

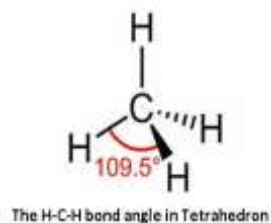
Unit V: Cycloalkanes	
<b>A</b>	Stabilities – Baeyer's strain theory, limitation of Baeyer's strain theory, Coulson and Moffitt's modification, Sachse Mohr's theory (Theory of strainless rings).
<b>B</b>	General Method of Preparation and Reactions of: Cyclopropane and Cyclobutane
	Reference: 1. Arun Bhal. A Text Book of Organic Chemistry, 22 <sup>nd</sup> Edition Page no: 618 2. P L Soni. Text Book of Organic Chemistry, 29 <sup>th</sup> Edition Page no: 2.58 & 2.477

### Baeyer's Strain Theory

**Baeyer's theory is based upon some assumptions that are helpful to understand instability of cycloalkane ring systems.**

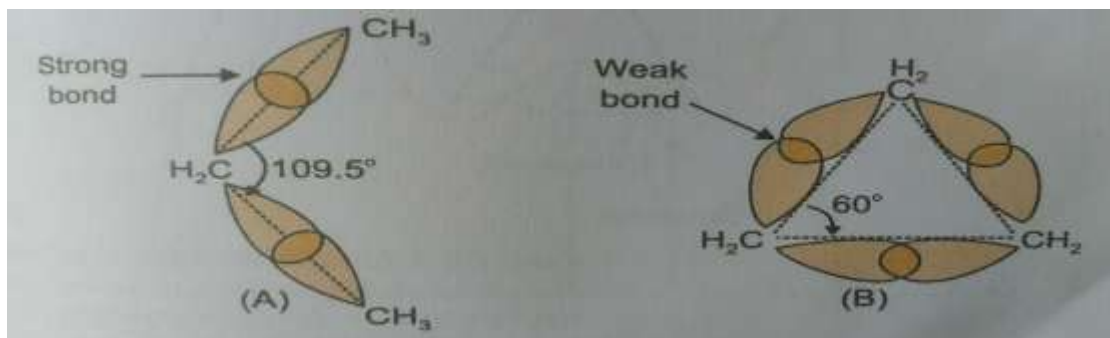
1. All ring systems are planar. Deviation from normal tetrahedral angles results in to instable cycloalkanes.
2. The large ring systems involve negative strain hence do not exists.
3. The bond angles in cyclohexane and higher cycloalkanes (cycloheptane, cyclooctane, cyclononane, etc.) are not larger than  $109.5^\circ$  because the carbon rings of those compounds are not planar (flat).

Adolf Baeyer (1885). Proposed a theory to explain the relative stability of the first few cycloalkanes on the fact that the normal angle between any pair of bonds of carbon atom is  $109^\circ 28'$  (or  $109.5^\circ$ ) in tetrahedral geometry (methane molecule).



**Baeyer** postulated that any deviation of bond angles from the normal tetrahedral value would impose a condition of internal strain on the ring. This is called Angle Strain, which determined the stability of the ring.

Baeyer proposed that the optimum overlap of atomic orbitals is achieved for bond angle of  $109.5^\circ$  (for carbon atom, in a molecule if it is  $sp^3$  hybridized and orbital overlap is maximum). In short, it is ideal bond angle for alkane compounds that produces maximum bond strength and stable molecule.



**Fig.1: Orbital overlap between (A) Propane (B) Cyclopropane. Maximum overlap occurs in propane**

For an open chain compound (propane), when carbon is connected to other two carbon atoms, it is  $sp^3$  hybridized and utilize these hybrid orbitals to form the bonds (strong sigma bonds)(Fig.1). In cyclopropane, the carbon atom don't use these hybrid orbitals to form the bonds hence, the bond (bent bond) is weaker as compare to usual carbon-carbon bond. This is described as Angle Strain.

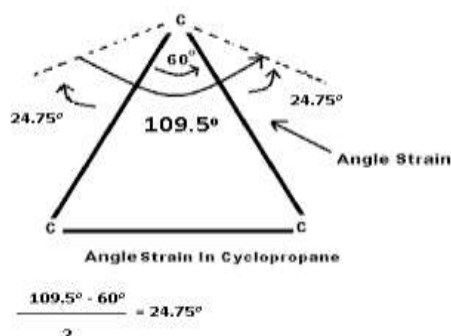
If bond angles deviate from the ideal then the ring produce strain. Higher strain produces higher instability, increased reactivity and increases heat of combustion. In simple higher the deviation lesser the instability.

Baeyer observed different bond angles for different cycloalkanes and also observed some different properties and stability. On this basis, he proposed angle strain theory. The theory explains reactivity and stability of cycloalkanes.



**Table 1: Angale strain of first few cycloalkanes**

Compound	Bond angle	Deviation	Angle strain
Cyclopropane	$60^\circ$	$49.5^\circ$	$24.75^\circ$
Cyclobutane	$90^\circ$	$19.5^\circ$	$9.75^\circ$
Cyclopentane	$108^\circ$	$1.5^\circ$	$0.75^\circ$
Cyclohexane	$120^\circ$	$10.5^\circ$	$-5.27^\circ$



The ring of cyclopropane is triangle. All the three angles are of  $60^\circ$  in place of  $109.5^\circ$  (normal bond angle for carbon atom) this implies that the normal tetrahedral angle between two bonds is compressed to  $60^\circ$  and that each of the two bonds involved is pulled in by  $24.75^\circ$  (**Table 1**). The value  $24.75^\circ$  then represents the angle strain or the deviation through which each bond bends from the normal tetrahedral direction.

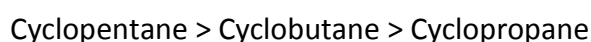
In same manner, cyclobutane is square and the bond angles are of  $90^\circ$  in place of  $109.5^\circ$  (normal bond angle for carbon atom) to adjust them into square ring system (angle strain  $9.75^\circ$ )

The deviation for cyclopropane and cyclobutane ring systems then normal tetrahedral angle will produce strain in ring. The ring strain will make them unstable as compare to molecules having tetrahedral bond angle. According to Baeyer cyclopropane should be highly strained molecule and most unstable compare to cyclobutane. The triangle ring therefore, be expected to open up on slightest provocation and thus releasing the strain within it. This is actually so cyclopropane undergoes ring opening reactions with  $\text{Br}_2$ ,  $\text{HBr}$  and  $\text{H}_2$  to give open chain addition products.

Cyclopentane (angle strain  $0.75^\circ$ ) consider to be under least strain and should be most stable. Thus it is not surprising that it does not undergo ring-opening reactions.

The angle strain in cyclohexane is higher than that in case of cyclopentane. This strain increase continuously with increase in the number of carbon atoms in the ring. According to the theory, cyclohexane and the higher cycloalkanes should become increasingly unstable and hence more reactive. Contrary to this prediction, cyclohexane and the higher members are found to be quite stable, they do not undergo addition reaction instead they react by substitution reaction. Thus the theory satisfactorily accounts for the first three cycloalkanes, but it is not valid for cyclohexane and higher members.

According to Baeyer, the relative order of stability for some common cycloalkanes is as under



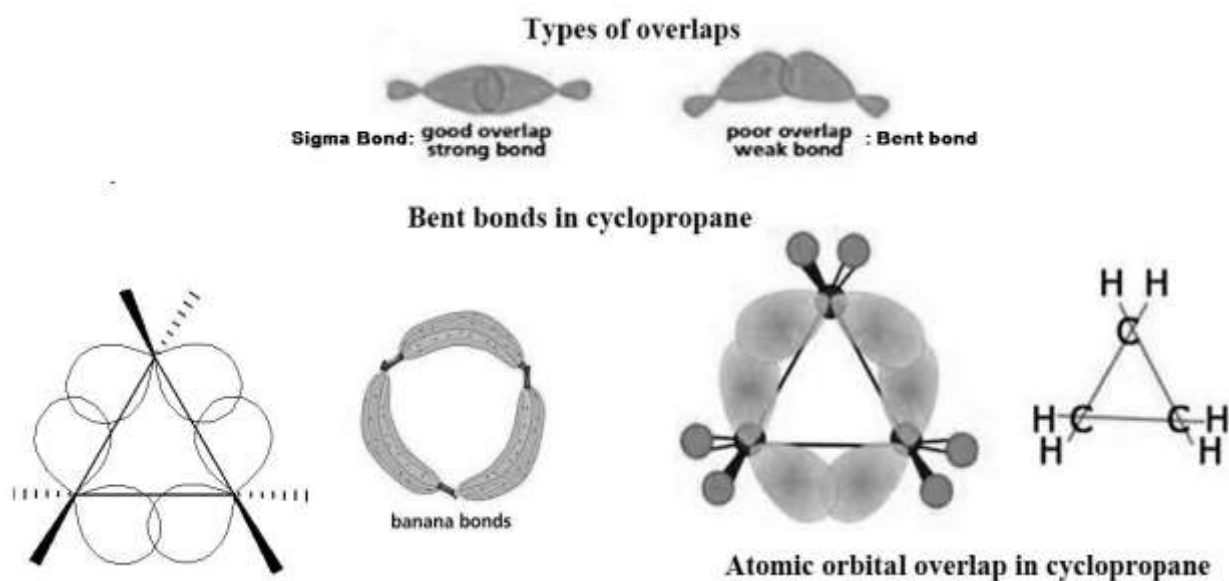
### Limitations of Baeyer's angle strain theory

- 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 wrinkled (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.



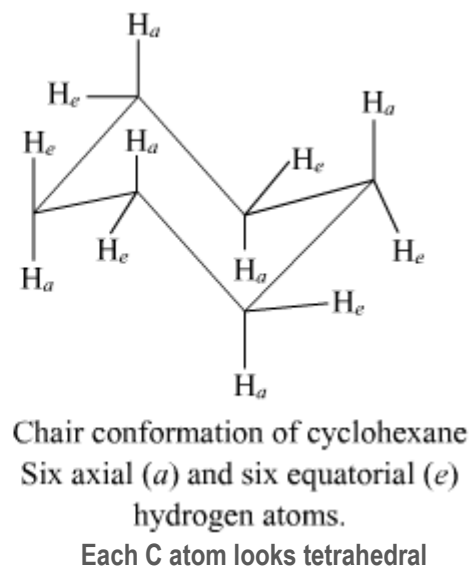
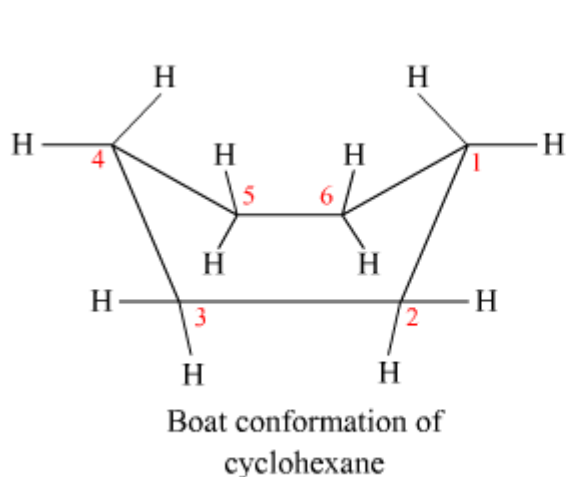
Note that sigma bond (strong bond) involves end-on-overlap and pi bond involves side-long overlap. Bent bond is intermediate between sigma and pi bonding. The overlap being neither end-on nor side-long. This makes the overlap less efficient than sigma overlap and the cyclopropane C-C bonds weaker than normal C-C sigma bonds.

According to Baeyer's strain theory, the configuration of cyclopropane is triangle with carbon valency angles  $60^\circ$ . This value is impossible as the carbon valence angle can never be less than  $90^\circ$  (when these are pure p-orbitals). The angles are more than  $90^\circ$  when hybridisation occurs. Coulson-Moffitts proposed that the smallest carbon valency angle which once can reasonably expect to have is  $104^\circ$ . Therefore, suggested that in cyclopropane only a partial overlap of the  $sp^3$  hybrid orbitals occurs, so C-C-C bond angle is decreased slightly from  $109.5^\circ$  to  $104^\circ$  and the H-C-H angle increased to  $120^\circ$  compare to normal tetrahedral angle. This decrease in overlap results in weakening of the bond and therefore partially explains the instability of cyclopropane. In case of cyclobutane, also has bent bonds but the decrease in overlap is less than in the case of cyclopropane. Cyclobutane is, therefore more stable (not participate in ring-opening reactions) and less reactive than cyclopropane.

### Sachse-Mohr Theory (Theory of Strainless Rings)

According to Baeyer, the carbon atoms of a ring are all in the same plane. The strain was calculated on the assumption that cyclic rings are planer. The strain is minimum for cyclopentane and goes on increasing as the size of the ring increases. Hence, members higher than cyclopentane should be increasingly unstable but Hermann Sachse, soon pointed out that large rings need not be strained, because the carbons need not be coplanar.

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 ( $109.5^\circ$ ) 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.

In chair cyclohexane there are two types of positions, axial and equatorial. The axial positions point perpendicular to the plane of the ring, whereas the equatorial positions are around the plane of the ring. Mohr (1918) further elaborated this theory and applied it to compounds with the two rings fused together.

#### References For

Unit V:

Part B: General Method of Preparation and Reactions of Cyclopropane and Cyclobutane are:

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