CHEM F111 : General Chemistry
Semester II: AY 2017-18

Lecture 31 (06-04-2018)

Conformational isomers (conformers).
Rotating about bonds (Bond breaking not required)

Configurational isomers: (Bond breaking required)
▪**Enantiomers.**
▪**Diastereomers**

Conformations of ethane, propane and butane

Eclipsed **Staggered** **Skew**

Torsional Strain: It is the resistance to twisting (torsion) as molecule rotates toward an eclipsed conformation.

Miscellaneous examples: X-C-C-Y containing compounds (where X and Y are electronegative groups) adopt gauche rather than anti conformations.

Hydrogen bonding

Stabilization accrues from σ → σ* interactions

Solvent polarity affect

➢ In cyclopropane or cyclobutane, one pair of bonds to each carbon cannot assume the tetrahedral angle, but must be compressed to 60^0 or 90^0 to fit the geometry of the ring.

➢ These deviations of bond angles from the "normal" tetrahedral value cause the molecule to be **strained,** and hence to be unstable compared with molecules in which the bond angles are tetrahedral.

➢An increase in energy when bond angles deviate from the optimum tetrahedral angle of 109.5° is called **angle strain**.

➢Cycloalkanes with more than three carbon atoms in the ring are not flat molecules. They are puckered to reduce strain.
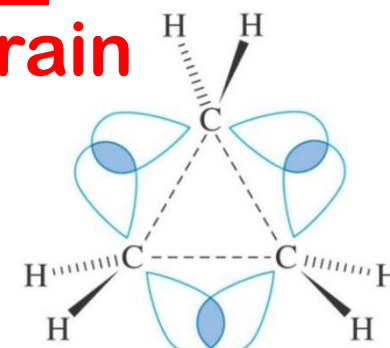
Cyclopropane and Cyclobutane
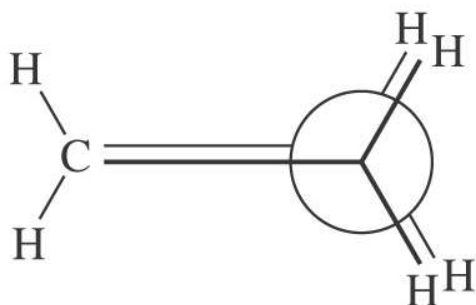
Newman projection of cyclopropane
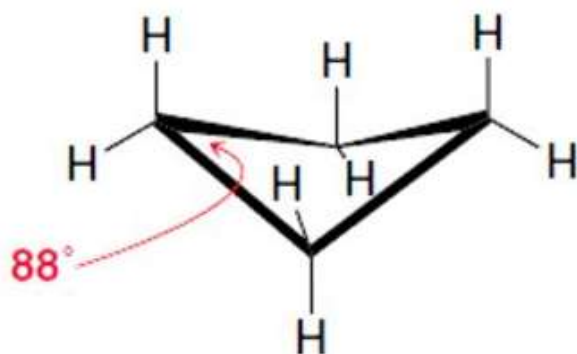
Necessarily Planer

109.5° tetrahedral angle
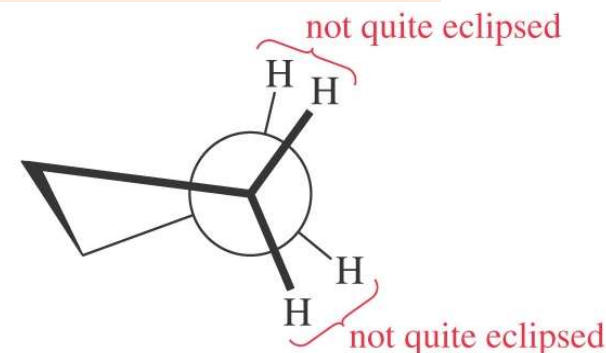
60°

49.5° angle compression
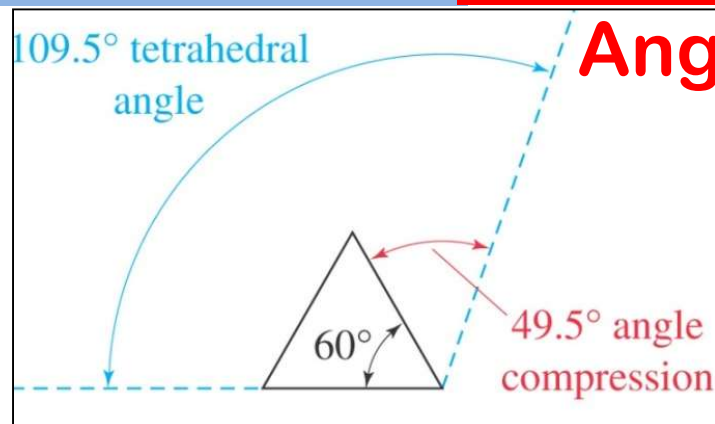
Angle strain

"bent bonds" nonlinear overlap

Torsional strain because of eclipsed hydrogens

Ring Strain = Angle strain + Torsional strain

88°

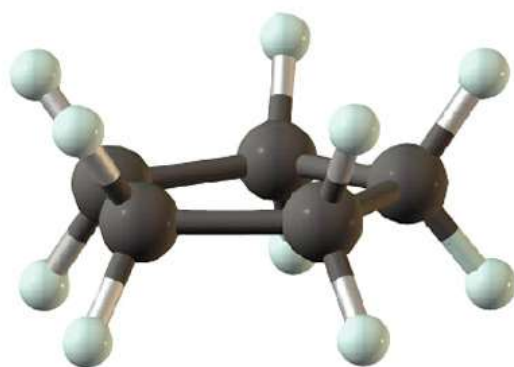Torsional strain partially relieved by ring-puckering (non-planar)

not quite eclipsed

not quite eclipsed

Newman projection of one bond

Ring opening reactions relieves the strain leads to more stable open chain compounds. More strained means more unstable and more prone to undergo ring opening reactions.

Cyclopentane
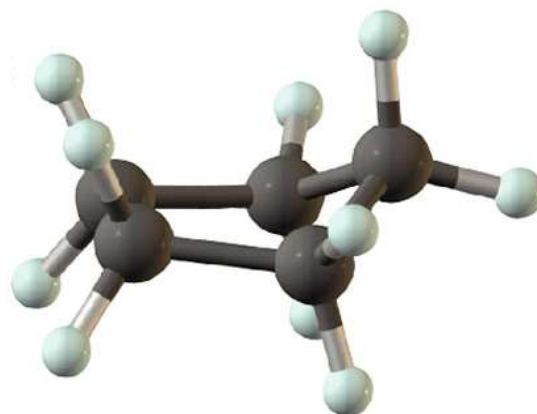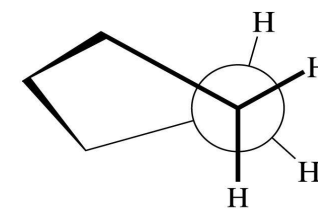
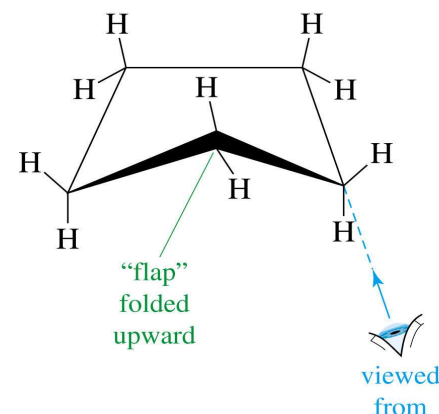- If planar, angles would be 108° but all hydrogens would be eclipsed.

H   H
H   H   H
H   H
          H
H
H

"flap"
folded
upward

viewed
from

Newman projection
showing relief of
eclipsing of bonds

Planar conformation

Puckered envelope conformation

envelope

- Puckered conformer reduces torsional strain. Puckering from planar cyclopentane reduces torsional strain.
- The conformation of minimum energy is a puckered "envelope" conformation.

Cyclohexane

The angles of a regular hexagon (120°) considered to be planar, are some what larger than the tetrahedral angle. Thus, cyclohexane molecule should have an angles strain of 10.5°. In reality, cyclohexane adopts a puckered "chair" conformation, which is more stable than any possible other conformation.
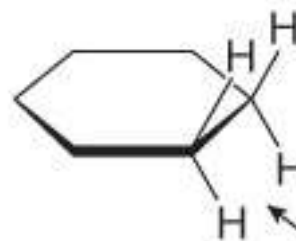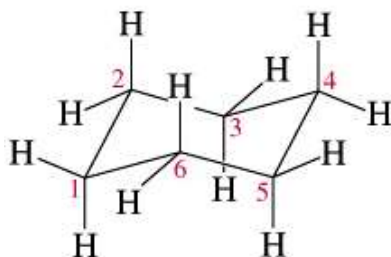
Planar cyclohexane

angle strain

120°
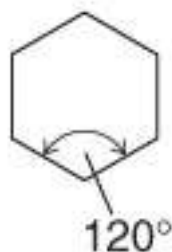
The internal bond angle is >109.5°.
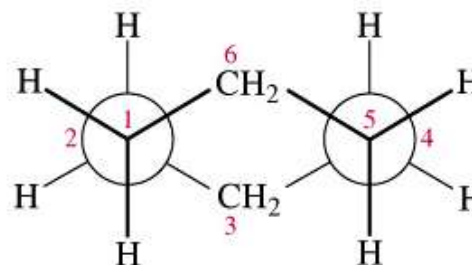
torsional strain

All H's are aligned.

Chair conformation

chair conformer of cyclohexane

Newman projection of the chair conformer

ball-and-stick model of the chair conformer of cyclohexane

Cyclohexane

Boat conformation: A puckered conformation of a cyclohexane ring in which carbons 1 and 4 are bent toward each other.

- There are four sets of eclipsed C-H interactions
- Another destabilizing feature is the fact that two of the "axial" hydrogens become **flagpole** hydrogens.
- A boat conformation is less stable than a chair conformation by 27 kJ (6.5 kcal)/mol.

1   4

"Flagpole" interaction

Eclipsed conformations

H
H   H
H
HH   HH

Cyclohexane
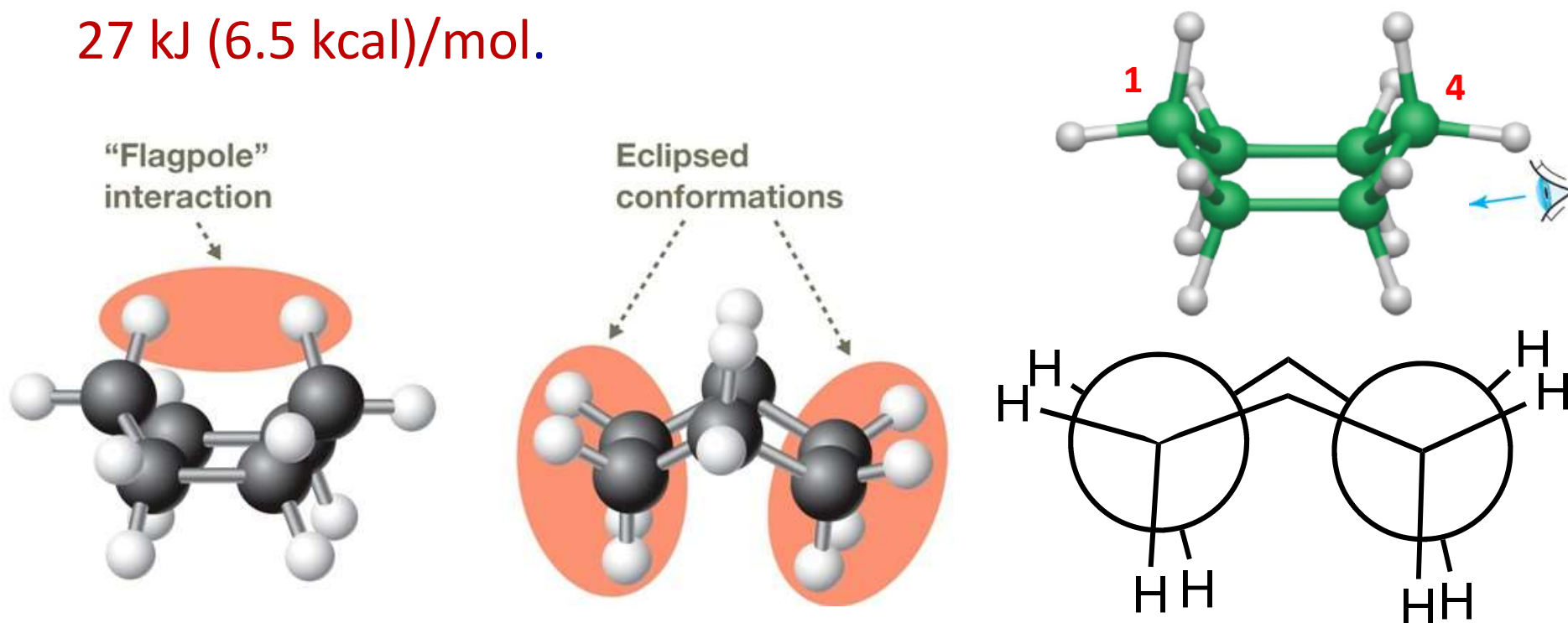
Twist-boat conformation

The **twist relieves some of the torsional strain of the boat** and moves the flag-pole hydrogens further apart reducing the steric strain. Consequently the twist boat is slightly more stable than the boat.

- Approximately 41.8 kJ (5.5 kcal)/mol less stable than a chair conformation
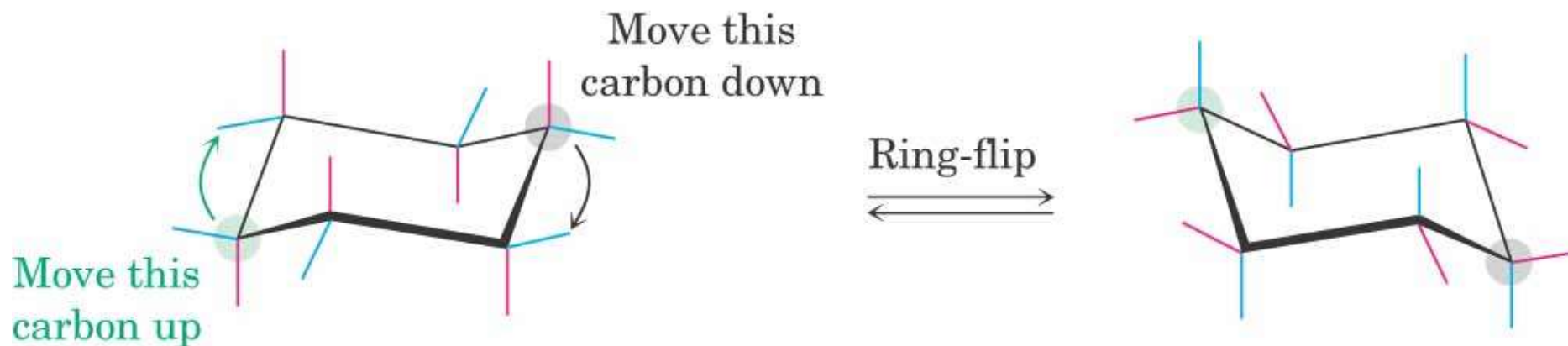- Approximately 6.3 kJ (1.5 kcal)/mol more stable than a boat conformation
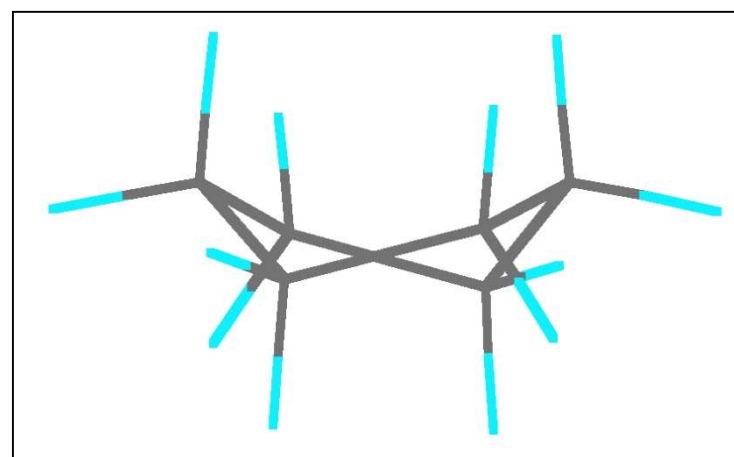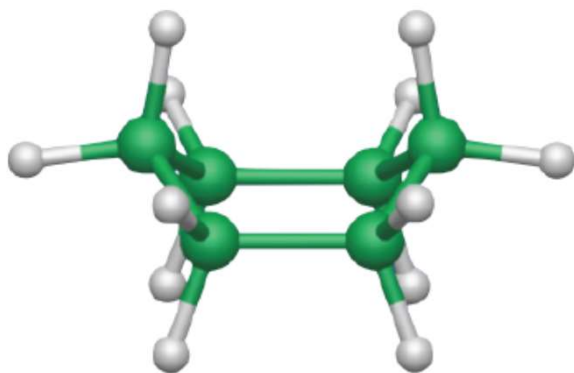
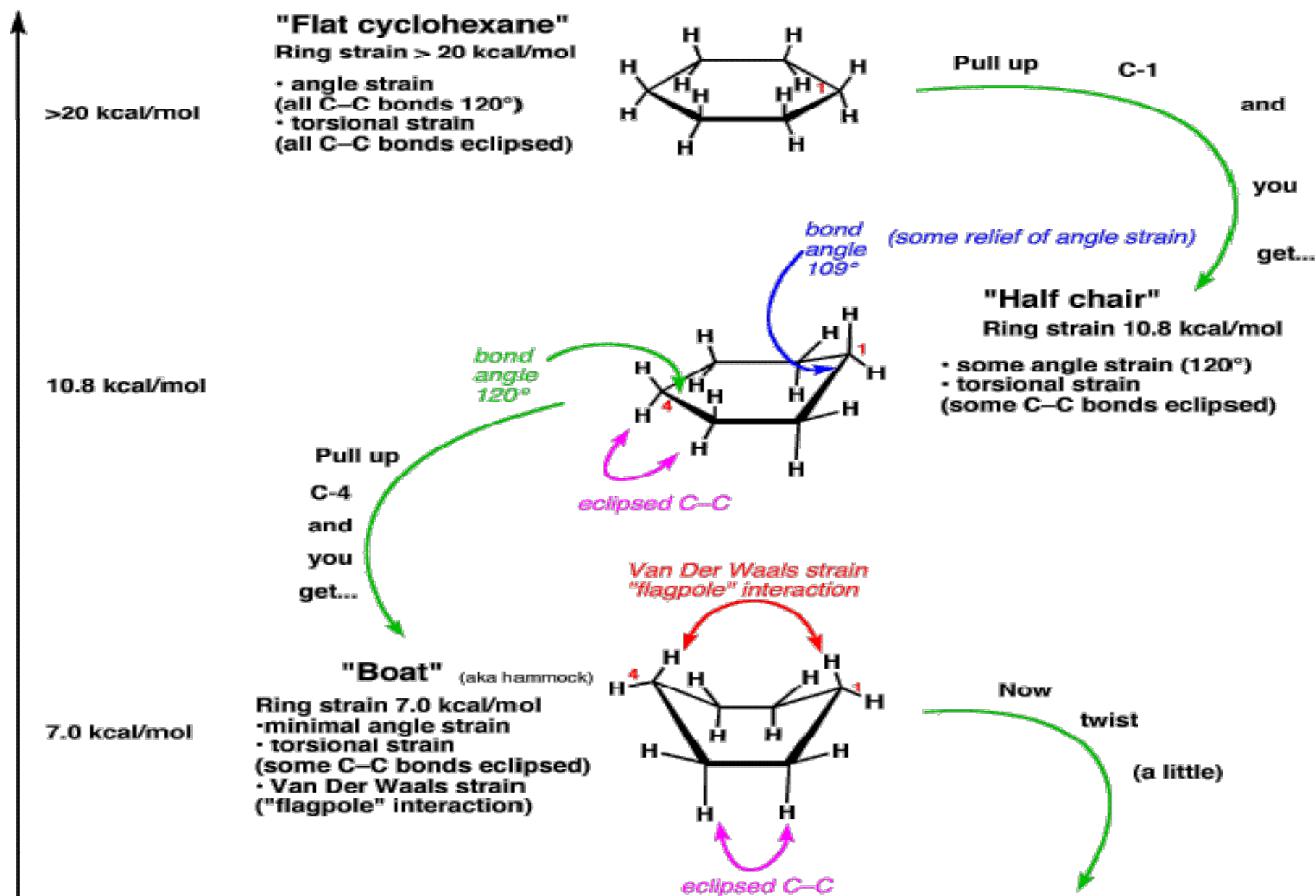# conformational analysis of cyclohexane

Move this
carbon down

Ring-flip

Move this
carbon up
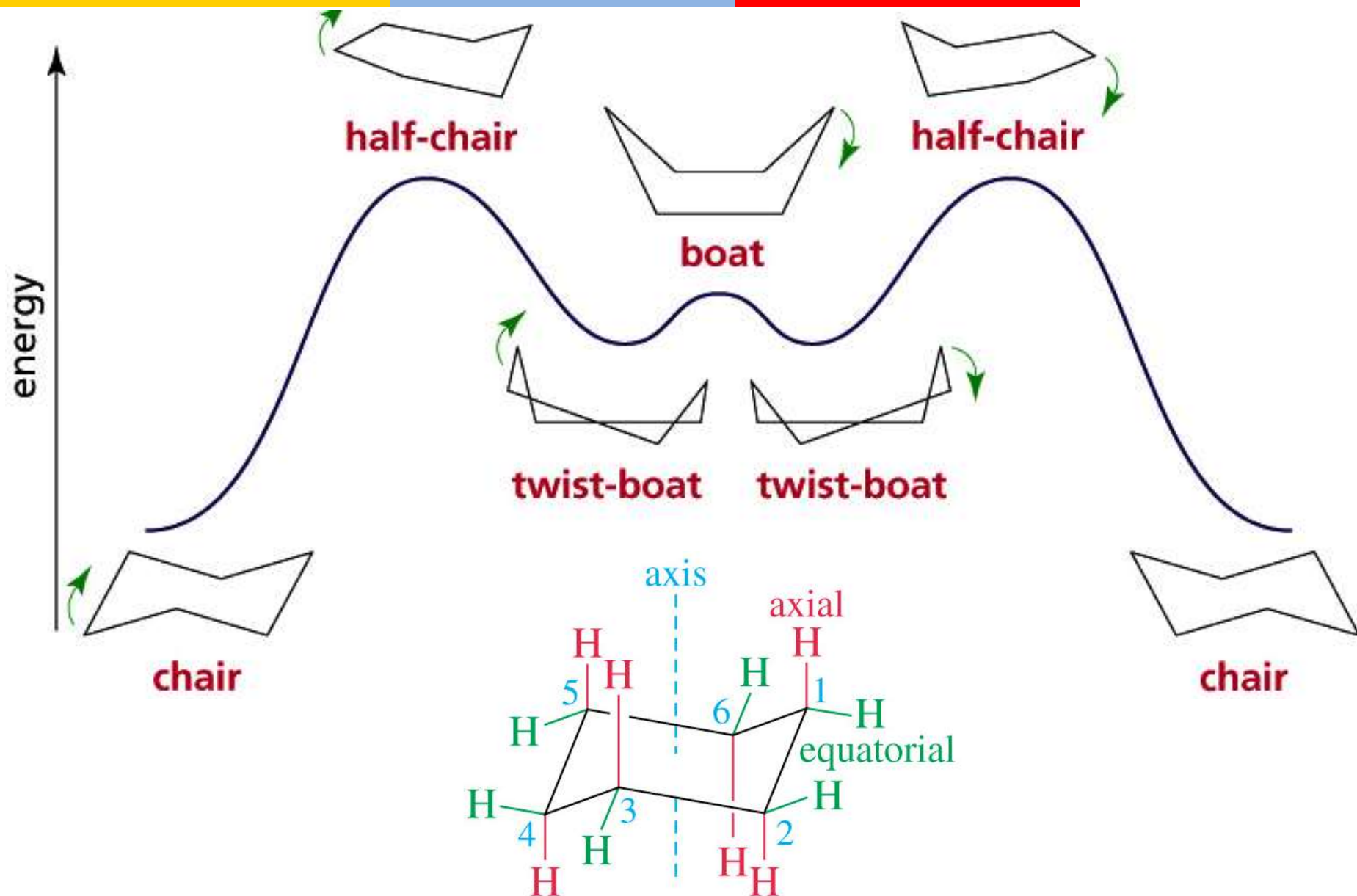
Flipping Chair Conformations

- All axial bonds become equatorial

- All equatorial bonds become axial

- All "up" bonds stay up

- All "down" bonds stay down

>20 kcal/mol

"Flat cyclohexane"

Ring strain > 20 kcal/mol

· angle strain
(all C–C bonds 120°)
· torsional strain
(all C–C bonds eclipsed)

Pull up

C-1

and

you

get...

bond angle 109°

(some relief of angle strain)

"Half chair"

Ring strain 10.8 kcal/mol

· some angle strain (120°)
· torsional strain
(some C–C bonds eclipsed)

10.8 kcal/mol

bond angle 120°

eclipsed C–C

Pull up

C-4

and

you

get...

Van Der Waals strain
"flagpole" interaction

"Boat" (aka hammock)

Ring strain 7.0 kcal/mol
·minimal angle strain
· torsional strain
(some C–C bonds eclipsed)
· Van Der Waals strain
("flagpole" interaction)

7.0 kcal/mol

Now

twist

(a little)

eclipsed C–C

11

5.5 kcal/mol

Now push C-1 down

"Twist Boat"

Ring strain 5.5 kcal/mol

-relief of Van Der Waals strain through twisting
- minimal angle strain
- torsional strain
(some eclipsed C–C bonds)

often drawn this way →
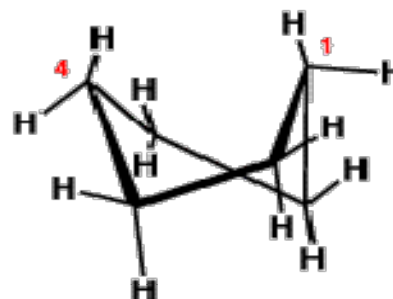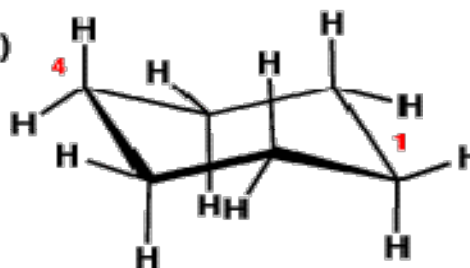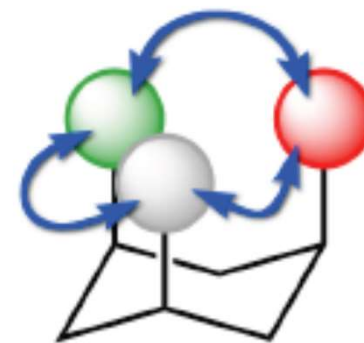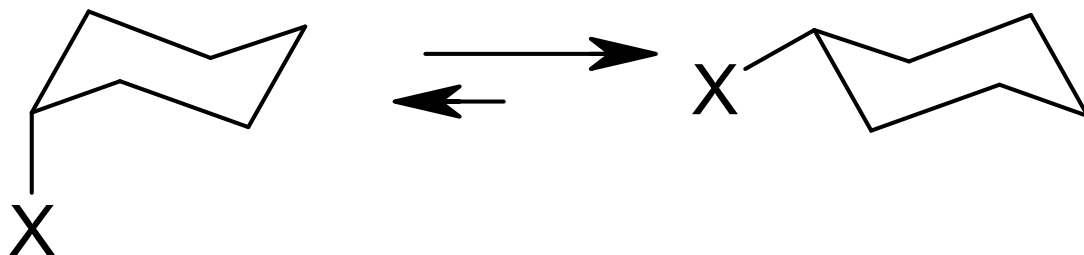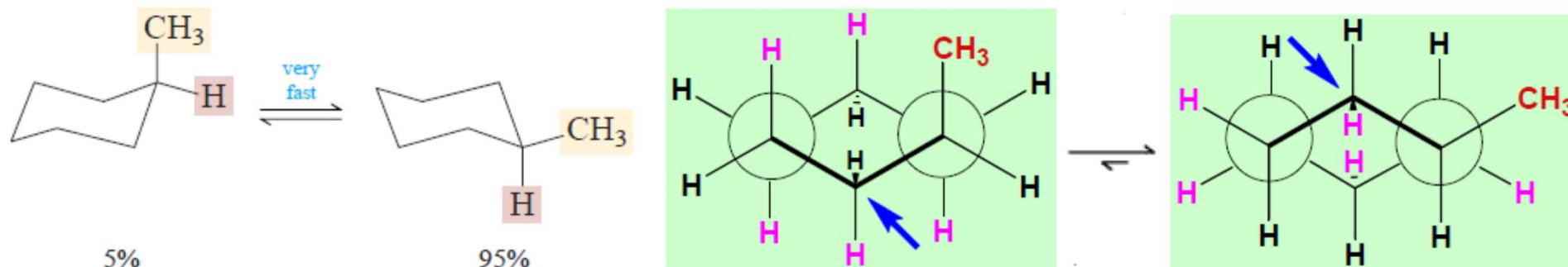
"Chair"

Ring strain 0 kcal/mol

· no angle strain (all bonds 109°)
· minimal torsional strain
(all C–C bonds staggered)

0 kcal/mol

monosubstituted cyclohexanes

Strain of one H-X 1,3-diaxial interaction in kJ/mol

X	$E_{axial} - E_{equatorial}$	X	$E_{axial} - E_{equatorial}$
-H	0.0	-COOH	2.9
-CN	0.4	$-CH_3$	3.8
-F	0.5	$-CH_2CH_3$	4.0
-Cl	1.0	$-CH(CH_3)_2$	4.6
-Br	1.0	Ph	6.3
-OH	2.1	$-C(CH_3)_3$	11.4

1-methylcyclohexane

Less stable   more stable by 7.6 kJmol⁻¹

$$\Delta G° = -RT \ln K_{eq} \qquad\longrightarrow\qquad \Delta G° = -2.303RT (\log K_{eq})$$

$$\log K_{eq} = \frac{-7.6 \text{ kj/mol}}{2.303(8.314\times10^{-3} \text{ kj/mol°K})(273+25)°K} = 1.33$$

$$K_{eq} = 10^{1.33} = 21$$

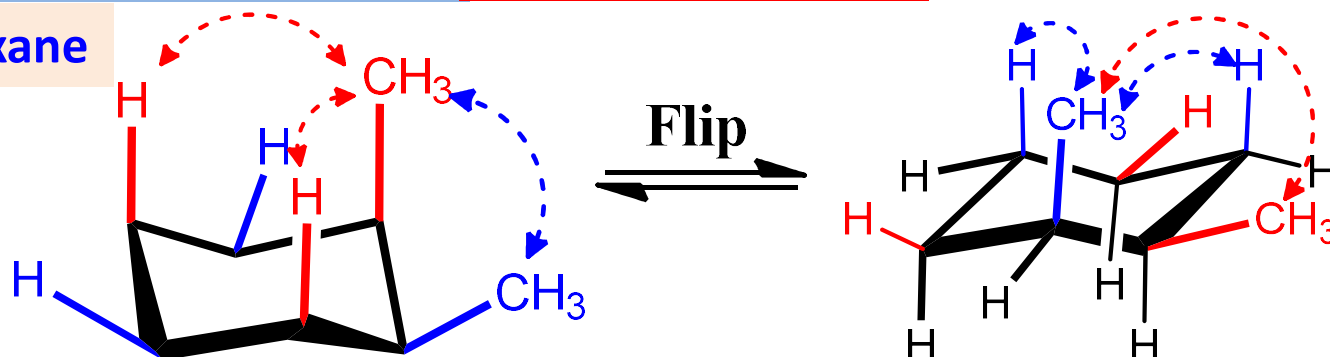$$K_{eq} = \frac{\text{Equatorial-Me conformer}}{\text{Axial-Me conformer}} = 21 = \frac{21}{1}$$

Equatorial-Me conformer: $\dfrac{21}{22}$ x 100 = 95%   Axial-Me conformer: $\dfrac{1}{22}$ x 100 = 5%
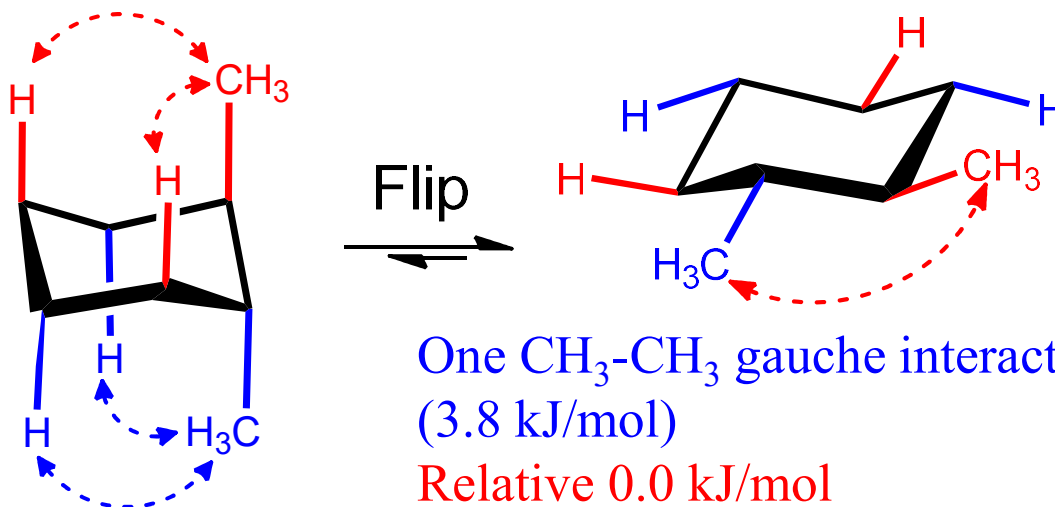
Disubstituted Cyclohexanes

cis-1,2-Dimethylcyclohexane

Two CH_3-H 1,3-diaxial interaction
+ One CH_3-CH_3 gauche
(7.6 kJ/mol + 3.8 kJ/mol)
Total strain =11.4 kJ/mol

Two CH_3-H 1,3-diaxial interaction
+ One CH_3-CH_3 gauche
(7.6 kJ/mol + 3.8 kJ/mol)
Total strain =11.4 kJ/mol
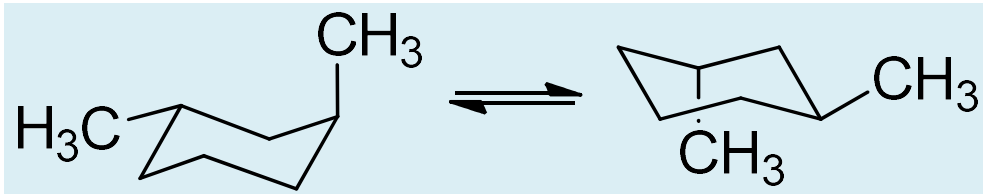
trans-1,2-Dimethylcyclohexane

Four CH_3-H 1,3-diaxial interaction
(15.2 kJ/mol)
Relative 11.4 kJ/mol

One CH_3-CH_3 gauche interaction
(3.8 kJ/mol)
Relative 0.0 kJ/mol
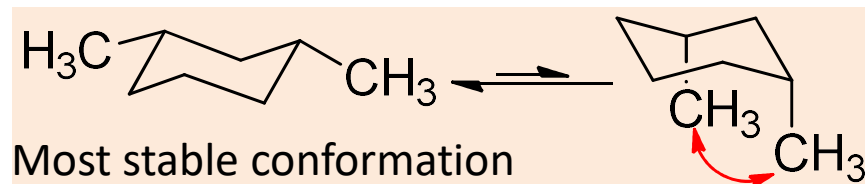
Disubstituted Cyclohexanes
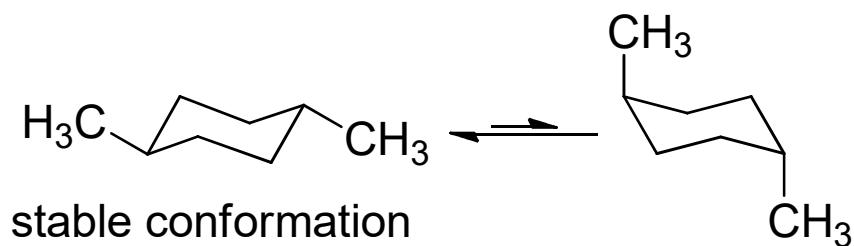
trans-1,3-Dimethylcyclohexane

Two CH$_3$-H 1,3-diaxial interaction
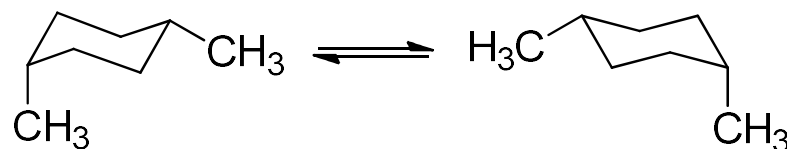(7.6 kJ/mol); Total strain =7.6 kJ/mol

cis-1,3-Dimethylcyclohexane

Most stable conformation

Relative 0.0 kJ/mol

trans-1,4-Dimethylcyclohexane

stable conformation
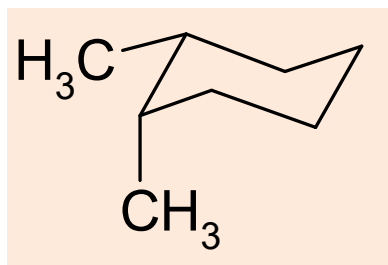
Relative 0.0 kJ/mol

cis-1,4-Dimethylcyclohexane

Two CH$_3$-H 1,3-diaxial interaction
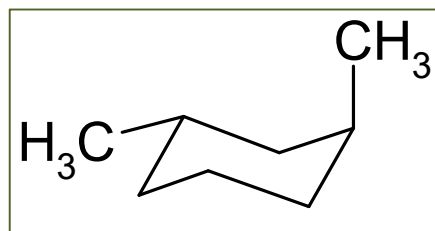(7.6 kJ/mol); Total strain =7.6 kJ/mol
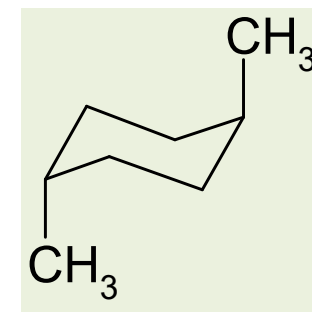
Disubstituted Cyclohexanes

Can you name these dimethylcyclohexanes?

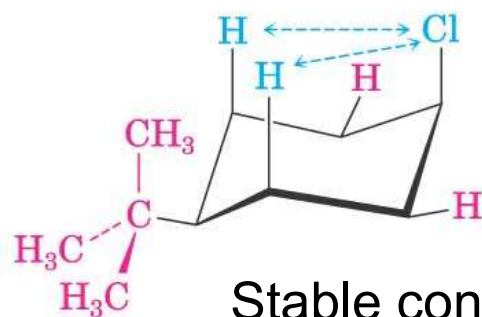*cis*-1,2-dimethylcyclohexane

equatorial - axial

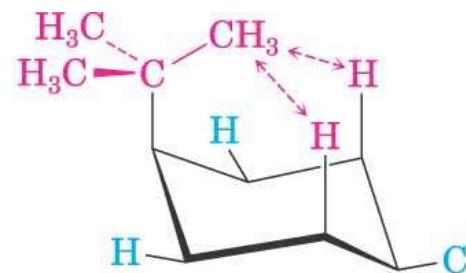*trans*-1,3-dimethylcyclhexane

equatorial - axial

trans-1,4-dimethylcyclohexane

axial-axial or diaxial

Which of these represent the most stable conformation possible?
What is energy difference in the corresponding most stable and
least stable conformation?

Stable conformation

$2 \times 1.0 = 2.0$ kJ/mol steric strain

$2 \times 11.4 = 22.8$ kJ/mol steric strain

<u>Notice for Quiz Test-03</u>

Quiz Test-03 will be conducted during 07-04-2018 (Saturday) to 12-04-2018 (Thursday) in the regular Tutorial Classes.

Syllabus: L-24 to L-31 of Course Hand-out.

Assignment-03 Test is scheduled on **18-04-2018 at 17.30 hrs**.