—CH_2—CH_2—CN$ $CH_3—CH_2—CH_2—NC$

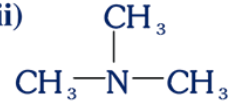
(v) Nitro and Nitrite ⟶  and $CH_3—CH_2—O—NO$

(vi) Amide and Oxime ⟶  and $CH_3—CHNOH$ and $CH_3CH_2–N=O$

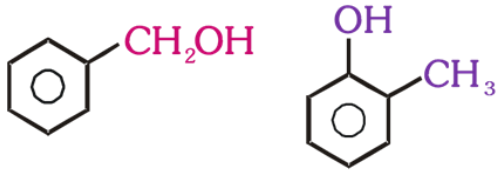
(vii) 1°, 2°, 3° amines

(i) $CH_3—CH_2—CH_2—NH_2$

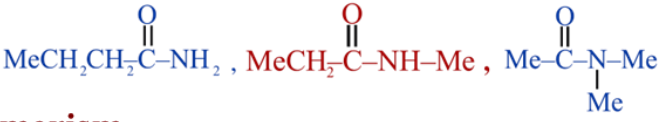
(ii) $CH_3—NH—CH_2—CH_3$

(iii) 

(viii) Alcoholic and phenolic compounds



(ix) 1°, 2°, 3° amide



Metamerism

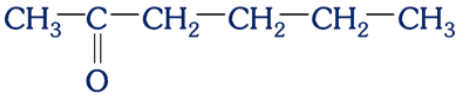
Same molecular formula, same polyvalent Functional group but different alkyl groups attached to polyvalent Functional group on either side.

$CH_3—CH_2—NH—CH_2—CH_3$

N–Methyl propanamine

$CH_3—NH—CH_2—CH_2—CH_3$

N–Ethyl Ethanamine



2–Hexanone

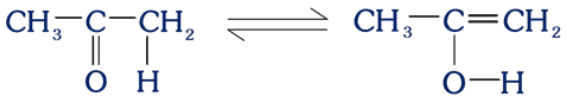
3–Hexanone

MIND MAP

Structural Isomerism

Tautomerism

Tautomerism was introduced by "Laar".
It Arises due to rapid oscillation of an atom, usually hydrogen, between 2 polyvalent atoms in a molecule.

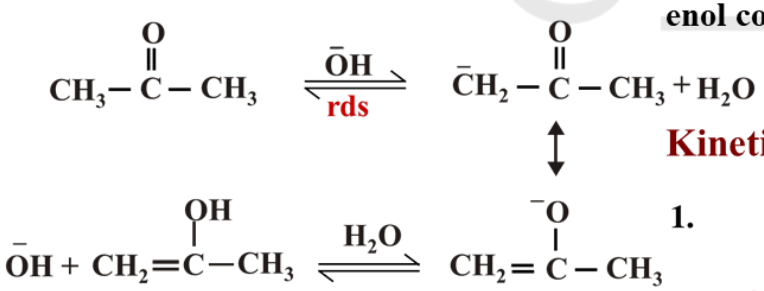


keto — ene + ol = enol

→ Tautomers remain in dynamic equilibrium with each other
→ More stable isomer is present in higher concentration.
→ The process can be catalysed by acid as well as base

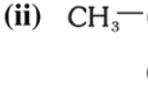
Mechanism

Base catalysed mechanism



Condition For Tautomerism

(i) 3 α H, how Tautomerism.

(ii)  6 α H, show Tautomerism

Enol Content

% amount of enol at equilibrium is known as enol content.

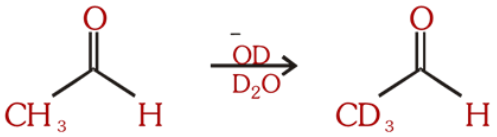
enol content ∝ stability of enol

enol content ∝ aromatization of enol

enol content ∝ stability of enolate ion

enol content ∝ Intramolecular H-bonding

Kinetic Isotopic Exchange

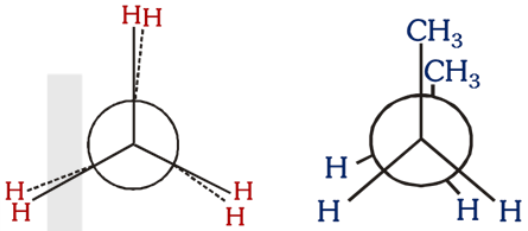
1. 

Conformational Isomerism

Conformational isomerism is a form of stereoisomerism in which the isomers can be interconverted just by rotations about single bonds.

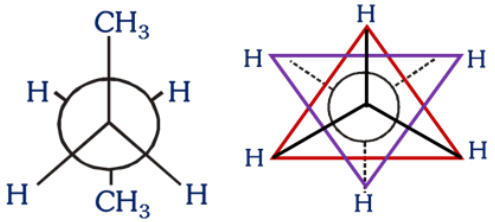
(i) Eclipsed Conformation:

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



(ii) Staggered Conformation:

Conformations in which valency triangle are opposite and most priority group are also opposite then known as staggered/anti conformation.



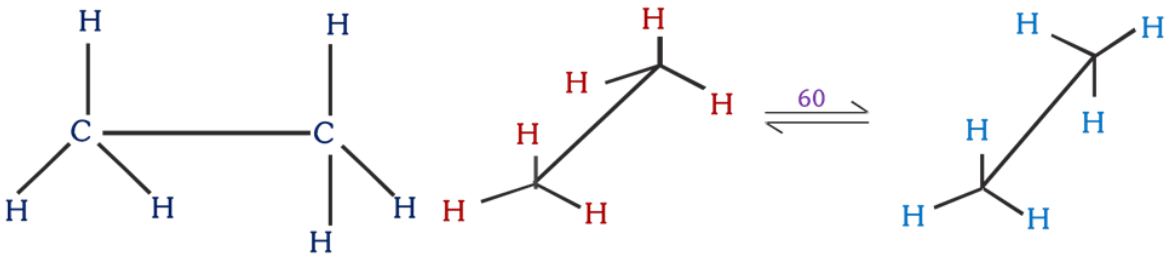
Structural Isomerism

MIND MAP

Structural Isomerism

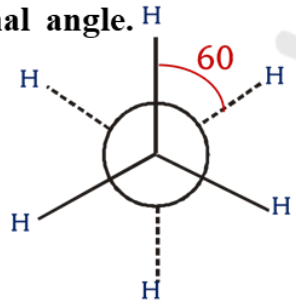
(iii) Skew Conformation : All other conformations are known as Skew Conformations.

Conformers of ethane [CH3—CH3]

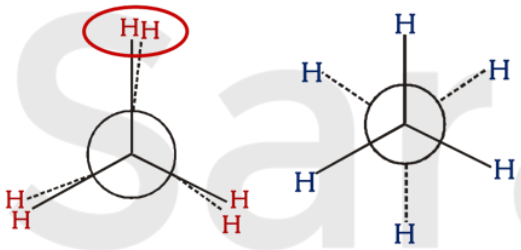


Eclipsed **Staggered**

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



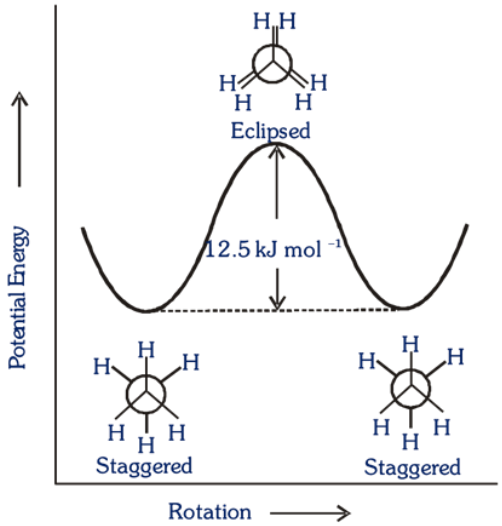
Eclipsed form - in this form distance between 2C–H bonds is minimum so maximum repulsion or minimum stable.
Staggered form - in this form distance between 2C–H bonds is maximum so minimum repulsion so maximum stable.



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

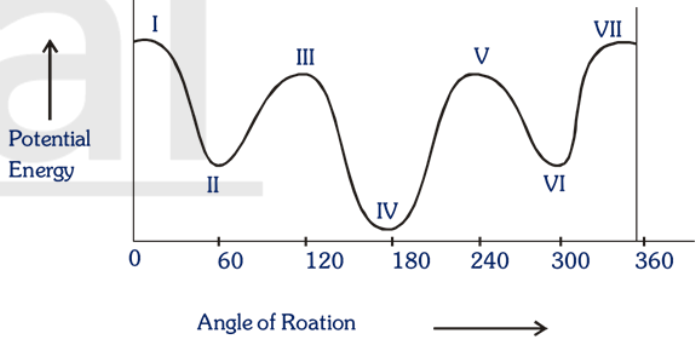
Stability order :Staggered > Skew > Eclipsed.

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 ethane

Conformational analysis 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

Dipole Moment In Conformational Analysis

Dipole Moment (μ)

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

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

$$x_a + x_g = 1$$

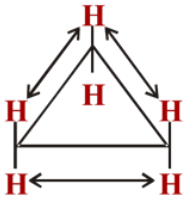
Conformational Analysis Of Cycloalkane

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 s bond rotation is observed so larger ring acquires non-planar orientation to avoid eclipsing.

Eclipsing



repulsion (eclipsing)

→ planar

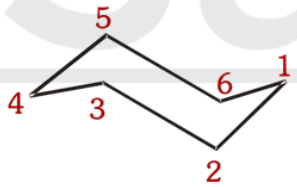
MIND MAP

Structural Isomerism

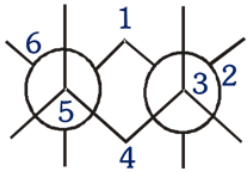
Conformational analysis of cyclohexane

(i) Chair form : Experimental evidences show that cyclohexane is non-planar. If we look at the models of the different conformations that are relatively 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.

The chair form is the most stable conformation of cyclohexane.

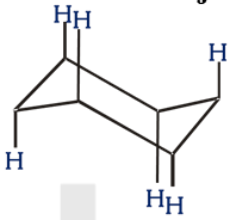


Chair conformation



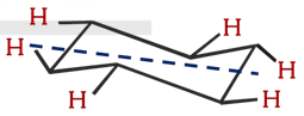
Chair conformation(all staggered bonds)

The 12 hydrogen atoms of chair conformation of cyclohexane can be divided into two groups. Six of the hydrogens are called axial hydrogens, hence their bonds are parallel to a vertical axis that passes through the ring centre. These axial bonds are directed up & down on adjacent carbons.

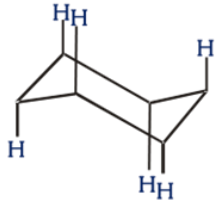


Axial C–H bonds

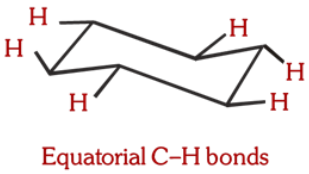
The second set of six hydrogens called equatorial hydrogens are located approximately along the equator of the molecule.



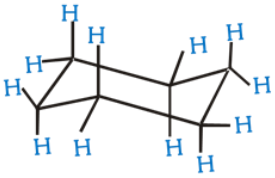
Equatorial C–H bonds



Axial C–H bonds



Equatorial C–H bonds



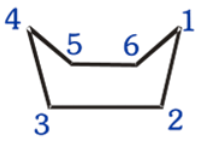
Axial & equatorial bonds together

MIND MAP

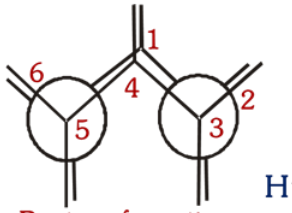
Structural Isomerism

(ii) Boat Form

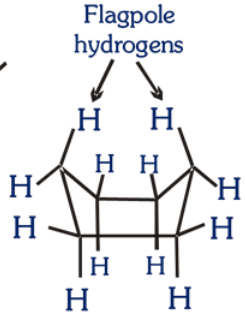
Another conformation which is known as boat conformation has exactly eclipsed conformations.



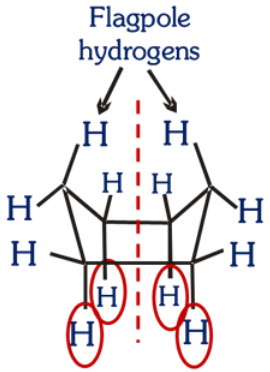
Boat conformation



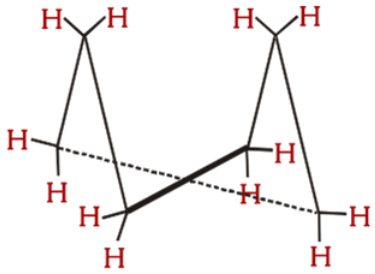
Boat conformation
(all eclipsed bonds)



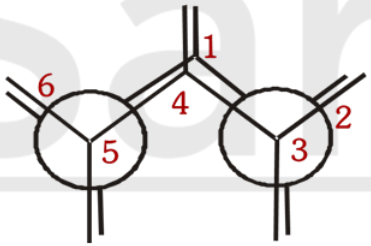
In boat form of cyclohexane 6 hydrogens are equatorial, 4 hydrogens are axial and two hydrogens are flagpoles. It is an unstable conformation of cyclohexane due to repulsion among axial hydrogens and due to repulsion caused by crowding between the "flagpole" hydrogens.



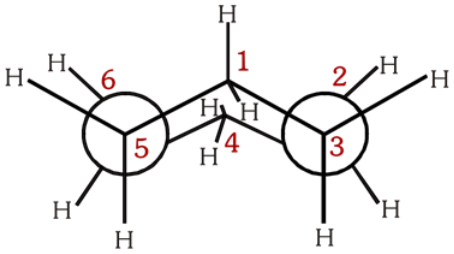
(iii) Twist Boat Conformation



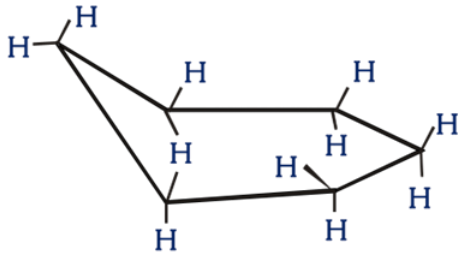
Boat conformation



Twist Boat conformation



(iv) Half Chair Conformation



Stability Order

Chair > Twist boat > Boat > Half Chair