

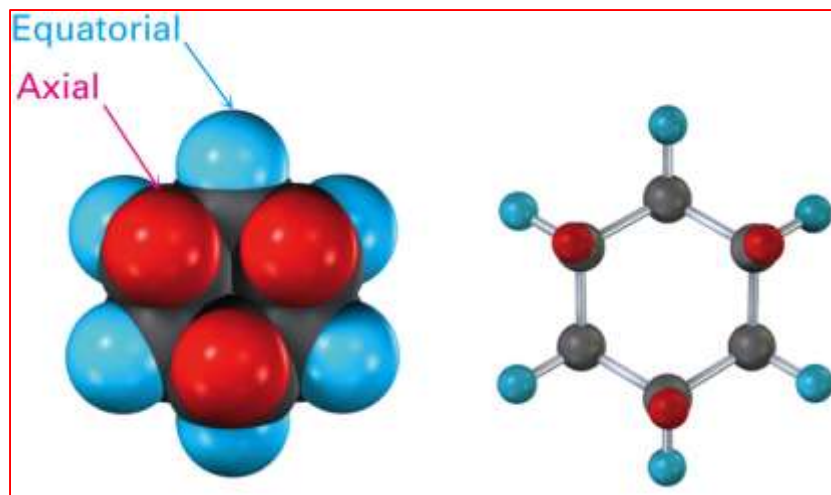
Module : Stereochemistry

Conformational Analysis of Cyclohexane

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Dept. of Chemistry

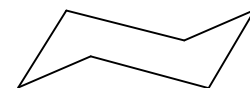
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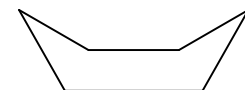
Conformations of Cyclohexane

* Sachse's suggestion(1890) : CH exists in Folded form. All nuclear carbons do not lie in one plane.

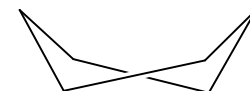
1. Chair Conformation



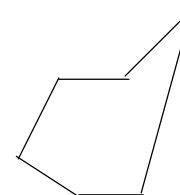
2. Boat Conformation



3. Twist Conformation or Skew Boat Conformation

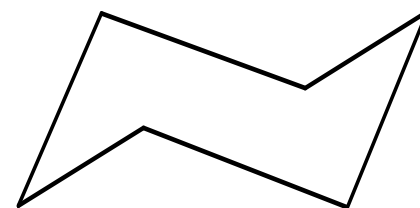


4. Half Chair Conformation



Chair Conformation

- Shape : Like a Chair
- No. of Carbon atoms : 06
- All Carbon atoms : sp^3 hybridised
- Bond angle between any two bonds : $109^{\circ} 28'$
- No. of Hydrogen atoms : 12
- Two sets of Hydrogen atoms : 06 + 06
 - a) Axial hydrogen atoms
 - b) Equatorial hydrogen atoms

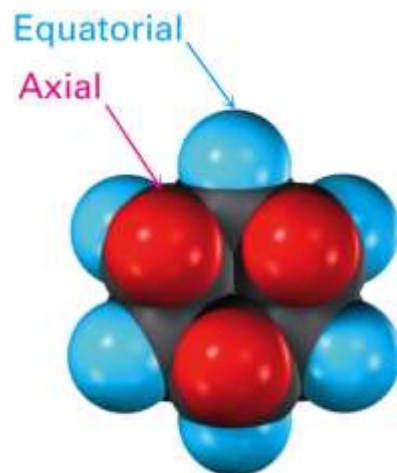
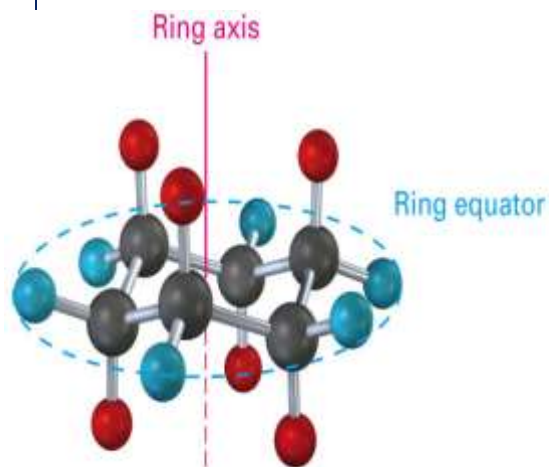


Axial and Equatorial Bonds in Cyclohexane

There are two kinds of positions for substituents on the cyclohexane ring

Axial positions – 6 axial positions perpendicular to ring and parallel to ring axis. Bonds in these positions are axial bonds and atoms/grs. are axial

Equatorial positions – 6 equatorial positions are in rough plane of the ring around the equator, i. e. Projecting outwards the ring. Bonds in these positions are equatorial bonds and atoms /grs are equatorial

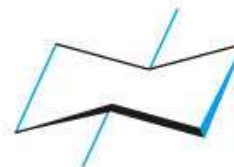


Axial and Equatorial Bonds in Cyclohexane

Axial bonds: The six axial bonds, one on each carbon, are parallel and alternate up-down.



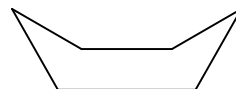
Equatorial bonds: The six equatorial bonds, one on each carbon, come in three sets of two parallel lines. Each set is also parallel to two ring bonds. Equatorial bonds alternate between sides around the ring.



Completed cyclohexane

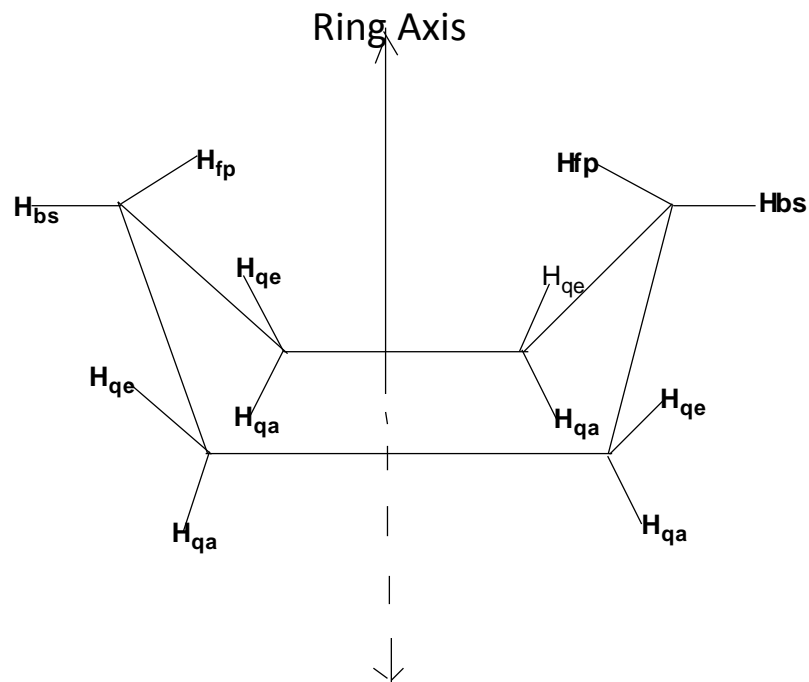


Boat Conformation of Cyclohexane



- Shape : Like a boat
- No. of Carbon atoms : 06
- All Carbon atoms : SP^3 hybridised
- Bond angle between any two bonds : $109^{\circ} 28'$
- No. of Hydrogen atoms : 12
- Four types of Hydrogen atoms : 2 + 2 + 4 + 4
 - a. Flag pole Hydrogen atoms : 2
 - b. Bow-sprit Hydrogen atoms : 2
 - c. Quasi axial Hydrogen atoms : 4
 - d. Quasi equatorial Hydrogen atoms : 4

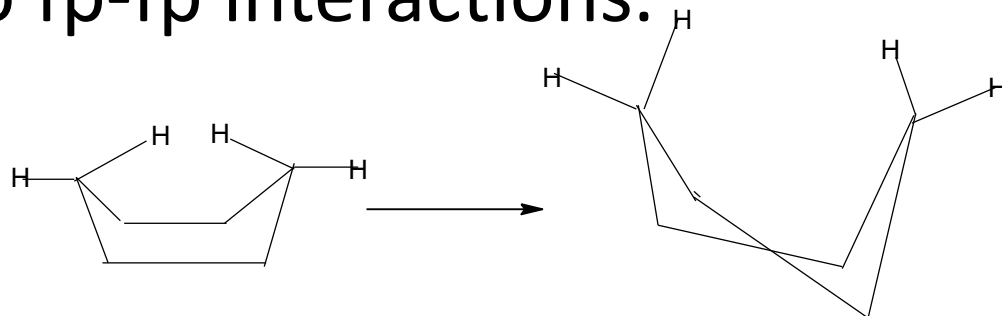
Types of Hydrogen atoms in Boat Conformation



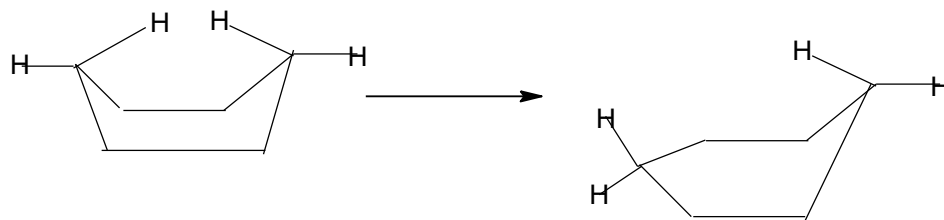
fp : Flag Pole, bs : Bow – sprit , qa : quasi axial, qe : quasi eqautorial

Twist Boat and Half Chair Conformations

- **Twist Boat** : Twisting of the boat results in release in steric strain due to fp-fp interactions.



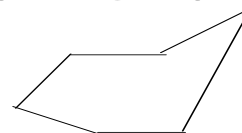
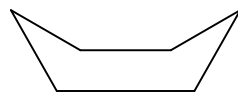
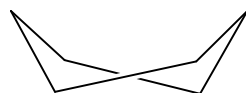
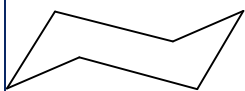
- **Half Chair Conformation** : If C_1 or C_4 of chair conformation is brought in the average plane of the ring, the resulting conformation is known as Half chair conformation



Stability of Conformations of Cyclohexane

- Decreasing Order of Stability

Chair > Twist Boat > Boat > Half Chair



Explanation

Stability

Factors contribute to instability of conformations

1. Bond distortion strain
2. Charge repulsion strain
3. Bond opposition strain
4. Steric strain

In cyclohexane due to ring puckering and uncharged nature bond opposition and charge repulsion strain are irrelevant.

Bond opposition and steric strain contribute to internal strain in CH.

Different conformations of CH differ in internal strain and hence in PE content.

1. chair conformation: Bond opposition and steric strain are minimum.

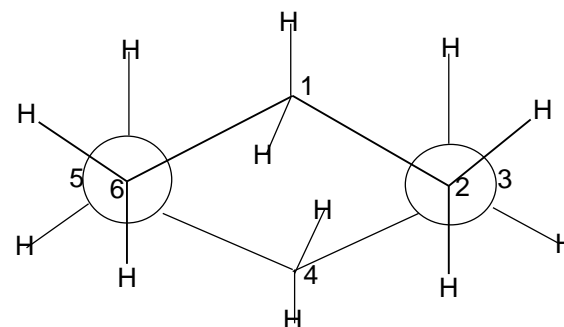
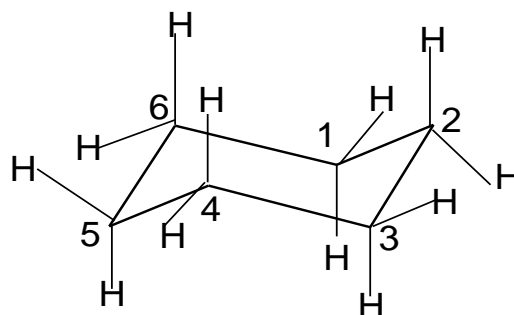
a) C-H bonds are perfectly staggered

∴ Bond opposition strain is minimum.

b) 'H' atoms on adjacent carbon atoms have enough space for their accommodation.

(Sum of van der Waal's is 2.5\AA° , where as 'a' and 'e' H atoms on adjacent C atoms are separated by 2.3° .)

∴ Steric strain is minimum.



Therefore PE content of chair conformation is minimum.

Hence it is most stable.

- **Boat Conformation:** suffers from two strains

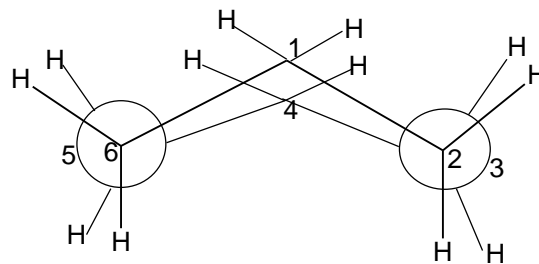
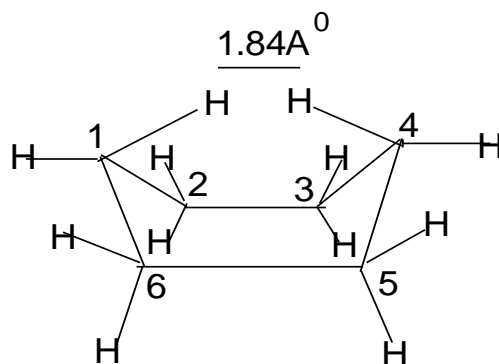
1. Bond opposition strain: C-H bonds on the sides are eclipsed.

2. Fp – Fp interaction: Distance between two Fp Hs is 1.84\AA

Distance required is 2.5\AA

These two strains make boat conformation highly strained.

It has 29.71kJ/mol more energy than chair conformation.



Therefore boat conformation is less stable than chair conformation.

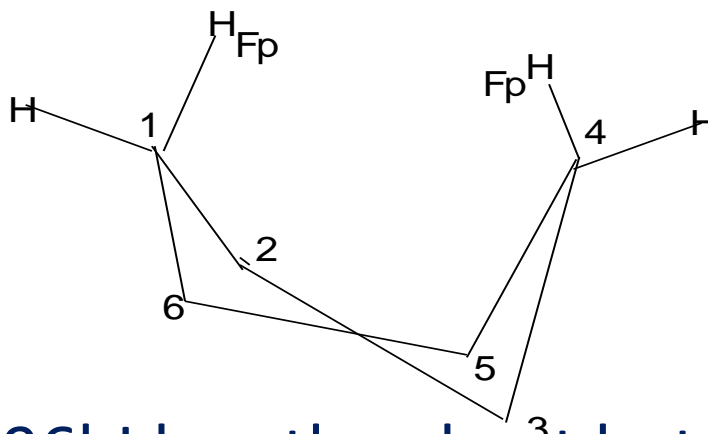
Thermodynamic calculations : 0.1 to 0.2 % boat form i.e. 1 or 2 molecules per thousand.

Twist or Skew boat Conformation:

Less torsional strain as compared to boat conformation.

Flag pole Hs are away from each other.

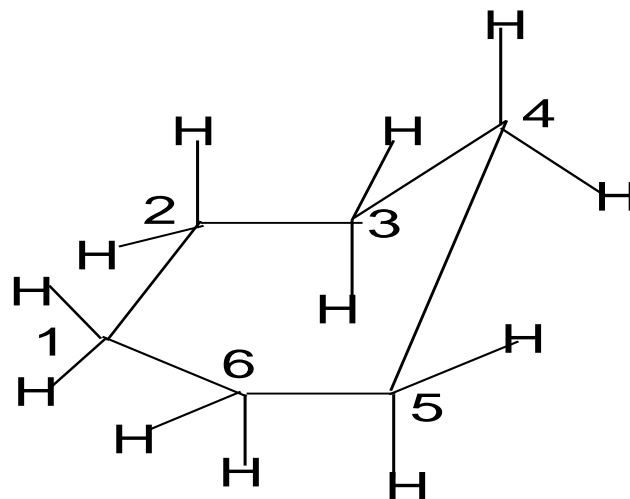
C2, C3, C5 and C6 become non-planer.



Energy content : 6.696kJ less than boat but 23.02kJ more than chair.

Therefore more stable boat but less stable than chair.

- **Half chair conformation:** Suffers from angle strain

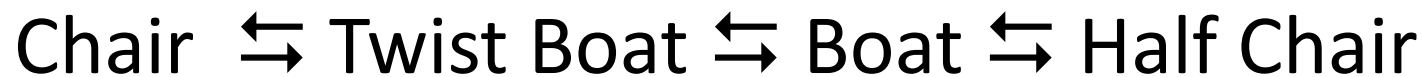


It has 46.04kJ more energy than chair conformation. Maximum energy content than any other conformation. There it is least stable.

- Isolation of any conformation of CH is not possible because :

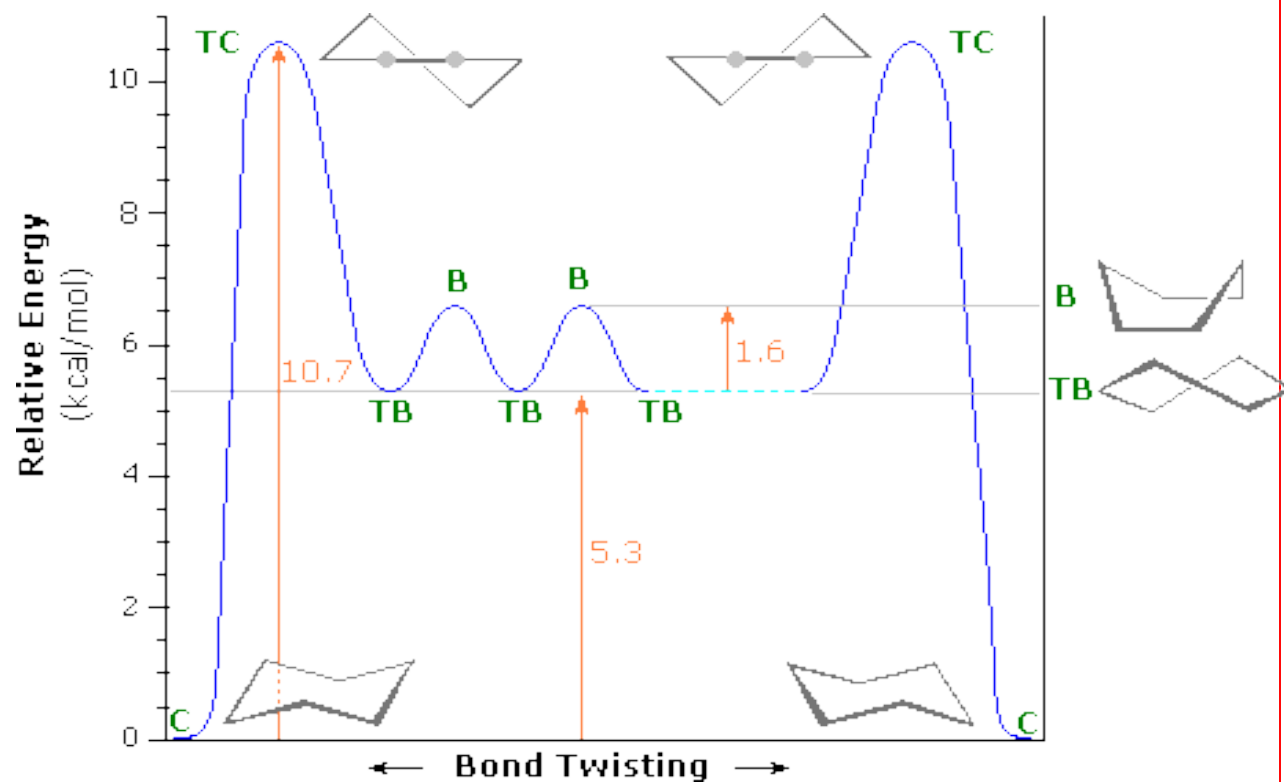
At RT the average energy content of CH is more than sufficient to overcome this small barrier.

There exists a dynamic equilibrium between different conformations of CH.



Energy Profile diagram

- Boat 29.7kJ/mol
- TB : 23.02kJ/mol
- HC: 46.04kJ/mol



Locking of Conformation

- In substituted cyclohexane small substituent may acquire either axial or equatorial position.

e.g.

But with increase in size of the substituent 1,3-diaxial interactions become very severe increasing internal PE. Thereby stability is decreased.

Very large substituents like t-butyl prefer to lie in equatorial position only to avoid 1,3 – diaxial interactions

The existence in only one conformation is termed as locking of conformation.