

Baeyer's Angle Strain Theory

For B.Sc. Sem-II

Organic Chemistry: US02CCHE01

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Introduction

- Van't Hoff and 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 stability.
- On this basis, he proposed angle strain theory.
- The theory explains **reactivity and stability of cycloalkanes**.
- Baeyer proposed that the **optimum overlap of atomic orbitals** is achieved for bond angle of 109.5° . In short, it is **ideal bond angle** for alkane compounds.
- Effective and optimum overlap of atomic orbitals produces **maximum bond strength and stable molecule**.
- If bond angles deviate from the ideal then ring produce **strain**.
- Higher the strain **higher the instability**.
- Higher strain produce **increased reactivity** and increases **heat of combustion**.
- Baeyer proposed “**any deviation of bond angle from ideal bond angle value (109.5°) will produce a strain in molecule. Higher the deviation lesser the instability**”.

Que.1 Discuss Baeyer's angle strain theory using concept of angle strain.

- **Baeyer's theory is based upon some assumptions as following.**
 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 exist.
 3. The bond angles in cyclohexane and higher cycloalkanes (cycloheptane, cyclooctane, cyclononane.....) are not larger than 109.5° because the carbon rings of those compounds are not planar (flat) but they are puckered (Wrinkled).

- These assumptions are helpful to understand instability of cycloalkane ring systems.

Que. 2 Cyclopropane is more prone to undergo ring opening reaction than cyclobutane or cyclopentane

Que. 3 Cyclopropane is more reactive than cyclobutane and cyclopentane

- The ring of cyclopropane is triangle. All the three angles are of 60° in place of **109.5° (normal bond angle for carbon atom)** to adjust them into triangle ring system.
- In same manner, cyclobutane is square and the bond angles are of 90° in place of **109.5° (normal bond angle for carbon atom)** to adjust them into square ring system.
- 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.
- So, cyclopropane and cyclobutane will easily undergo **ring opening reactions** to form more stable open chain compounds.
- Now compare the stability of cyclopropane and cyclobutane

The bond angle in cyclopropane is 60° .

The normal tetrahedral bond angle value is 109.5° .

That is why, deviation = (normal tetrahedral bond angle) – (actual bond angle)

$$\text{Deviation} = 109.5^\circ - 60 = 49.5^\circ$$

The bond angle in cyclobutane is 90° .

The normal tetrahedral bond angle value is 109.5° .

That is why, deviation = (normal tetrahedral bond angle) – (actual bond angle)

$$\text{Deviation} = 109^{\circ} 5' - 90 = 19.5^{\circ}.$$

Deviation for cyclopropane is 49.5°

Deviation for cyclobutane is 19.5°

The deviation is higher for cyclopropane than cyclobutane therefore cyclopropane is more prone to undergo ring opening reactions.

As a result of this, the strain is more in cyclopropane as compare to cyclobutane. It will make **cyclopropane less stable than cyclobutane**. So, cyclopropane easily undergoes ring opening reaction as compare to cyclobutane.

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

Cyclopentane > Cyclohexane > Cyclobutane > Cyclopropane

Actual observed order of stability for these cycloalkanes is as under.

Cyclohexane > Cyclopentane > Cyclobutane > Cyclopropane

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

Baeyer also proposed some facts for cyclohexanes that stood incorrect later on.

- Cyclohexane is **unstable** ring due to **higher ring strain**.
- It is difficult to synthesize for **cyclohexane** and higher ring systems as deviation from the normal **tetrahedral value (109.5°) would be larger**.
- The larger deviation will result into **more strain** and the ring system will be unstable.

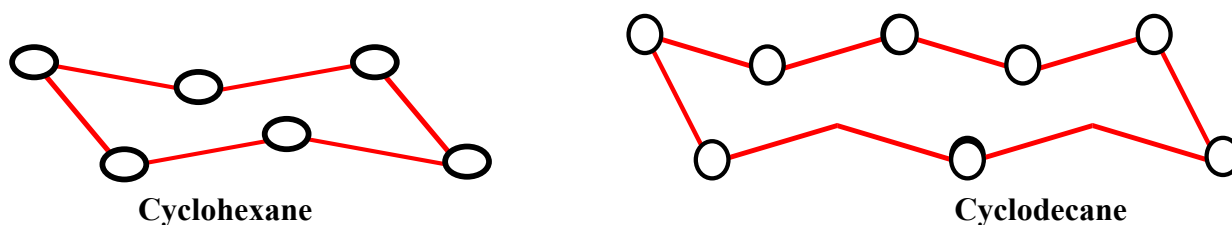
In conclusion, Baeyer proposed that ring systems smaller or larger than cyclopentane or cyclohexane are unstable due to higher ring strain. Therefore, he assumed that cyclopropane

and cyclobutane easily undergo ring opening reaction whereas larger ring systems are difficult to synthesize.

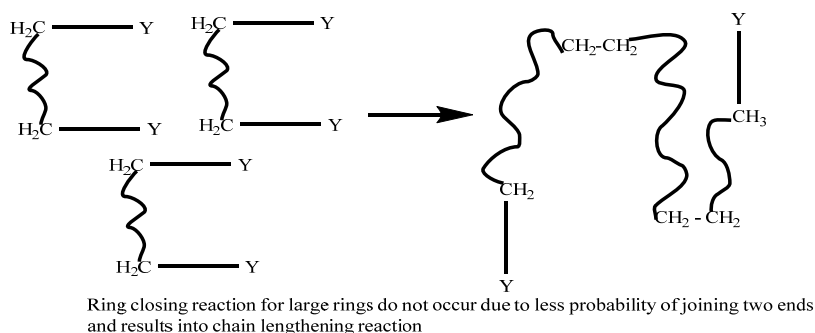
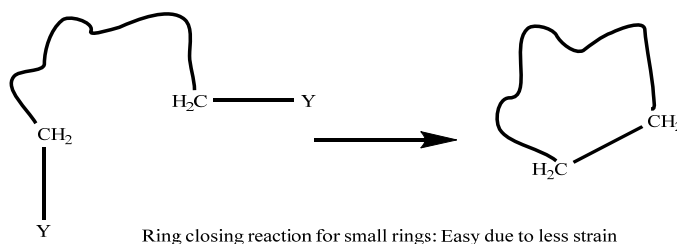
Que. 4 Why larger rings are difficult to synthesize?

Baeyer explained why synthesis of larger ring is difficult. (Baeyer was incorrect in presuming the larger ring systems are flat)

- It is difficult to explain the formation of larger ring system on the basis of angle strain.
- Because, larger ring systems **are not flat or planar** that was assumed by Baeyer.
- These larger ring systems are **puckered (wrinkled)** to eliminate possible angle strain.



- If we want to synthesize large ring system then the open chain **should be long** but in this case it is difficult for both ends to join and form the ring.
- Instead of this, end of an **open chain will join with end of another compound** and result into a **different compounds**.



Although it is difficult to synthesize large rings according to Baeyer theory, there are several methods for preparation of large rings. Such methods are carried out in **highly diluted solutions of dihalides** in which the chain lengthening reactions would not occur but ring closing reactions will take place.

Five and six membered ring systems (Cyclopentane and Cyclohexane) are favourable to synthesize as they are large enough to free from strain and small enough to undergo ring closure reactions.

Que.5 Discuss Baeyer's angle strain theory using heat of combustion data

Que.6 Define heat of combustion and discuss the stability of cyclopropane and cyclobutane with respect to heat of combustion.

Que.7 Cyclopropane is more prone to undergo ring opening reaction than cyclopentane using heat of combustion.

Que.8 Cyclopropane is more reactive than n-alkane.

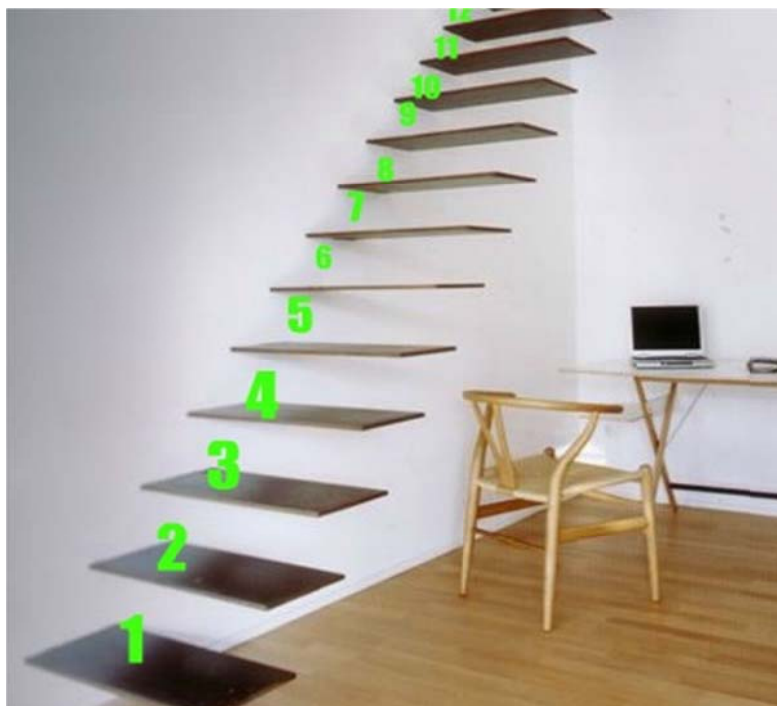
Heat of Combustion and Relative Stability of Cycloalkanes

- The **amount of heat evolved** when **one mole** of compound is burned in **carbon dioxide and water** is referred as **heat of combustion**.
- Heat of combustion is important property to know the stability and other valuable information.
- The information from heat of combustion is important to understand the Baeyer's theory and its limitations.

**For open chain compound heat of combustion for CH₂ group is
157.4 Kcal/Mole**

Ring Size	Heat of Combustion/CH₂ Kcal/Mole	Ring Size	Heat of Combustion/CH₂ Kcal/Mole
3	166.6	10	158.6
4	164.0	11	158.4
5	158.7	12	157.6
6	157.4	13	157.8

7	158.3	14	157.4
8	158.6	15	157.7
9	158.6	16	157.2



Understanding of heat of combustion and stability (if one jump from first stair then energy will be lower but if one jump from higher stairs then the energy will be higher that causes instability)

Calculation of heat of combustion for cyclopropane

Heat of combustion =

(No. of Carbon atom in the ring) × (heat of combustion for that ring per CH₂) – heat of combustion for normal alkane per CH₂

Heat of Combustion for Cyclopropane

Number of carbon in cyclopropane = 3

Observed heat of combustion for cyclopropane = 166.6 Kcal/mole

Observed heat of combustion for n-propane = 157.4 Kcal/mole

$$\begin{aligned}\text{Therefore, Heat of Combustion for cyclopropane} &= 3 \times (166.6 - 157.4) \\ &= 27.6 \text{ Kcal/mole}\end{aligned}$$

Similarly one can calculate heat of combustion for cyclobutane and cyclopentane those are 26.4 and 6.5 Kcal/mole respectively.

- Upon examination of data, it can be seen that **cyclopropane and cyclobutane** evolve **more energy per CH₂ group** than its open chain compound and that may be the reason for **the instability and their tendency to undergo chain opening reactions easily**. Heat of combustion value for cyclopropane and cyclobutane are higher than open chain compounds (9.2 and 7.0 Kcal/mole respectively). According to data, cyclopropane is less stable than cyclobutane. For these ring systems Baeyer's theory was correct.
- Now if we examine data for **cyclopentane**, then it can be seen that the value for **heat of combustion is higher than open chain compound (157.4 Kcal/mole)**. The value is **much higher than** the open chain compound for Baeyer's most stable compound, cyclopentane.
- For other larger ring systems, the values for heat of combustion are very close to the open chain compound that indicates stability of those compounds. Here Baeyer's theory was incorrect to justify this stability.

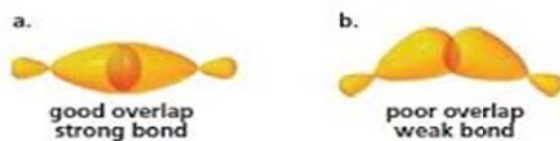
Que.9 Discuss Baeyer's angle strain theory using orbital picture of covalent bond

Que.10 Cyclopropane group acts as substituent.

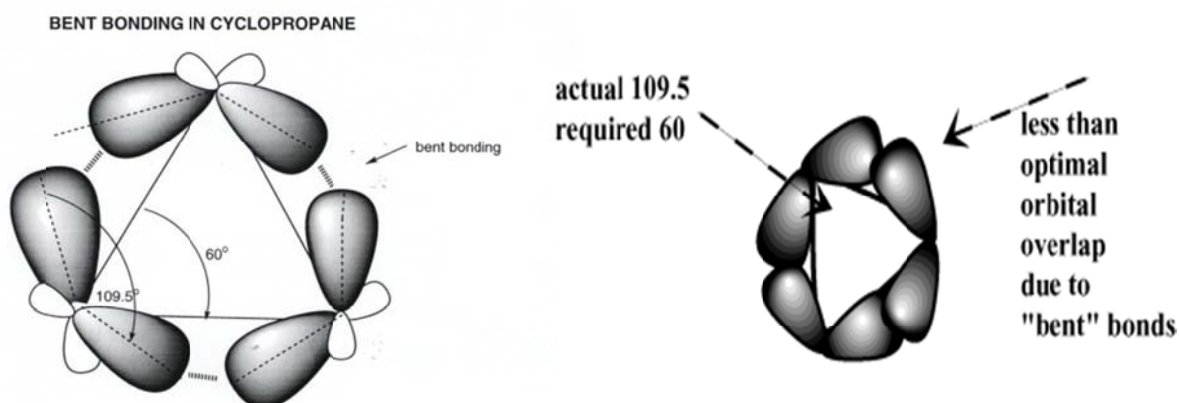
Orbital Picture of Angle Strain

- We know that, for the bond formation **effective atomic orbital overlap** is required.
- For carbon atom, in a molecule if it is **sp³ hybridized** then the bond angle is **109.5°** and orbital overlap is maximum.
- This is the reason for **highly stable compounds**.
- For an open chain compound, when carbon is connected to other two carbon atoms, it is **sp³ hybridized** and utilize these hybrid orbitals to form the bonds.
- In cyclopropane, the **bond angle is 60° instead of 109.5°**.

- The carbon atom do not use sp^3 hybridized orbitals to form the bond.
- Hence, the bond is **weaker** as compare to usual carbon-carbon bond.



Types of overlaps

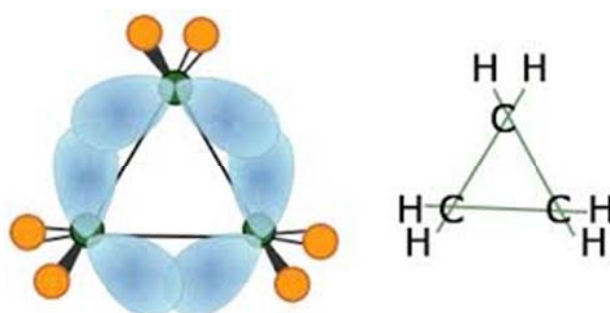


NOTE THAT SIGMA BONDING INVOLVES "END-ON OVERLAP" AND PI BONDING INVOLVES "SIDELONG" OVERLAP. SIGMA BONDING IS STRONGER THAN PI BONDING. **BENT BONDING** IS INTERMEDIATE BETWEEN SIGMA AND PI BONDING, THE OVERLAP BEING NEITHER END-ON NOR SIDELONG. THIS MAKES THE OVERLAP LESS EFFICIENT THAN SIGMA OVERLAP, AND THE CYCLOPROPANE C-C BONDS WEAKER THAN NORMAL C-C SIGMA BONDS. THIS IS DESCRIBED AS **ANGLE STRAIN**.

carbon frame of cyclopropane

Bent bonds in cyclopropane

Bonding in cyclopropane



Atomic orbital overlap in cyclopropane

Que. 11 Discuss successfulness and unsuccessfulness of Baeyer angle strain theory.

Que. 12 Limitation of Baeyer's angle strain theory.

Que. 13 What is wrong with Baeyer's angle strain theory? Why it is not applicable to ring larger than four carbon atoms?

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.