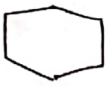
CYCLOALKANES

Cycloalkanes are alkanes that contain ring of carbon atoms. They are may be mono cyclic, bicyclic or polycyclic. Monocyclic ring are usually classified into four catagorie; small ring (three and 4 memberd); normal ring (5 and 6 memberd); medium ring (8 to 11 memberd) and large ring (more than 11 atoms).

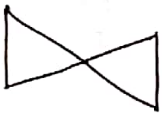
Nomenclature of cycloalkanes

cyclopropane

cyclobutane



cyclohexane

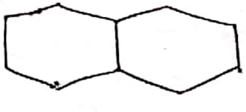


Spiro -[2,2] pentane

Spiro [4,5] decane.

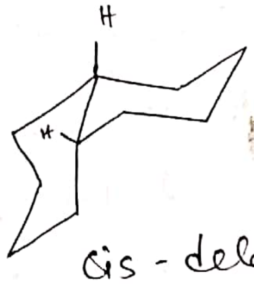
→ Spiro cyclic

fused bicyclic

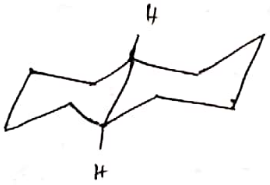


Bicyclo[4,4,0] delane (delalin).

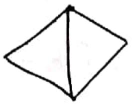
Delalin shows cis-trans isomerism –



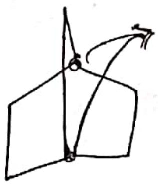
Cis - delalin



trans - delalin.

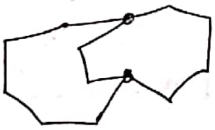


Bicyclo {1,1,0] butane.



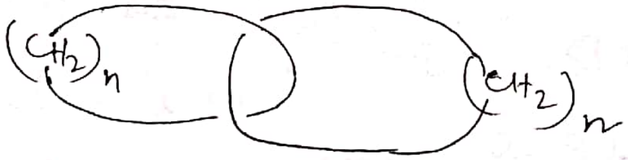
bridgehead Carbons.

bicyclo {2,2,1] heptane
(norborane)



bicyclo {5,4,2] tridelane

bridge bicyclic



Catenane ($n \geqslant 18$)

Stabilities of cycloalkanes :-

Theoritical aspect :-

Bayer strain theory :-

As in cycloalkane, the angle between any pair of bonds deviate from ideal bond angle

So molelule to be ~~sta~~ strained. To account for the above stability or instability order of cycloalkanes Bayer proposed his strain theory which is known as the Bayer strain theory. According to this theory, the cycloalkanes have the planner structure and here the C—C—C bond angle is given by $\frac{2n-4}{n} \times 90°$ where 'n' is the member of ring element. Now this bond angle deviates from the normal tetrahedral angle of 109°28' and thereby a strain is introduced. The strain often called the bond angle strain or Bayer strain is defined as

$$\frac{1}{2}(109°28' - \text{Calculated bond angle})$$

n	Bayer strain
3	$\frac{1}{2}(109°28' - 60°) = 24°44'$
4	$\frac{1}{2}(109°28' - 90°) = 9°44'$
5	$\frac{1}{2}(109°28' - 108°) = 44'$
6	$\frac{1}{2}(109°28' - 120°) = -5°16'$

Limitation :-

① According to Baayer, cyclopentane is more stable than cyclohexane but experimentaly the opposite is true.

(ii) Baeyer assumed all ring are flat. but most of the ring are puckered.

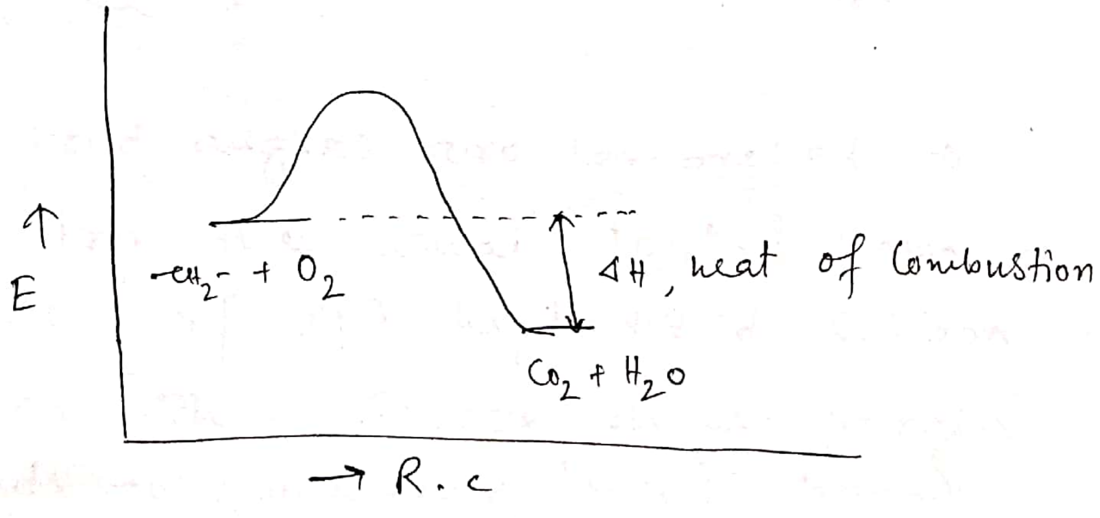
(iii) It is not measured by quantum mechanical calculation.

(iv) It is applicable for monocyclic ring only.

Experimental aspect :-

Heats of Combustion

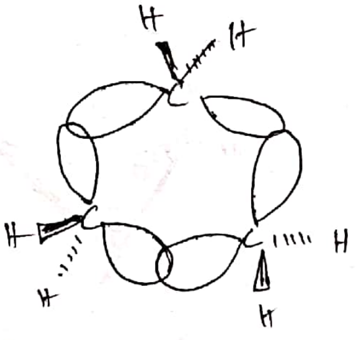
The heat of Combustion is the amount of heat released when a compound is burned with an excess of O_2 in a sealed container called a bomb calorimeter.

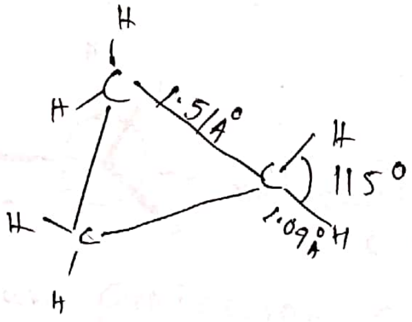


Thus higher the magnitude of heat of combustion per methylene group in comparison to that of n-alkane lower is the stability of cyclo-alkane.

Ring size	Heat of combustion per $-CH_2-$, K.cal/mole
3	166.6
4	164.0
5	158.7
6	157.4
7	158.3
8	158.6

Cyclopropane



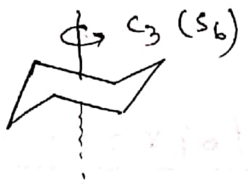


The bond angles are compressed to 60° from the usual 109.5° bond angle of sp^3 hydridized carbon atoms. This severe angle strain leads to non linear 'bent' bonds.

Cyclohexane :-

Sachse and Mohr proposed two nonplaner forms for cyclohexane which are free from Baeyer strain. These are ① chair form ⓘⓘ Boat form.

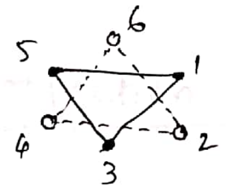
① chair form

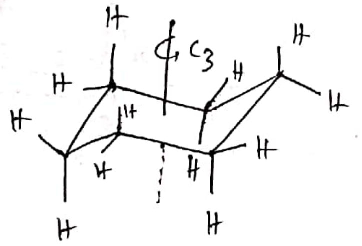


$$C_3 + 3C_2(\perp^r \text{ to } C_3) + 3\sigma_d + S_6 + i$$

$$\Rightarrow D_{3d}$$

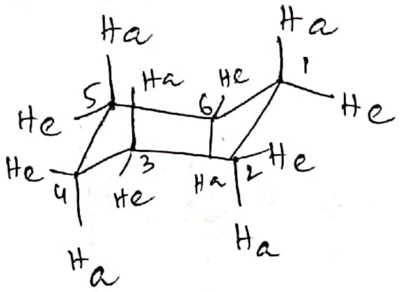
The presence of the above elements of Symmetry in the chair form of the Cyclohexane will be more clear from the following model





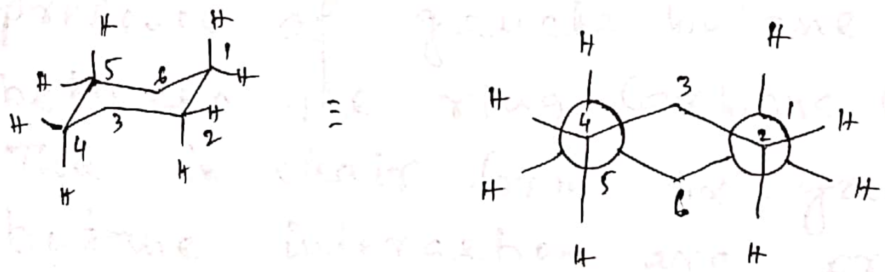
® Axial bonds :- Six 'C—H' bonds are parallel to the C_3 axis of the cyclohexane ring. These are called axial bonds, which are symbolized as 'a'.

® Equatorial bonds :- Six 'C—H' bonds make an angle (19°) with horizontal plane of the rings. These are called equatorial bonds and are symbolized by 'e'.

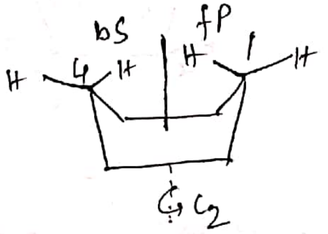


The interaction between 1e, 2e and 1e, 2a Substituents is known as 1,2-interaction while that between 1a, 3a is known as 1,3 interaction or '<u>Synaxial interaction</u>'. when H is substituted by a bulkier group with longer bond length, the 1,2 interaction does not increase in the same proportion as the 1,3 interaction which is thus more severe.

<u>Newman projection formula:-</u>



<u>Boat form:-</u>



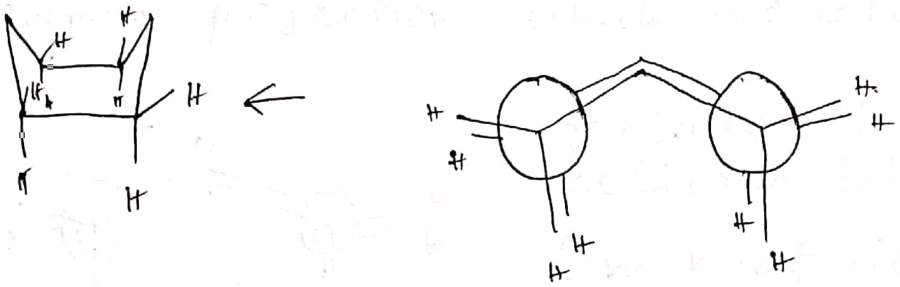
$C_2 + 2\sigma_v$

$\Rightarrow C_{2v}$.

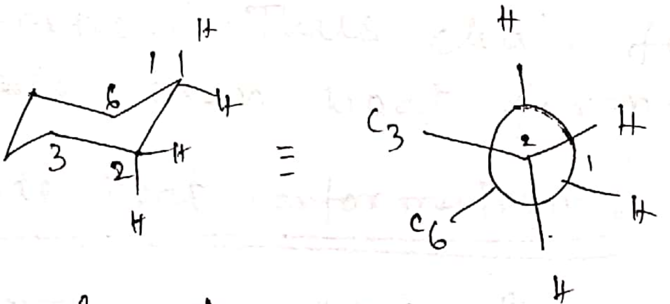
Normal equatorial and axial bonds at C-1 and C-4 designated flagpole;

abbreviated as 'fp' and the other bowsprit abbreviated as 'bs'.

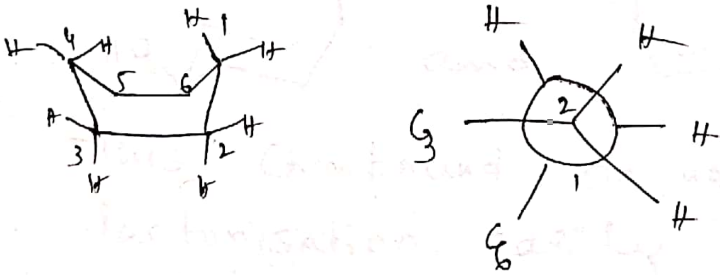
Newman projection



Stability of chair and boat form

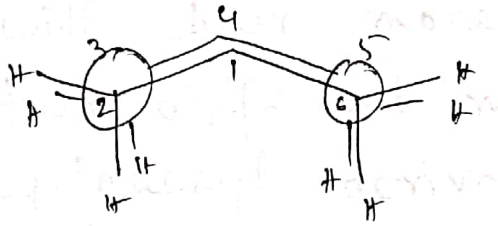


Now looking along the bond C_2-C_1 we have the following newman projection, which indicates the presence of gauche butane interaction between the ring carbons C_3 and C_6. Thus in chair form six gauch butane interaction are present.



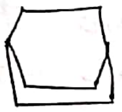
Now looking along C_2-C_1, which indicates the presence of gauch butane interaction. Thus there are four gauch-butane interactions looking along C_2-C_1, C_1-C_6, C_3-C_4, C_4-C_5.

Again looking along C_2-C_3 and C_6-C_5, we have the following Newman projection, which indicates the



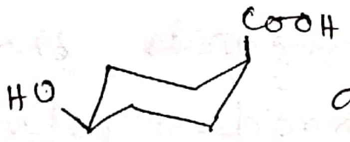
presence of two eckipsed interaction. In boat form there are another strain due to "bs-fp" interaction. Thus chair form is more stable than boat form.

Stable boat Conformations:

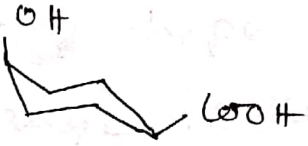


The case of bicyclo(2,2,2) octane in which the cyclohexane ring system is forced to be in the boat form.

Let us consider the case of cis-4-hydroxy cyclohexane carboxylic acid which can exist in ether of the following two chair forms



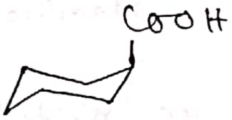
and



This compound on heating undergoes lactonisation easily. Obviously the str of lactone is boat form.

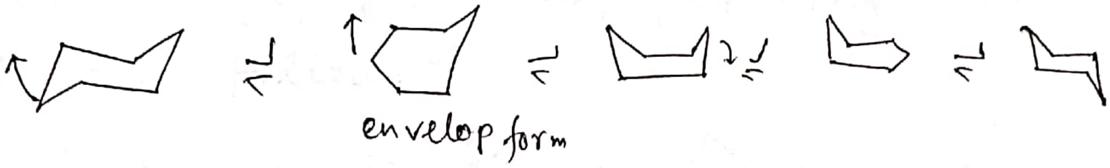
Topomerisation or flipping

As we have seen in the chair form of cyclohexane there are two types of bonds namely axial and equatorial bonds. Now the difficulty was that with chair model there should have two different mono substituted cyclohexyl derivatives, such as hexahydrobenzoic acids. One equatorially substituted and the other axially substituted

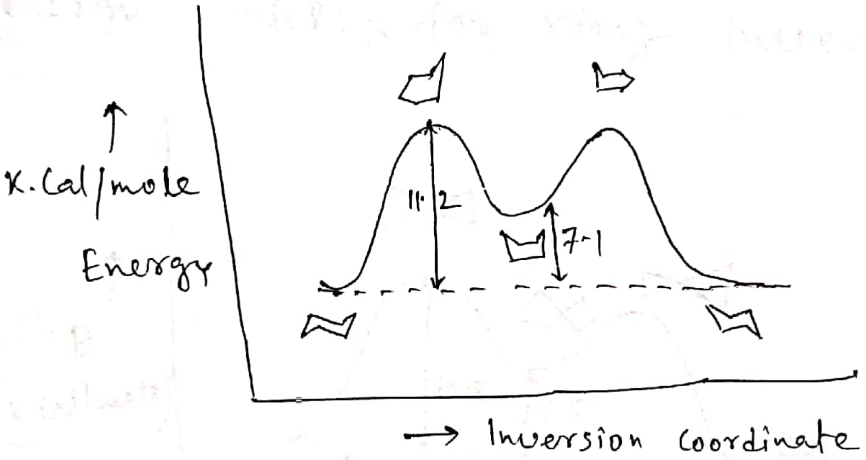


But such isomers were never found. Now to explain the non existance of two forms, there is an equilibrium between the two forms and that the two models vibrate from one to the other so rapidly the net average is a planar molelule. This ~~change called~~ type of Conformational change is known as ring inversion, topomerisation or flipping.

Now the ring inversion may proceed through the following pathway –



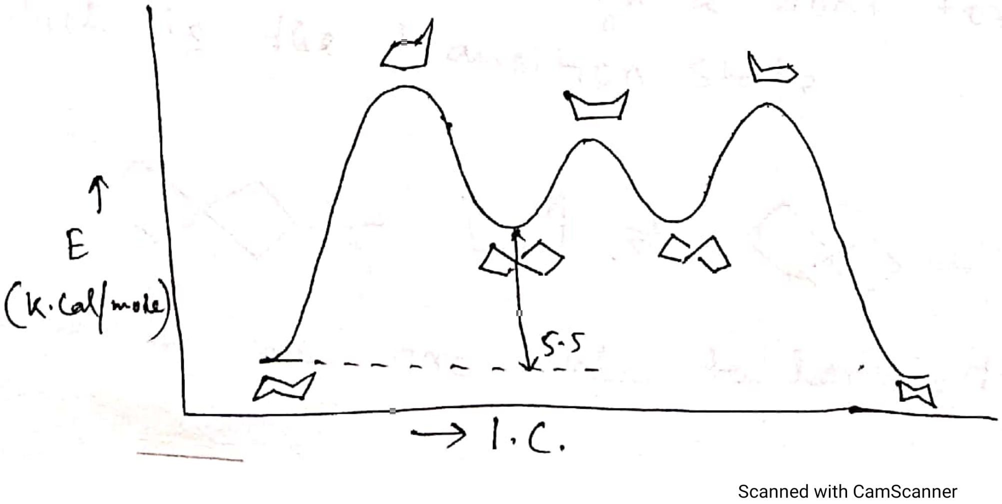
Thus we have following energy profile for the ring inversion.



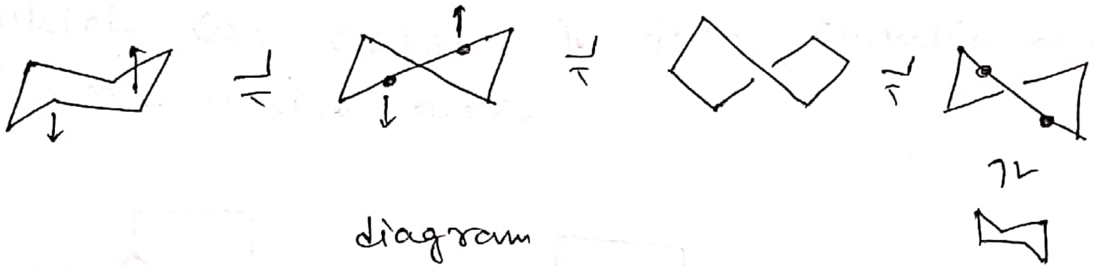
This pathway of ring inversion is called σ - Pathway.

During transformation of chair form to boat form one may obtain a form in which both bs - fp interaction and eclipsing interactions are some what absent. This form is called the twist boat form. So its energy is less than that of boat form.

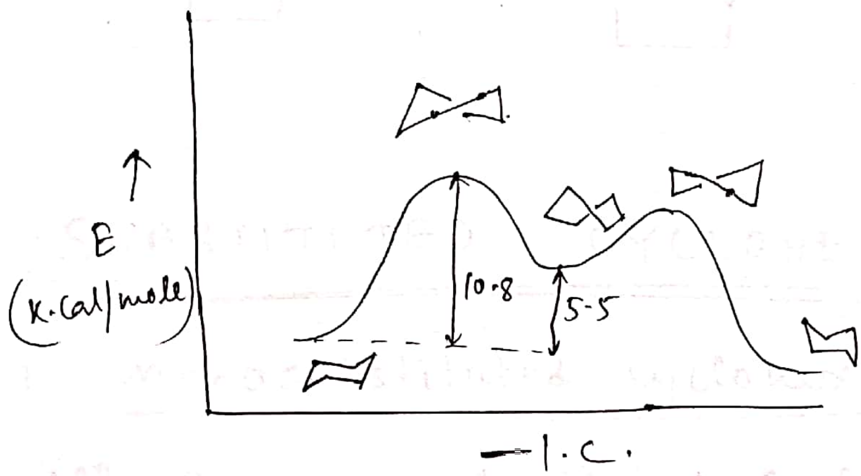
Now energy profile diagram is –



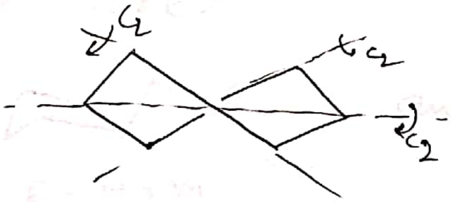
According to Hendrikson, the most probable pathway (C_2 pathway) for ring inversion is as follows —



energy profile diagram for ring inversion is –



Twist Boat Form



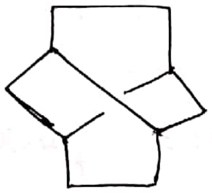
$3C_2 \Rightarrow D_2$

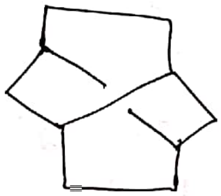
$C_2, 2C_2$ ($\perp^r C_2$)

Two enantiomeric twist boat forms are interconvertible by a process called pseudorotation through a boat form which is the transition state.

Now if we are able to lock the

pseudorotation in twist boat form then we do expect enantiomerism. This is actually the case in twistane which can exist in two enantiomeric forms which are



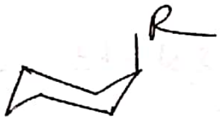


SUBSTITUTED CYCLOHEXANE

1. Monosubstituted cyclohexane.

All the monosubstituted cyclohexane can exist in two diastereoisomeric forms which are

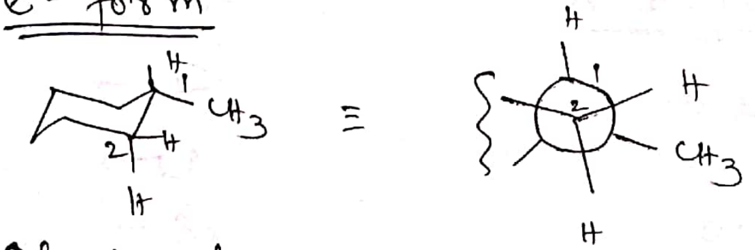
and



e-form a-form

Now the difference in energy of methyl cyclohexane between the a-form and e-form can be estimated from an inspection of the models.

e-form



Obviously there is no extra gauch