For updated version, please click on
http://ocw.ump.edu.my

Organic Chemistry

Alkanes (2)

by
Seema Zareen & Dr. Izan Izwan Misnon
Faculty Industrial Science & Technology
seema@ump.edu.my; iezwan@ump.edu.my

Expected Outcomes

In the end of this chapter, student will have the ability to:

- Classify carbons and hydrogens in alkanes
- Draw and identify IUPAC nomenclature of alkane and cycloalkane compounds
- Describe characteristics and physical properties of alkanes

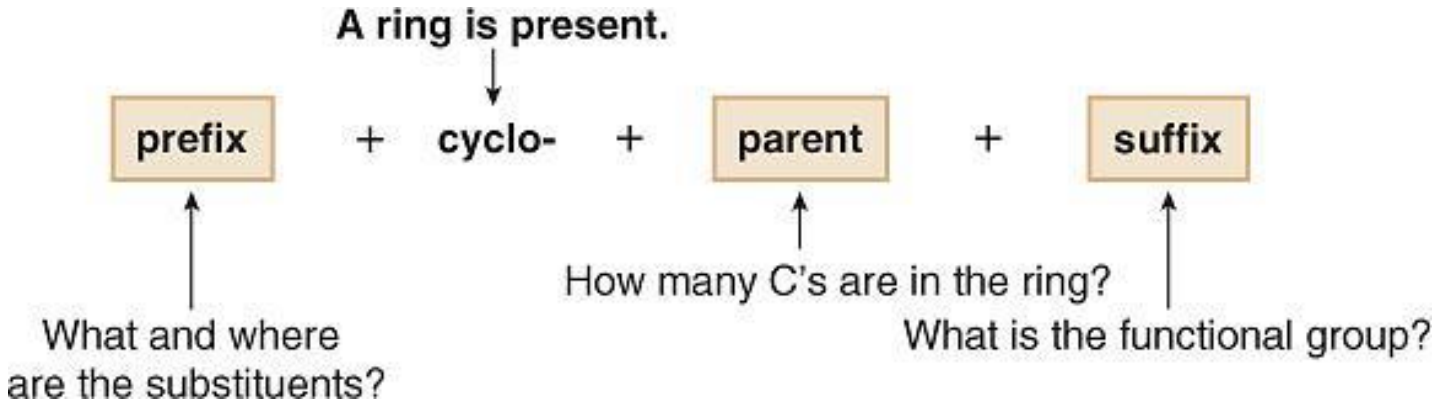
Contents

- Alkanes
- Physical properties
- Nomenclature
- Alkanes reaction mechanisms

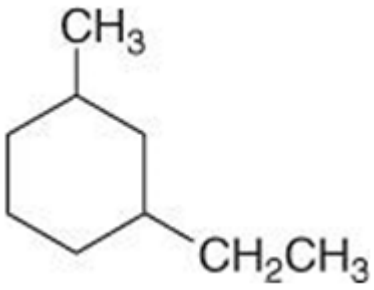
Cycloalkanes

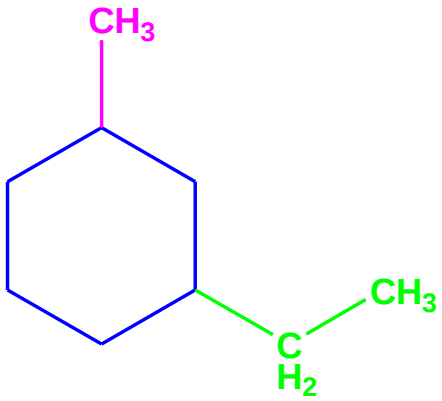
- Rings of carbon atoms (CH_2 groups)
- Formula: C_nH_{2n}
- Nonpolar, insoluble in water
- Compact shape
- Melting and boiling points similar to branched alkanes with same number of carbons

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

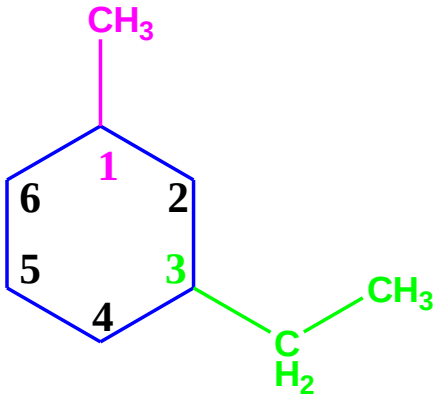


1. Find the **parent cycloalkane**.

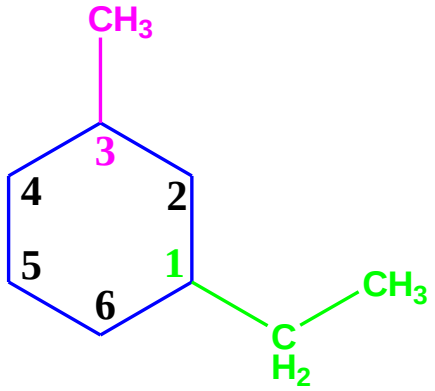




Parent Carbon = cyclohexane
Substituent = 2 (methyl and ethyl)

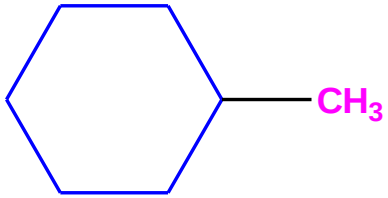


3-ethyl-1-methylcyclohexane

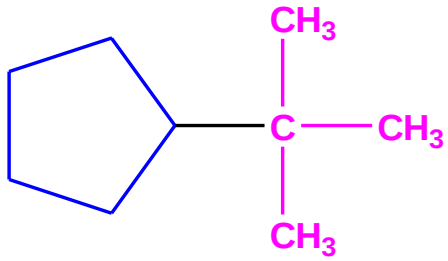


1-ethyl-3-methylcyclohexane

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

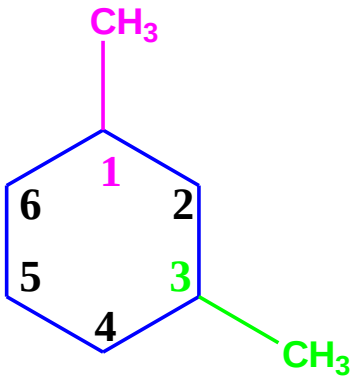


Methylcyclohexane

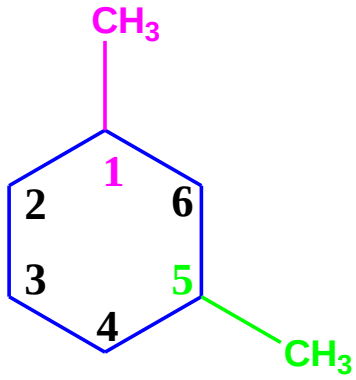


tert-butylcyclopentane

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.

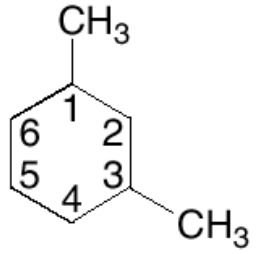


1,3-dimethylcyclohexane



1,5-dimethylcyclohexane

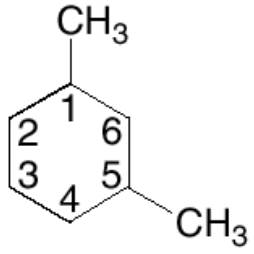
numbering clockwise



CH_3 groups at C1 and **C3**
The 2nd substituent has a lower number.

Correct: **1,3-dimethylcyclohexane**

numbering counterclockwise

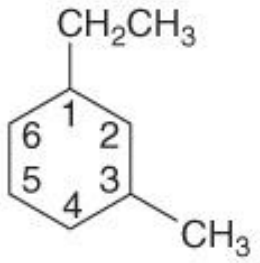


CH_3 groups at C1 and **C5**

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.

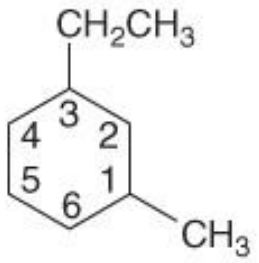


- **e**thyl group at **C1**
- **m**ethyl group at **C3**

earlier letter ⟶ lower number

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

Begin numbering at the methyl group.



- **m**ethyl group at **C1**
- **e**thyl group at **C3**

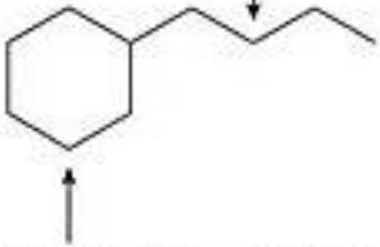
Incorrect: 3-ethyl-1-methylcyclohexane

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.

Two contrasting examples—
Naming compounds containing both a ring and a long chain of carbon atoms

more carbons in the ring

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



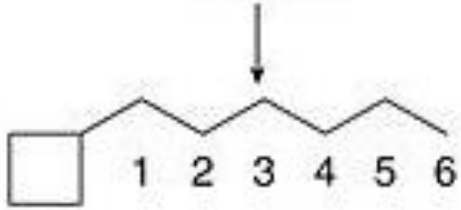
6 C's in the ring—**cyclohexane**

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

Answer: butylcyclohexane

more carbons in the chain

6 C's in the chain — a **hexane**

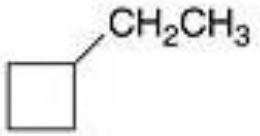


4 C's in the ring—a **cyclobutyl** group

Name as a *hexane* with a substituent.

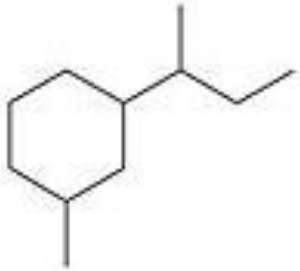
Answer: 1-cyclobutylhexane

Examples of cycloalkane nomenclature



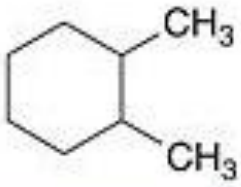
ethylcyclobutane

[No number is needed with only one substituent.]



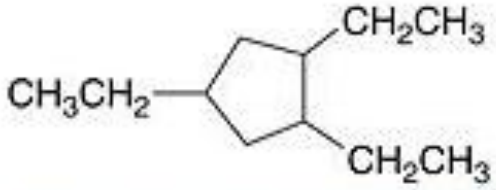
1-*sec*-butyl-3-methylcyclohexane

[Assign the lower number to the 1st substituent alphabetically: the **b** of **b**utyl before the **m** of **m**ethyl.]



1,2-dimethylcyclohexane

[Number to give the 2nd CH_3 group the lower number: 1,2- not 1,6-.]

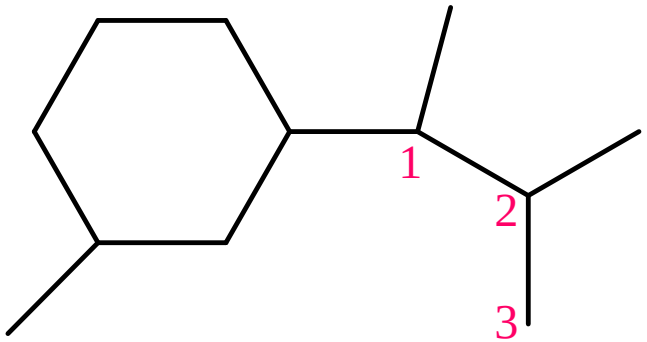


1,2,4-triethylcyclopentane

[Number to give the 2nd CH_3CH_2 group the lower number: 1,2,4- not 1,3,4- or 1,3,5-.]

Naming complex substituents:

- If the branch has a branch, number the carbons from the point of attachment.
- Name the branch of the branch using a locator number.
- Parentheses are used around the complex branch name (sub-branch name ends in –yl).



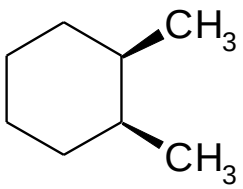
1-methyl-3-(1,2-dimethylpropyl)cyclohexane

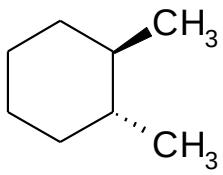
Cis/Trans isomerism in Cycloalkanes

In contrast to C-C single bonds in alkanes, the C-C single bonds in a cycloalkane do not undergo free rotation.

Look at a model. In order to rotate about the single bond, the C-C single bond would have to break. This sigma bond is too strong to break under ordinary conditions.

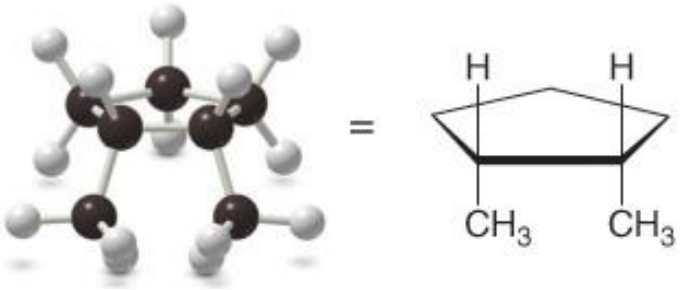
Because of this restricted rotation, cycloalkanes with two or more substituents exhibit **cis/trans isomerism**



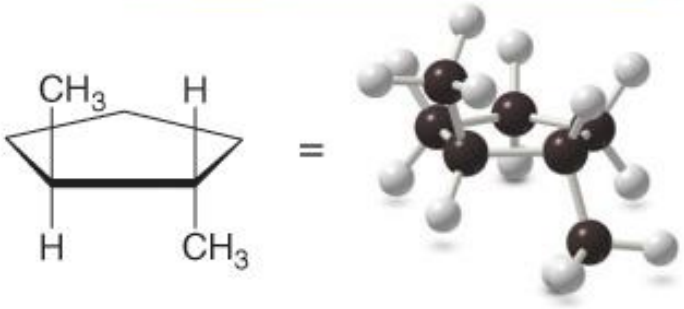


- The prefixes **cis** and **trans** are used to distinguish these isomers.
- The **cis isomer** has two groups on the same side of the ring.
- The **trans isomer** has two groups on opposite sides of the ring.

cis-1,2-dimethylcyclopentane

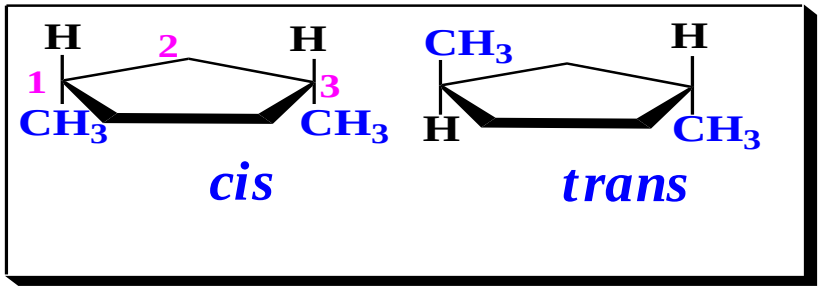


trans-1,2-dimethylcyclopentane

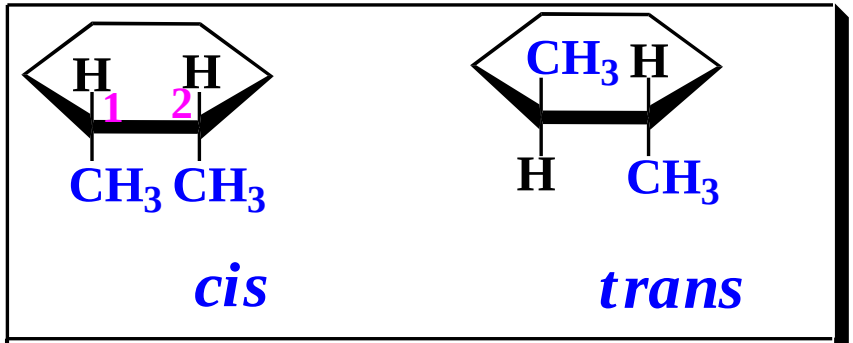


Additional Examples of *cis*- and *trans*- Isomers

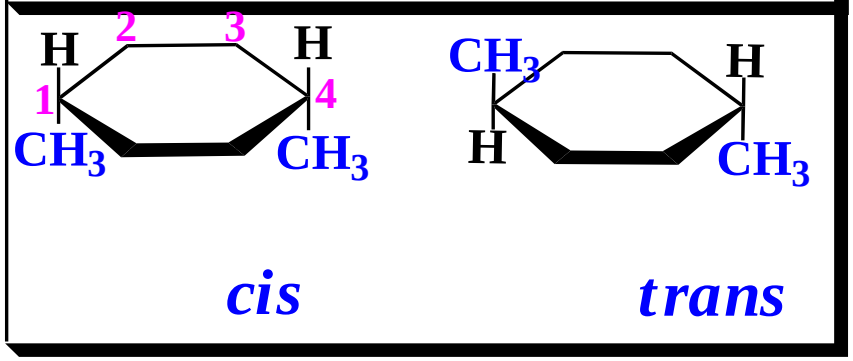
These examples are all shown as planar structures to more easily illustrate the stereochemical relationships.



1,3-dimethylcyclopentanes



1,2-dimethylcyclohexanes

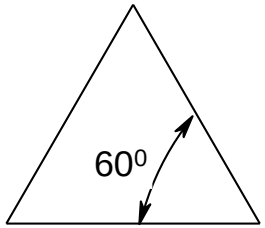


1,4-dimethylcyclohexanes

Conformations and Stabilites of Cycloalkanes

Cycloalkanes possess types of strain that do not exist in noncyclic alkanes

Angle Strain – the amount of strain due to deviation from normal bond angle.



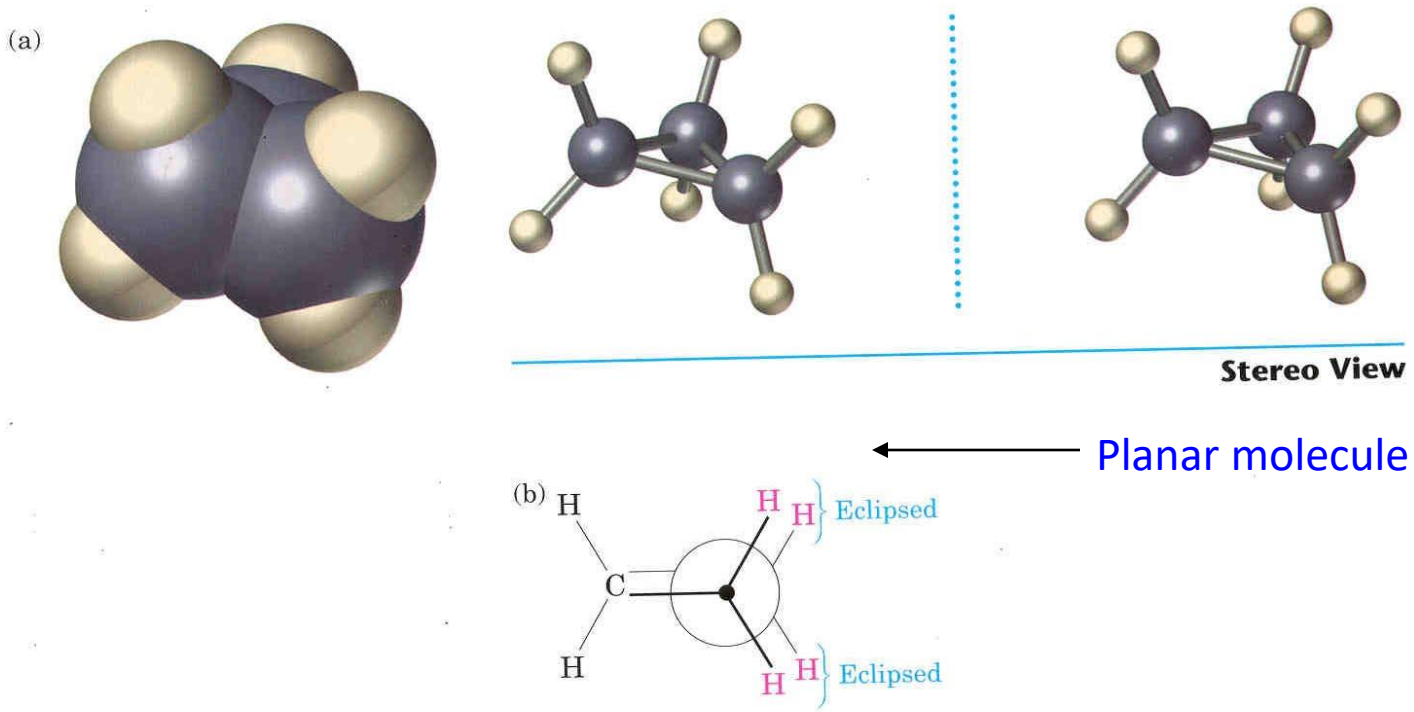
Cyclopropane

What is the normal bond angle for an sp^3 carbon?

109.5°

Deviation 109.5 – 60 = 49.9°

Cycloalkanes, eg cyclopropane, also possesses torsional strain because of eclipsed bonds.



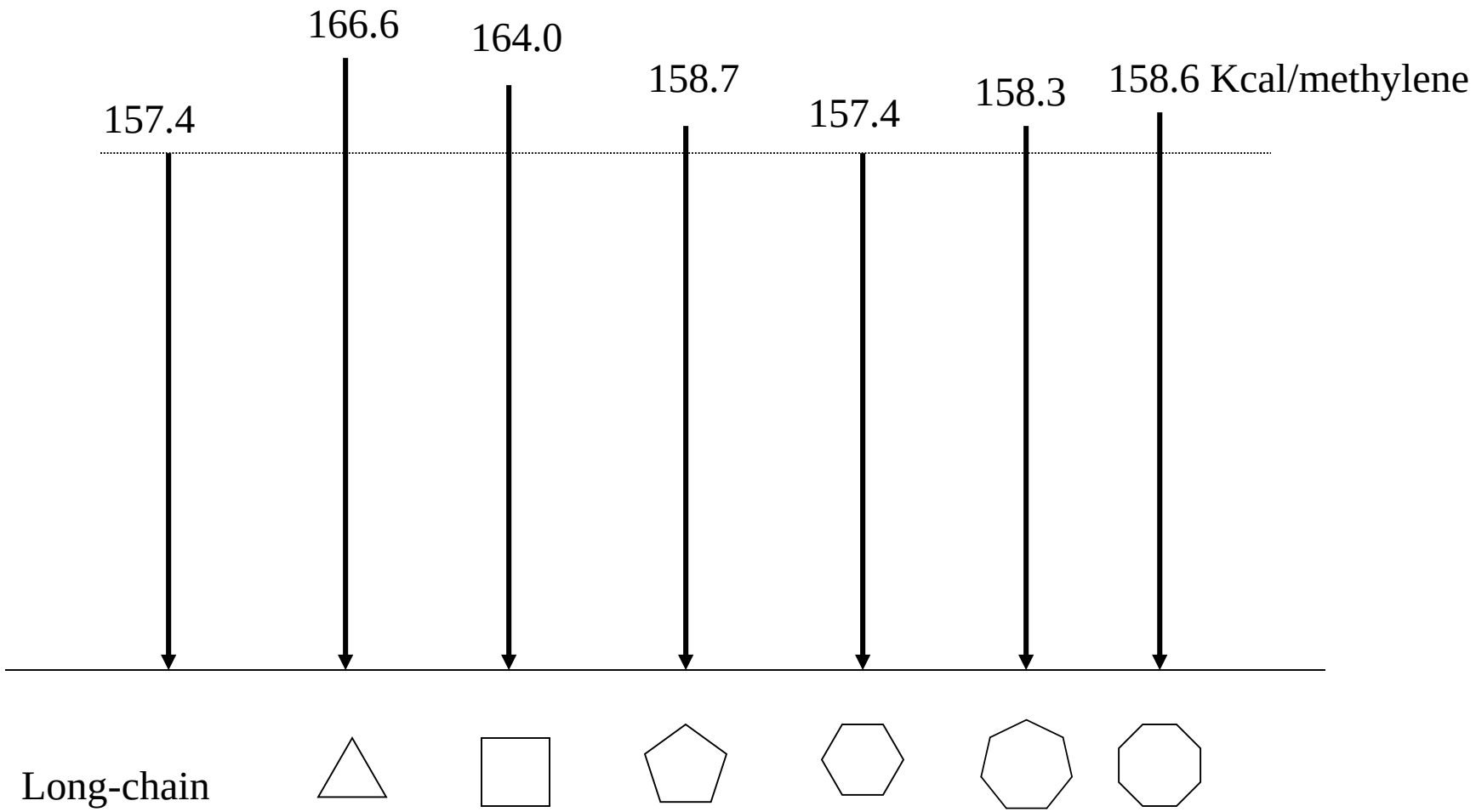
Cycloalkanes

Ring Strain – total strain (sum of torsional and angle strain) in a cycloalkane compared to a open, noncyclic reference compound.

- Strain is measured by determining the heats of combustion for the different cycloalkanes and expressing the values obtained, in kcal or Kj/mol, in the form of 'per $-CH_2-$' (methylene) group.
- 5- and 6-membered rings are the most stable. In fact cyclohexane is considered to be free of ring strain.

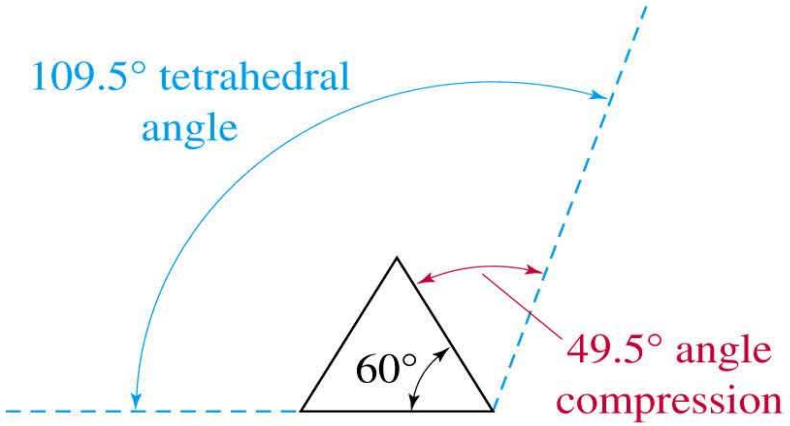
Heats of Combustion

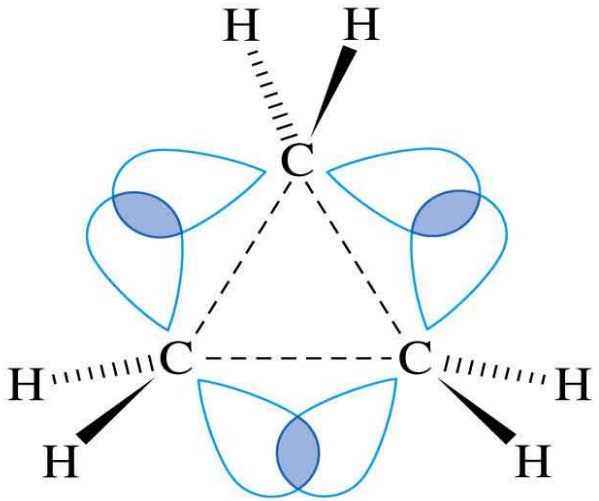
Alkane + O_2 → CO_2 + H_2O



Cyclopropane

- Large ring strain due to angle compression
- Very reactive, weak bonds

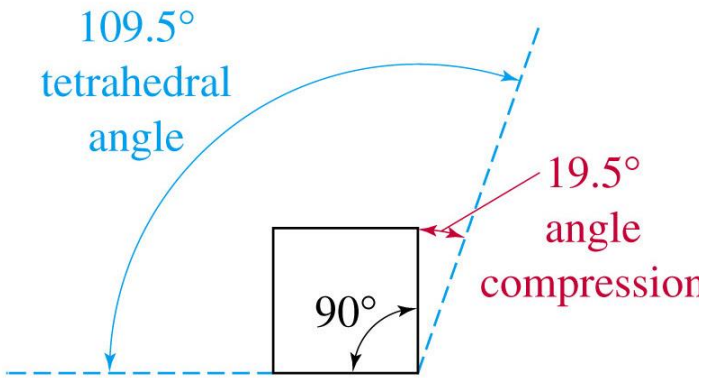


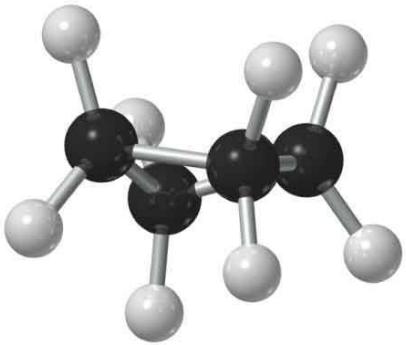


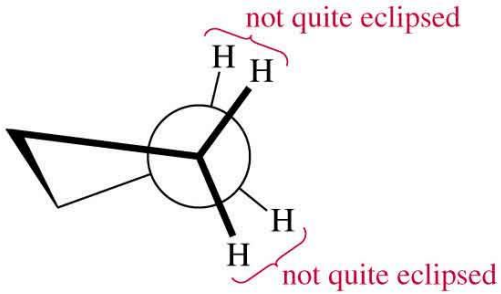
"bent bonds"
nonlinear overlap

Cyclobutane

- Angle strain.
- Torsional strain partially relieved by ring-puckering



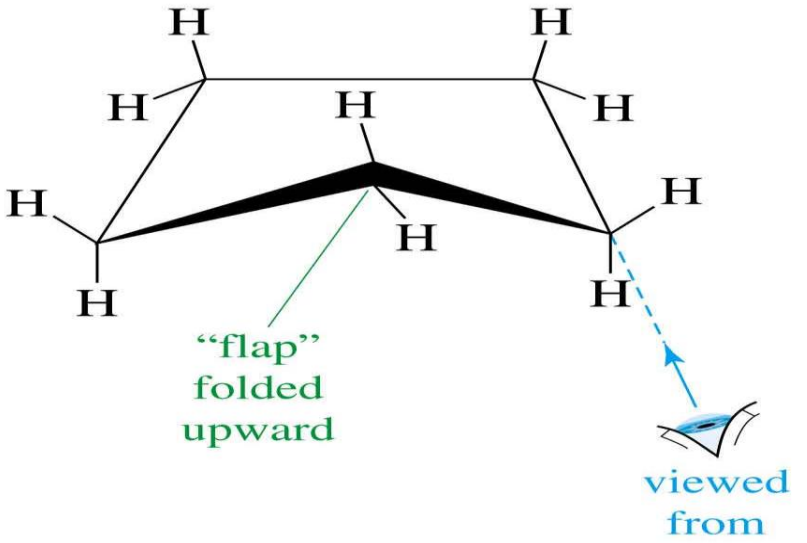


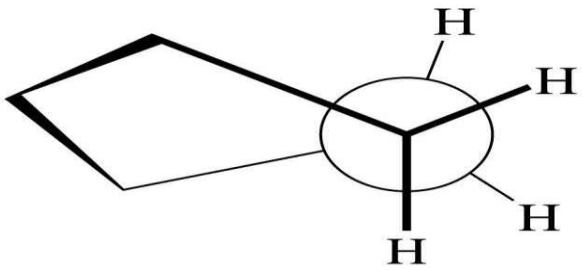


Newman projection of one bond

Cyclopentane

- If planar, angles would be 108°, but all hydrogens would be eclipsed.
- Puckered conformer reduces torsional strain.



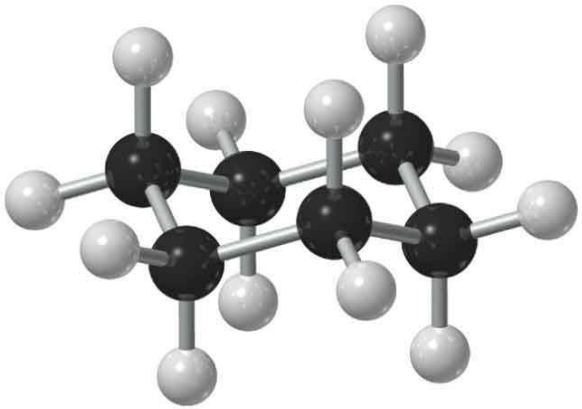


Newman projection showing relief of eclipsing of bonds

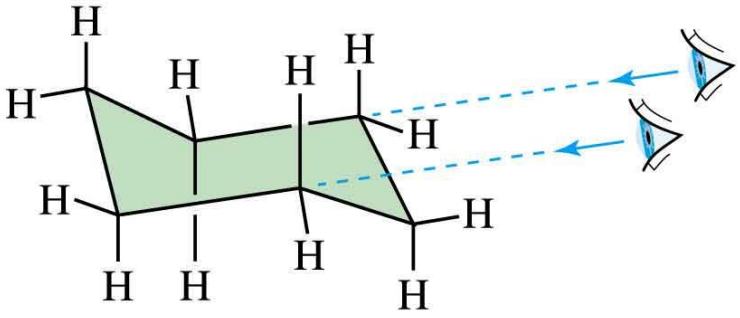
Cyclohexane

- Combustion data show that it is unstrained.
- Angles would be 120°, if planar.
- The chair conformer has 109.5° bond angles and all hydrogens are staggered.
- No angle strain and no torsional strain.

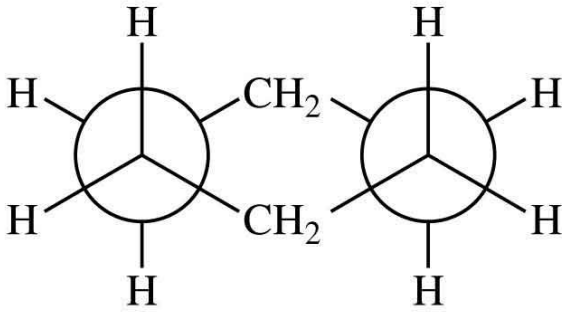
Chair Conformer



chair conformation

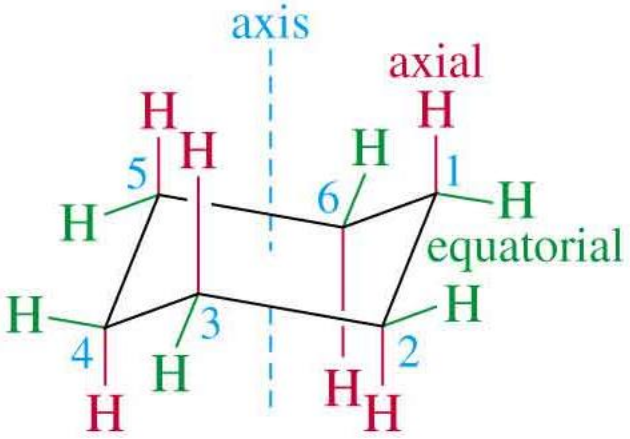


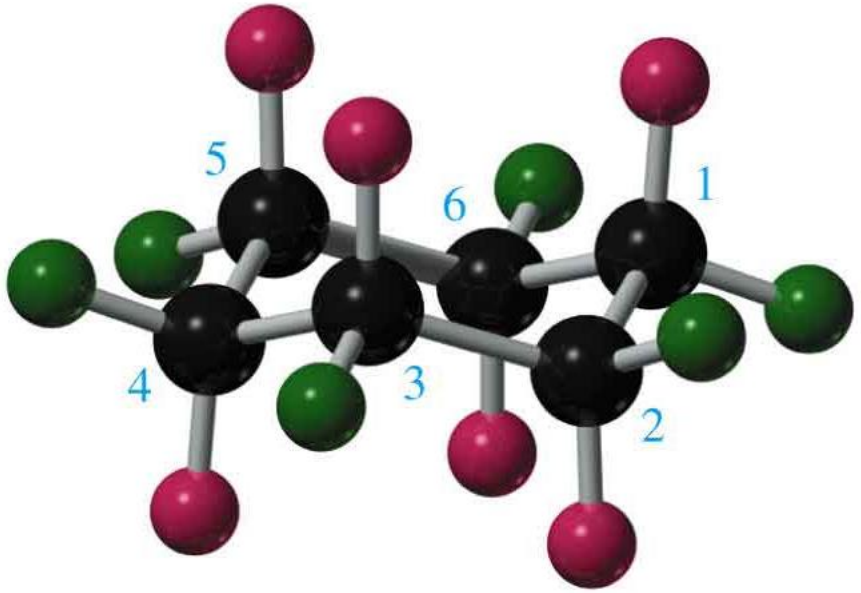
viewed along the “seat” bonds



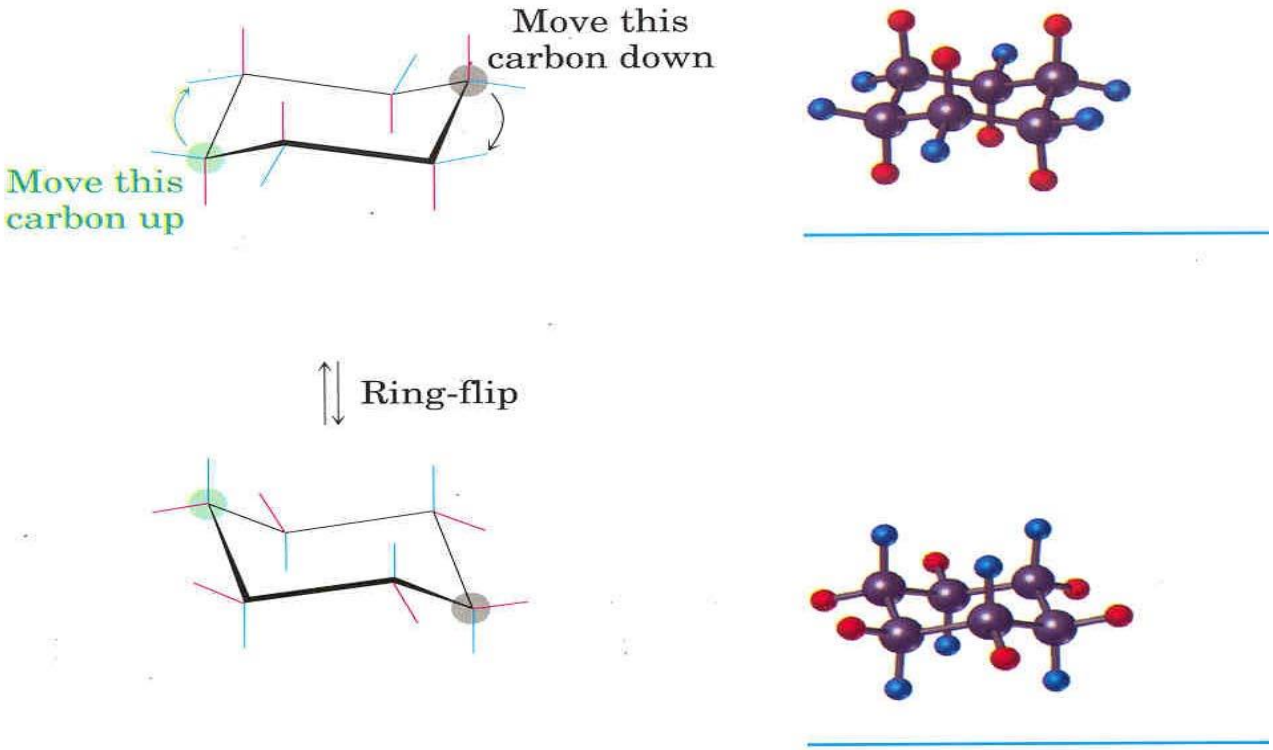
Newman projection

Axial and Equatorial Positions (Chair Conformer)





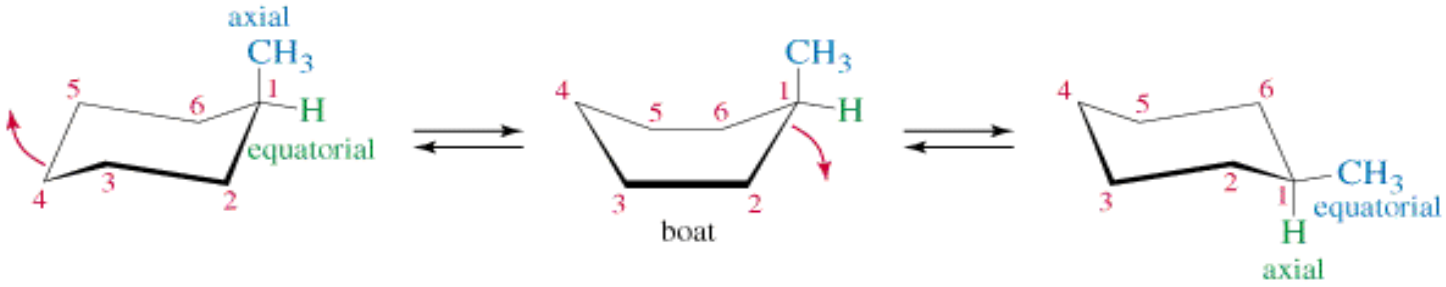
Interconversion of Chair Conformations or "Ring Flipping"

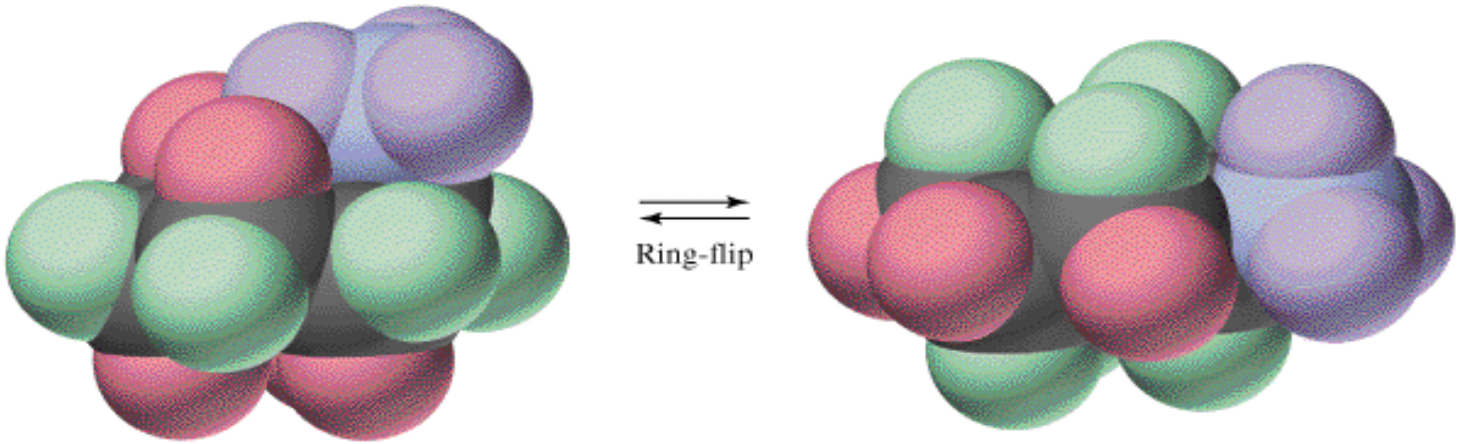


- The axial and equatorial positions exchange during this process
- At room temperature the cyclohexane ring rapidly flips back and forth between two equivalent chair conformations.
- What if we have an alkyl group replacing a hydrogen ?

Monosubstituted Cyclohexanes:

Methylcyclohexane has two possible chair conformations which are interconvertible through ring flipping. In one conformation the methyl group occupies an axial position and an equatorial one in the other conformation. Studies showed that the latter conformation (*equatorial* methyl) is more stable by 7.6 KJ/mol, compared with the other conformation (*axial* methyl) . In the equilibrium mixture the stable conformation constitutes 95% of the mixture.



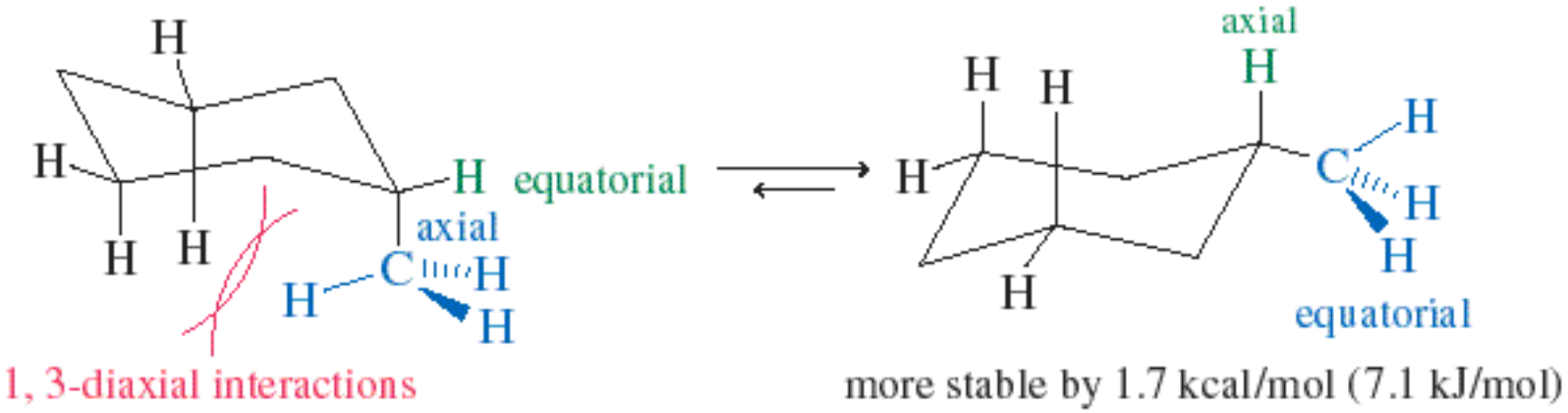


CH_3 axial

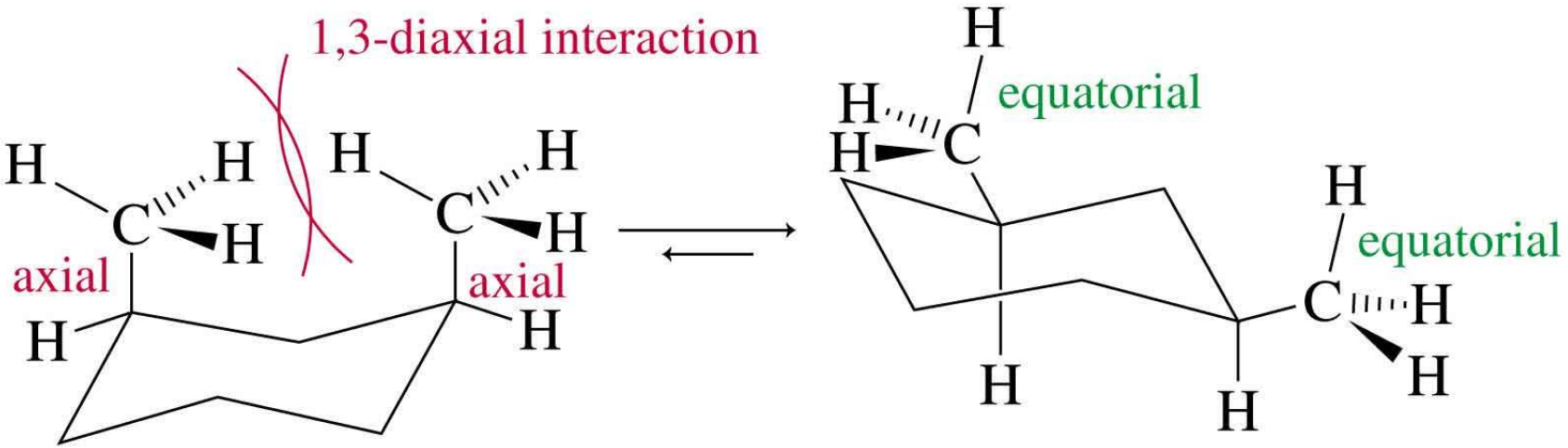
CH_3 equatorial

Why is the conformation in which the methyl group of methylcyclohexane in axial position, less stable than the other conformer ?

The reason is: 1,3-diaxial interactions (repulsions)

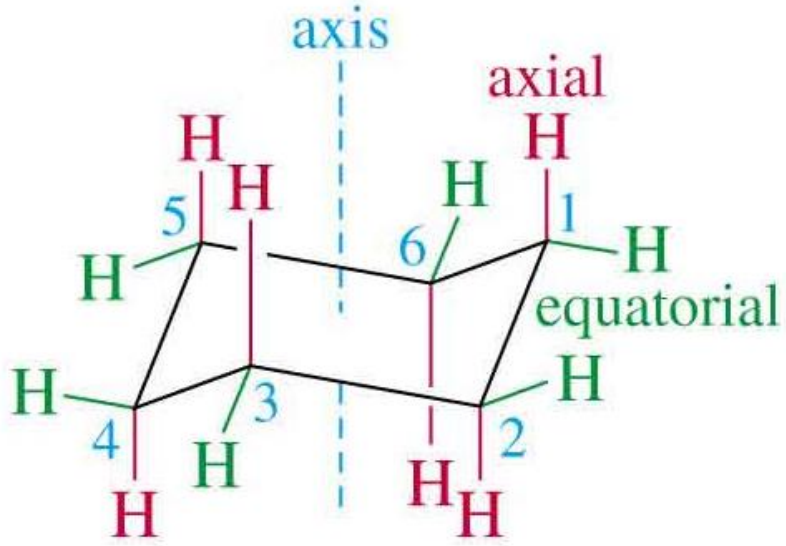


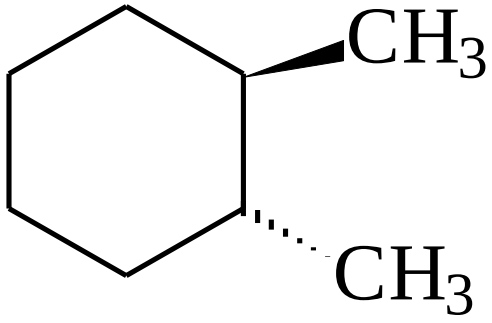
Disubstituted Cyclohexanes



Cis-Trans Isomers

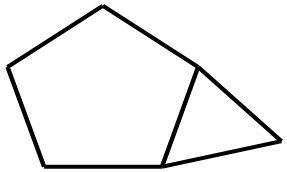
Bonds that are cis, alternate axial-equatorial around the ring.



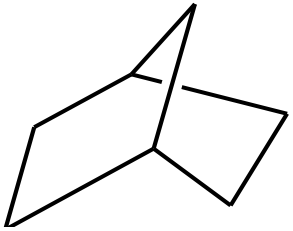


Bicyclic Alkanes

- Fused rings share two adjacent carbons.
- Bridged rings share two nonadjacent C's.
- Fused or bridged compounds containing two rings are named as 'bicyclo'. The number of carbons attached to the two junction carbons' (in every direction; in order of decreasing length) is indicated between square brackets. Note the use of dots.
- Use the name of the alkane corresponding to the total number of carbon atoms in the rings as the parent name.



bicyclo[3.1.0]hexane



bicyclo[2.2.1]heptane

bicyclo[4.2.0]octane

bicyclo[5.1.0]octane