

STABILITY OF CYCLOALKANES

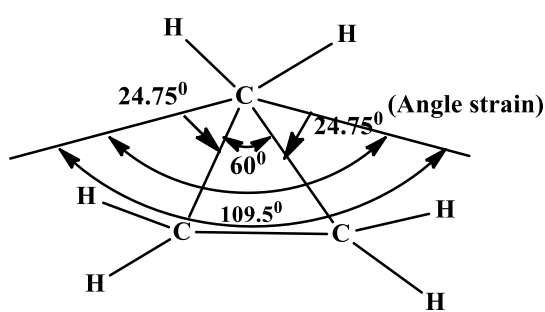
1. Baeyer's strain theory

- In 1885, Adolf Von Baeyer proposed a theory to explain the relative stability of the first few cycloalkanes. This theory named after him, accounted for the act of opening of cyclopropane and cyclobutane rings as also the stability of the cyclopentane ring.
- Van't Hoff & Lebel proposed tetrahedral geometry of carbon, the bond angle is of $109^{\circ}28'$ (or 109.5°) for carbon atom in tetrahedral geometry (methane molecule).
- Baeyer observed different bond angles for different cycloalkanes and also observed some different properties and stabilities. On this basis, he proposed angle strain theory. The theory explain reactivity and stability of cycloalkanes.

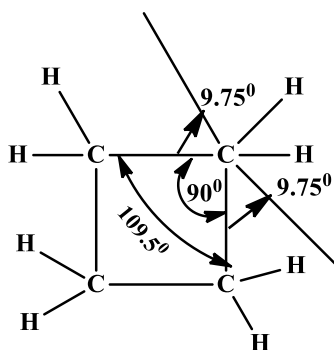
Baeyer's strain theory postulated that:

1. The carbons atoms constituting a ring lie in a same plane. Consequently, the bond angles between adjacent carbon atoms in a ring are no longer equal to the tetrahedral angle, i.e 109.5° . The deviation or distortion (straining or twisting) from the normal tetrahedral angle varies with the size of the ring.
 2. The deviation or distortion from the normal tetrahedral angle causes a strain and hence instability in the resultant molecule.
 3. The greater the distortion from the normal tetrahedral angle during the formation of the ring, greater the strain is also the constituents instability of the ring.
 4. More stable ring system is, more easily it is formed.
- The distortion in a C-C-C angle is in different ring systems (this distortion is often referred to as **Angle strain**) can be calculated as following: **in the cyclopropane ring,**
 - In the cyclopropane ring , each carbon occupy the corner of an equilateral triangle so that the C-C-C angle is 60° . This means that the angle strain in the cyclopropane = $\frac{1}{2} (109.5 - 60^{\circ})$

$$= 24.75$$



Angle strain in Cyclopropane



The C-C-C in cyclobutane is 90° as each carbon is situated at the corner of the square.

Therefore, the angle of strain in cyclobutane = $\frac{1}{2} (109.5^{\circ} - 90^{\circ}) = 9.75^{\circ}$.

The internal bond angle of an alicyclic compound can be calculated by,


By applying Formula

$$\text{Internal bond Angle} = \frac{180(n-2)}{n}$$

where n= no. of carbon atoms

eg. Cyclobutane = $\frac{180(2)}{4} = 90^{\circ}$

The relevant angle of strain for the various ring system

Angle strain	
Cyclopentane 	$\frac{1}{2} (109.5^{\circ} - 108^{\circ})$ $= \frac{1}{2}(1.5^{\circ}) = 0.75^{\circ}$
Cyclohexane (6)	$\frac{1}{2} (109.5^{\circ} - 120^{\circ})$ $= -5.25^{\circ}$
Cycloheptane (7)	$\frac{1}{2} (109.5^{\circ} - 128.58^{\circ}) = -9.54^{\circ}$
Cyclooctane (8)	$\frac{1}{2} (109.5^{\circ} - 135^{\circ})$ $= -12.62^{\circ}$

The magnitude of the distortion and not sign measures the strain in the molecules.

As five and six member rings involve the least distortion in their angle. They should be relatively the most stable ring system further, the fact that rings containing seven or more carbon atoms were unknown at that time was also taken into consideration by Baeyer's to be evidence in support of this theory.

Note: Angle strain:

Baeyer's assumed that all cycloalkanes are planar and thus calculate the angles through which each of the valence bonds was deflected from the normal direction in the formation of the rings. This is called angle strain.

- According to Bayer the relative order of stability for some common Cycloalkane > cyclohexane
Cyclopentane > cyclohexane > cyclobutane > cyclopropane

Actual observed order of stability for these cycloalkanes:

Cyclohexane > cyclopentane > cyclobutane > cyclopropane

According to Baeyer's the bond angle in cyclopentane is 108° (geometry is pentagonal) that is very close to tetrahedral angle (109.5°), so it is almost free from ring strain.

2. In conclusion, Baeyer proposed that ring system smaller or larger than cyclopentane and cyclohexane are unstable to higher ring strain. Therefore, he assumed that cyclopropane and cyclobutane easily undergo ring opening reaction whereas longer or larger ring system are difficult to synthesis.

(Angle strain): Which determine the stability of the ring.

Limitations:

1. Baeyer was not able to explain the effect of angle strain in the larger ring systems.
2. According to Baeyer cyclopentane should be much stable than cyclohexane but practically it is reverse.
3. Larger ring systems are not planar/but puckered to eliminate angle strain.
4. Larger ring systems are not possible according to Baeyer as they have negative strain but they exist and are much stable.
5. A C=C bond is known to be formed easily (By dehydrogenation of alkyl halides or dehydration of alcohols), although it should be difficult to form on the basis of Baeyer's strain theory.

Coulson and Moffitt's modification in Cyclopropane:

Cyclopropane has a triangular planar structure due to which, the bond angle between carbon-carbon bonds is expected to be 60° . This is far less than the thermodynamically stable angle of 109.5° as per the sp^3 hybridisation of the carbon atoms. Due to this there is a considerable amount of ring strain in the cyclopropane molecule.

In addition to this angular strain, cyclopropane also suffers additional torsional strain.

The torsional strain is due to the co-planar arrangement of the carbon atoms which leads to the eclipsed arrangement of the -CH bonds.

Important characteristics of Cyclopropane rings are –

- A) C-C bonds are shorter than in alkanes (1.54 Å)

$$(1.51 \text{ \AA} < 1.54 \text{ \AA})$$

- B) H-C-H angle is opened up to 115° vs 106° in propane.

- C) -C-H bonds are more acidic $pK_a = 46$ vs 51 of propane.

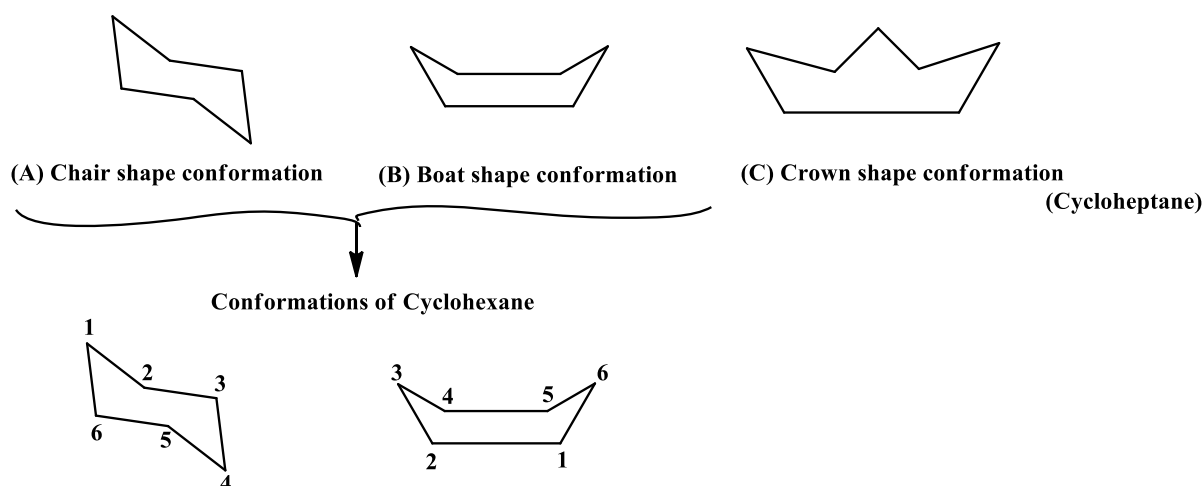
- D) Strain energy = 27.5 kcal/mol.

- E) The C-C bond strength in cyclopropane is considerably weaker (65 kcal/mole) than for a typical C-C bond (80-85 kcal/mole).

It has been suggested that significant rehybridisation occurs in cyclopropanes and bonding between carbon centres occurs in terms of “bent” bond (**Coulson and Moffitt’s Model**) where in the C-C bonds are bent outwards so that the inter orbit angle is 104° which consequently reduces the level of bond strain. So it is intermediate between sigma & π bonding. These bonds are also sometimes called “**Banana bonds**”. Hence, the C-C bonds have more p-character than normal while C-H bonds have more s-characters. Hence, the ring strain weakens the C-C bonds of the cyclopropane rings. Therefore, cyclopropane is much more reactive than alkanes or other higher ring systems.

Sachse Mohr’s theory of strainless rings:

According to this theory, “the carbon atom in five membered and smaller rings can lie in a single plane as postulated by Baeyer, but in six membered and larger rings they lie in different planes. Therefore, the angle strain calculated for each rings by Baeyer on the basis of their planarity is not correct. A ring with 6 or more Carbon atoms can assumed “puckered “ arrangement, so that there is little distortion of the normal tetrahedral angles and there is a negligible angle strain in the molecule. The two puckered forms of cyclohexane. These two puckered forms can be interconverted by just rotation about single bonds or truly the conformation of cyclohexane. Similarly, rings larger than six member can also have almost negligible angle strain by using puckered conformation.



- In the boat form carbon 1,2,4,5 lie in same plane and carbon 3 and 6 above the plane.
- In the chair form carbon 2,3,6,5 lie in same plane and carbon 1 above the plane and 4 below the plane.