B.Sc.(H) Chemistry
Semester - II
Core Course - III (CC-III)
Organic Chemistry - I

III. Chemistry of Aliphatic Hydrocarbons

C. Cycloalkanes and Conformational Analysis

Dr. Rajeev Ranjan
University Department of Chemistry
Dr. Shyama Prasad Mukherjee University, Ranchi

Cycloalkanes and their Stereochemistry

Syllabus : Types of cycloalkanes and their relative stability, Bayer’s strain theory, Energy diagrams of cyclohexane: Chair, Boat and Twist boat forms - Relative stability with energy diagrams.

Coverage:

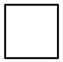
1. Nomenclature of Cycloalkanes
2. Stabilities of Cycloalkanes
3. Conformations of Cyclohexane and Substituted Cyclohexanes.

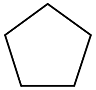
Goals:

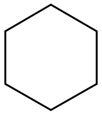
1. Be able to estimate the relative energies of the different conformations of cycloalkanes.
2. Be able to draw chair conformations of cyclohexanes, showing equatorial and axial positions.
3. Be able to estimate the relative energies of the conformations of substituted cyclohexanes.
4. Understand the meaning of torsional, steric, angle and ring strain and be able to apply them to the conformations of alkanes and cycloalkanes.
5. Understand how the stabilities of cycloalkanes are measured.
6. Understand why cyclohexane is the most stable cycloalkane.

Nomenclature of Cycloalkanes

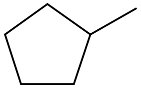

Cyclopropane

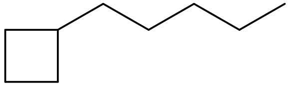

Cyclobutane


Cyclopentane

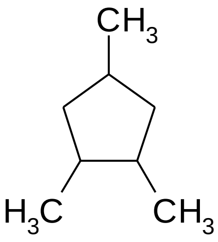

Cyclohexane

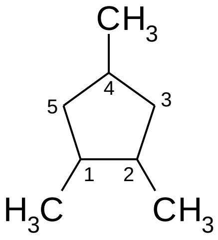
1. Find the parent. Simply count the number of carbon atoms in the ring. If the number is larger than the number in the substituent, then it is named as a cycloalkane.


Methylcyclopentane


Cyclobutylpentane

2. Number the Substituents. C-1 always has a substituent attached. Number so that the second substituent has the lowest number possible, etc, etc.

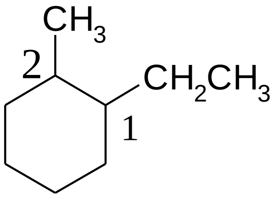




1,2,4-trimethylcyclopentane

Not 1,3,4-trimethylcyclopentane

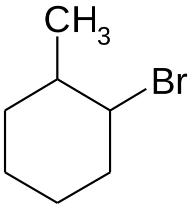
a. If two or more alkyl groups have potentially the same number, number alphabetically.



1-ethyl-2-methylcyclohexane

Not 1-methyl-2-ethylcyclohexane

b. Treat other substituents exactly like alkyl groups.



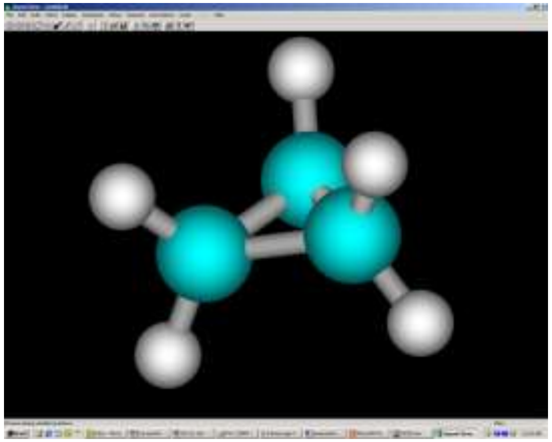
1-Bromo-2-methylcyclohexane

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.

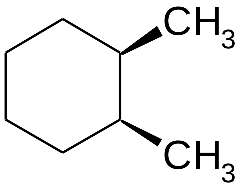
Why not?

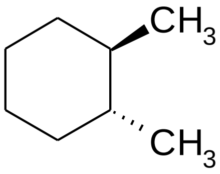
Look at a model. In order to rotate about the single bond, the C-C single bond would have to break. This sigma bond is too strong to break under ordinary conditions.



Cyclopropane

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



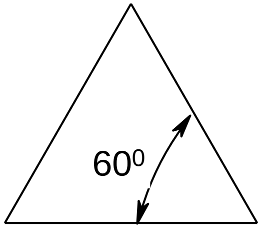


Question: Are the above cycloalkanes constitutional or stereoisomers? Answer: Stereoisomers

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

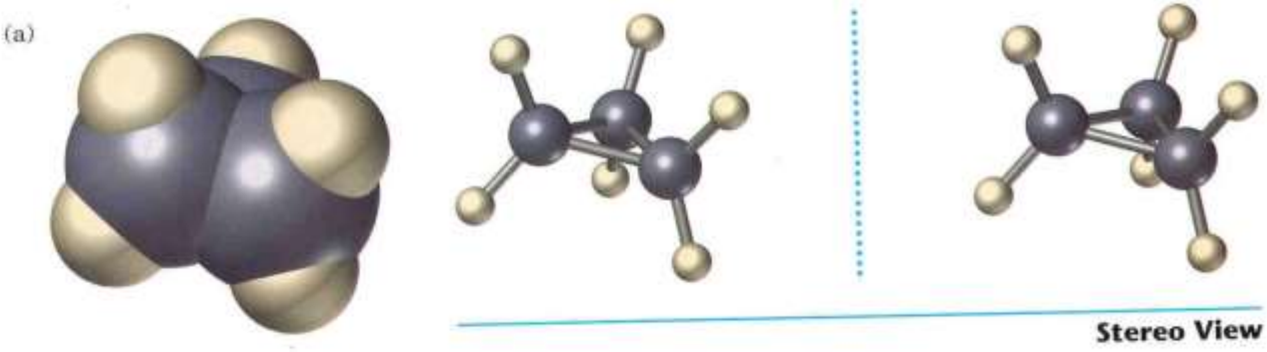
What is the normal bond angle for an sp^3 carbon?

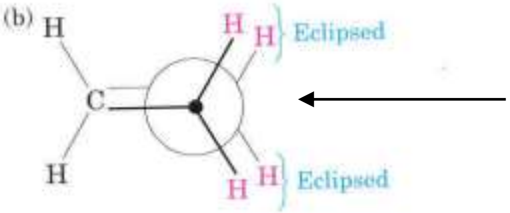
109.5^o

Deviation 109.5 – 60 = 49.9^o

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

Cyclopropane also possesses torsional strain because of eclipsed bonds.





Planar molecule

How much torsional strain (kcal/mol) does it possess?

Answer: You figure it out.

Ring Strain in Cycloalkanes

Baeyer Strain Theory

Johann Friedrich Wilhelm
Adolf von Baeyer

- First graduate student of Kekule'
- Developed theory that cycloalkanes possess different amounts of strain or stability, depending on the size of the ring.
- Awarded Nobel Prize in 1905 for work with organic dyes.
- Total synthesis of indigo.

"I have never set up an experiment to see whether I was right, but to see how the materials behave".

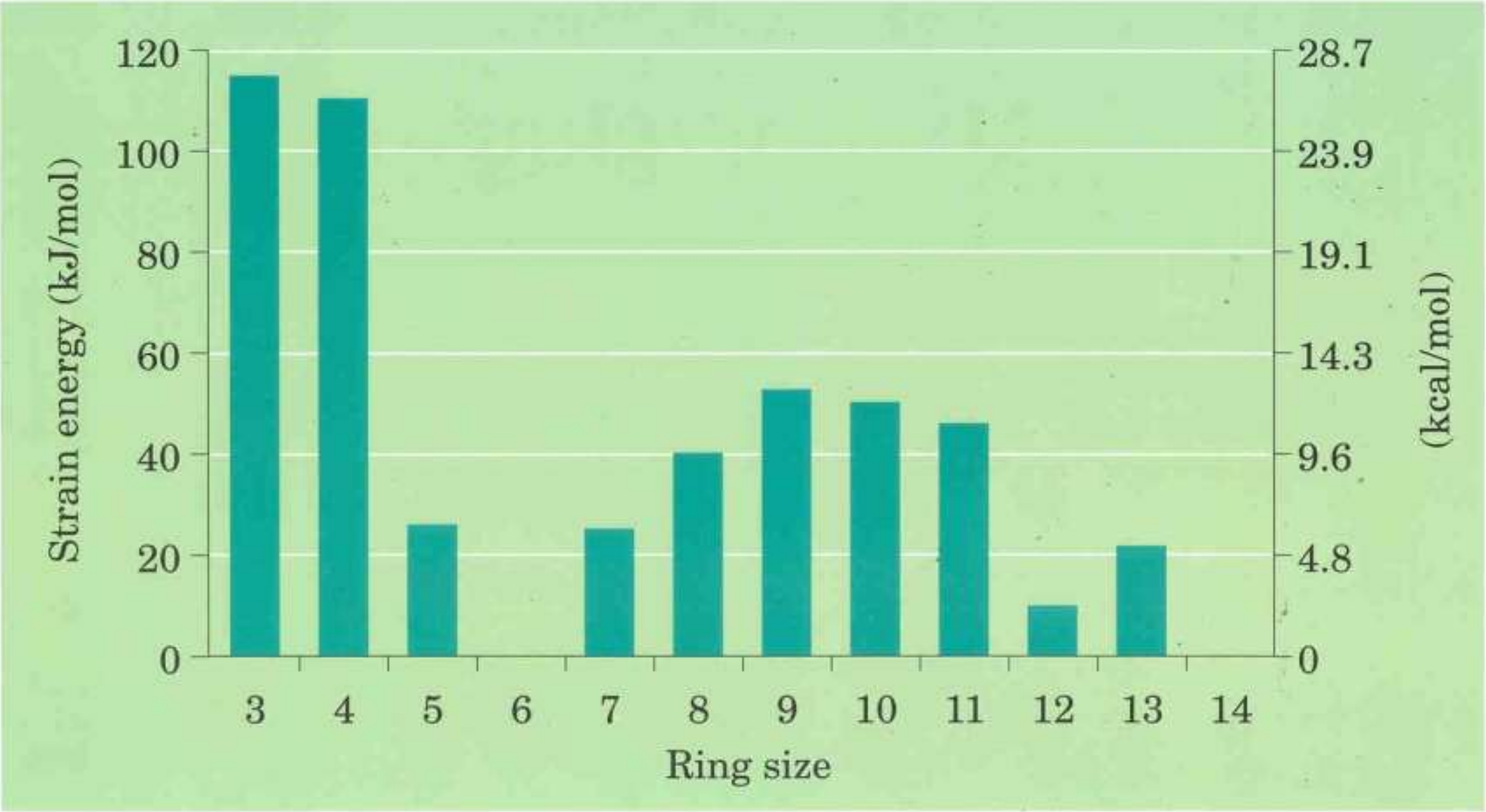
Ring Strain in Cycloalkanes

The relative stabilites of cycloalkanes are determined by measuring their heats of combustion.

$$[\text{-CH}_2\text{-}]_n + 3/2nO_2 \rightarrow nCO_2 + nH_2O + \text{Heat}$$

The more heat per CH_2, the less stable the alkane.

Ring Size	Heat per CH_2 kcal/mol	Ring Strain per CH_2, kcal/mol	Total Ring Strain, kcal/mol
Long-Chain Alkane	157.4	0.0	0.0
3	166.6	9.2	27.6
4	164.0	6.6	26.4
5	158.7	1.3	6.5
6	157.4	0.0	0.0
7	158.3	0.9	6.3
8	158,6	1.2	9.6


120
100
80
60
40
20
0
Strain energy (kJ/mol)
28.7
23.9
19.1
14.3
9.6
4.8
0
(kcal/mol)
3
4
5
6
7
8
9
10
11
12
13
14
Ring size

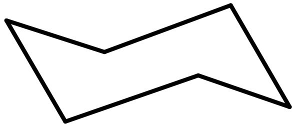
Cyclohexane is free of ring strain? Why?

1. All Bonds are staggered and therefore no torsional strain.

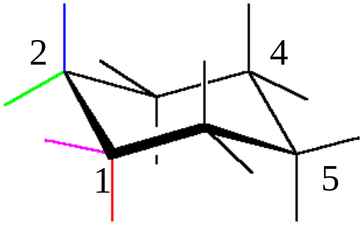
2. All bond angles are near 109.5^0 so no angle strain.

3. It does possess steric strain (internal gauche interaction)
   but no more than a noncyclic alkane.

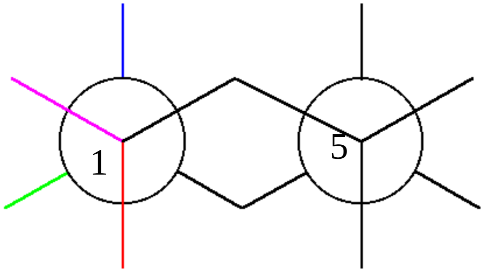
Cyclohexane – the most stable conformation of cyclohexane is the chair.



Chair conformation showing only carbon atoms

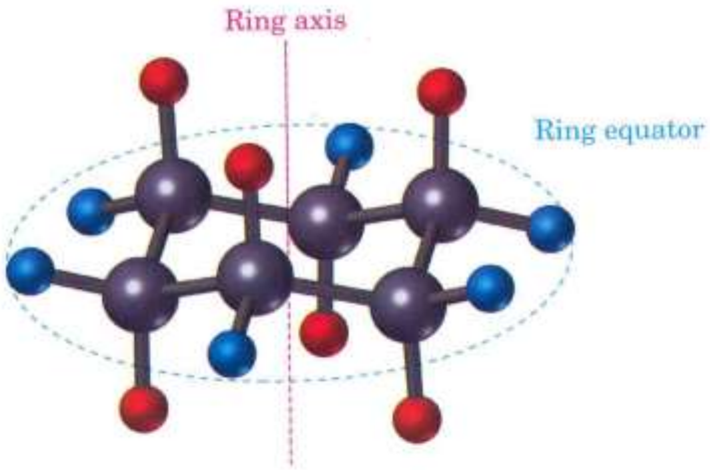


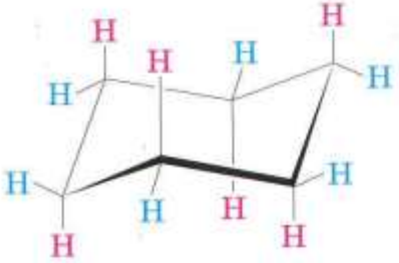
Chair conformations showing positions of hydrogens



Newman projection shows that all bonds are staggered. Bond angles are about 109.5^o

Equatorial and Axial Hydrogens of Cyclohexane



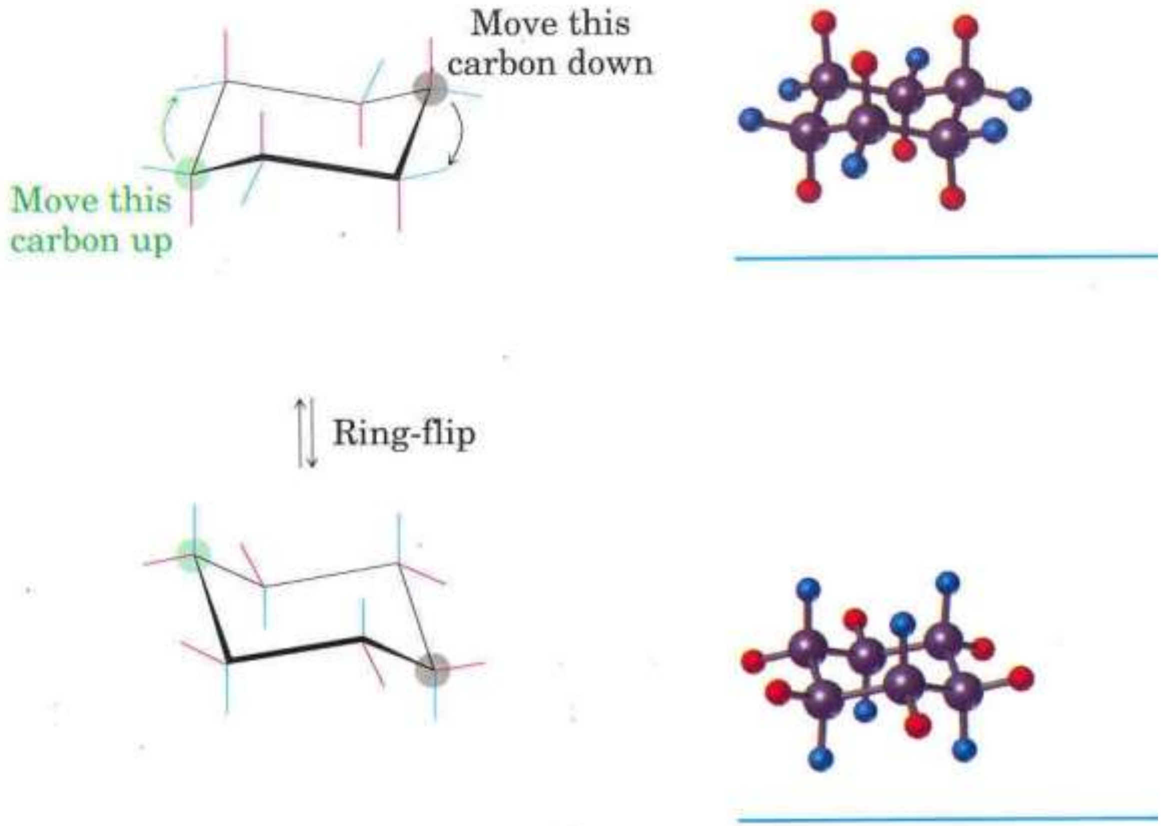


Six axial hydrogens point straight up (3) and straight down (3).

Six equatorial hydrogens point out away from the ring.

The axial and equatorial hydrogens are exchangable by a process called "ring flipping".

Interconversion of Chair Conformations or "Ring Flipping"



The axial and equatorial positions exchange during this process

You need to be able to draw a cyclohexane ring!

1. Draw two parallel lines, slanted downward and slightly offset.

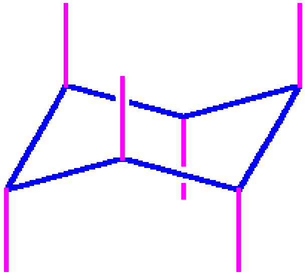
2. Connect two lower carbons to topmost carbon.

3. Connect two upper carbons to bottommost carbon.

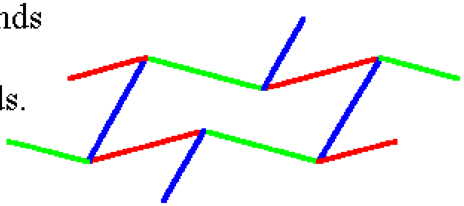
4. Note parallel bonds.

You also need to be able to draw in the equatorial and axial positions.

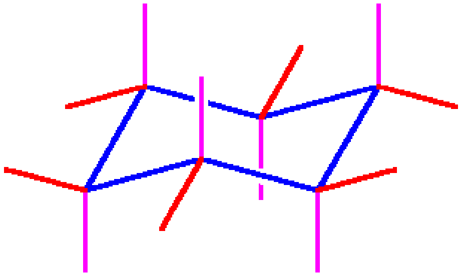
1. Draw axial bonds perpendicular to the "plane" of the molecule.



2. Draw equatorial bonds pointing out and parallel to ring bonds.



3. Combine.



Other Conformations of Cyclohexane

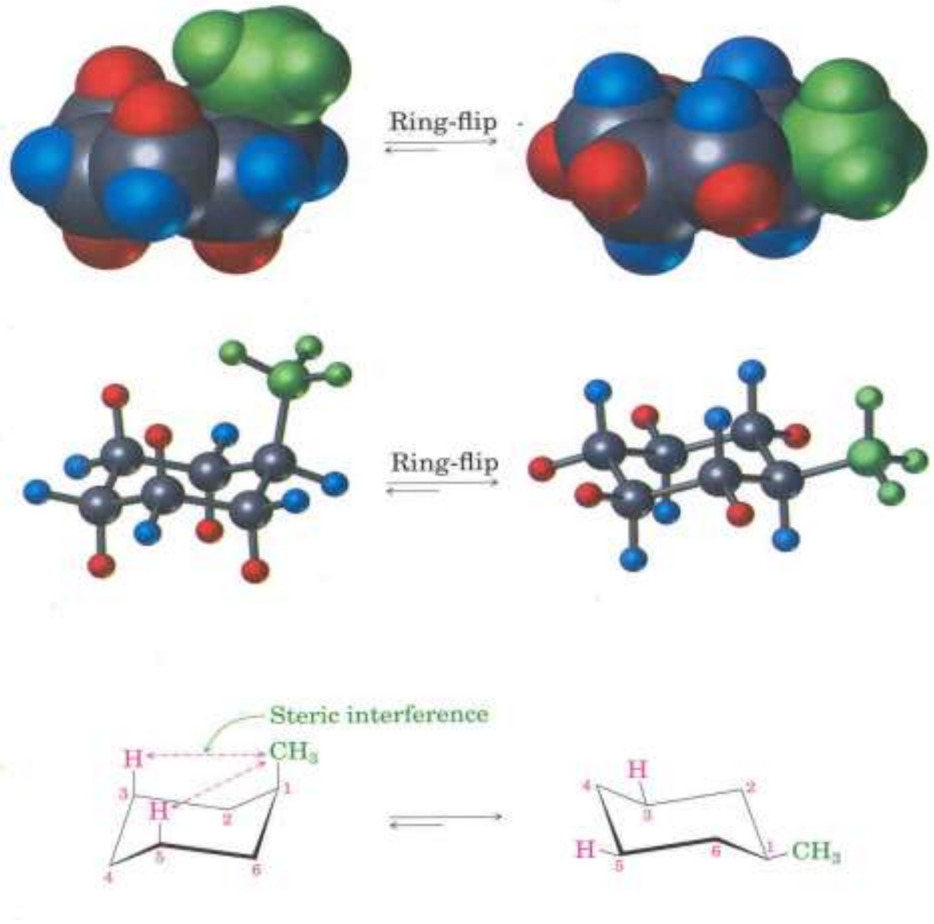
Chair 1 → Half Chair 1 → Twist Boat 1 → Boat → Twist Boat 2 → Half Chair 2 → Chair 2

What are the shapes and energies of these other conformations?

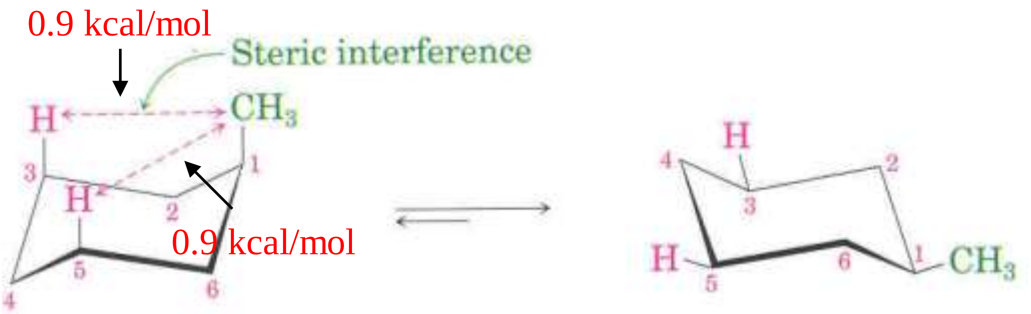
Monosubstituted Cyclohexanes

Methylcyclohexane

Axial Conformer $\rightleftharpoons$ Equatorial Conformer



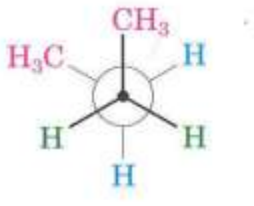
The equatorial conformer is more stable by 1.8 kcal/mol due to a steric interaction between the axial methyl and two axial hydrogens. These interactions are termed 1,3-diaxial interactions.



2 x 0.9 = 1.8 kcal/mol
5%

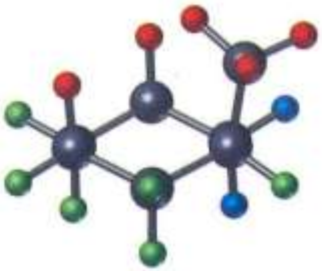
0.0 kcal/mol
95%

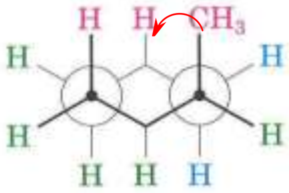
These 1,3-diaxial interactions are really gauche interactions in disguise! Remember that a gauche interaction for butane is worth 0.9 kcal/mol.



Gauche butane (3.8 kJ/mol strain)

0.9 kcal/mol

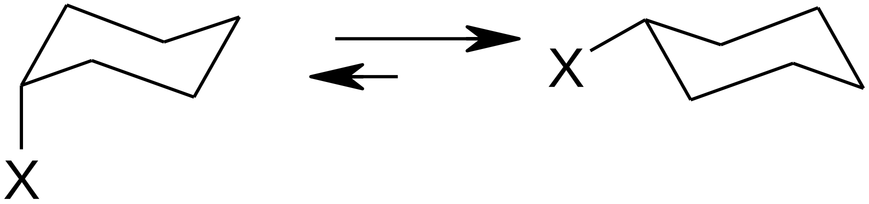




Axial methylcyclohexane (7.6 kJ/mol strain)

1.8 kcal/mol

Other Substituents



X	$E_{axial} - E_{equatorial}$ kcal/mol
-H	0.0
-F	0.24
-C≡N	0.2
-Cl	0.50
-Br	0.50
$-CH_3$	1.8
$-CH_2CH_3$	1.9
$-CH(CH_3)_2$	2.2
$-C(CH_3)_3$	5.4

Disubstituted Cyclohexanes

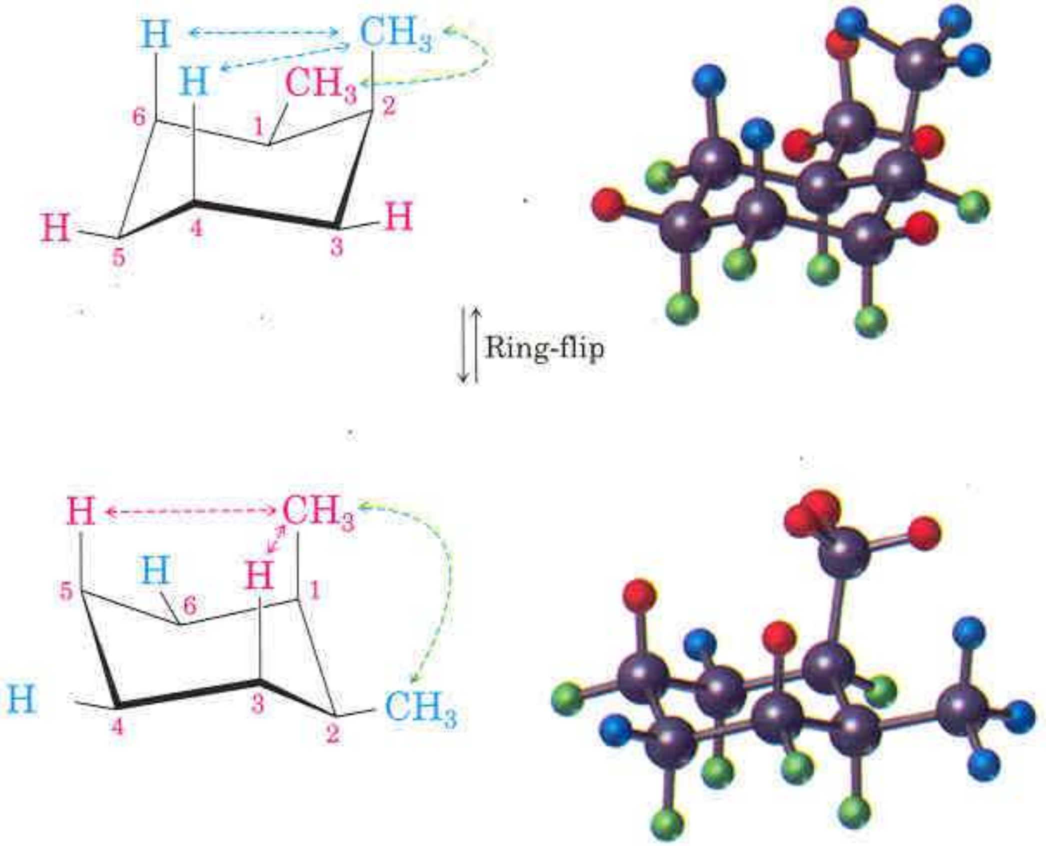
cis-1,2-Dimethylcyclohexane

One gauche
interaction (3.8 kJ/mol)
Two CH_3–H diaxial
interactions (7.6 kJ/mol)
Total strain: 3.8 + 7.6 = 11.4 kJ/mol

0.9 + 1.8 = 2.7 kcal/mol

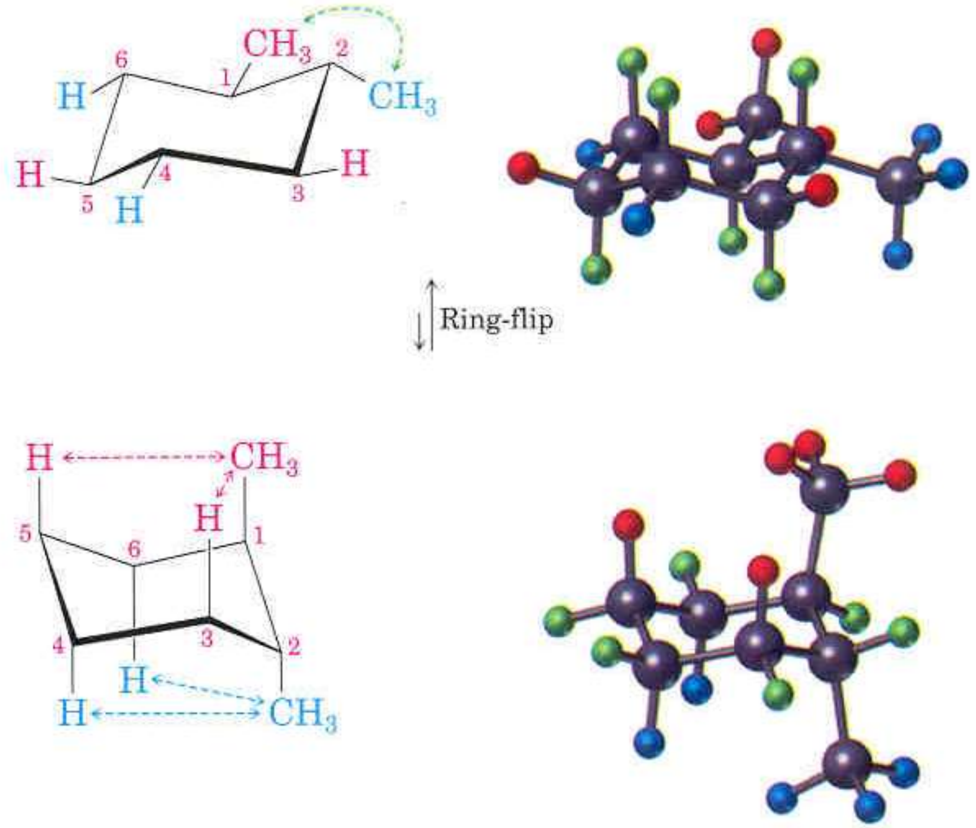
One gauche
interaction (3.8 kJ/mol)
Two CH_3–H diaxial
interactions (7.6 kJ/mol)
Total strain: 3.8 + 7.6 = 11.4 kJ/mol

0.9 + 1.8 = 2.7 kcal/mol



Disubstituted Cyclohexanes

***trans*-1,2-Dimethylcyclohexane**



One gauche interaction (3.8 kJ/mol)

0.9 kcal/mol

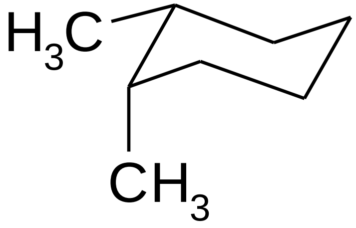
Relative 0.0 kcal/mol

Four CH$_3$–H diaxial interactions (15.2 kJ/mol)

3.6 kcal/mol

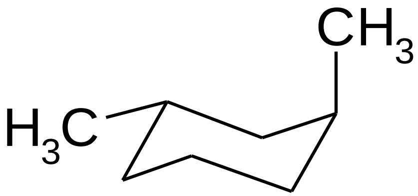
Relative 2.7 kcal/mol

Can you name these dimethylcyclohexanes?



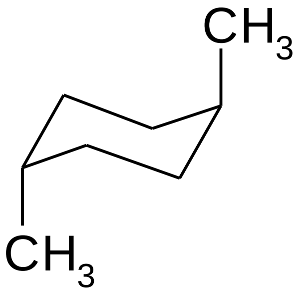
cis-1,2-dimethylcyclohexane

equatorial - axial



trans-1,3-dimethylcyclhexane

equatorial - axial

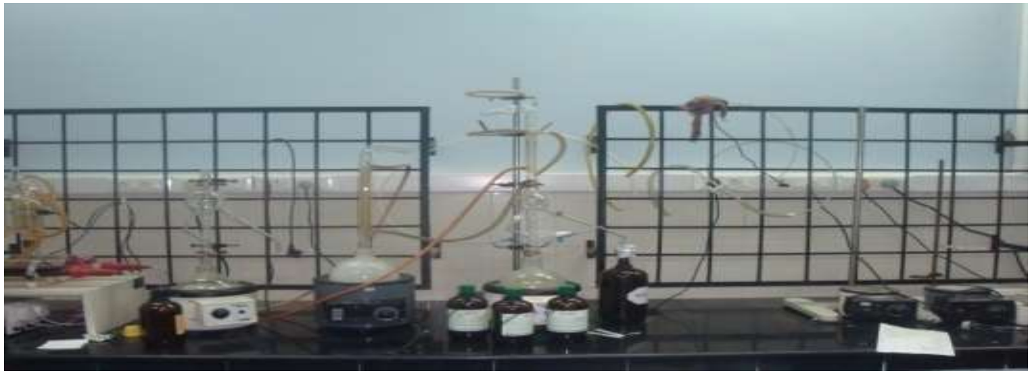


trans-1,4-dimethylcyclohexane

axial-axial or diaxial

Which of these represent the most stable conformation possible?

Thank You



Dr. Rajeev Ranjan
University Department of Chemistry
Dr. Shyama Prasad Mukherjee University, Ranchi