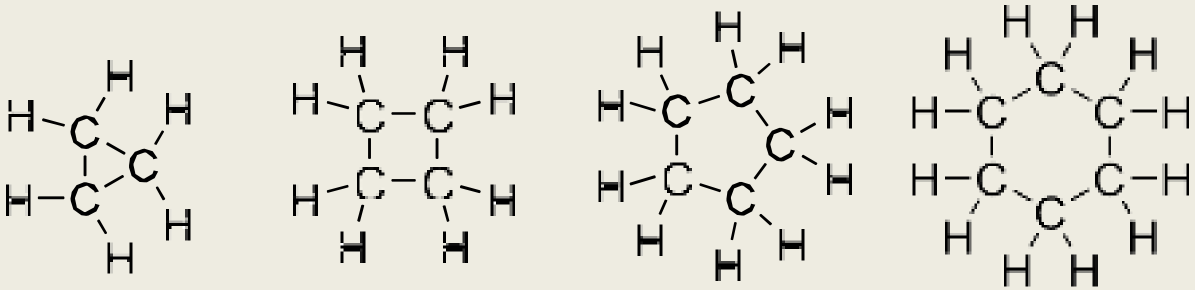
CYCLOALKANES

---Mr. Sandip N. Badeliya
Associate Professor,
SIPS, Dhanap, Gandhinagar

Cycloalkanes

Definition

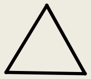
- Cycloalkanes are alkanes which have some of their carbon atoms arranged in a ring. Rings of different sizes beginning with three carbons are possible.



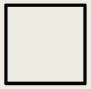
- Cycloalkanes are saturated since all the carbon atoms that make up the ring are single bonded to other atoms.
- Because of the ring, a cycloalkane has two fewer hydrogens than an acyclic (noncyclic) alkane with the same number of carbons.
- The general molecular formula for cycloalkanes is C_nH_{2n}

Nomenclature of Cycloalkanes

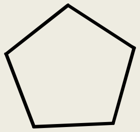
- Cycloalkanes are commonly drawn as line structures whereby each vertex represents a carbon understood to be connected to an appropriate number of hydrogens to give carbon four bonds.
- Cycloalkanes are named by adding the prefix “cyclo” to the ‘alkane’ name that has the same number of carbon atoms as those in the ring.
- These most common cycloalkanes are represented as shown below:



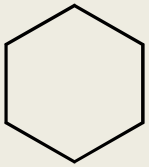
Cyclopropane



Cyclobutane



Cyclopentane



Cyclohexane

Nomenclature of Cycloalkanes

Substituted Cycloalkanes

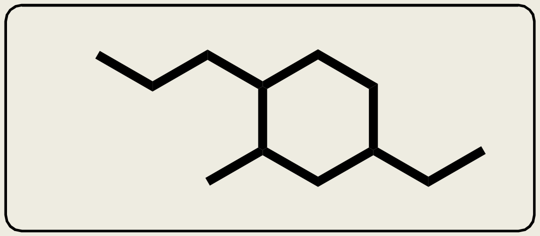
The rules for naming cycloalkanes are similar to those used for straight-chain alkanes:

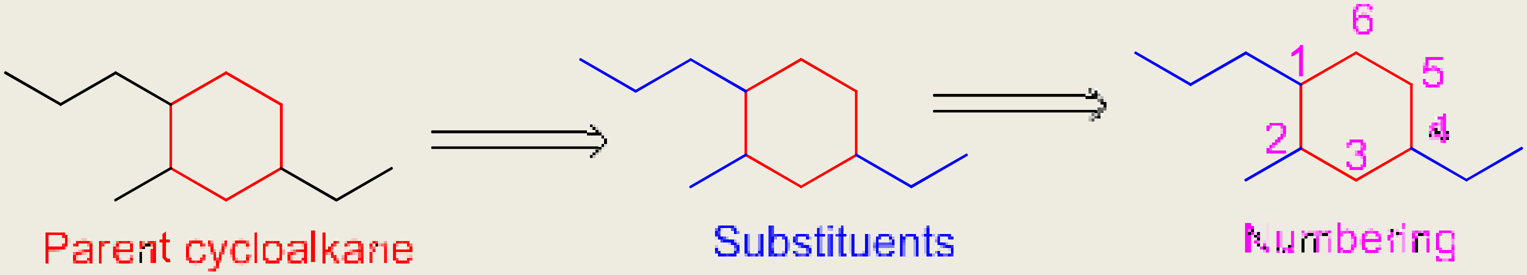
i. The parent ring is the largest ring in the molecule.
ii. The parent name is generated by adding the prefix cyclo- to the name of the alkane with the same number of carbons.
iii. Identify the substituents and their location by numbering the ring from the carbon containing substituents so as to give the substituents the lowest possible location numbers.
iv. Alphabetize the substituents in the full name of the cycloalkane.

Nomenclature of Cycloalkanes

Substituted Cycloalkanes

Refer to the cycloalkanes below to illustrate the nomenclature of cycloalkanes.





Parent name: **Cyclohexane**

Substituents

1-Propyl
2-Methyl
4-Ethyl

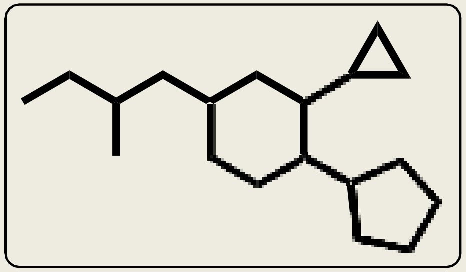
Alphabetize the substituents

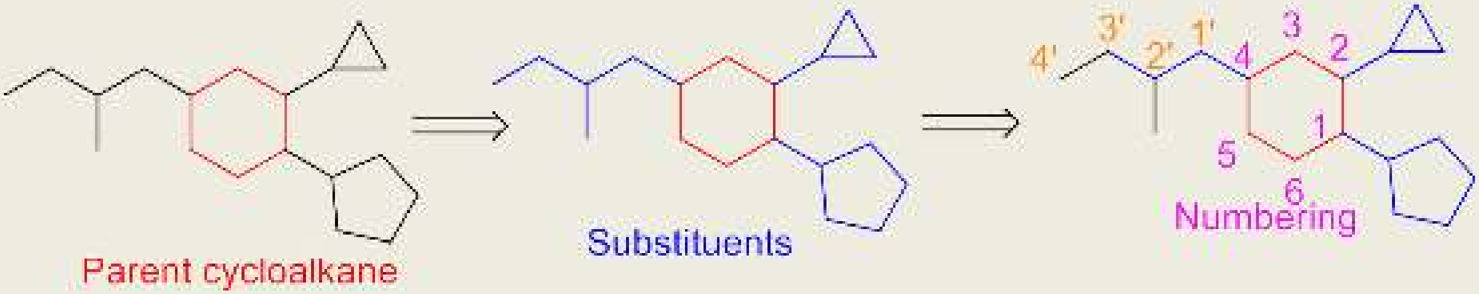
Complete name: **4-Ethyl-2-methyl-1-propylcyclohexane**

Nomenclature of Cycloalkanes

Substituted Cycloalkanes

Larger rings take precedence over smaller rings.





Parent name: **Cyclohexane**

Substituents ↓

1-Cyclopentyl
2-Cyclopropyl
4-(2'-Methylbutyl)

Alphabetize the substituents

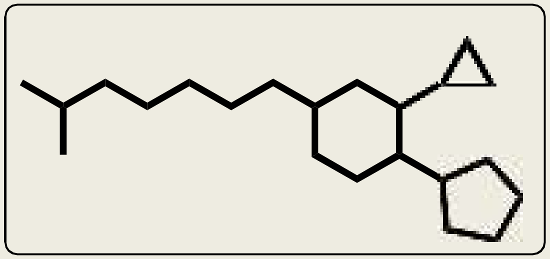
↓

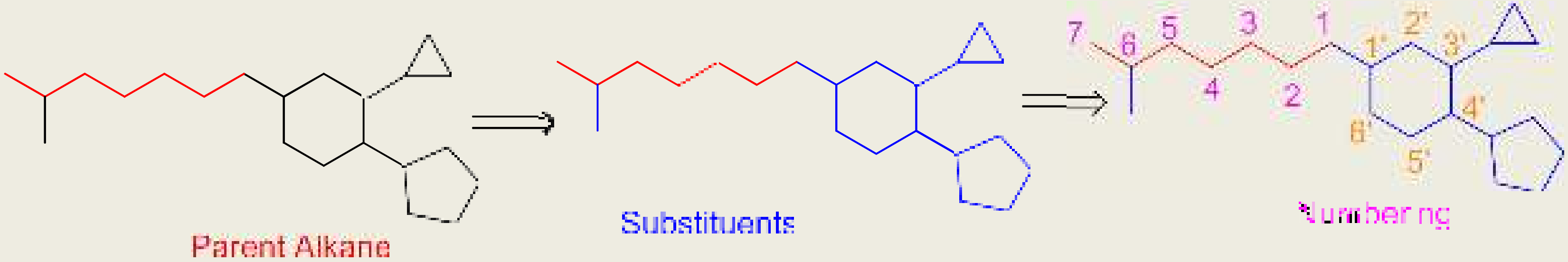
Complete name: **1-Cyclopentyl-2-cycloppropyl-4-(2'-methylbutyl)cyclohexane**

Nomenclature of Cycloalkanes

Substituted Cycloalkanes

If the alkyl group has a longer carbon chain than any of the rings, the straight chain system will be the parent chain.





Parent name: **Heptane**

Substituents ↓ 1-(4'-Cyclopentyl-3'-cyclopropylcyclohexyl)
6-Methyl

Alphabetize the substituents

↓

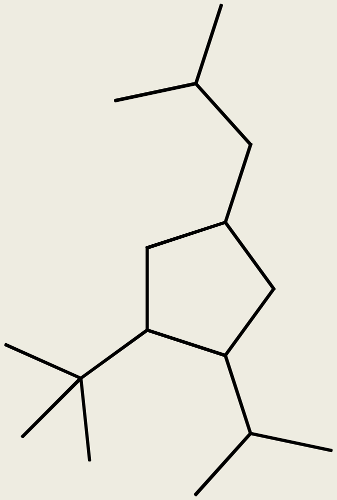
Complete name: **1-(4'-Cyclopentyl-3'-cyclopppropylcyclohexy)-6-methyheptane**

Practice Questions

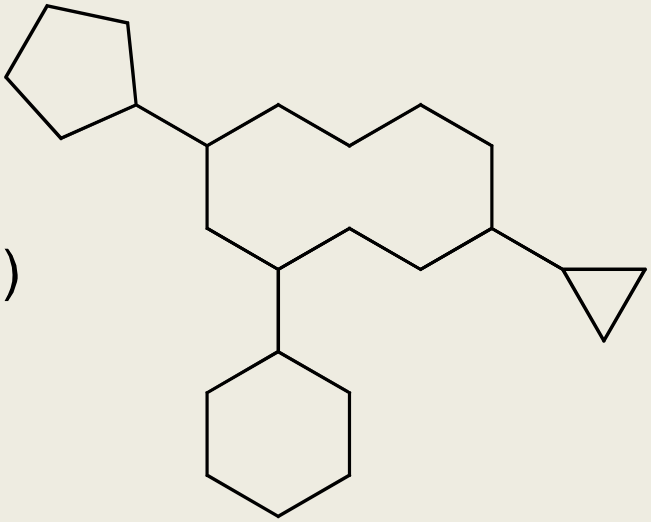
Nomenclature of Cycloalkanes

Provide the IUPAC names of the following cycloalkanes

(i)

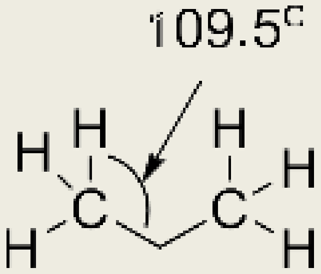


(ii)

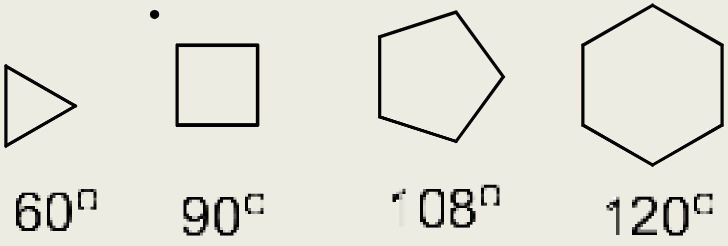


Conformations of Cycloalkanes

The bond angles in straight chain alkanes is normally 109.5^0. This is expected for a tetrahedral arrangement of bonds that are not restricted.



Internal Bond Angle



$$\text{Bond angle} = \frac{(n-2)}{n} \times 180$$

n= number of carbons in ring

However, when the carbon atoms form part of a ring, the angle will be controlled by the requirements of the ring.

Stability of Cycloalkanes

- Bayer (1885) postulated a theory of angle strain for cycloalkanes in which the difference between a tetrahedral angle (109.5^{o}) and an internal angle of the appropriate polygon is used as a measure of stability.
- The deviation of bond angles from the tetrahedral angle causes the molecule to be strained and hence unstable compared with molecules with tetrahedral bond angles.

Polygon	Internal angle	Polygon	Internal angle
3	60	7	129
4	90	8	135
5	108	9	140
6	120	10	144

Stability of Cycloalkanes

- Since the angles of a regular pentagon (108^{o}) are very close to the tetrahedral angle (109.5^{o}), the cycloalkane with the least angle (Bayer) strain is cyclopentane.
- Considering that the angles of a regular hexagon (120^{o}) are somewhat larger than the tetrahedral angle, Baeyer concluded (incorrectly) that there is a certain amount of strain in cyclohexane.
- Further, he suggested that as one proceeds to cycloheptane, cyclooctane etc, the deviation of the bond angles become progressively larger and the molecules would become progressively more strained. This has largely been found to be incorrect.

Baeyer Theory vs Experimental Facts

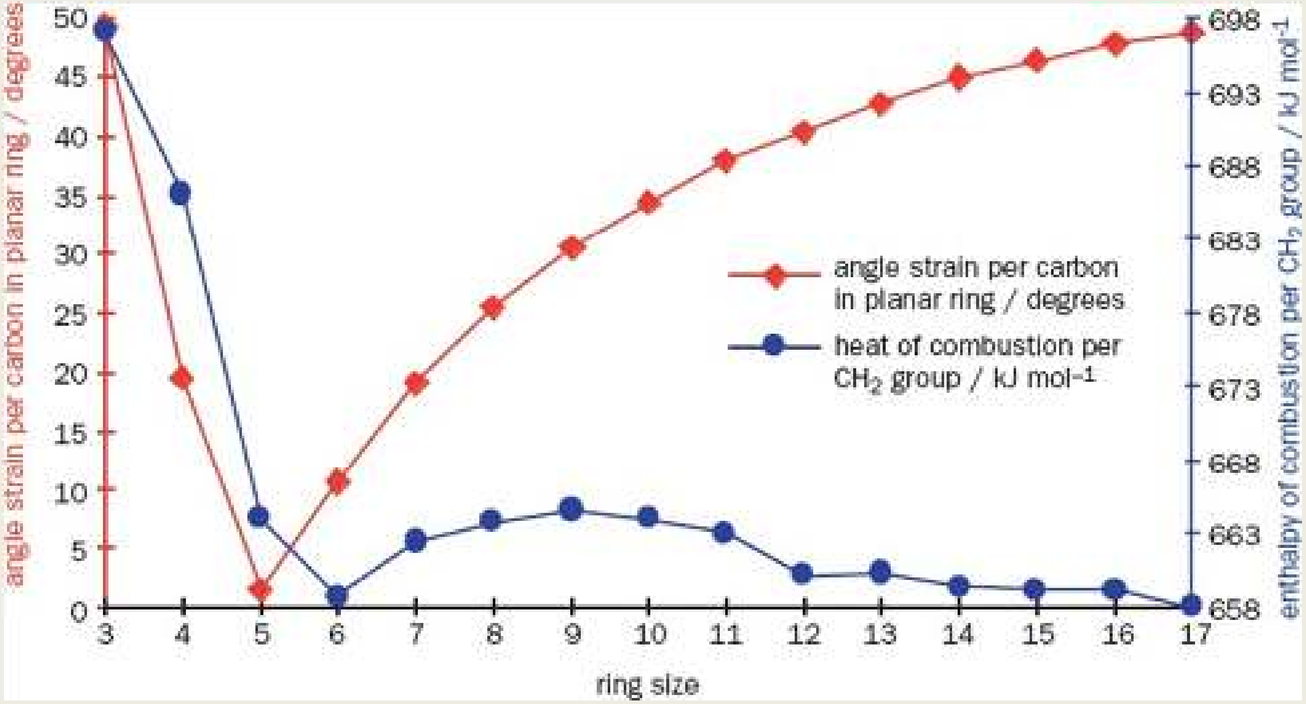
- Heats of combustion can often furnish valuable information on the relative stabilities of compounds.

Ring size	**Heat of combustion per CH_2 (kcal/mol)**	**Ring size**	**Heat of combustion per CH_2 (kcal/mol)**
3	**166.6**	**7**	**158.3**
4	**164.0**	**8**	**158.6**
5	**158.7**	**9**	**158.8**
6	**157.4**	**10**	**157.4**
Heat of combustion for an open chain alkane per –CH_2- is 157.4 kcal/mol			

- Apparently, cyclohexanes are just as stable as straight chain alkanes.

Baeyer Strain vs Heats of Combustion

- When the heats of combustion of other larger ring cycloalkanes is considered, a clearer picture emerges.



- The Bayer theory appears to apply to cycloalkanes from three carbons (cyclopropane) to five carbons (cyclopentane), but fails for larger ring sizes.

Where Does the Baeyer Theory Fail?

The Baeyer theory fails for larger rings because:

- The angles that Baeyer used for each ring were based on the assumption that the rings of all cycloalkanes are planar.
- In fact, all cycloalkanes except cyclopropane are not planar (flat).
- The reality is that cycloalkanes tend to adopt puckered three dimensional conformations that allow all the bond angles to be nearly tetrahedral.

Conformations of Cycloalkanes

The stability of cycloalkanes are influenced by a combination of three factors:

i. Baeyer strain or angle strain: The strain due to expansion or compression of bond angles. There is increase in energy when bonds deviate from the optimum tetrahedral bond angle of 109.5^o.

ii. Torsional strain or bond strain: The strain due to the eclipsing of bonds on neighbouring atoms. There is increase in energy when there are eclipsing interactions.

iii. Steric strain: The strain due to the repulsive interactions when atoms approach each other too closely. There is increase in energy when atoms are forced too close to one another.

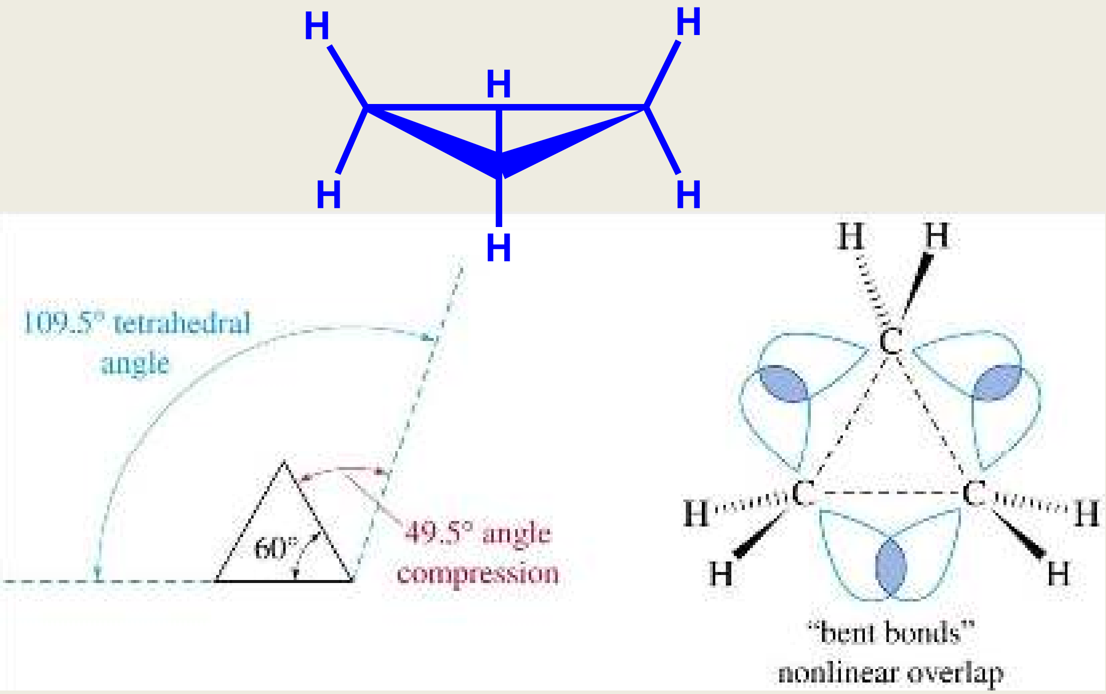
Conformations of Cycloalkanes

- The ring strain of a cycloalkane is a combination of the effects of angle strain, torsional strain and steric strain.
- The various arrangements in space that are available to a molecule by rotation about single bonds is its conformations.
- The investigations of various conformations of a molecule and their relative stabilities is known as conformational analysis.
- We will look at the conformational analysis of cyclopropanes, cyclobutanes, cyclopentanes and cyclohexanes to identify the lowest energy conformers.

Cyclopropanes

Structure and Bonding

- These are three membered ring carbocycles of formular C_3H_6 and a ring bond angle of 60°.

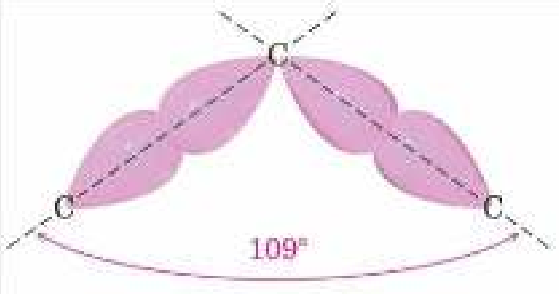


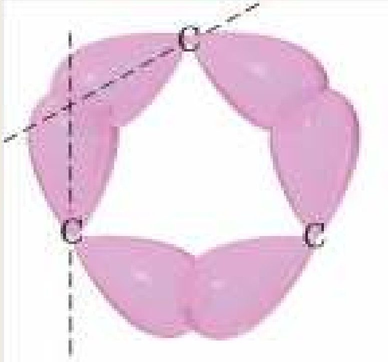
- This significant angle compression relative to the tetrahedral bond angle leads to strain in the cyclopropane.

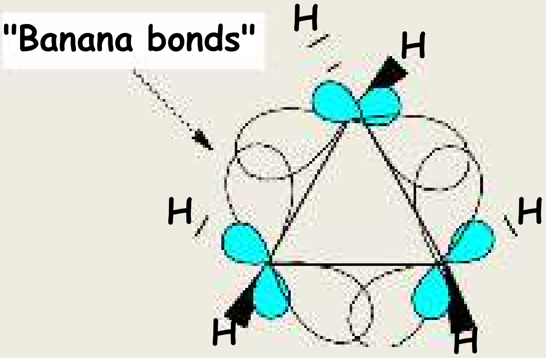
Cyclopropanes

Bonding

- The bonds in cyclopropane rather than being straight are curved like a banana.



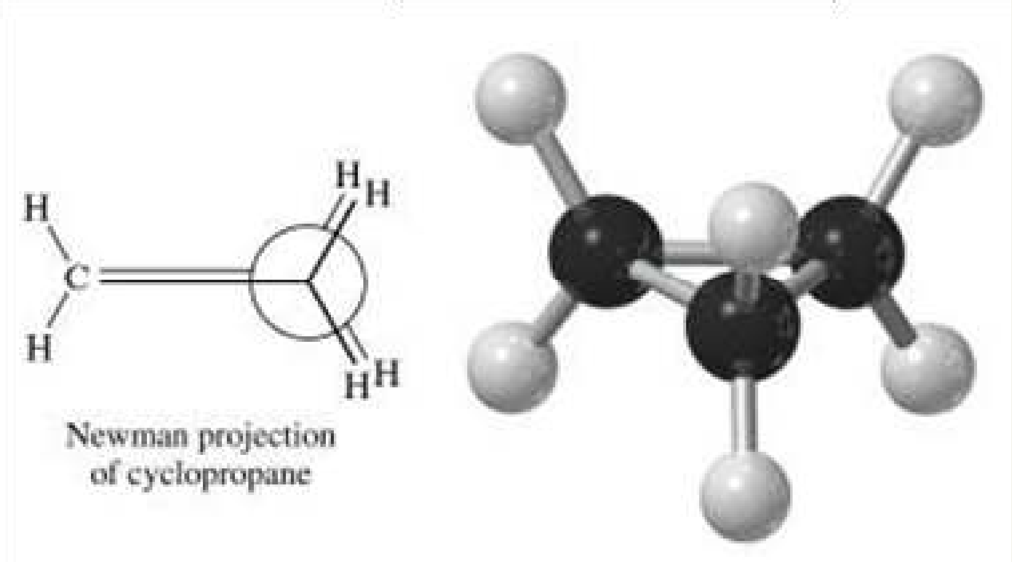




- Since the orbitals in cyclopropane are at wrong angles for good overlap, there is a significant angle strain (Baeyer strain) in the ring.

Cyclopropanes
Bonding

- Since all 6 C-H bonds in cyclopropane are eclipsed, this leads to bond strain (torsional strain) in the cyclopropane.

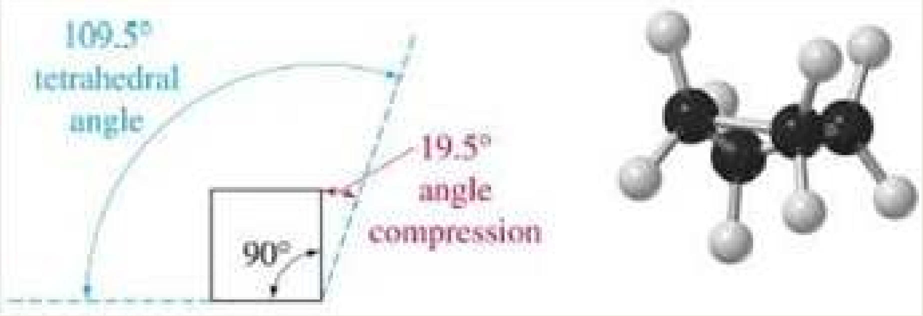


- As a result of angle strain and torsional strain, cyclopropane is very unstable and therefore more reactive than straight chain alkanes.
- The ring opening reactions of cyclopropane serve to relieve this strains.

Cyclobutanes

Bonding

- Cyclobutane is a four membered carbocycle of formula C_4H_8.
- Just like cyclopropane, the bond angles in cyclobutane are strained as a result of angle compression compared to related linear or unstrained hydrocarbons.

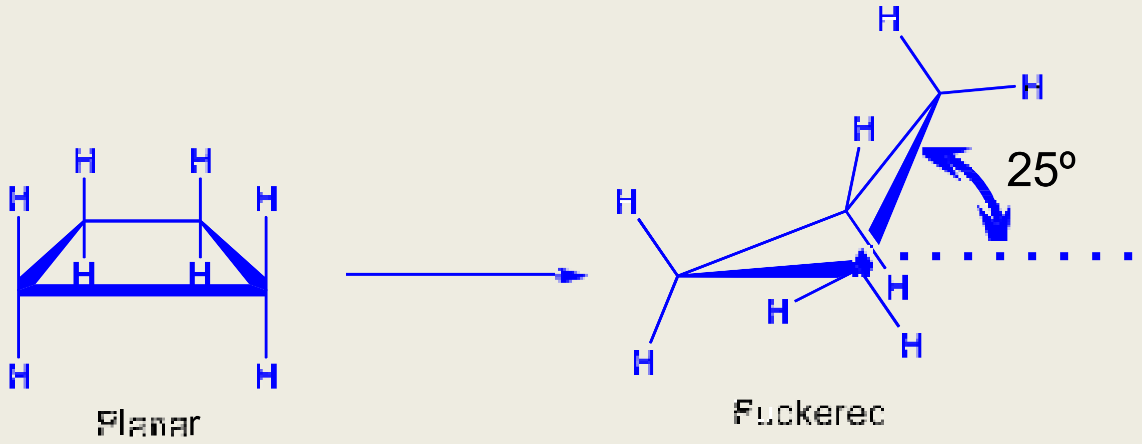


- As a result of angle strain, cyclobutane is unstable above 500^{o}C.
- But unlike cyclopropane, cyclobutane has slighltly greater freedom of rotation.

Cyclobutanes

Conformations

- One can envisage two extreme forms of cyclobutane: A planar form and a bent form (referred to as the puckered form).

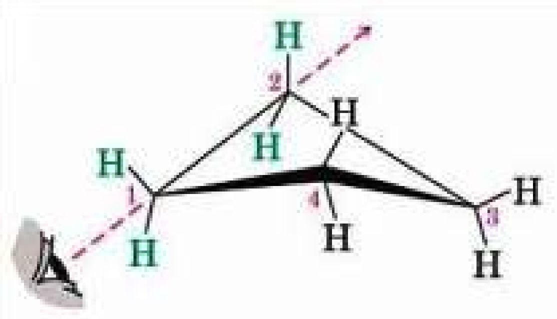


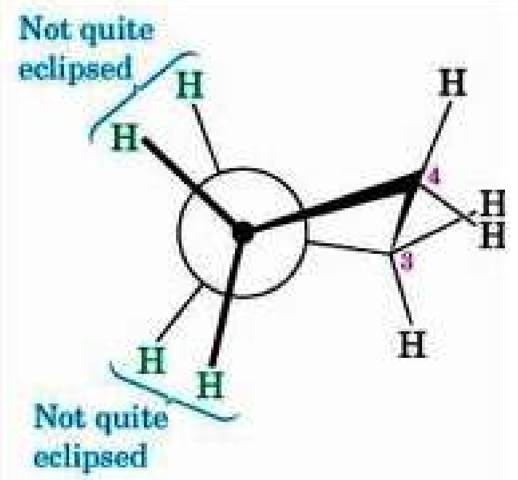
- The planar cyclobutane has all its 8 C-Hs in an eclipsed arrangement with bond angles of 90^{o}, while the puckered conformation has a bond angle of 88^{o}.
- Although the puckered conformation increases the angle strain, it significantly reduces the torsional strain.

Cyclobutanes

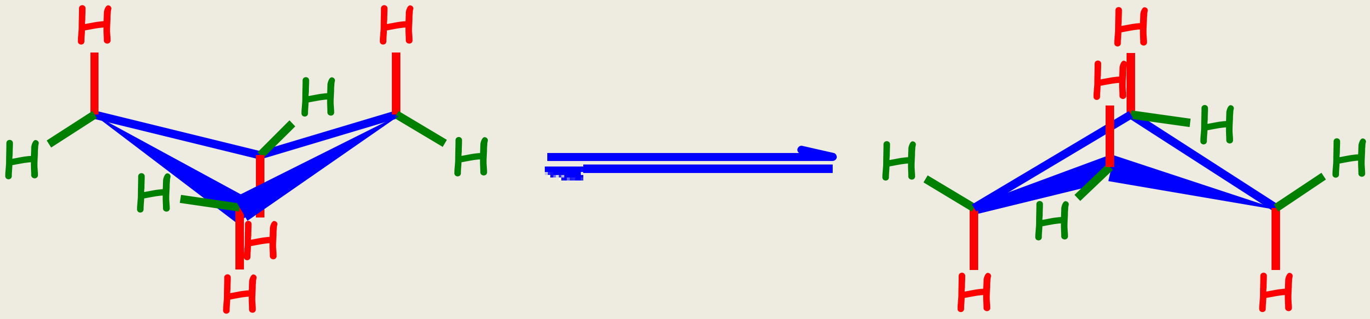
Conformations

- Cyclic molecules minimize the angle strain and torsional strain in them by ring puckering (bending).





- Cyclobutane consists of two puckered conformations which are in rapid equilibrium.



Cyclobutanes

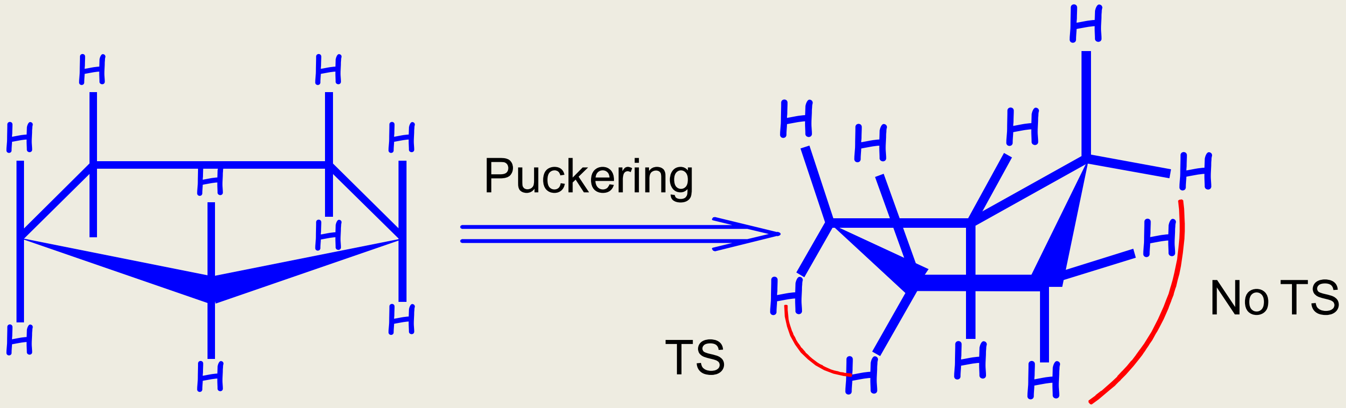
Conformations

- Note how in the puckered conformation of cyclobutane there are two different kinds of C–H bonds and hence two different kinds of H atoms. There are those C–H bonds that are nearly anti to other C–H bonds, and there are those C–H bonds that are nearly anti to C–C bonds.

- When we will look at cyclohexanes, we will see that this has great significance in the stability of the cyclohexane rings.

Cyclopentanes

- Cyclopentane is a five membered carbocycle of formula C_5H_{10}.



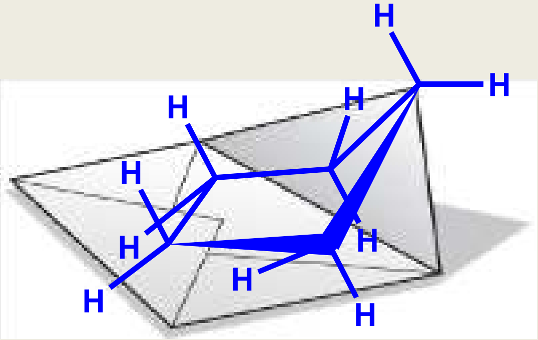
Planar conformer

Envelope conformer

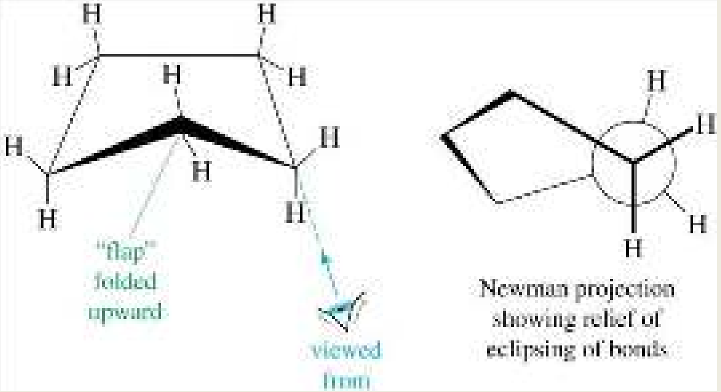
- There are two extreme conformations of cyclopentane (the planar and envelope conformations).
- In the planar conformation, postulated in the Baeyer theory, the bond angle in the ring is 108° and all 10 C-H bonds are eclipsed.

Cyclopentane

(The Envelope Confomer)



- In the envelope conformation, four carbons are on the plane, while the fifth carbon is out of plane, sort of like the flap of an envelope.
- The number of eclipsed hydrogens is reduced at the expense of angle strain, the bond angle is 105º.

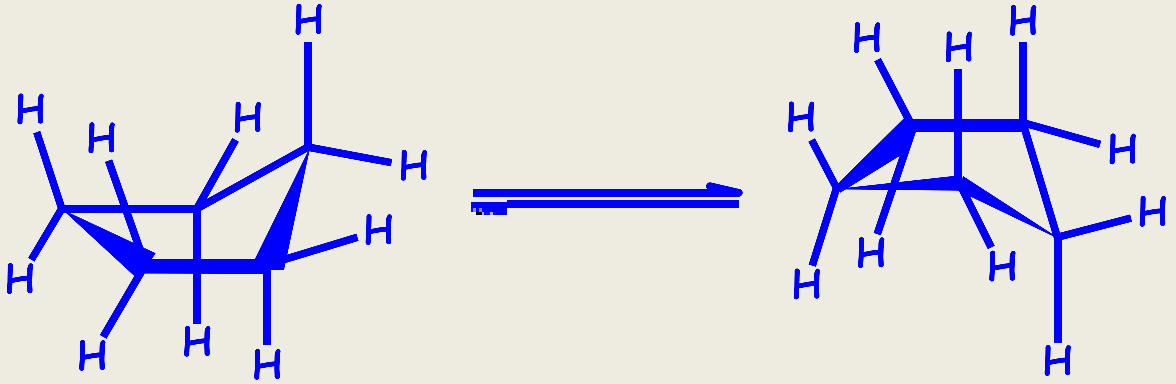


Newman projection showing relief of eclipsing of bonds

Cyclopentane

(The Envelope Confomation)

- The envelop conformation undergoes a rapid conformational change in which the carbon at the envelope alternates.

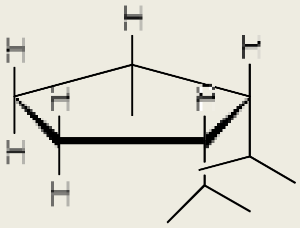


- Suppose the different C atoms in the ring are non-identical, i.e. have different substituents. How do we know which C atom in cyclopentane will pucker?

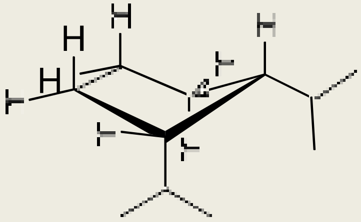
Substitued Cyclopentanes

(The prefered Envelope Confomation)

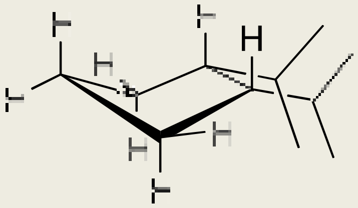
- When we have substituted cyclopentanes, puckering occurs preferably involving the substituted carbon to generate the envelope conformer with reduced tortional strain.



Eclipsed planar



Staggered Envelope



Eclipsed Envelope

- For 1,2-diisopropylcyclopentane, the prefered conformer of lowest energy is the staggered envelope.