STEREOCHEMISTRY OF CYCLIC COMPOUNDS

Monocyclic ring compounds are classified into four categories according to the number of carbon atoms in the ring:

(a) Small rings: comprising 3 or 4 atoms (i.e. 3 or 4 membered ring);

(b) Normal or common rings: comprising 5 to 7 atoms (i.e. 5 to 7 membered ring);

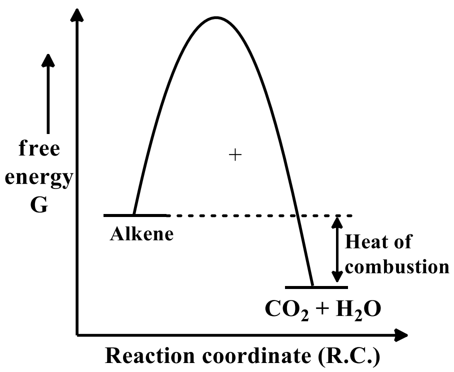
(c) Medium rings: comprising 8 to 11 atoms (i.e. 8 to 11 membered ring);

(d) Large rings: with more than 11 atoms. (i.e. more than 11 membered ring.)

Strain of a molecule affects the chemical stability and the chemical stability may be measured in various ways—

(i) by heat of formation (ii) heat of combustion, (iii) dipole moment measurement (iv) absorption spectra etc.

One of the most convenient method to work with in respect to hydrocarbon is the heat of combustion. This gives a measure of thermodynamic stability and is the total strain.



As we have with increasing thermochemical stability the heat of combustion value decreases. Experimentally it has been found that the heat of combustion value gradually decreases up to six membered ring i.e. stability increases. But heat of combustion value increases from 7 to 11 membered ring (stability decreases) and from the twelve –membered onwards attains the stability similar to six membered ring.

There are different types of strains in cycloalkanes are as follows —

1. Baeyer Strain or angle strain:

The ideal angles of sp3, sp2 and sp hybrid C-atoms are $109^0 28'$, 120^0 and 180^0 respectively. But due to geometrical requirements of some cyclic molecules or due to van der Waals' repulsive force among nonbonded atoms or groups, the bond angles in some molecules are deviated from their normal angles. This distortion of bond angle develops a strain which is called Baeyer strain or angle strain.

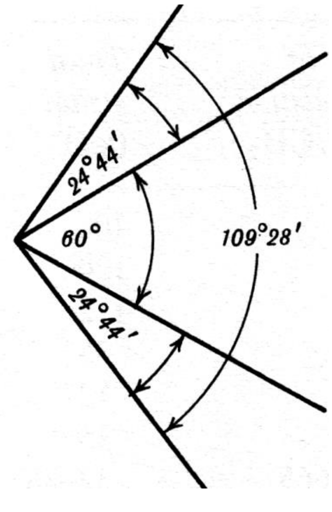
The magnitude of angle strain increases with increase in deviation of the bond angle from normal value.

Thus the Baeyer strain is a consequence of deforming bond angles from their optimal tetrahedral value of about $109^0 28'$

Baeyer assumed that ring forming atoms are arranged in a coplanar regular poygonal fashion (accepting the Kekule model, benzene like) with a bond angle same as the internal angle of the polygon. So the bond angle deviates from normal valence angle. The distortion in bond angle is the angular deviation of the bond from its normal angular orientation and is given as

Distortion, D =½ [normal valence angle — true bond angle of regular polygon].

Larger the value of angular distortion (D), greater is the destabilising strain in the molecule. This type of strain arising due to distortion in bond angle is known as **Baeyer strain or angle strain**.



According to Baeyer, five and six membered rings form most readily and are the most stable because they involve the least Baeyer strain (or less distortion) from the normal valency angle.

If all the rings are assumed to be planar, the distortions for each ring-size can be readily calculated,

In cyclopropane the planar geometrical angle is 60^0 (for regular triangle)

The distortion will be (D) = $\frac{1}{2}[109^0 28' — 60^0) = + 24^0 44'$

The distortion of the bond angle has been assumed to be equally shared between the two bonds.

In cyclohexane, the distortion is (D) = $\frac{1}{2}[109^0 28' — 120^0) = - 5^0 16'$

Thus the angle strain of cyclopropane is higher than that of cyclohexane.

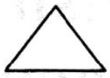
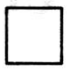
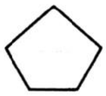
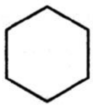
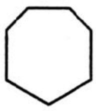
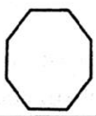
Q 1.24. What are the limitations of Baeyer's strain theory? 2 **C.U. 2000**

<u>Ans</u>: (i) Baeyer's strain theory is based on a mechanical concept of valency and on the assumption that all the rings are planar, which is incorrect. For example: cyclopentane ring remains in puckered envelope form, cyclohexene ring also remains in non planar chair form. Baeyer ignored the tetrahedral model founded by Le Bel and van't Hoff.
(ii) Quantum mechanical calculations do not permit very large distortions of band angles.

Q 1.61. Discuss the relative stability of cyclopropane and cyclohexane in the light of Baeyer Strain theory. 2 **C.U. 2014**

Ans: Baeyer assumed the planar structure of the ring compounds and the amount of strain is proportional to the angular distortion which would be half the difference between the tetrahedral angle ($109^0 28'$) and the internal angle of a regular polygon.
Angular distortion or angle strain, D =½ [$109^0 28'$) — internal angle of regular polygon].
According to the theory,
The angle strain or angular distortion for cyclopropane = ½[$109^0 28'$ — 60^0) = + $24^0 44'$
The angle strain or angular distortion for cyclohexane = ½[$109^0 28'$ — 120^0) = - $5^0 16'$

From the above angle strain comparison of the two, indicates cyclopropane is highly strained and thus much less stable compared to cyclohexane.

Cycloalkane	Proposed polygonal geometry	Internal angle of the polygon (=180°-360°/n)	Proposed angle strain = 1/2 [109°28]-bond angle
cyclopropane		60°	+24°44′
cyclobutane		90°	+9°44′
cyclopentane		108°	+0°44′
cyclohexane		120°	–5°16′
cycloheptane		128°34′	–9°33′
cyclooctane		135°	–12°46′

The magnitude of angle strain is low for cyclopentane and cyclohexane. In all other polygonal arrangements of cycloalkanes the magnitude of angle strain is quite large.

The angle strain gradually increases with increase in the difference of the size of the polygon from regular pentagon. Thus, cyclopentane should be the most stable cycloalkane, but actually, the stability of cyclohexane is greater than cyclopentane. Further, large cycles are found to be even more stable than cyclohexane. This fact cannot be explained by only considering the Baeyer's strain with planar geometry of the cyclic molecules.

In fact, stable arrangements of cyclic frames of all alicycles except cyclopropane are nonplanar. The ring atoms are arranged in a nonpolar zigzag fashion with a tendency to maintain the normal valence angle. In the small cycles viz cyclopropane and cyclobutane, the normal valence angle cannot be maintained. The bond angles between the ring forming atoms are reduced due to the required geometry of three and four membered rings. In these rings, there arises a clear distortion in bond angle from the normal valence angle so that the angle strain becomes an important destabilising strain in these small rings.

In the larger cycles, the angle strain is relieved suubstantially, but other kinds of strains like torsional strain (Pitzer strain or bond opposition strain), nonbonded or van der Waals' interaction etc. become important contributors towards their stability. In some cases, these strains are alleviated to some extent at the cost of deviation of bond angles as well as compression or elongation of bonds.

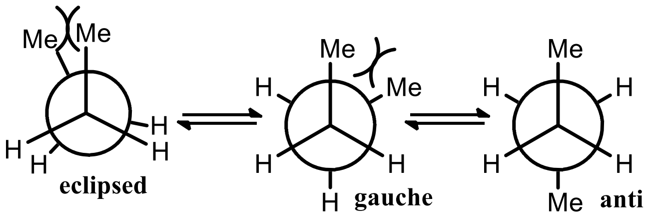
For example, to get relief from eclipsing strain and transannular strain, the bond angles in cyclononane and cyclodecane become as large as 124^0. Thus the net stability can be accounted theoretically not only by Baeyers' strain but also on the basis of all different types of strains.

2. **Torsional strain or bond opposition strain or Pitzer strain :**
Rotation around the bond in a molecule develops different conformations. In these conformations the bonding and nonbonding electrons on adjacent atoms repel each other in different magnitude depending on torsion angle.

The bond pair—bond pair repulsion along with the steric interaction between the substituents on adjacent atoms at a particular torsion angle develops a strain which is known as Pitzer strain or bond opposition strain or torsional strain.

For example, the potential energy of gauche conformer of n-butane (torsion angle = 60°) is greater than its anti form (torsion angle = 180°). Therefore, the torsional strain of gauche butane is greater than anti butane. The eclipsed conformation (torsion angle = 0°) suffers the torsional strain to the maximum extent.

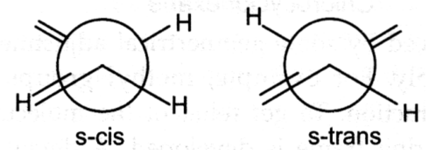
In eclipsed form, there is van der Waals' repulsion between two Me groups and C-C σ-bonded electron pair repulsion i.e. Pitzar strain is maximum. so it is least stable



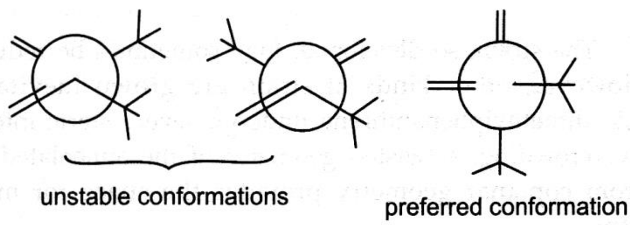
The anti form is most stable because it has no Pitzar strain as the two Me groups are in opposite direction and the bonded electron pairs are far apart

The eclipsing torisonal strain is also present in coplanar arrangement of cyclic ring compounds. Thus in cyclobutane and cyclopentane there is a great deal of bond opposition or torsional strain as these rings adopt nearly coplanar carbon skeleton.

When an apparently stable geometrical arrangement of a molecule suffers excessive torisonal strain, the geometry of the molecule may even change to get rid of the severe torsional strain. For example, the stable geometrical arrangements of buta-1,3-diene are s-cis and s-trans coplanar arrangements but the s-trans is more stable due to lack of Pitzar strain.



But 2,3-ditert-butylbuta-1,3-diene suffers severe torisonal strain in either of s-cis and s-trans conformations due to presence of bulky Me_3C— group. The ethylenic carbon atoms remain in nonplanar arrangement to get rid of this torsional strain although the resonance stabilisation is sacrificed.



I-Strain (Internal Strain): I-Strain is the strain usually in the cyclic molecules due to its specific geometry. This includes angle strain, bond opposition strain, strain due to nonbonded interaction etc.

CYCLOHEXANE

The planar geometry of cyclohexane is very unstable due to angle strain (Baeyer strain) and large torsional strain (Pitzer strain). The cyclohexane has two puckered (nonplanar) forms which are free from Baeyer strain. These forms are named as **(i) Chair form and (ii) Boat form,** because of their similarities in physical appearances with chair and boat respectively.

The stable form of cyclohexane is the chair form, which is also called rigid form in the sense that it resists distortion.

Characteristics of the chair conformation:

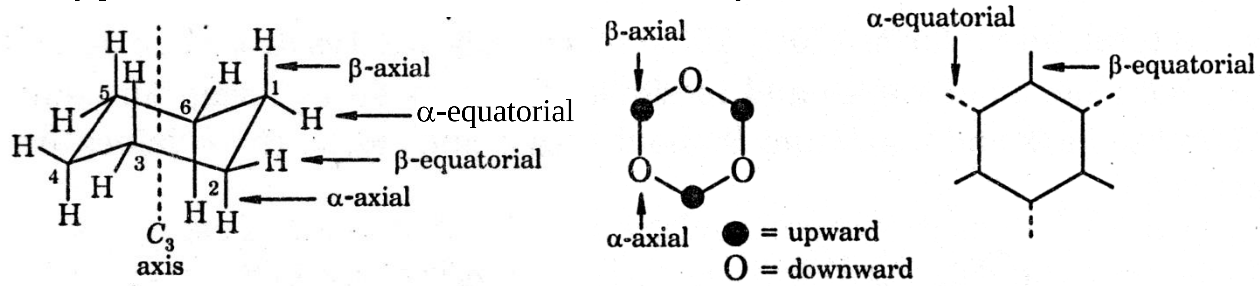
[A] Geometry:

1. C—C bond length = 0.1528 nm (152.8 pm) C—H bond length = 0.1119 nm (111.9 pm)

2. C—C—C bond angle = $111^0 05$ (instead of 109 °28′)

Dihedral angle = 56^0 (instead of 60^0)

The increased C—C—C bond angle makes the chair conformation slightly flattened so, that the dihedral angles between adjacent C—C bonds are 56° and the vertical C—H bonds (axial) are not exactly parallel to the C3 axis but lean outwards from it by 7^0.



3. The opposite sides of the chair are parallel,

C_1—C_2 bond is parallel to C_4—C_5 bond, C_2—C_3 bond is parallel to C_5—C_6 bond, C_3—C_4 bond is parallel to C_1—C_6 bond,

4. The C—H bonds are in a staggered arrangement

5. C_1, C_3, and C_5 atoms are up carbon atoms, they constitute upper plane and C_2, C_4, and C_6 atoms are down carbon atoms, they constitute down plane. The distance between these two planes are 0.05 nm.

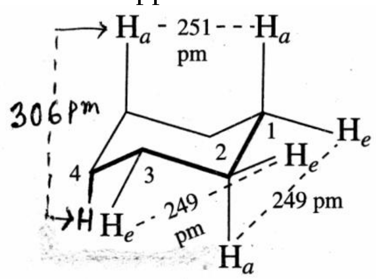
6. The chair form has two geometrically different sets of C-H bonds. In one set, six C-H bonds are parallel to the C_3 axis (principal axis) are called **axial bonds.** Three of these axial bonds are directed upward and the other three downward. Conventionally, upward bonds are called **'β'** bonds and downward bonds are '**α**' bonds. Axial bonds are, therefore may be β—axial or α—axial.

In the other set, the six C—H bonds make an angle of 109°28' with the perpendicular axis of the ring or ± 19°28' with the horizontal plane containing any three alternate carbon atoms of the ring. These are called equatorial bonds and are symbolised as 'e'. Like axial bonds, they are also classified as **α** and **β**, when projected downward and upward respectively.

The axial hydrogens - are homotopic relative to each other because they are interchangeable their positions by C_3 axis of symmetry. The same is true in case of equatorial hydrogens. However, the axial set of hydrogen atoms is diastereotopic with the equatorial set. These two sets are related neither by a symmetry axis (not homotopic), nor by symmetry plane (not enantiotopic).

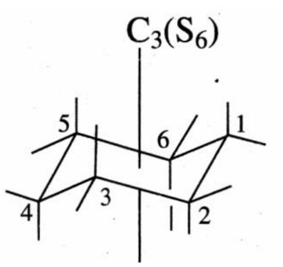
7. Strain: The chair form has no Baeyer's strain due to absence of angular distortion.

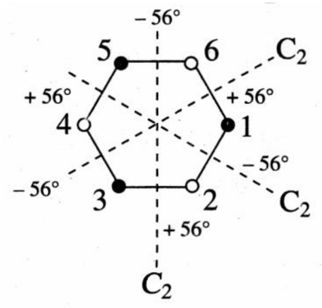
Torsional strain or bond opposition strain or pitzer starin nil.



The vander waal redii of two H atoms (120+120) =240 pm. But the distances between any two H-atoms are greater than twice the van der Waals radius of H atom. Therefore, there is no non- bonded (vander waal) interaction in chair form of cyclohexane.

[B] Symmetry:

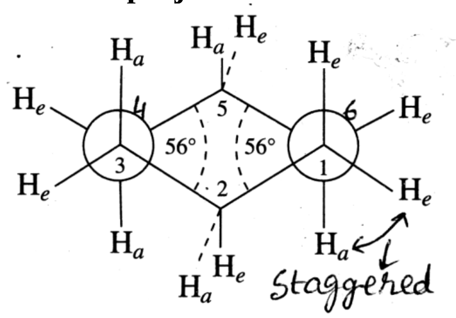


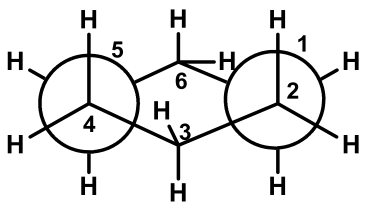


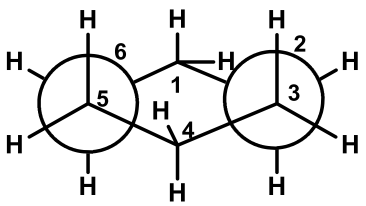
(i) Principal axis: C_3-axis passing through the centre of the ring.
(ii) $3C_2$-axis passing through the midpoint of the opposite bonds and perpendicular to the principal axis.
(iii) $3\sigma_v$ planes (more accurately σ_d), passing through diagonal carbon atoms, which intersect at C_3 and bisect the angles between the two C_2 axes. Each σ-plane contains four H atoms.
(iv) A centre of or inversion centre (i) is present at the centre of the ring. ($i \equiv S_2$).
(v) one S_6-axis coincident with the C_3 axis.
(v) Symmetry number =6
(vi) point group symmetry= D_{3d}

Q 1.4. What are the symmetry elements present in the chair form of cyclohexane? 4 **C.U. 1993**

Newman projection of chair form:



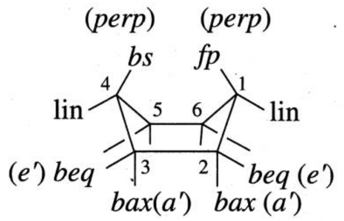




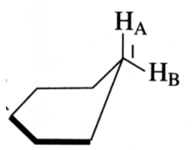
Interactions:
(i) Gauche butane interactions: In the above structure, two pairs of n-butane units (2-3-4-5 and 2-1-6-5) are seen in Newman projection with dihedral angle of 56° in each.
Any consegutive four carbon atoms form a gauche butane unit and since there are six such units (1-2-3-4, 2-3-4-5, 3-4-5-6 etc.), the enthalpy of cyclohexane chair may be computed as 3.3 x 6 or 19.8 kJ mol^{-1} with respect to a hypothetical all-anti chair conformation.
(ii) Syn diaxial interaction: In case of substituted cyclohexane, the interaction between 1e, 2e and 1e, 2a substituents is known as **1, 2-interaction**, while that between la, 3a is known as **1, 3-interaction or synaxial interaction.**

One significant difference between the two types of interactions is that while the le, 2e and le, 2a bonds are skewed, the la, 3a bonds are parallel. As a result, 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.

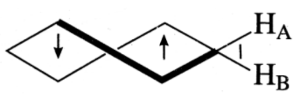
There are some other conformations of cyclohexane these are as follows—



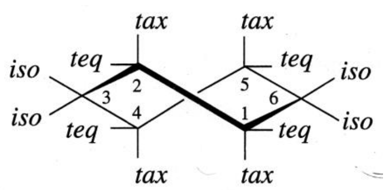
Boat conformation



half boat / envelope



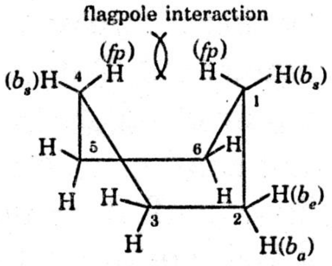
half-chair

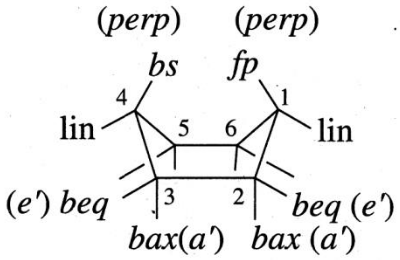


twist form

Some characteristic of boat conformations:

Another conformation of cyclohexane, which is free from angle strain, is boat form, usually represented in the form shown below—





1. In boat conformation, there are four types of C—H bonds. They are designated as flagpole (fp), bowsprit (bs), boat-equatorial (b_e or *beq*) and boat-axial (b_a or *bax*). Linear (lin)

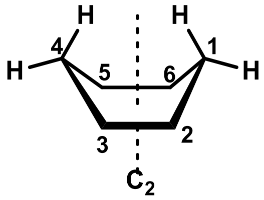
The distance between different C—H bonds in boat conformation is given below.

2a, 3a— 0.227 nm =227pm

2e, 3e— 0.227nm =227pm

1fp, 4bs.—183nm = 183pm

2. Symmetry elements in boat conformation:



(i) one C_2-axis passing through the centre of the ring, which is principal axis.

(ii) one σ_v passing through the $C_1$and C_4 carbon atom and perpendicular to the principal axis.

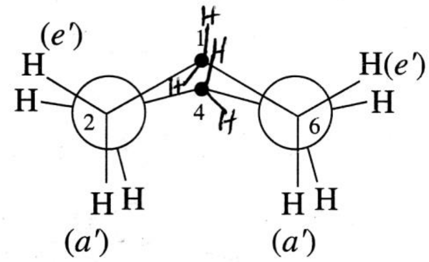
(iii) point group symmetry= C_2

(iv) Symmetry number = 2

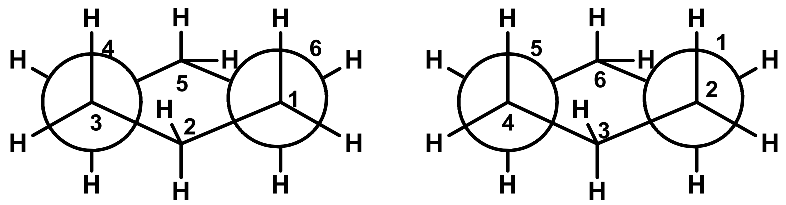
Q 1.26. Draw the chair and boat conformations of cyclohexane and show the symmetry elements possessed by them. 2 **C.U. 2001**

Q 1.40. What are the symmetry elements present in the boat form of cyclohexane ? 1 **C.U. 2008**

Newman projection of boat conformation:



Eclipsed butane interactions



gauche-butane interactions

Q 1.15. Draw boat conformation of cyclohexane in Newman projection. 1 **C.U. 1997**

Interactions:

Eclipsed butane interaction: C_1-C_2-C_3-C_4 and C_1-C_6-C_5-C_4 they make two eclipsed butane units, so there is two eclipsed butane interactions.

There is other four gauche butane interactions.

The distance between two H-atoms at C1 and C4 is 183 pm as a result there is severe non bonded interaction between these H-atoms this is known as **flagpole—bowsprit (fp—bs) (non bonded) interaction.**

Thus total enthalpy of boat form = 4g.b. int. + 2 e.b. int. + 1fp.-bs. Int.

= 4x3.3 + 2(18-26) + fp—bs

=(49.2 KJ/mole + fp-bs) to (65.2 KJ/mole + fp-bs)