Successfulness of Baeyer's angle strain theory

- Baeyer rightly proposed that **cyclopropane and cyclobutane**are flat molecule and having angle of **60° and 90°** those are much deviated from the **ideal tetrahedral value of 109.5°** hence these ring systems are **unstable and easily undergo ring opening reactions**. There is much angle strain in cyclopropane and cyclobutane.
- Baeyer also proposed that **cyclopentane** is not need to be planar but it is **planar** as in that condition the angle is much near to ideal tetrahedral angle

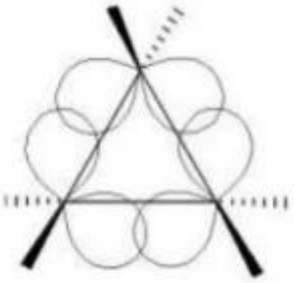
Unsuccessfulness of Baeyer's angle strain theory

- Baeyer was not able to explain the effect of angle strain in larger ring systems.
- According to Baeyer **cyclopentane should be much stable than cyclohexane but practically it is reversed**.
- **Larger ring systems are not possible** according to Baeyer as they have negative strain but **they exist and much stable**.
- Larger ring systems **are not planar** but puckered to eliminate angle strain.

Coulson-Moffitt Model or Concept of Maximum Overlap of Carbon Orbitals (Bent bond/Banana bond Theory)

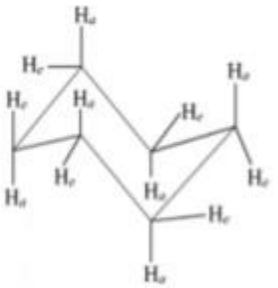
- A bent bond, also known as a banana bond, is a type of covalent chemical bond with geometry somewhat indicative of a banana.
- The term itself is a general representation of electron density or configuration resembling a similar "bent" structure within small ring molecules, such as cyclopropane (C_3H_6) or as a representation of double or triple bonds within a compound that is an alternative to the sigma and pi bond model.

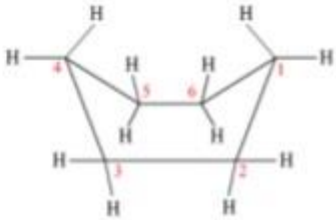
Types of overlaps



Sachse-Mohr Theory (Theory of Strainless Rings)

Sachse Mohr's theory proposed that higher member ring can become free from strain if all the ring carbons are not forced into one plane. They exhibit in two non-planar 'folded' or 'puckered' conformations both of which are completely free from strain. These are strainless as the carbon atoms lie in different planes and the normal valency angle (109.5°) is retained. These are called the '**Chair' Form or the 'Z' Form** and the '**Boat' Form or the 'C' Form** because of their shapes.





The chair conformation is the most stable conformation of cyclohexane.

Conformational analysis

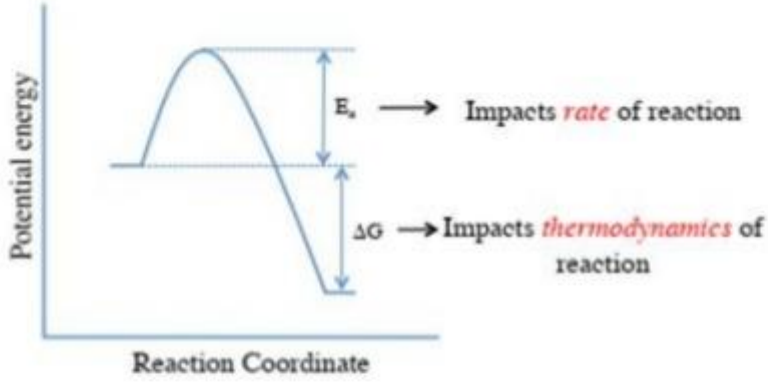
The various arrangements in space that is available for a molecule by rotation about single bond its conformation. There are in principle an infinite number of conformations, but a molecule will adopt a geometry that minimises total energy; this minimum energy is given by

$$\text{Esteric} = E(r) + E(q) + E(f) + E(d))$$

Where, E(r) = stretching energy, E(q) = strain energy, E(f) = torsion energy, E(d) = non-bonding interactions.

The investigation of various conformations of a molecule and their stabilities is known as conformational analysis.

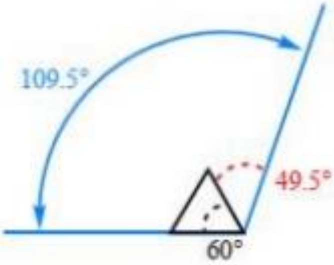
Understanding the differences in energy with conformational analysis allows prediction of relative rates of compounds.

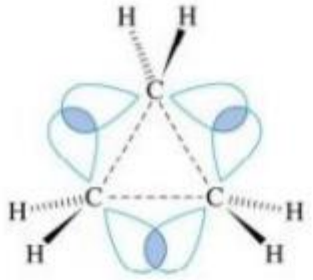


Conformation of Cyclopropane:

In cyclopropane, the three carbon atoms lie in a plane. All C-C bond lengths are same and three carbons form an equilateral triangle. The hybridization at each carbon atom is Sp^3.

The bonding electrons principally lie outside the triangular internuclear line resulting in bent bonds. There are three strained bonds and six eclipsed hydrogens.

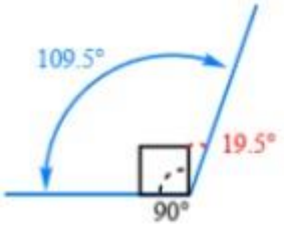


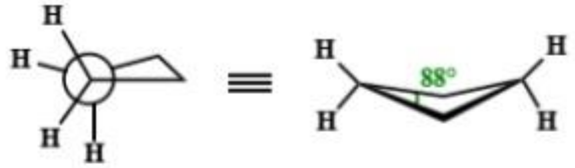


Newmann projection of cyclopropane.

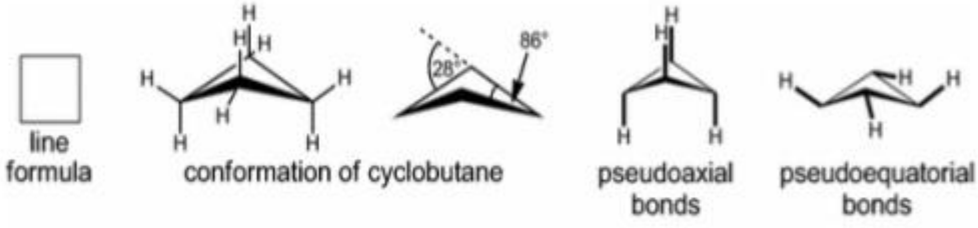
Conformation of Cyclobutane:

Cyclobutane has internuclear angle of 90o. There are four strained bonds and eight eclipsed hydrogens.

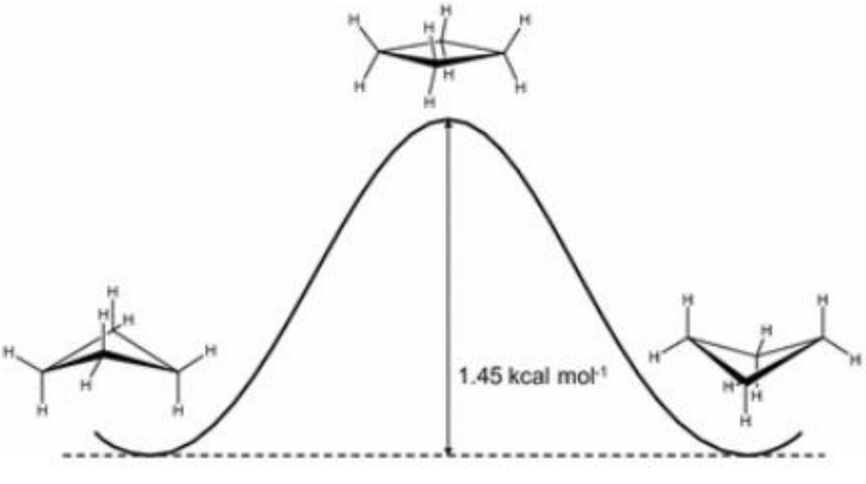




Cyclobutane is not planar but puckered i.e. one $-CH_2-$ group bent at an angle of about 25°. The molecule flips from one puckered conformation to other.



Due to bent at angle of about 25° from plane of three ring carbons there will be reduction in the eclipsed hydrogen interaction and compensate for the increase in bond angle strain.



Conformation of Cyclopentane:

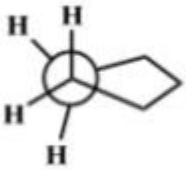
If the structure of cyclopentane is planar, the C-C-C bond angle will be 108° which is so close to normal tetrahedral bond angle of 109°.28' that is no significant strain effect would be expected.

However, in such structure all of the hydrogens are completely eclipsed and it would have considerable torsion strain resulting from ten H---H eclipsing interactions.

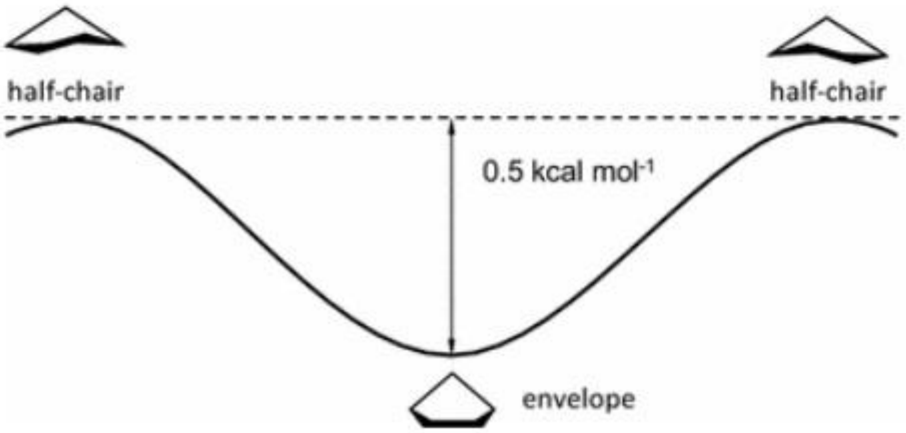
Planar
All C-atoms in one plane

Envelope
Four C-atoms in one plane

Half-chair
Three C-atoms in one plane

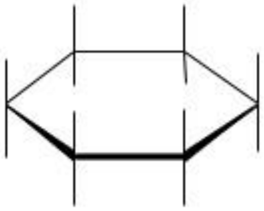


Torsional strain is reduced by moving one or two carbon away from the plane. This results in an increase in angular strain. Carbon atoms move in and out of the plane rapidly, resulting in an illusion of rotation of the molecule. This phenomenon is termed as **pseudo-rotation**. The actual structure is of open envelope shape. In which four carbon atoms lie in plane and one above or below it.



Conformation of Cyclohexane:

A planar structure of cyclohexane is clearly improbable. The bond angle would be 120° i.e. 10.5° larger than the ideal tetrahedral angle. Also every C-C bond in such structure would be eclipsed. The resulting angle and eclipsing strain would severely destabilize this structure.



Planar

E_{rel} = Very large

If two carbon atoms on opposite side of six member ring are lifted out of the plane, much of the angle strain can be eliminated. It can form Chair conformation or Boat conformation.

In 1950, interconversion of chair conformation and the different orientation bond was elucidated by D. H. R. Barton.

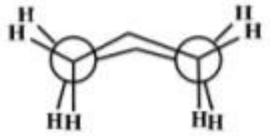
Chair conformation:

It is non planar puckered conformation. All bonds are fully staggered therefore Pitzer strain is minimized. The bond angles are not exactly 109°.28' but 111°. Relative energy is zero (four carbons are planar, one puckered up and one puckered down)

Cyclohexane forms a number of different conformers. However, structure other than the chair conformation suffers torsional strain, angular strain or both.

Boat Conformation:

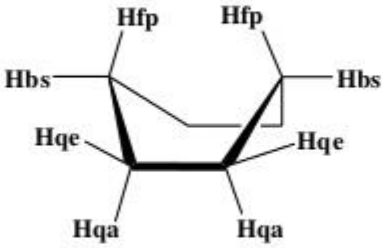
Even though boat conformation is free from angular strain. However, in addition to the torsional strain resulting from 4 H---H eclipsing interactions, it also has a flagpole interaction between the hydrogen atoms on 1- and 4-carbon atoms. Hence, it has higher energy than chair conformation of about 25 KJ/mol or 6.0 Kcal/mol.



The eclipsing interaction can be relieved by slightly twisting two C-C bonds resulting in new conformation called twist boat conformation.

In boat conformation there are four types of hydrogens

1. Flag pole hydrogen – 2 Nos (**Hfp**)
2. Bow spirit hydrogen – 2 Nos (**Hbs**)
3. Quasi axial hydrogen – 4 Nos (**Hqa**)
4. Quasi equatorial hydrogen – 4 Nos (**Hqe**)



Twist Conformation:

It is more stable than the boat conformation, but less stable than than chair conformation. The flagpole interactions and torsional strain in the boat conformation are reduced in the twist conformer.

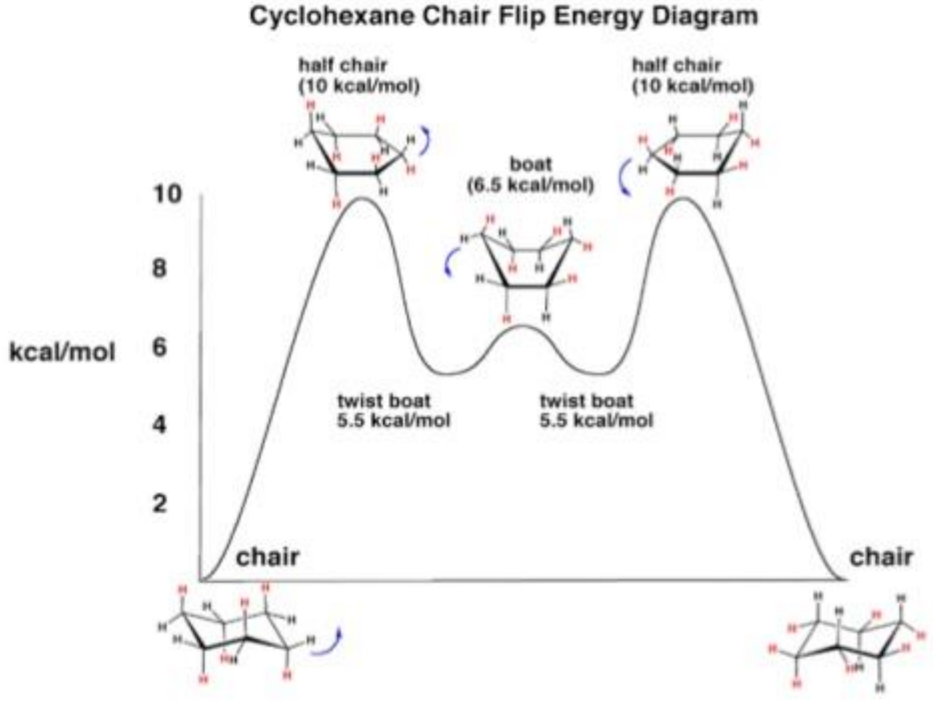
The twist boat has energy of about 21 KJ/mol or 5.5 Kcal/mol which is lower than boat conformer.

Half chair conformation:

It is a transition state conformation. The half chair conformer lies about 43 KJ/mol or 10 Kcal/mol above chair conformation. It has five carbons lie in plane and one puckered out of plane.

Stability order of cyclohexane conformers:

Chair > Twist boat > Boat > Half chair

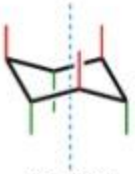


On careful examination of cyclohexane we find that the twelve hydrogens are not structurally equivalent.

Equatorial Bonds: These are three sets of two parallel bonds, each of which are parallel to two of the bonds in the ring. Equatorial bonds alternate from slightly up to slightly down orientation on moving from one carbon to the next.

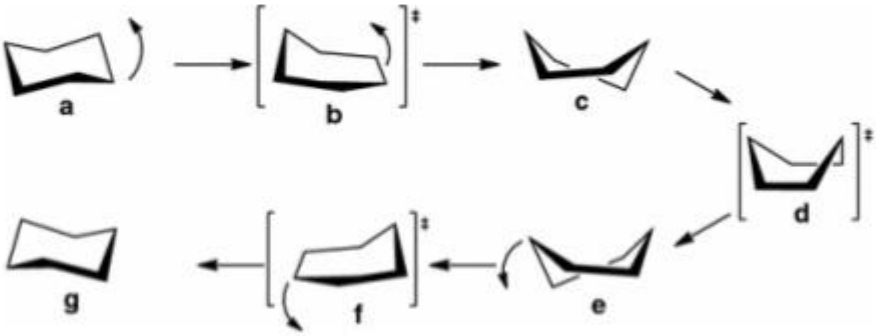
Equatorial Bonds

Axial Bonds: They are parallel to each other and to the principal axis, but perpendicular to the average plane of the ring. There are three bonds facing up and three facing down.

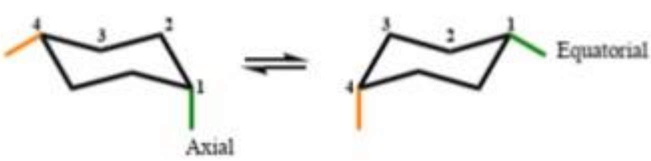


Axial Bonds

An inversion of a cyclohexane chair involves all of the conformations of cyclohexane. Starting with a chair conformation **a**, cyclohexane first passes through a "half-chair" conformation **b**. The half-chair, as expected, has a very high energy and is only a transition state, which gives rise to the actual conformation—twist-boat **c**. Next, the twist-boat conformation flips into the alternative twist-boat conformation **e**. The transition state for this flip is the boat conformation **d**. Then, the cyclohexane molecule passes through another half-chair transition state **f** (mirror image of the first one) and finally arrives at the alternative chair conformation **g**. At room temperature cyclohexane interconvert from one chair form to another referred to as ring inversion or ring flipping.



Axial and equatorial bonds also undergo interconversion, when a chair conformation flips to the other. However, their relative orientations in space do not change.

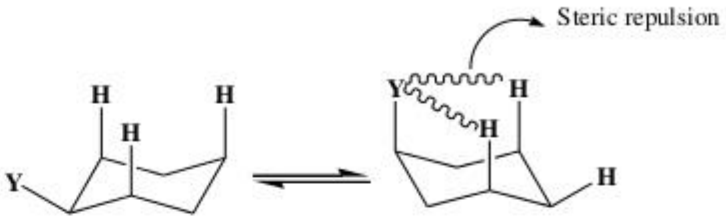


Since two equilibrium chairs are in rapid equilibrium all twelve hydrogen have 50% equatorial and 50% axial character.

Conformations of substituted cyclohexanes:

Monosubstituted cyclohexanes:

The axial and equatorial positions have different spatial orientations. In chair-chair interconversion, substituent's moves from equatorial to axial and vice versa. Bigger substituent's has more steric interaction in an axial position than in equatorial. Hence, the chair conformation which has the larger group on equatorial is more stable.



Y = equitorial

Y = axial

When larger group occupies the axial position there is a steric repulsion between the substituent and the axial hydrogens which are three carbons away. These repulsive effects are called 1, 3 –diaxial interactions. It destabilizes the axial conformer about 1.8 Kcal/mol compared to equatorial conformer.

1, 3 –diaxial interactions is approximately equivalent to one gauche butane interaction of 0.9 Kcal/mol. Since in axial methyl cyclohexane two gauche butane type of interaction between axial methyl and two ring C-C bond destabilizes the axial conformer while such interactions does not exists when methyl group is in equatorial.