

# cycloalkanes.

Introduction, Nomenclature, Isomerism, Synthesis, properties and stability of different ring compounds.

Chemists class rings as small,normal, medium, and large depending on their size.

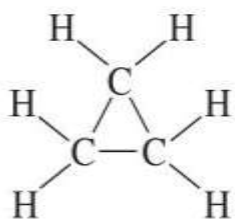
- small,  $n = 3$  or  $4$
- normal,  $n = 5, 6,$  or  $7$
- medium,  $n = 8$ –about  $14$
- large,  $n >$  about  $14$

This is because these different classes all have different properties and synthetic routes to making them

**Cycloalkanes have molecular formula  $C_nH_{2n}$  and contain carbon atoms arranged in a ring.** In organic chemistry, many common molecules are cyclic.

Cycloalkanes are simply alkanes that are cyclic.

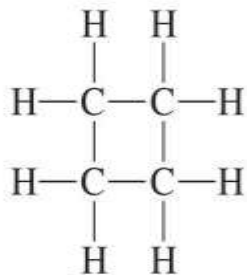
Just add cyclo-before their name. (The opposite of cyclic is acyclic).



or



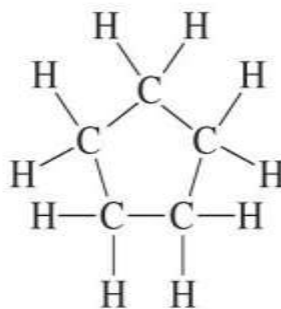
cyclopropane  
 $C_3H_6$



or



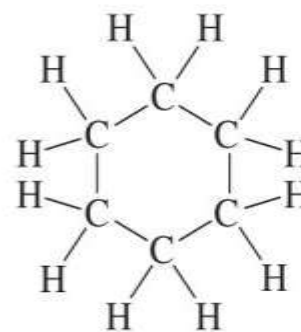
cyclobutane  
 $C_4H_8$



or



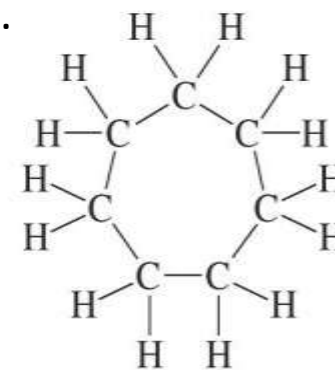
cyclopentane  
 $C_5H_{10}$



or



cyclohexane  
 $C_6H_{12}$

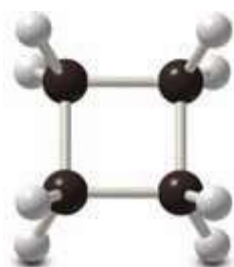
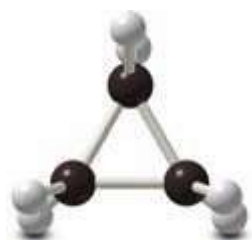


or

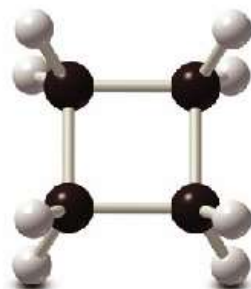


cycloheptane  
 $C_7H_{14}$

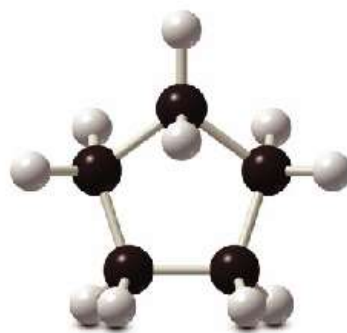
# Ball model of common cycloalanes.



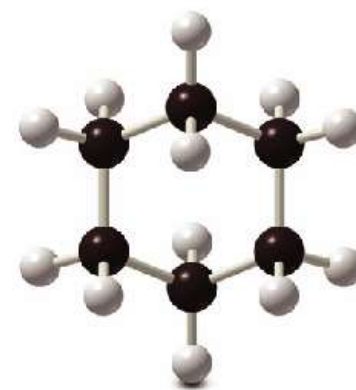
cyclopropane  
 $C_3H_6$



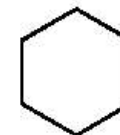
cyclobutane  
 $C_4H_8$



cyclopentane  
 $C_5H_{10}$



cyclohexane  
 $C_6H_{12}$



# Nomenclature of Cycloalkanes

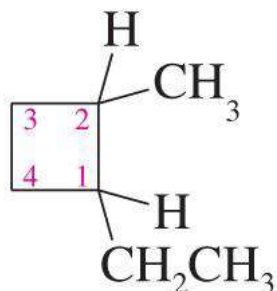
This is the same as for alkanes, although two extra rules apply.

Rule A: Decide whether the cyclic or acyclic portion contains more carbons. This determines the base name. (Alkyl substituted cycloalkane or cycloalkane substituted alkane).

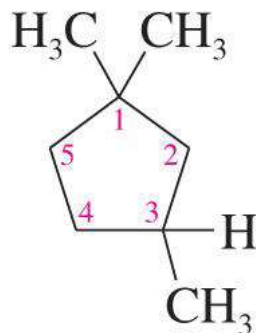
Rule B: Carbons are numbered to give the lowest numbers for substituted carbons .

Numbering starts at the most substituted carbon, and goes around in order to give the lowest numbers.

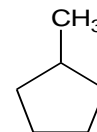
Examples:



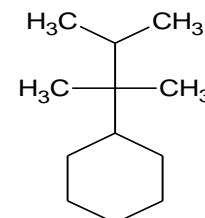
1-ethyl-2-methylcyclobutane



1,1,3-trimethylcyclopentane

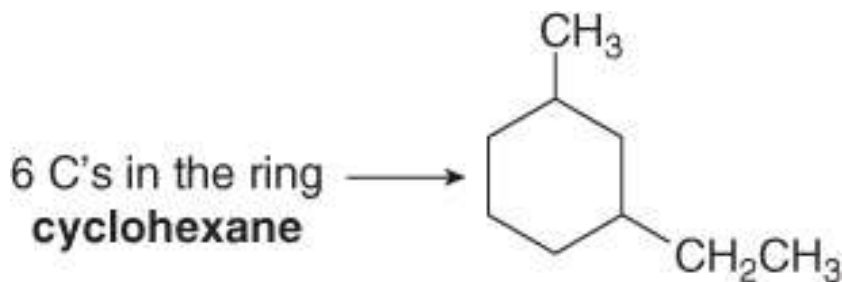
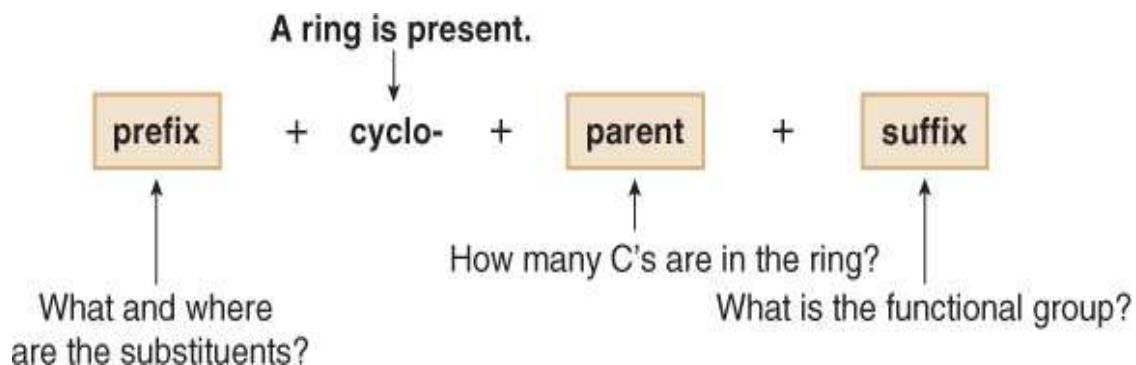


methylcyclopentane

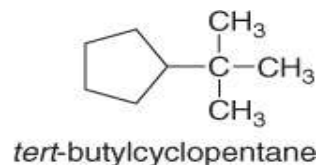
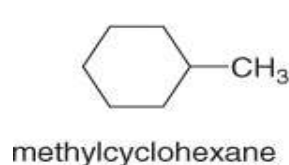


(2,3-dimethylbutan-2-yl)cyclohexane

Cycloalkanes are named by using similar rules, but the prefix cyclo- immediately precedes the name of the parent

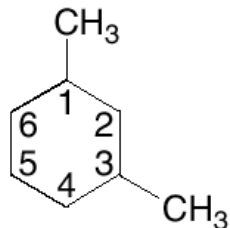


Name and number the substituents. No number is needed to indicate the location of a single substituent.



For rings with more than one substituent, begin numbering at one substituent and proceed around the ring to give the second substituent the lowest number.

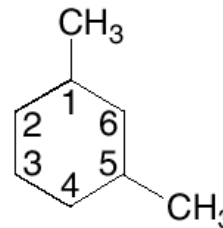
**numbering clockwise**



CH<sub>3</sub> groups at C1 and **C3**  
The 2<sup>nd</sup> substituent has a lower number.

**Correct: 1,3-dimethylcyclohexane**

**numbering counterclockwise**

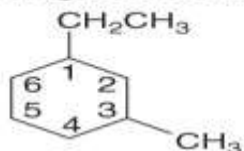


CH<sub>3</sub> groups at C1 and **C5**

**Incorrect: 1,5-dimethylcyclohexane**

With two different substituents, number the ring to assign the lower number to the substituents alphabetically.

Begin numbering at the ethyl group.

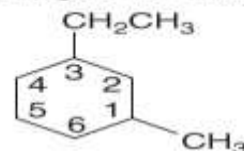


- ethyl group at **C1**
- methyl group at **C3**

earlier letter → lower number

**Correct:** 1-ethyl-3-methylcyclohexane

Begin numbering at the methyl group.



- methyl group at **C1**
- ethyl group at **C3**

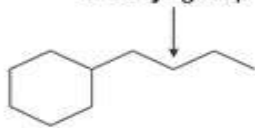
**Incorrect:** 3-ethyl-1-methylcyclohexane

Note the special case of an alkane composed of both a ring and a long chain. If the number of carbons in the ring is greater than or equal to the number of carbons in the longest chain, the compound is named as a cycloalkane.



more carbons in the ring

4 C's in the chain —  
a **butyl** group



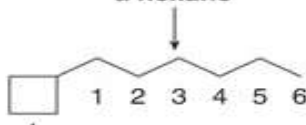
6 C's in the ring — **cyclohexane**

Name as a **cyclohexane** with a substituent.

**Answer: butylcyclohexane**

more carbons in the chain

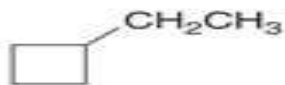
6 C's in the chain —  
a **hexane**



4 C's in the ring — a **cyclobutyl** group

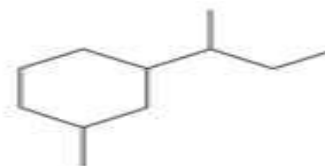
Name as a **hexane** with a substituent.

**Answer: 1-cyclobutylhexane**



**ethylcyclobutane**

[ No number is needed  
with only one substituent. ]



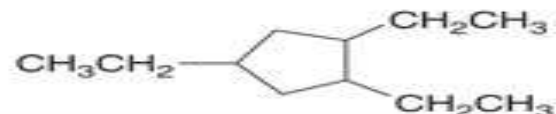
**1-sec-butyl-3-methylcyclohexane**

[ Assign the lower number to the 1<sup>st</sup> substituent  
alphabetically: the **b** of **butyl** before the **m** of **methyl**. ]



**1,2-dimethylcyclohexane**

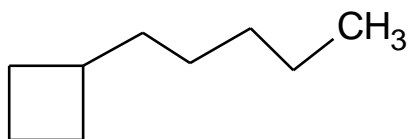
[ Number to give the 2<sup>nd</sup> CH<sub>3</sub> group  
the lower number: 1,2- not 1,6-. ]



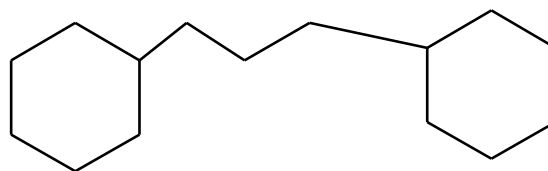
**1,2,4-triethylcyclopentane**

[ Number to give the 2<sup>nd</sup> CH<sub>3</sub>CH<sub>2</sub> group the  
lower number: 1,2,4- not 1,3,4- or 1,3,5-. ]

When a single ring system is attached to a single chain with a greater number of carbon atoms, or when more than one ring system is attached to a single chain, then it is appropriate to name the compounds as *cycloalkylalkanes*. For example.

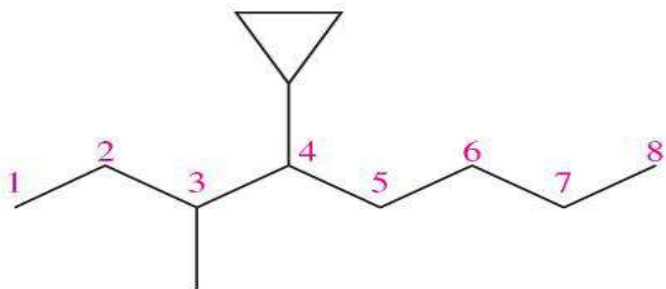


**1-Cyclobutylpentane**



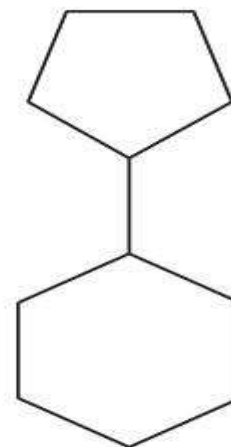
**1,3-Dicyclohexylpropane**

When there are more acyclic than cyclic carbons, the cyclic part becomes a cycloalkyl substituent.



4-cyclopropyl-3-methyloctane

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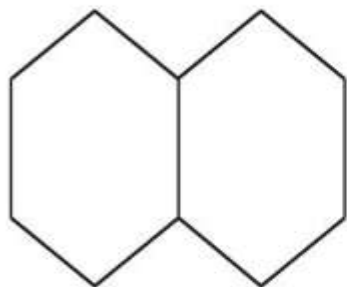
cyclopentylcyclohexane

# Nomenclature of Bicyclic compounds

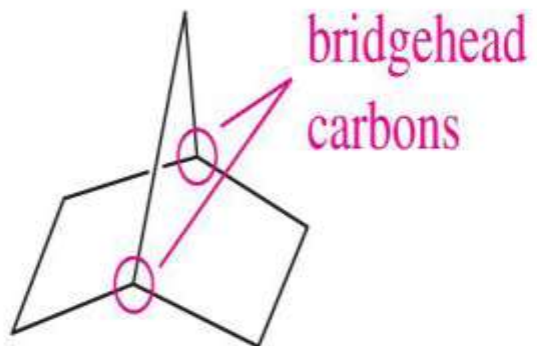
- Bicyclic Alkanes
- When two or more rings are joined, the molecule is said to be polycyclic.
- (A molecule with two joined rings is bicyclic, etc.)
- There are 3 ways that rings can be joined:
  - Fused
  - Bridged
  - Spirocyclic

- A) Fused Rings :  
Fused rings share two adjacent carbon atoms and the bond between them. (These are the most common).
- B) Bridged Rings:  
These share two non-adjacent carbon atoms (the bridgehead carbons) and one or more carbon atoms between them.
- C) Spirocyclic Compounds :  
The two rings share only one carbon atom. (These are comparatively rare).

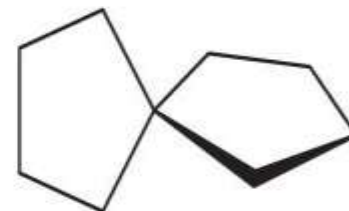
*fused bicyclic*



*bridged bicyclic*



*spirocyclic*



# Nomenclature of Bicyclic Alkanes

- Rule 1:

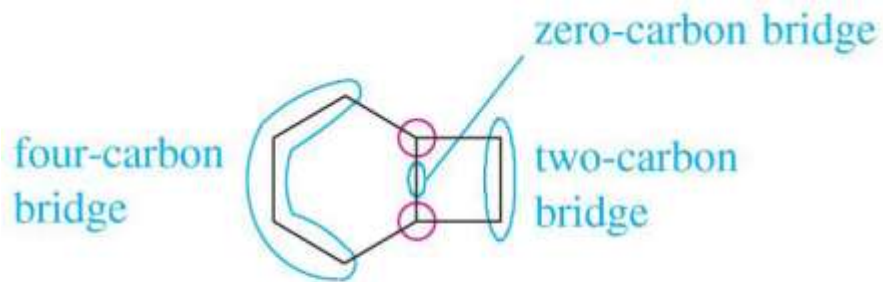
The name is based on the number of carbons in the ring systems.

- Rule 2:

This name is prefixed by bicyclo- (or spiro-), and square brackets with three (or two) numbers.

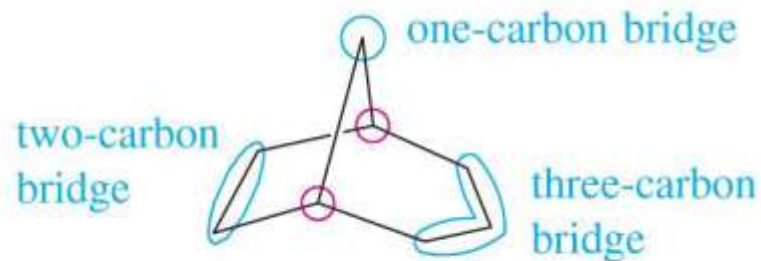
- Rule 3:

For fused and bridged compounds: count the carbon bridges around the shared atoms, and arrange the three numbers in decreasing order. (Spirocyclic systems only have two numbers, but the same rule applies).

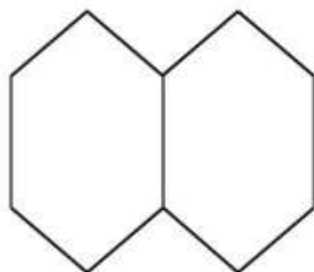


bicyclo[4.2.0]octane

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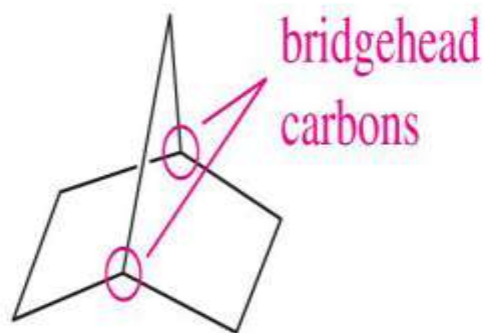


bicyclo[3.2.1]octane



bicyclo[4.4.0]decane  
(decalin)

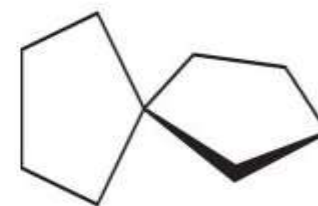
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bicyclo[2.2.1]heptane

(norbornane)

R.D.Pandey, Department of  
chemistry, SXC, Maitighar, KTM, Nepal



spiro[4.4]nonane



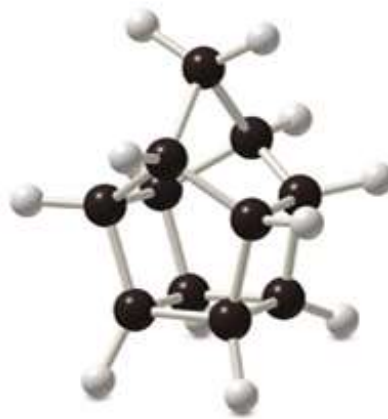
Some organic compounds are identified using common names that do not follow the IUPAC system of nomenclature. Many of these names were given long ago before the IUPAC system was adopted, and are still widely used. Additionally, some names are descriptive of shape and structure, like those below:



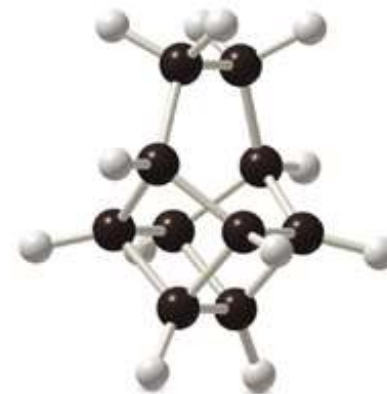
**cubane**



**housane**



**churthane**



**basketane**



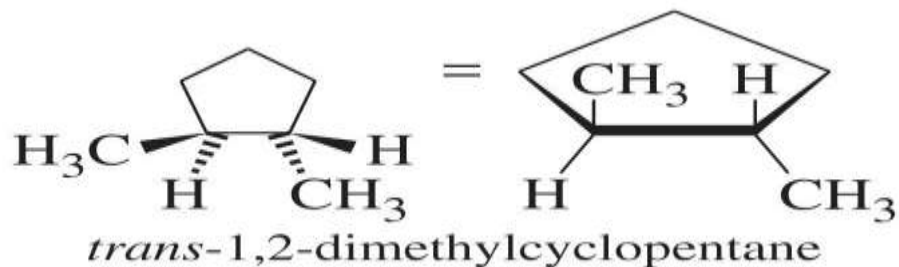
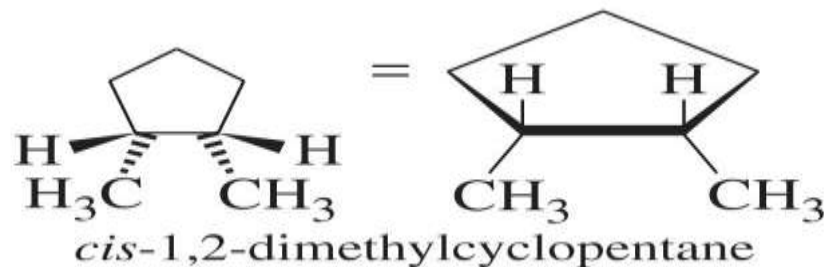
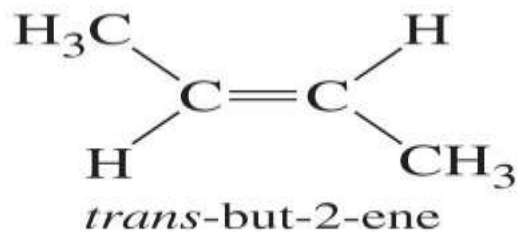
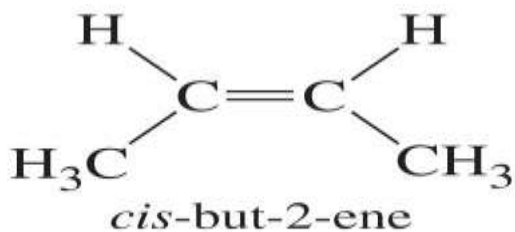
# Geometric Isomerism In Cycloalkanes

Open chain alkanes undergo free rotation about their C-C bonds.

Alkenes, with double bonds, cannot undergo free rotation.

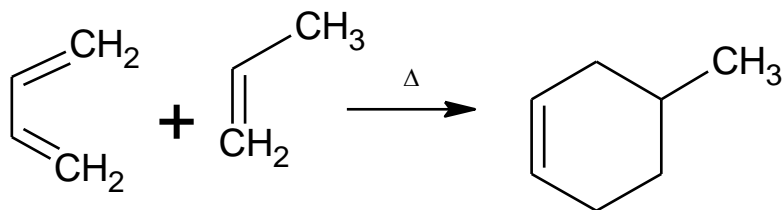
Cycloalkanes also cannot undergo free rotation.

Substituted cycloalkanes can also give rise to cis and trans isomers. The two adjacent carbon must have two different groups to show G.I.



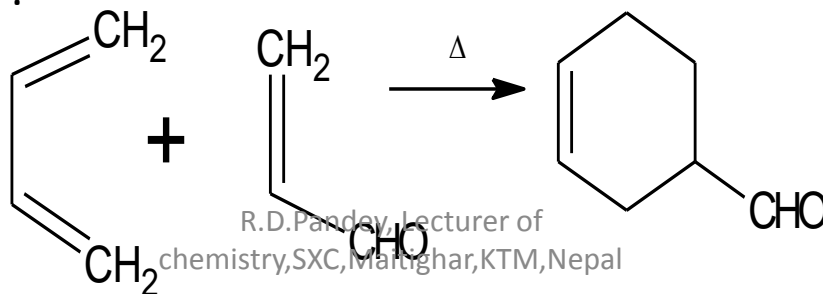
# Preparation of cycloalkane

**Diel's Alder reaction**: The addition of conjugated diene to another unsaturated molecule generally called Dienophile, gives adduct. This reaction is called Diel's Alder reaction. Diel's Alder reaction is an example of pericyclic reaction, a reaction that takes place in one step by a cyclic shift of electrons. It is an example of (4+2) cycloaddition reaction.

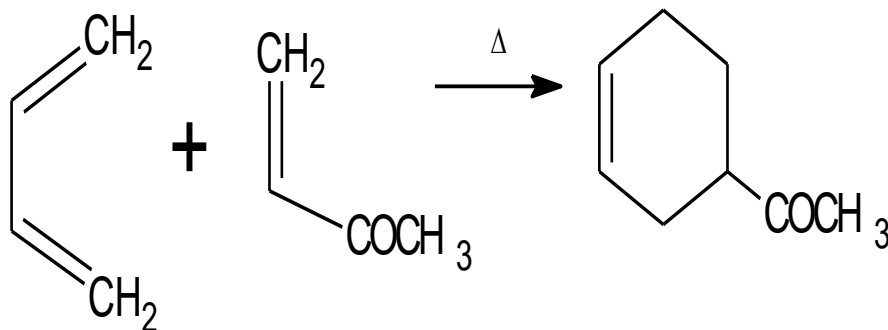


Diene(4

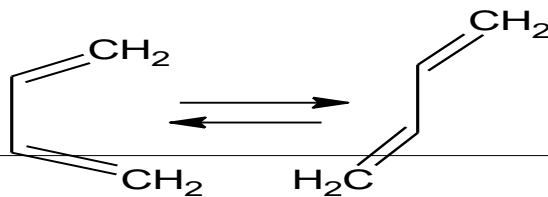
An electron withdrawing group bonded to one of the SP<sup>2</sup> carbon increases the reactivity of dienophile. Such group withdraw electron from the double bond making the Diel's Alder reaction easier to initiate by pumping a partial positive charge on a carbon of dienophile.



Dienes are activated by electron donating groups such as  $-\text{OCH}_3$ ,  $-\text{CH}_3$ ,  $-\text{N}(\text{CH}_3)_2$  etc.



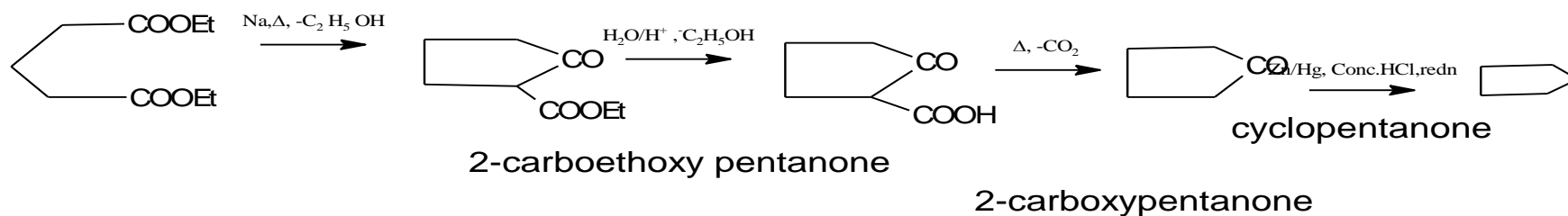
Bicyclic products are obtained if the dienophile is cyclic. This reaction was awarded nobel prize in chemistry in 1950. Only diene with s-cis configuration undergoes this type of addition.



S-cis configuration. S-trans configuration.  
R. D. Pandey, Lecturer of chemistry, SXC, Maitighar, KTM, Nepal

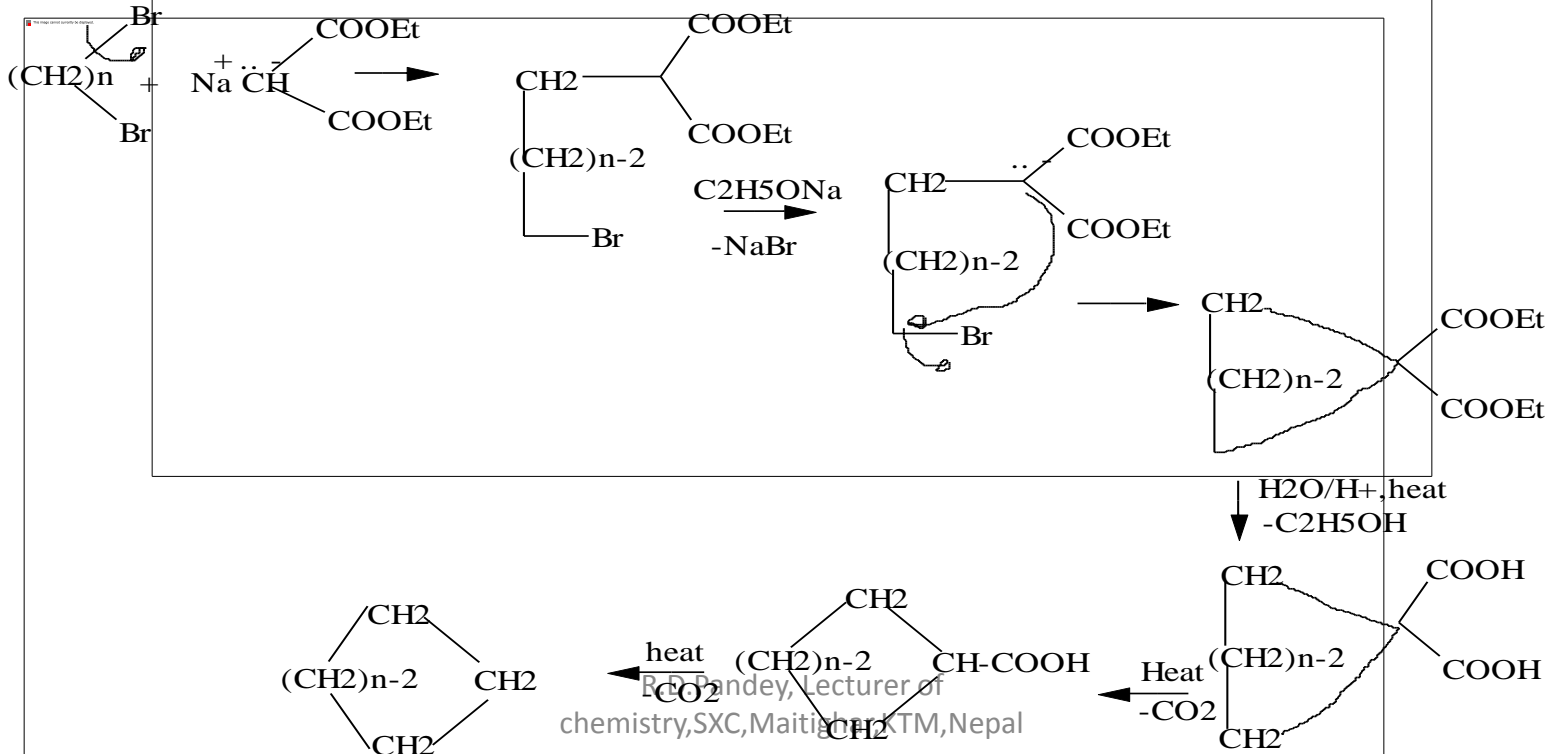
# From esters of dicarboxylic acid.

**Dieckmann's reaction:** Esters of dicarboxylic acid s when heated with sodium followed by hydrolysis cyclic ketone is formed which on Clemmensen reduction gives cycloalanes . It s an intramolecular Claisen condensation reaction. The addition of base to 1,6-diester causes the diester to undergo an intramolecular condensation ,thereby forming a five membered ring  $\beta$ - ketoester.



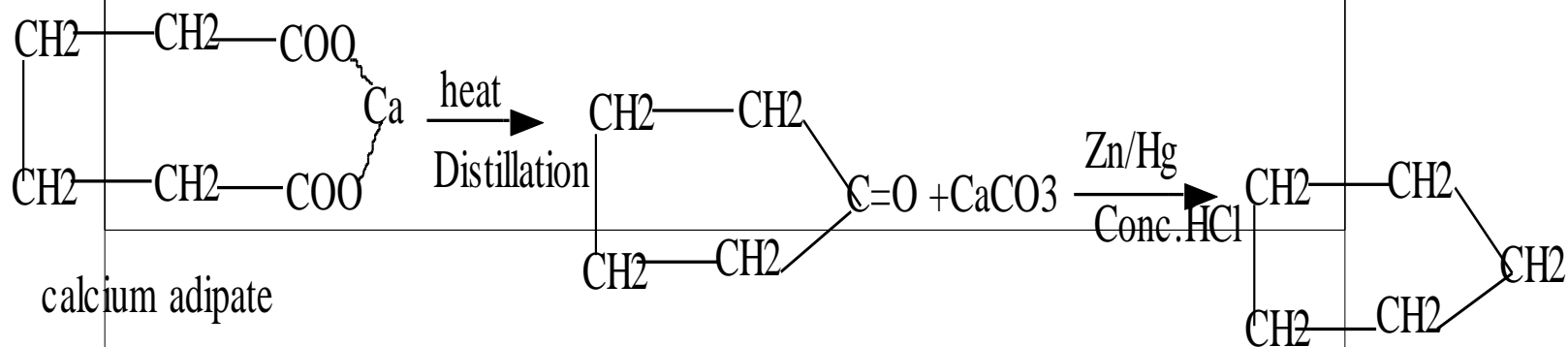
# From malonic ester

Perkin's method: This method is suitable for the synthesis of cycloalkane upto six membered ring and suggested by Perkin. When terminal dibromide is treated with malonic ester in presence of sodium ethoxide, a cycloalkane-1,1-dicarboxylic ester is formed which upon hydrolysis followed by heating gives the corresponding cycloalkane.



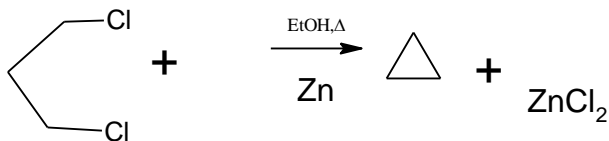
# From calcium, barium or thorium salt of dicarboxylic acid

- Wislicenus method: On heating Ca or Ba salt of dicarboxylic acids, cyclic ketone is formed which can be further reduced to cycloalkane by Clemmensen reduction using Zn-Hg/ conc.HCl.



# From $\alpha,\omega$ -dihalide

Freund's method: When  $\alpha,\omega$ -dihalogen compounds are heated with Zn or Na metal in presence of EtOH, cycloalkane is formed. 3,4,5,6 membered rings are prepared by this method. When two X-atoms are further than 1,6- position, they do not form ring compounds but undergo the Wurtz reaction.





# Physical Properties

- Cyclopropane and cyclobutane are gases and higher members are liquid.
- They are insoluble in water but soluble in organic solvent.
- Their m.p. and b.p. increases as their molecular wt. increases.
- Note that, compared with the corresponding straight-chain alkanes, the cycloalkanes have higher boiling and melting points as well as higher densities. These differences are due in large part to increased London interactions of the relatively more rigid and more symmetric cyclic systems.
- In comparing lower cycloalkanes possessing an odd number of carbons with those having an even number, we find a pronounced alternation in their melting points. This phenomenon has been ascribed to differences in crystal packing forces between the two series
- They are nonpolar, relatively inert compounds with boiling points and melting points that depend on their molecular weights. The cycloalkanes are held in a more compact cyclic shape, so their physical properties are similar to those of the compact, branched alkanes.

# Chemical properties.

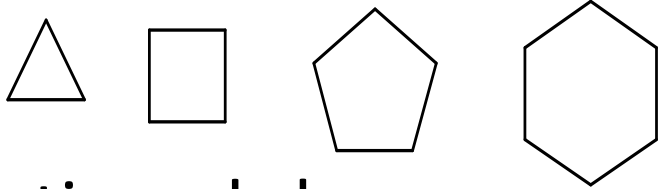
- The cycloalkanes resemble alkanes in chemical properties.
- They do not react with acid ,bases, oxidising agent and reducing agent.

Q.

## Discuss the stability of cycloalkane in terms of Bayer's strain theory.

- In order to explain the stability of cycloalkane, Adolf Von Bayer (1889) proposed a theory known as Bayer's strain theory. The main facts of this theory are as follows;
- i) the carbon is tetrahedral. The carbon atoms lie at the center of the tetrahedron and its four valences are directed towards the four corners of tetrahedron. The bond angle is  $109^{\circ} 28'$ .
- The deviation of bond from normal tetrahedron causes a strain in the molecule which is the cause of reactivity. Example the deviation of bond in alkene and alkyne makes them reactive.

- lii) Cycloalkanes are planar molecules i.e. all the carbon atoms forming the ring lie in the same plane. Thus cyclopropane is the equilateral triangle, cyclobutane is the square and cyclopentane and onwards are polygons.

- Iv) If these molecules are  Considered in the above mentioned shapes, then there is large deviation from the normal angle ( $109^{\circ}28'$ ). This strain is called "angle strain".

- The greater the deviation of bond from  $109^{\circ} 28'$ , the greater will be the angle strain. Consequently the more reactive will be the molecule. He calculated the deviation of bond by using the formula-  $d = \frac{1}{2}(109^{\circ} 28' - \alpha)$ , where, d is the deviation in bond angle from tetrahedral angle and  $\alpha$  is the observed angle in cycloalkane.
- The deviation of bond in cyclopropane =  $\frac{1}{2}(109^{\circ} 28' - 60^{\circ}) = 24^{\circ} 44'$ . Like wise in cyclobutane, cyclopentane and cyclohexane are respectively  $9^{\circ} 44'$ ,  $0^{\circ} 44'$ ,  $-5^{\circ} 16'$

- $\frac{1}{2}$  means deviation is equally shared between two bonds. +ve value for deviation shows the bond angle has been compressed and –ve value for the deviation show the bond angle has been expanded .
- From the above calculation, it is obvious that the deviation from the normal tetrahedral angle is maximum in cyclopropane causing maximum strain in the molecule(Bayer's most unstable compound).Hence it is the most reactive.

- The deviation in cyclobutane is less than cyclopropane causing less strain in the molecule. The deviation of bond in cyclopentanes is least .It is the most stable compound(Bayer's most stable).The deviation in cyclohexane and cycloheptane would go on increasing .Thus they will be less stable compound .Thus the synthesis of large ring would be very difficult because the deviation of bond would go on increasing.

- V) The more stable a ring system, more easily it can be synthesized.
- If Bayer's strain theory is accepted, stability of cyclohexane and other higher members should be lower than cyclopentane. But experimentally, cyclohexane and higher members have been found as stable as cyclopentane ring, why? This is opposed by heat of combustion data of cycloalkane.



# Factors affecting stability of cyclo-alkane

Besides torsional strain and steric strain, the conformations of cycloalkanes are also affected by **angle strain**.

Keep in mind the three different types of strain in organic molecules:

- **Torsional strain (pitzer strain): strain** caused by eclipsing interactions.

This is caused by the repulsion of the bonding electrons of one substituent with bonding electrons of another substituent on the adjacent atom.

- **Steric strain (Vanderwaals strain): strain** produced when atoms are forced too close to each other.

This is caused by atoms or groups approaching each other too closely i.e. nearer than vander waal's radi.

- **Angle strain(Baeyer's strain): strain** produced when bond angles deviate from  $109.5^\circ$  (for *sp*<sup>3</sup> hybridized atoms).

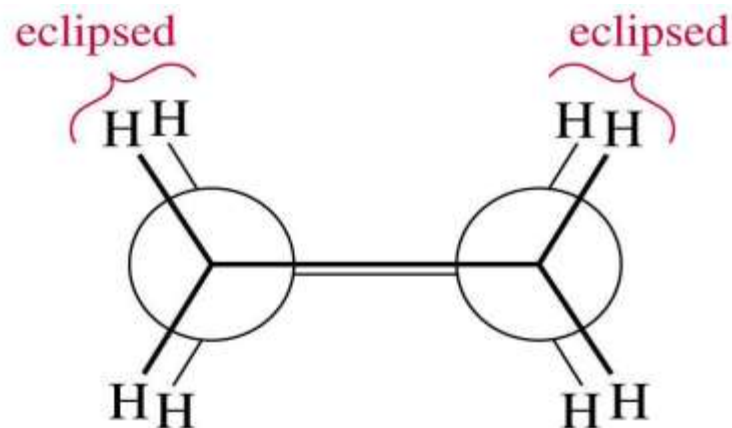
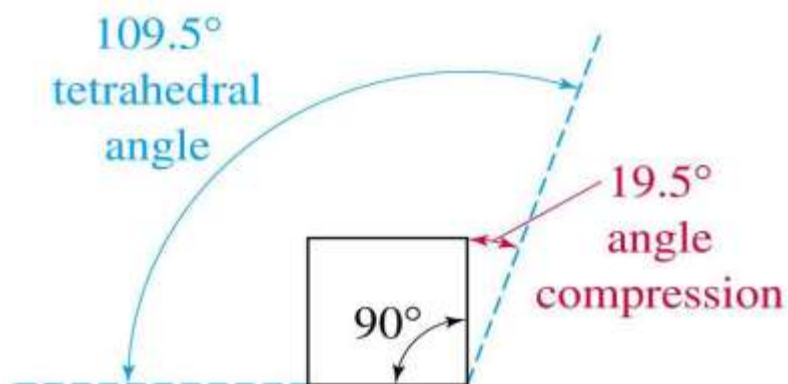
Cyclic compounds twist and bend in order to achieve a final structure which minimize the above three kinds of strain that can destabilize a cyclic compound.

# Ring Strain in Cycloalkanes

If a cycloalkane requires bond angles **different to  $109.5^\circ$**  then the  **$sp^3$  orbitals cannot overlap as efficiently as possible.**

This gives rise to **angle strain (Bayer strain).**

Consider planar cyclobutane:



Newman projection  
of planar cyclobutane

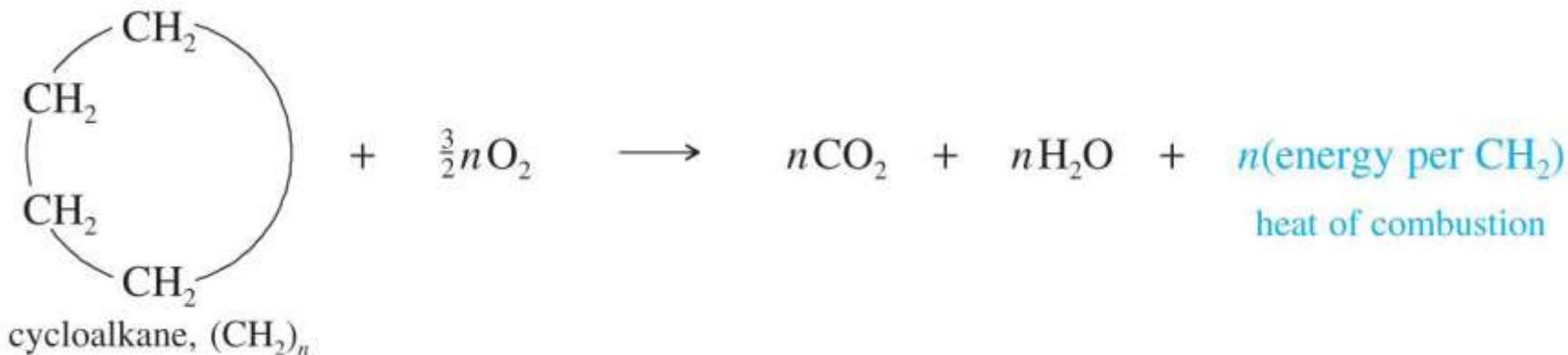
Along with the angle strain, there is also eclipsing of the hydrogens – torsional strain.

The combination of angle and torsional strains is called **Ring Strain.**

Calculation of Ring Strain

This is calculated through heats of combustion.

Already seen that alkanes can be combusted – so can cycloalkanes.



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The energy released is the **heat of combustion**, and this value can be **converted in useful information**

Ring Size	Cycloalkane	Molar Heat of Combustion	Heat of Combustion per CH <sub>2</sub> Group	Ring Strain per CH <sub>2</sub> Group	Total Ring Strain
3	cyclopropane	2091 kJ (499.8 kcal)	697.1 kJ (166.6 kcal)	38.5 kJ (9.2 kcal)	115 kJ (27.6 kcal)
4	cyclobutane	2744 kJ (655.9 kcal)	686.1 kJ (164.0 kcal)	27.5 kJ (6.6 kcal)	110 kJ (26.3 kcal)
5	cyclopentane	3320 kJ (793.5 kcal)	664.0 kJ (158.7 kcal)	5.4 kJ (1.3 kcal)	27 kJ (6.5 kcal)
6	cyclohexane	3951 kJ (944.4 kcal)	658.6 kJ (157.4 kcal)	0.0 kJ (0.0 kcal)	0.0 kJ (0.0 kcal)
7	cycloheptane	4637 kJ (1108.2 kcal)	662.4 kJ (158.3 kcal)	3.8 kJ (0.9 kcal)	27 kJ (6.4 kcal)
8	cyclooctane	5309 kJ (1268.9 kcal)	663.6 kJ (158.6 kcal)	5.1 kJ (1.2 kcal)	41 kJ (9.7 kcal)
	reference: long-chain alkane		658.6 kJ (157.4 kcal)	0.0 kJ (0.0 kcal)	0.0 kJ (0.0 kcal)

All units are per mole.

Note: Cyclopropane and cyclobutane are highly strained

Cyclopentane and cycloheptane have low ring strain .cyclohexane has no ring strain !

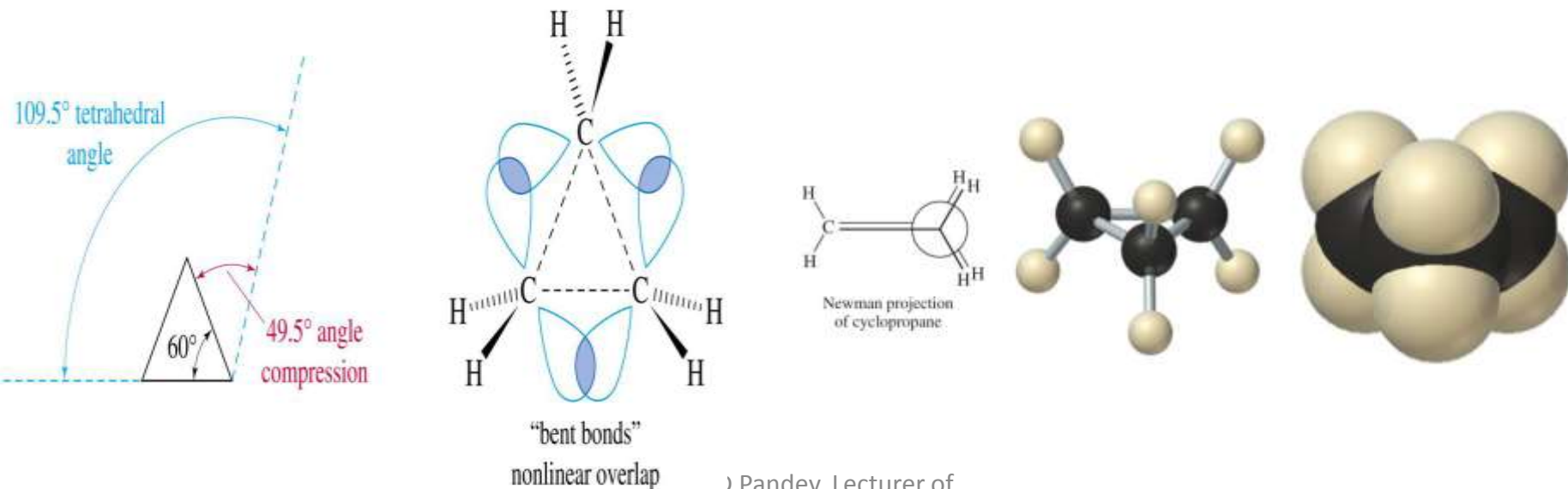
## Cyclopropane

Cyclopropane is the most strained cycloalkane . This is due to two effects: Angle Strain and Torsional Effects

Bonding Overlap is reduced because the **enforced 60° bond angle leads to poor overlap of the sp<sup>3</sup> orbitals.**

The three membered ring has to be planar, and all the C-H's are eclipsed.

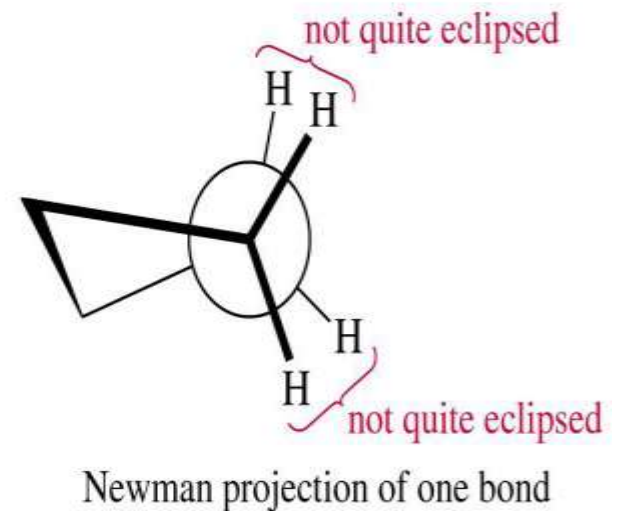
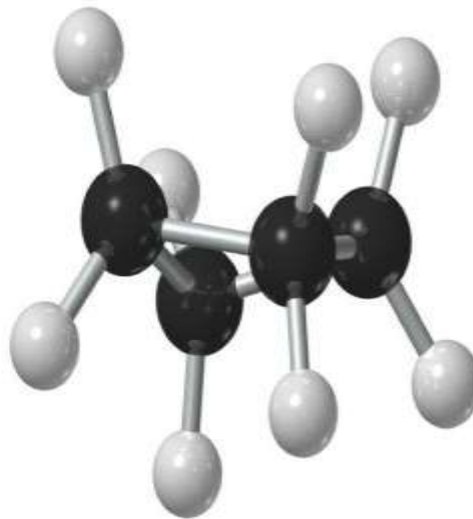
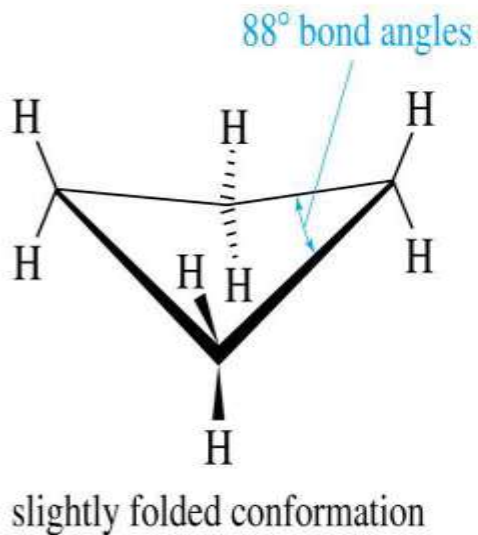
The angle strain is larger than the torsional effects for cyclopropane



- The carbon atoms of alkanes are *sp<sup>3</sup> hybridized*  $\Rightarrow$  *the bond angle is 109.5°*
- The internal angle of cyclopropane is 60° and departs from the ideal value by a very large amount — by 49.5°.
- **Angle strain: the potential energy rise resulted from compression of the internal angle of a cycloalkane from normal *sp<sup>3</sup>-hybridized carbon angle*.**
- The *sp<sup>3</sup> orbitals of the carbon atoms cannot overlap as effectively as they do in alkane (where perfect end-on overlap is possible).*
- The **C—C bonds of cyclopropane are “bent”  $\Rightarrow$  orbital overlap is less effectively (the orbitals used for these bonds are not purely *sp<sup>3</sup>*, they *contain* more *p* character)  $\Rightarrow$  the C—C bonds of cyclopropane are weaker  $\Rightarrow$  cyclopropane has greater potential energy.**

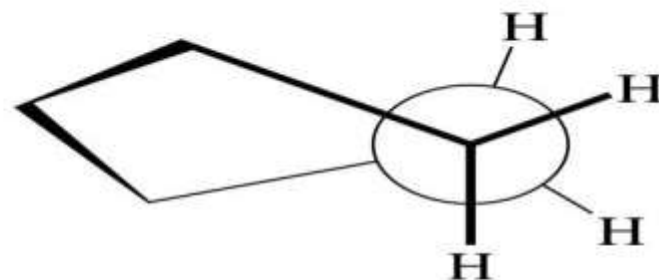
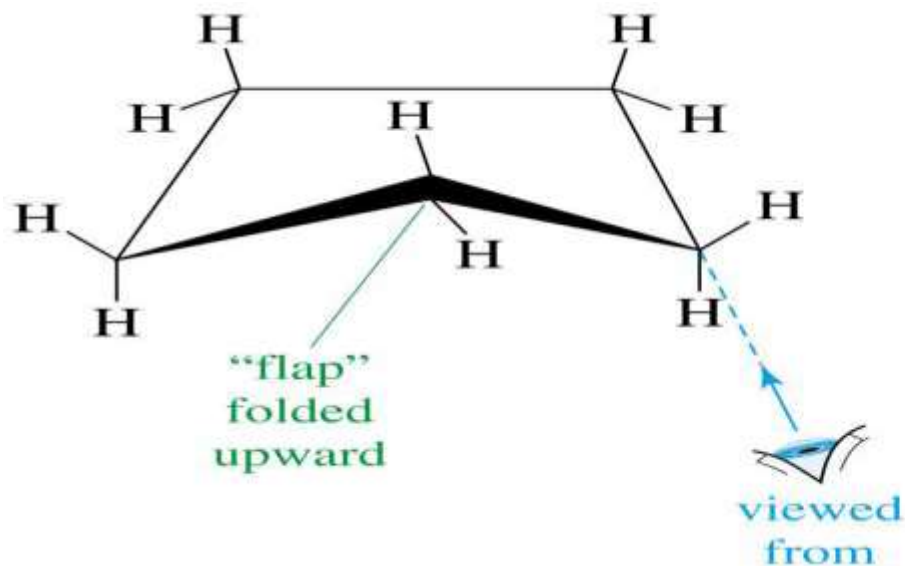
# Cyclobutane

Cyclobutane is **neither planar, nor a perfect square**. A planar geometry would force all the C-H bonds into eclipsing positions. Cyclobutane actually adopts a slightly puckered conformation like butterfly, with bond angles of  $88^\circ$ . This increases angle strain but reduces torsional strain.



# Cyclopentane

Cyclopentane has **little torsional strain and angle strain**. Cyclopentane is not planar either, since this also would require all C-H's to be eclipsing. The molecule adopts a puckered 'envelope' conformation, which reduces the torsional strain. The internal angles are  $108^\circ \Rightarrow$  very **little angle strain if it was planar**  $\Rightarrow$  considerably **torsional strain**. Cyclopentane is **flexible and shifts rapidly from one conformation to another**.



Newman projection showing relief of eclipsing of bonds

## Stability of cyclohexane

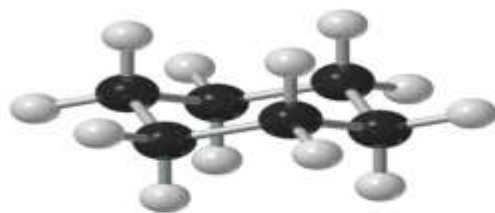
Cyclohexane : Sacche-Mohr concept of strainless ring:

Cyclohexane is by far the most common cycloalkane in nature and also in organic chemistry.

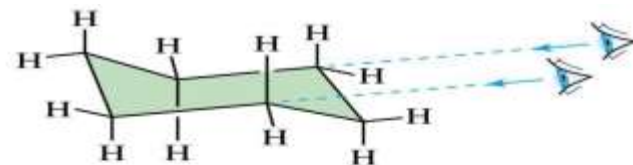
**Zero ring strain implies the bond angles must be  $109.5^\circ$  (no angle strain) and also no eclipsing interactions between the C-H bonds (no torsional strain).**

Boat and Chair Conformations

Cyclohexane adopts a puckered structure. The most stable conformation for cyclohexane is called the **chair conformation**.

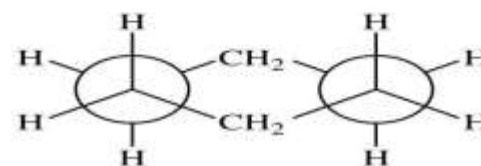


chair conformation



viewed along the "seat" bonds

In the chair conformation, all the bond angles are  $109.5^\circ$  and all the C-H bonds are staggered. (Zero ring strain)



Newman projection

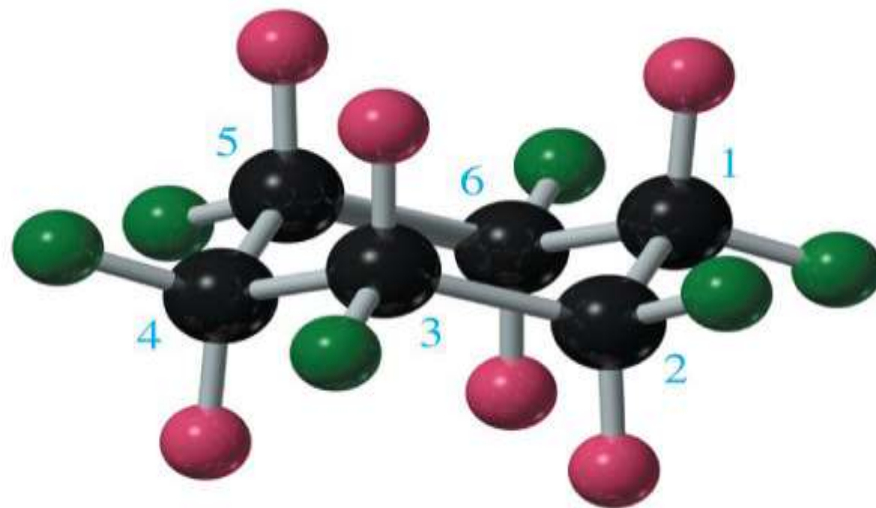
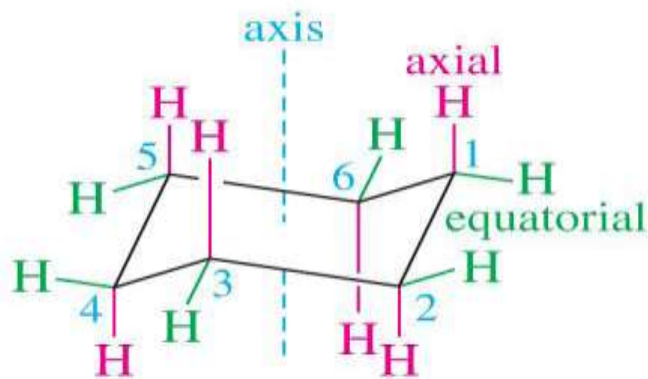


# Axial And Equatorial Positions

If we look at an instantaneous snapshot of cyclohexane in a chair conformation, there are 2 types of C-H bond. Six of the C-H bonds point straight up and down (axial bonds).

Six of the C-H bonds point out from the ring (equatorial bonds).

Notice the alternating pattern of the positions.



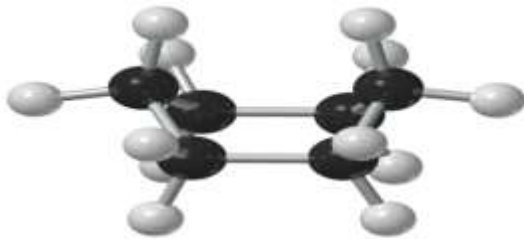
# Boat Conformation

Cyclohexane can also exist in another conformation called the **boat**. The boat is just a chair with the footrest flipped up.

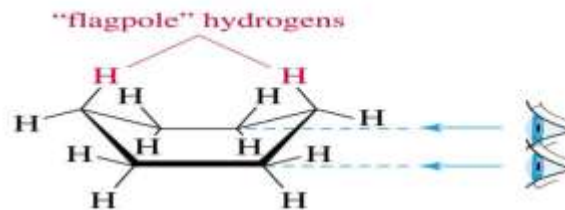
This also has bond angles of  $109.5^\circ$  and thus avoids any angle strain, but there is torsional strain.

The two hydrogens at the ends of the boat are in close contact, causing torsional strain. These flagpole hydrogens are eclipsed.

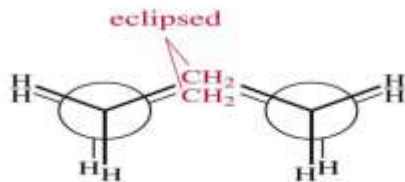
To avoid these unfavorable interactions, the boat conformation skews slightly, giving a twist boat conformation .



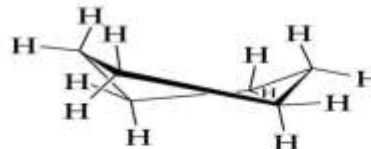
boat conformation



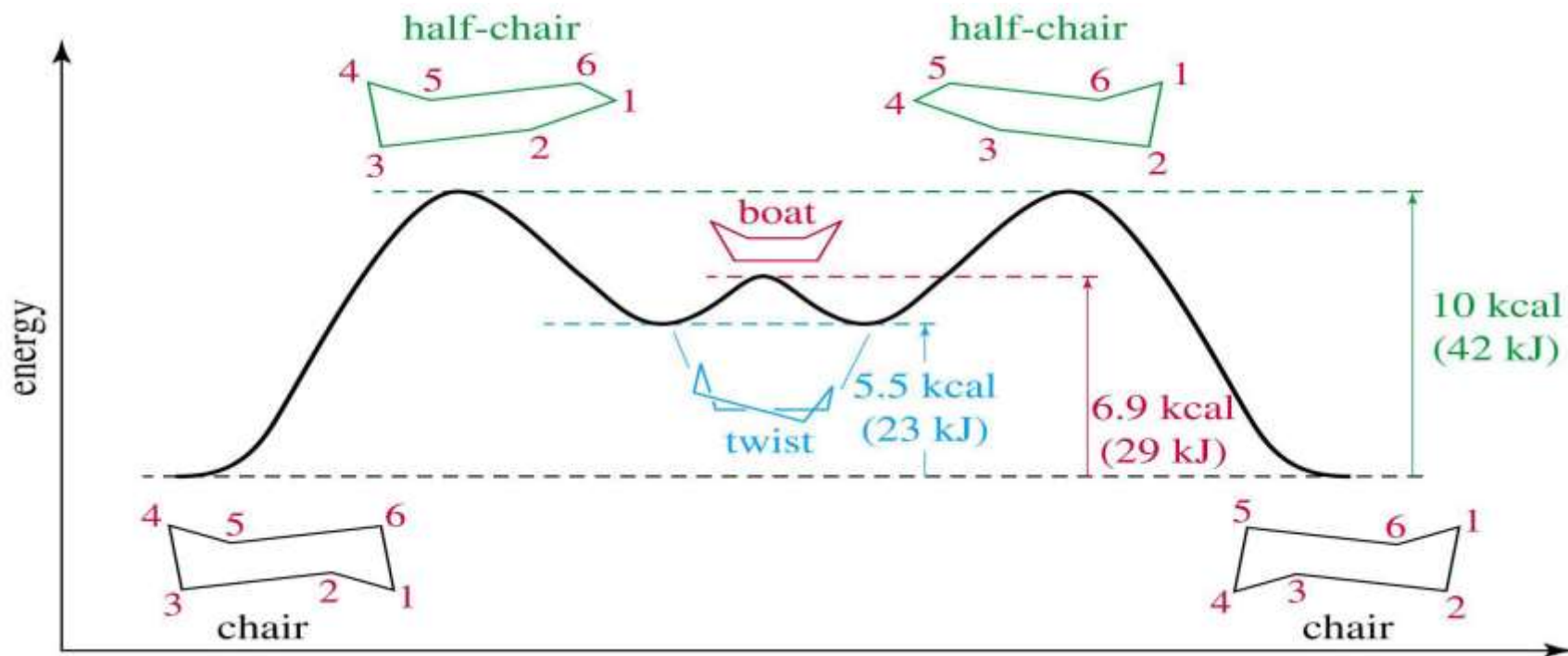
symmetrical boat



Newman projection



"twist" boat

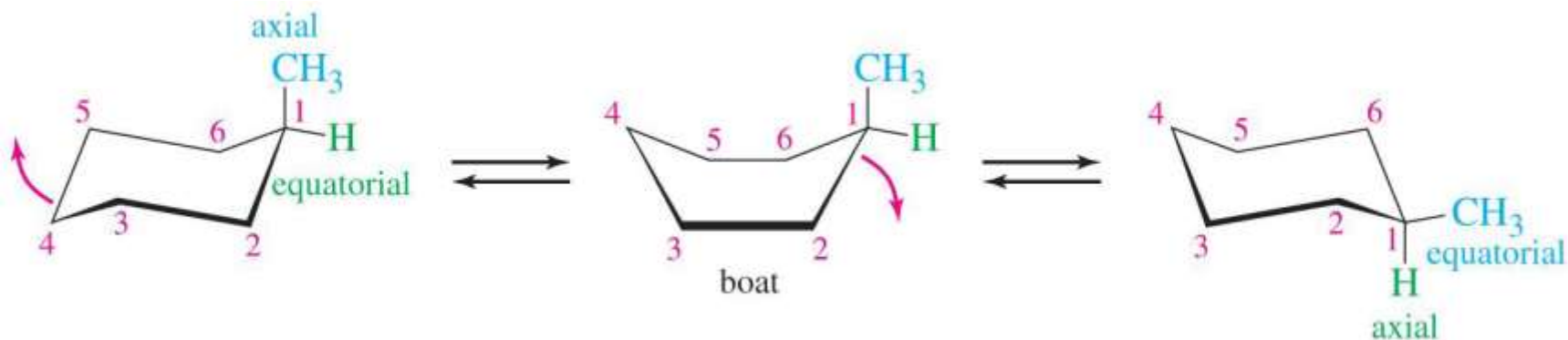


The chair is the **lowest energy conformation**, although since the energy barrier to ring flip is **fairly small**, there will always be some other conformations present.

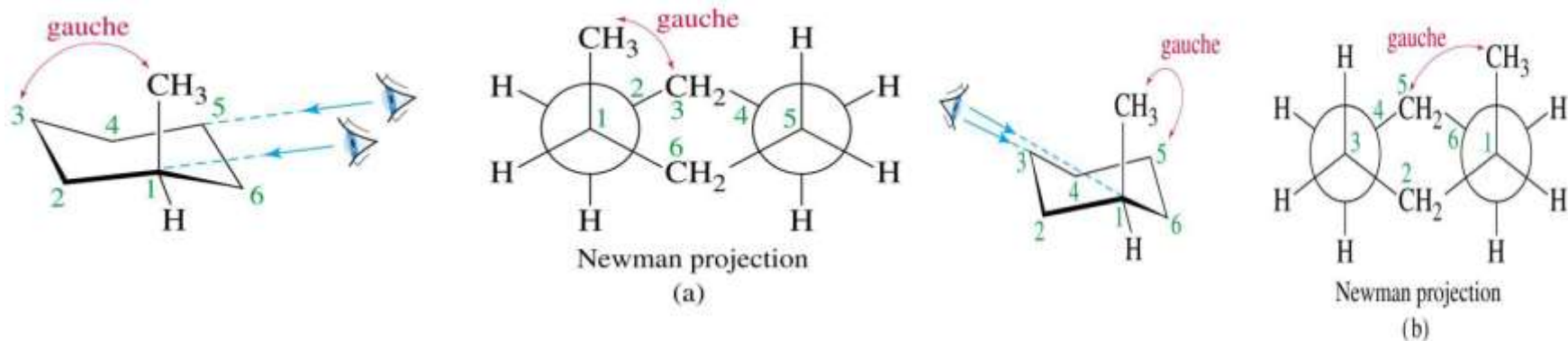
The half chair is the point of highest energy, and is not a stable conformation

## Conformations of Monosubstituted Cyclohexanes

A substituent on a cyclohexyl ring can occupy either an axial or equatorial position. Consider methylcyclohexane: The chair conformation with the methyl axial can interconvert via a boat conformation into a chair conformation with the methyl equatorial. The energy barrier for this is low, and this interconversion takes place rapidly at room temperature, although the conformation of lower energy predominates. It is found that the methyl equatorial conformation is 1.7kcal/mol lower in energy than the methyl axial conformation. Both chair conformations are lower in energy than the boat.



When the methyl group is **axial**, it is **gauche** to C3 and C5.

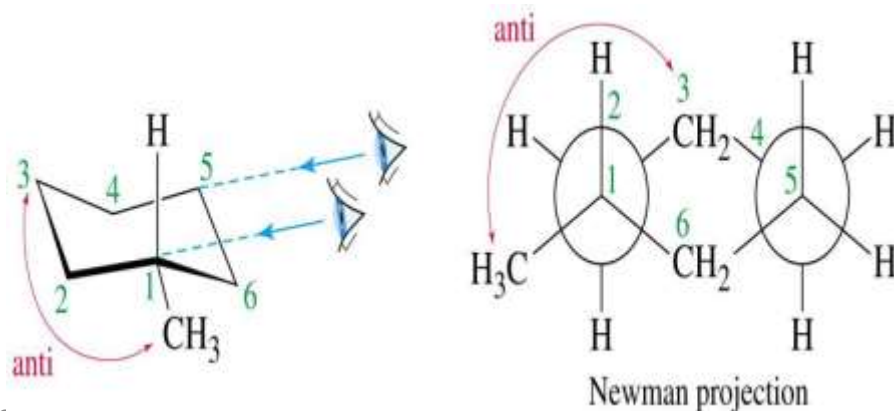


When the methyl is **equatorial**, it is **anti** to C3.

So axial methylcyclohexane has 2 gauche interactions (2 x 0.9kcal)

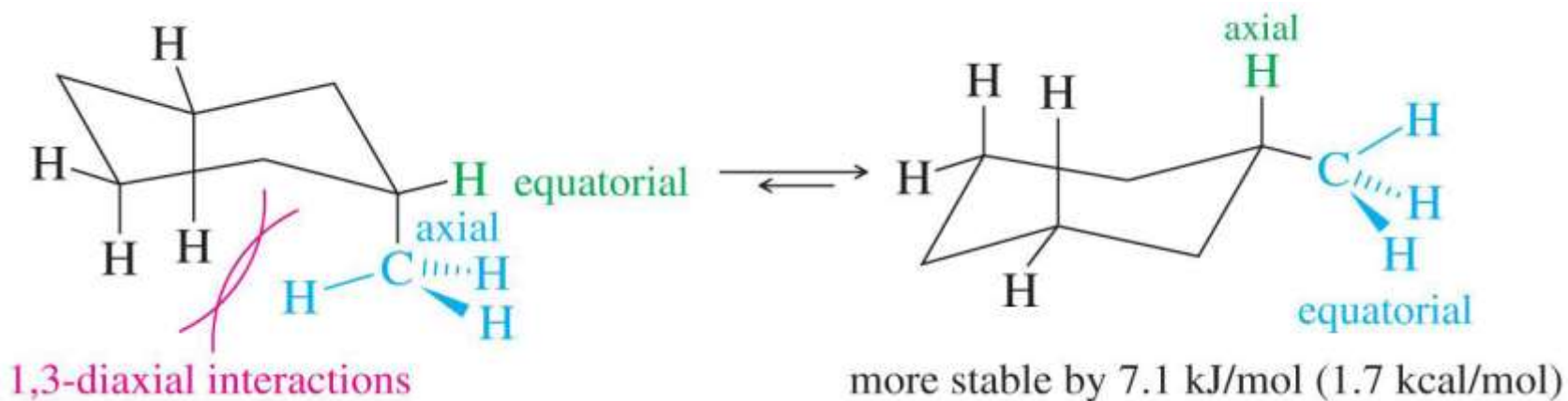
Equatorial methylcyclohexane has no gauche interactions.

Predict that **EQUATORIAL** is favored by **1.8kcal. (Good agreement).**



This gauche interaction is also known as a **1,3 diaxial interaction**. The axial substituents on C1 and C3 are close in space and their electron clouds repel one another.

Generally a larger substituent gives rise to a larger difference in energy between the axial and equatorial conformations.



# Industrial source.

- Petroleum from certain areas is rich in cycloalkane (in particular California), known to petroleum industry as naphthenes (mainly contains cyclohexanes, methylcyclohexane, methylcyclopentane, and 1,2-dimethylcyclopentane).
- Addition of hydrogen to aromatic compounds yields cyclic aliphatic compounds specially cyclohexane derivatives. For example, hydrogenation of benzene yields pure cyclohexane.





# Industrial source.