CH203 Lecture 7

September 23, 2010

John. A. Porco, Jr.

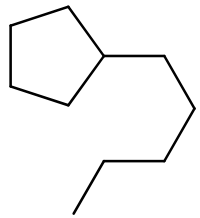
BOSTON UNIVERSITY

Department of Chemistry

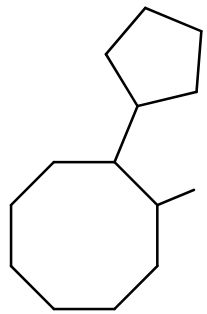
porco@bu.edu

From Last Lecture

The cycloalkane serves as the parent alkane if there are the same number of carbon atoms as the alkyl chain. E.g. pentylcyclopentane, not 1-cyclopentylpentane



Also, when naming cycloalkanes as substituents, *the cyclo- does count for determining alphabetical order*. For example: it would be 1-cyclopentyl-2-fluorocyclooctane, NOT 1-fluoro-2-cylopentylcyclooctane

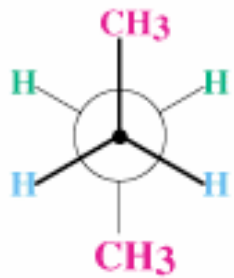


Review: Conformations of Butane

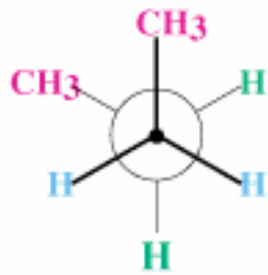
- **anti conformation** has two methyl groups 180° away from each other
- Rotation around the C2–C3 gives eclipsed conformation
- Staggered conformation with methyl groups 60° apart is **gauche conformation**

[kcal/mol]

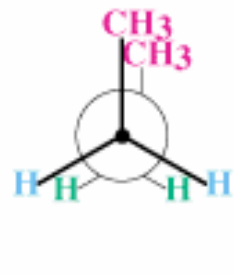
H,H eclipsed	1.0
CH3,H eclipsed	1.4
CH3,CH3 eclipsed	2.6
CH3,CH3 *gauche*	0.9



Anti



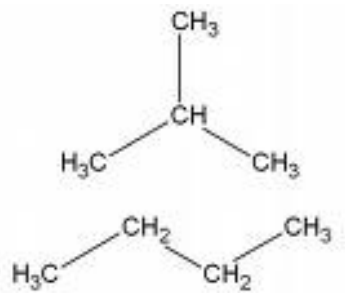
Gauche



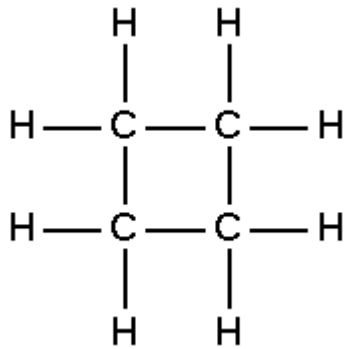
Least stable eclipsed

Review: Cycloalkanes

Cycloalkanes are chemical compounds with one or more carbon rings to which H atoms are attached according to the formula C_nH_{2n}. Cycloalkanes with a single ring are named analogously to their normal alkane counterpart



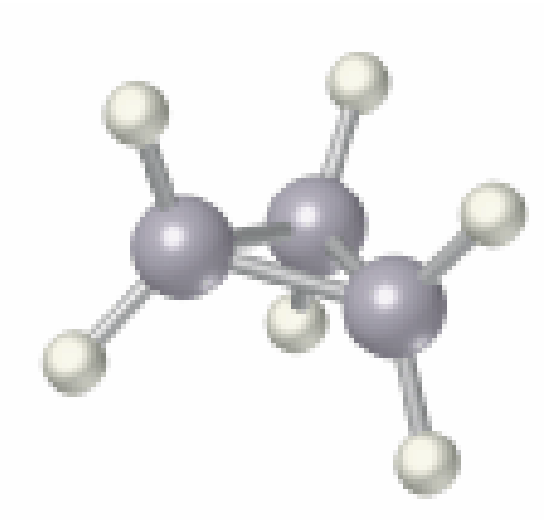
isobutane
butane

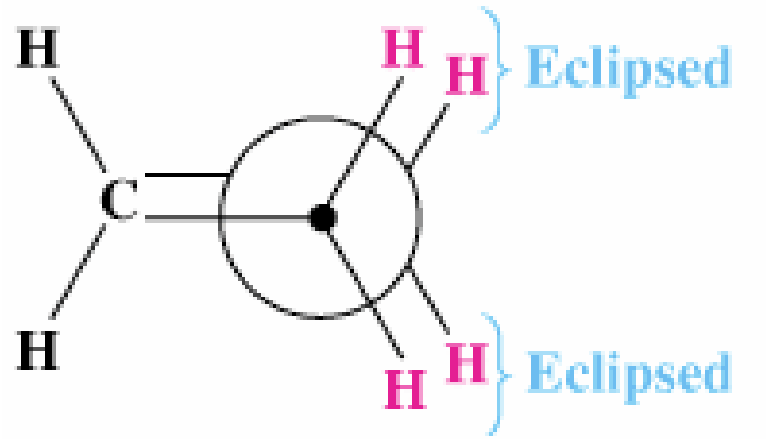


cyclobutane

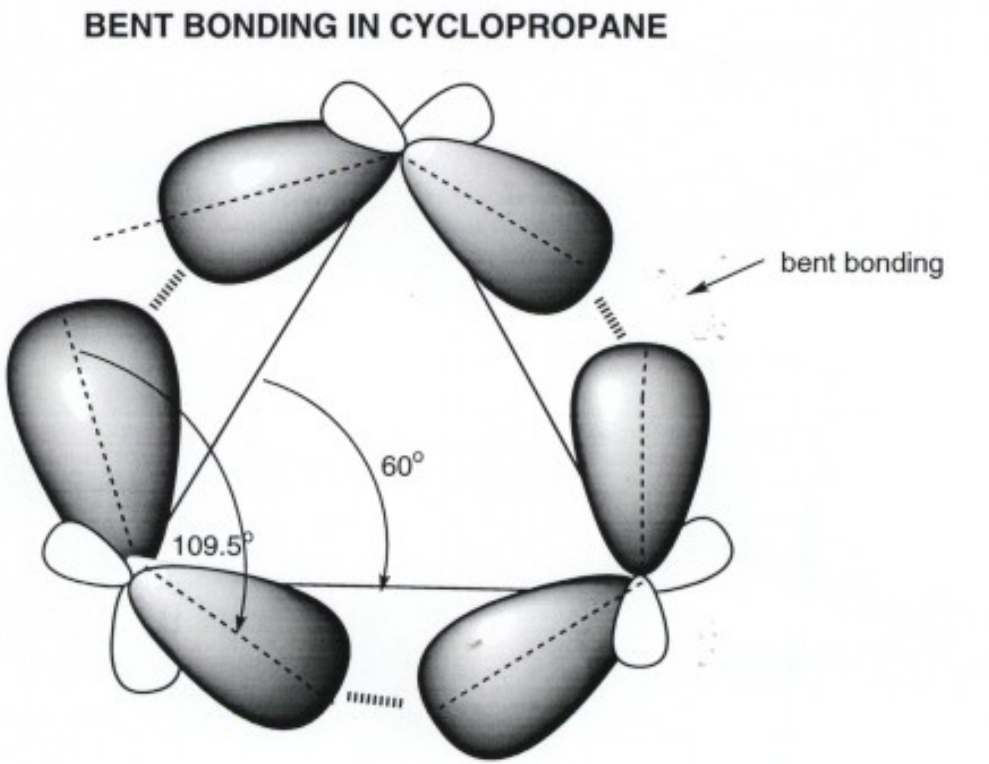
Cyclopropane: An Orbital View

- 3-membered ring must have planar structure
- Symmetrical with C–C–C bond angles of 60°
- Requires that sp^3 based bonds are bent (and weakened)
- All C-H bonds are eclipsed





Cyclopropane Ring Strain



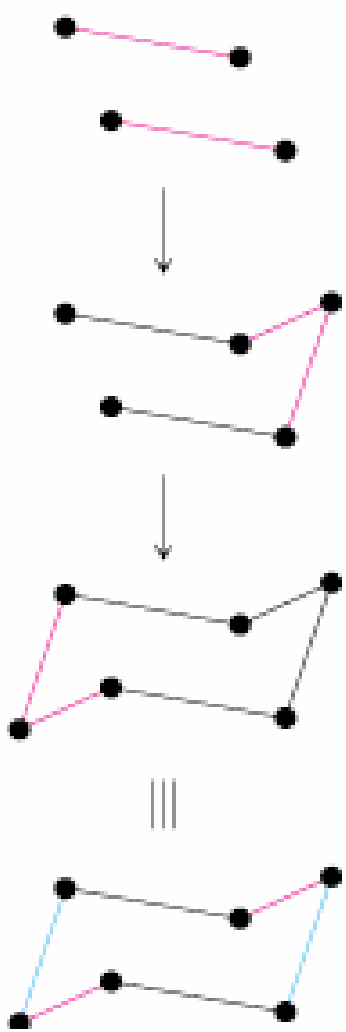
NOTE THAT SIGMA BONDING INVOLVES "END-ON OVERLAP" AND PI BONDING INVOLVES "SIDELONG" OVERLAP. SIGMA BONDING IS STRONGER THAN PI BONDING. **BENT BONDING** IS INTERMEDIATE BETWEEN SIGMA AND PI BONDING, THE OVERLAP BEING NEITHER END-ON NOR SIDELONG. THIS MAKES THE OVERLAP LESS EFFICIENT THAN SIGMA OVERLAP, AND THE CYCLOPROPANE C-C BONDS WEAKER THAN NORMAL C-C SIGMA BONDS. THIS IS DESCRIBED AS **ANGLE STRAIN.**

How to Draw Cyclohexane

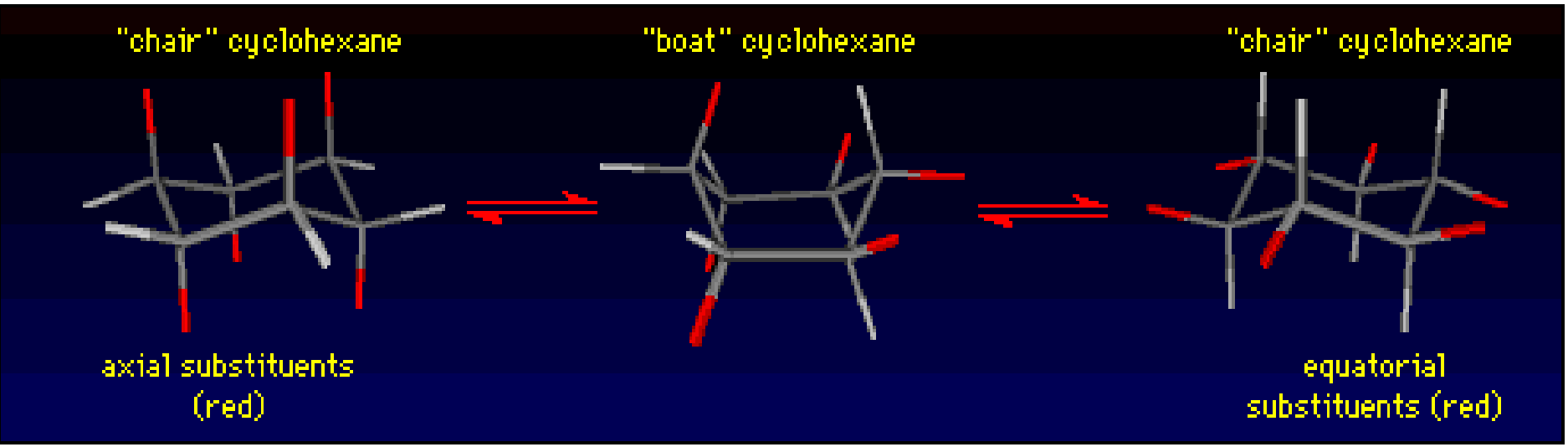
STEP 1 Draw two parallel lines, slanted downward and slightly offset from each other. This means that four of the cyclohexane carbon atoms lie in a plane.

STEP 2 Locate the topmost carbon atom above and to the right of the plane of the other four and connect the bonds.

STEP 3 Locate the bottommost carbon atom below and to the left of the plane of the middle four and connect the bonds. Note that the bonds to the bottommost carbon atom are parallel to the bonds to the topmost carbon.

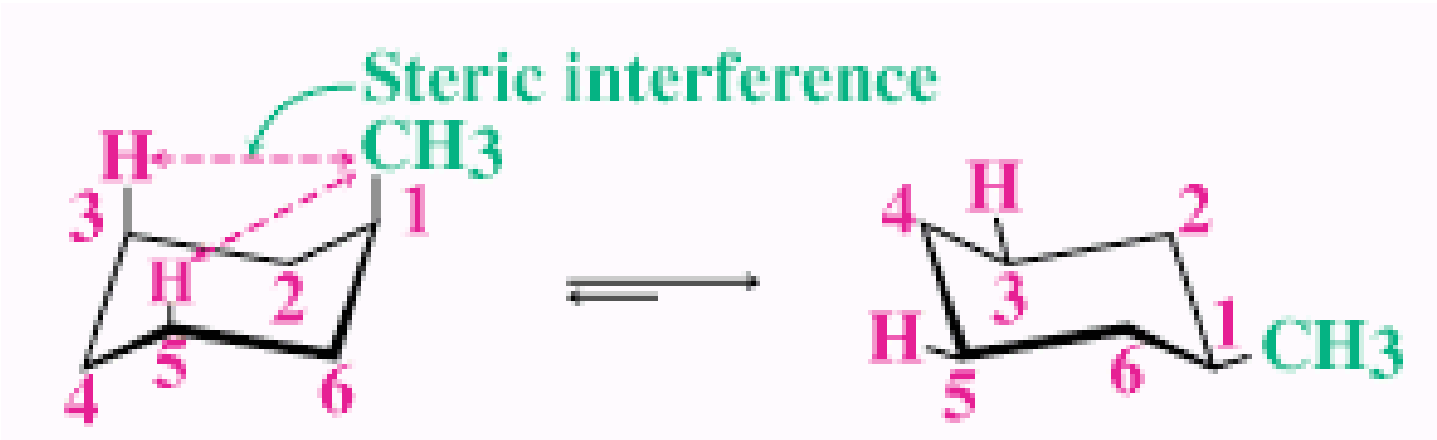


Chair-Chair Interconversion



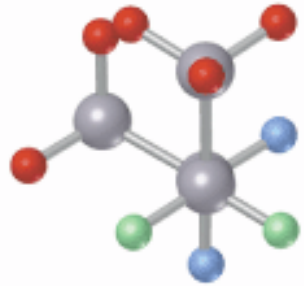
1,3-Diaxial Interactions

- Difference between axial and equatorial conformers is due to steric strain caused by **1,3-diaxial interactions**
- Hydrogen atoms of the axial methyl group on C1 are too close to the axial hydrogens three carbons away on C3 and C5, resulting in 1.8 kcal/mol (7.6 kJ/mol) of steric strain

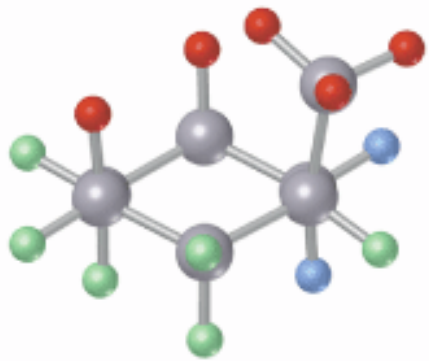


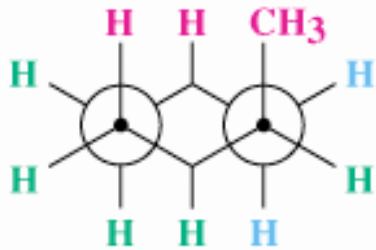
Relationship to Gauche Butane Interactions

- Gauche butane is less stable than anti butane by 3.8 kJ/mol because of steric interference between hydrogen atoms on the two methyl groups
- The four-carbon fragment of axial methylcyclohexane and gauche butane have the same steric interaction
- In general, equatorial positions give more stable isomer



Gauche butane
(3.8 kJ/mol strain)





Axial
methylcyclohexane
(7.6 kJ/mol strain)

Cycloalkanes & Ring strain

Lecture #7
9/23/10

- Cycloalkanes do not all have the same relative stability:

	kcal/mol	ring strain
△	27.4	115 kJ/mol
□	26.0	109 kJ/mol
⬠	6.4	27 kJ/mol
⬡	0	0 kJ/mol

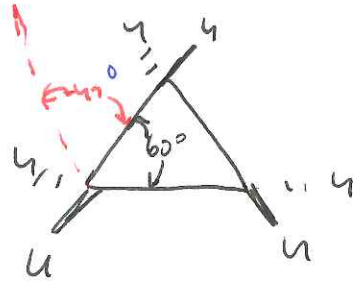
calcd from heats of combustion

$$(CH_2)_n + \frac{3n}{2} O_2 \rightarrow n CO_2 + n H_2O + \text{Heat}$$

↳ heat of combu. per CH_2 unit, then subtract a ref value derived from a strain-free "alkane" ↳ acyclic

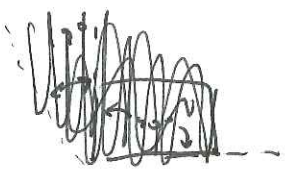
~~Baeyer strain theory~~

Origin of ring strain in △ & □

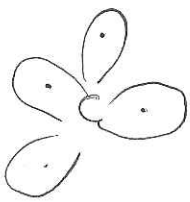


1) alkanes: sp^3 C
2) normal tet b. angle 109.5°
3) △: int ∠'s 60°
depart. from tetr. geo by 49.5°

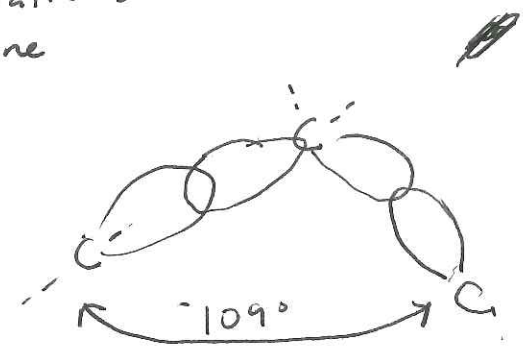
angle strain: caused by compression/expansion of bond angles



Orbital considerations for cyclopropane

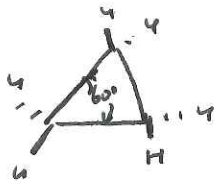


sp^3 C



typical alkane C–C

↑ end-on orbital overlap



In △, int. angles are 60° and depart from ideal sp^3 hybrid by 49.5°

angle strain

← not perfectly end-on and weaker ∴ more reactive

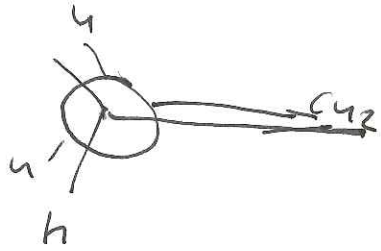
"bent" bonds

banana bonds

present if neighboring C–H bonds eclipse

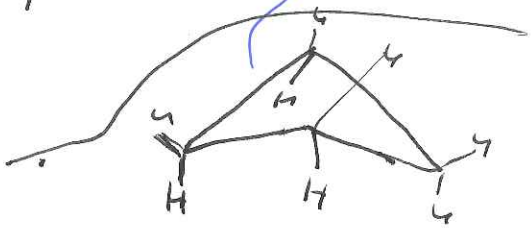
tors. strain

Cyclopropane also shows



eclipsed H's

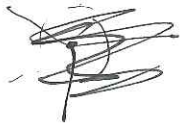
not quite eclipsed

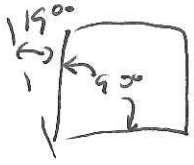


Cyclobutane

considerable ∡ strain

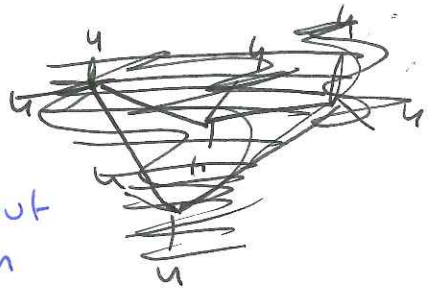
~ 88° int angles





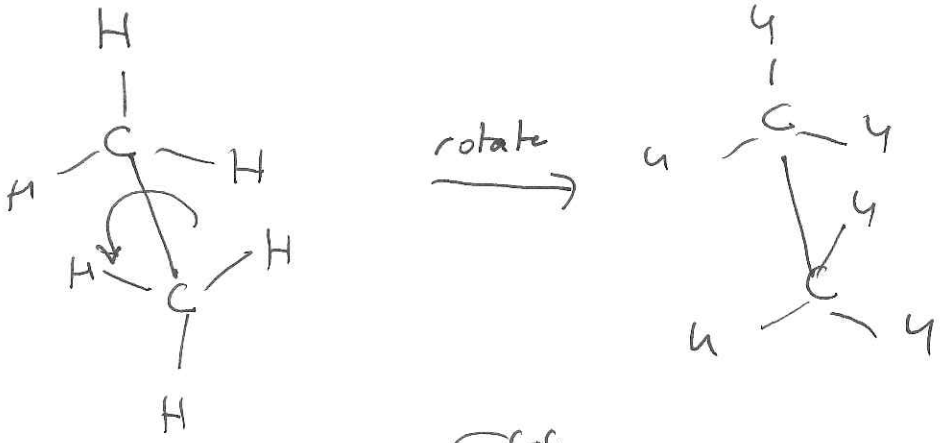
(if planar)

less angle strain, but more torsional strain



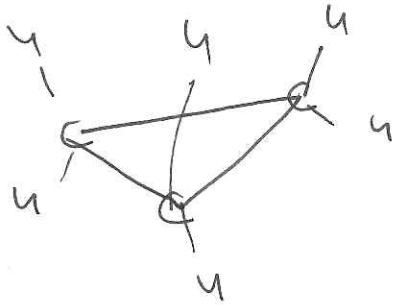
folding/puckering cyclobutane relieves some tors. strain

Cycloalkanes & Cis/trans Isomerism

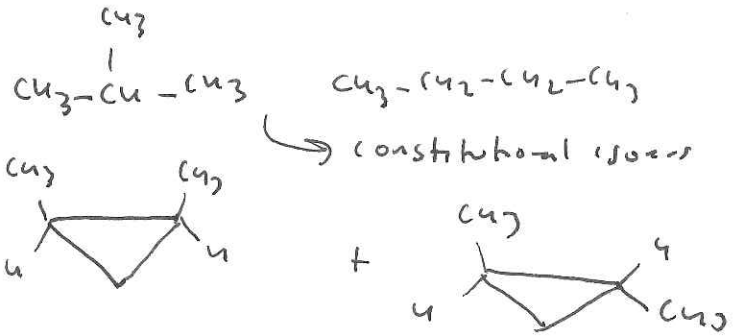


C-C

rotate around σ bond is possible and occurs freely

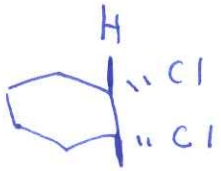


In contrast, △ is a rigid molecule & no bond rotation can take place around a cyclopropane C-C bond w/o breaking open the ring



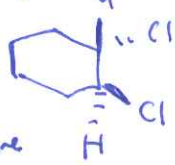
cis 1,2-diethyl cyclopropane

stereoisomers (same connections but different 3-D orientation.



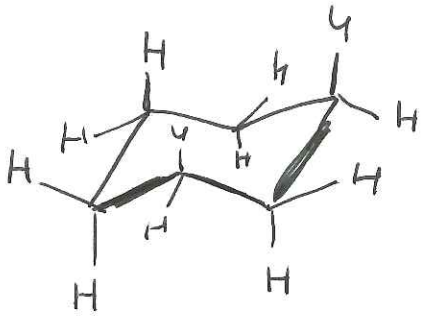
cis-1,2-dichloro cyclohexane

trans-1,2-diethyl cyclopropane

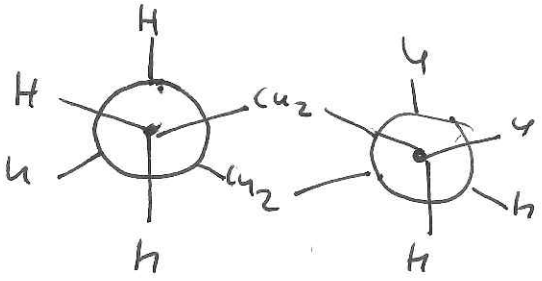


trans-1,2-dichlorocyclohexane

Conformations of Cyclohexane



"chair conformation"

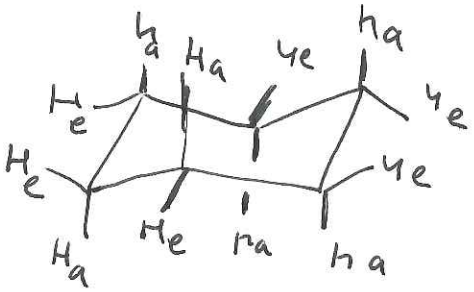


Newman projection

Use molecular model to confirm staggered arrangement: C-C bond angles 109.5°, free of torsional strain

like lounge chair back seat + footrest

One consequence of the chair conformation is that there are two kinds of substs for positions on the ring:

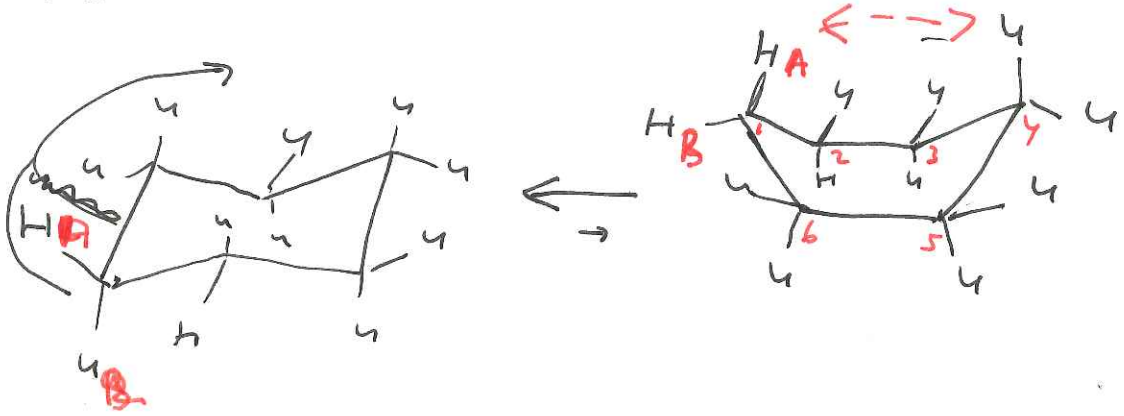


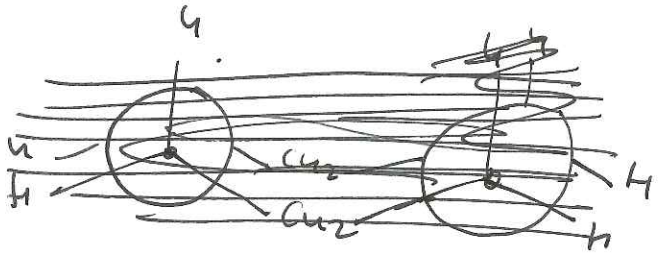
six each

Ha (axial): parallel to ring axis (⊥ to ring)

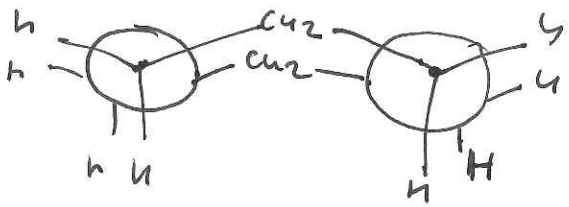
He (equatorial): in rough plane of the ring (around the ring equator)

By flipping one end of the chair form up (or down), we can assume the "boat conformation"



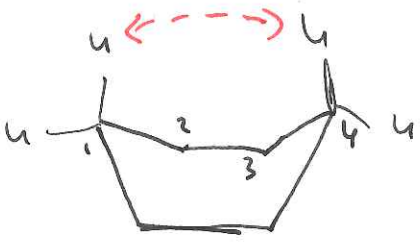


eclipsed conformations produce torsional strain



Newman obtained by sighting along C2-C3 and C5-C6 bonds

Boat- approx 30 kJ/mol (7 kcal/mol) higher than chair



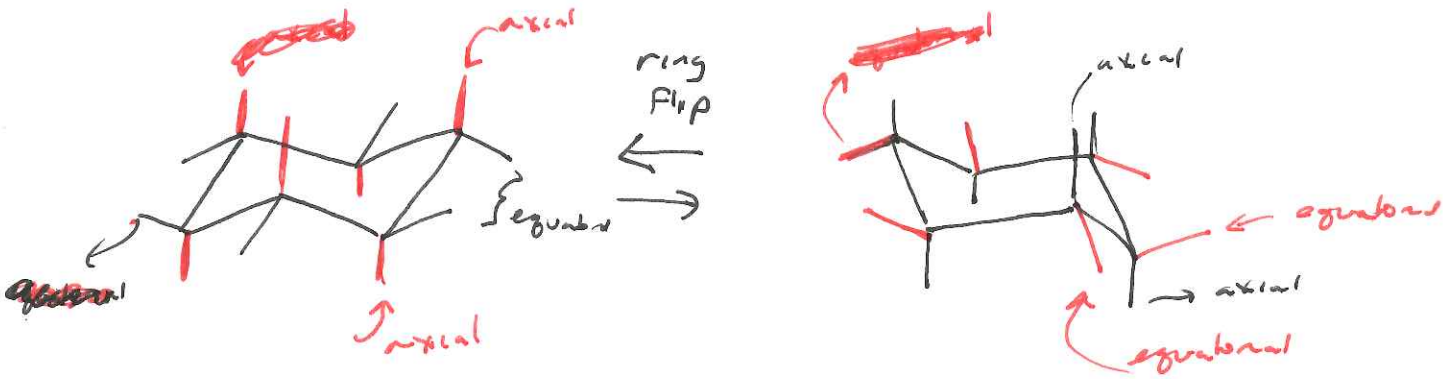
Additional interaction: 2 H's on C1 & C4 close enough to cause Van der Waal's repulsion

"flagpole" interaction

half chairs twist boats

energetics → ppn of molecules in chair conf.

Conformational mobility of cyclohexane

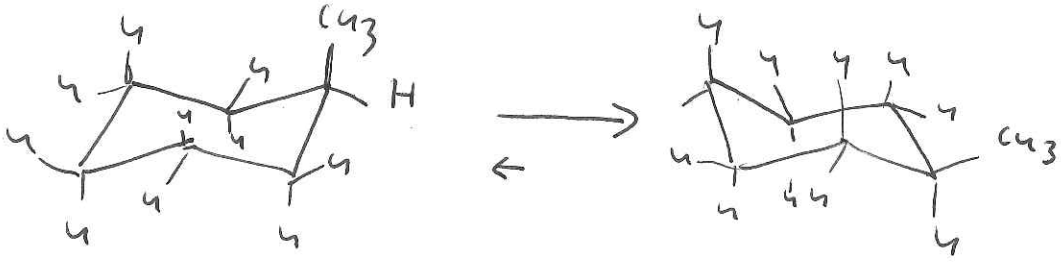


At room temperature, the cyclohexane ring flips back & forth rapidly btwn 2 equivalent chair conformations.

When the ring flips, all the bonds that were axial become equatorial and vice-versa

What happens when we replace one H atom by an alkyl substituent?

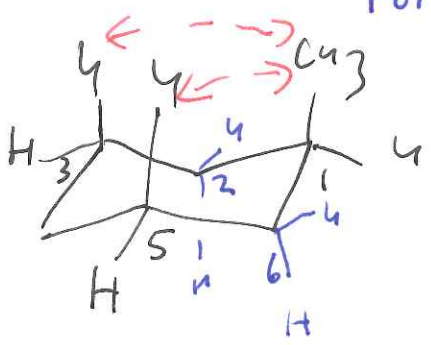
Methylcyclohexane

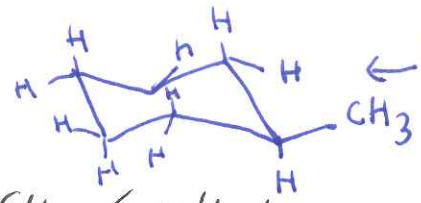


less stable

more stable by 7.5 kJ/mol] 1.8 kcal/mol

For a monosubst. cyclohexane





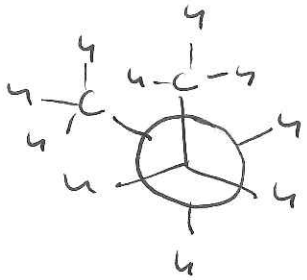
1,3 diaxial int. absent here

When the $-CH_3$ (methyl group) is axial, it is so close to the H atoms on C3 and C5 that the van der Waals forces btwn them are repulsive

Two conformers are not equally stable.

This type of steric strain is called a 1,3-diaxial interaction E' is minimized when the group is equatorial

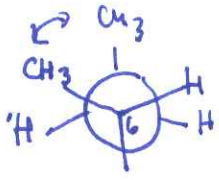
The strain caused by a 1,3-diaxial interaction in me-cyclohexane is the same as the strain caused by close prox. of H atoms in CH_3 groups of gauche butane.



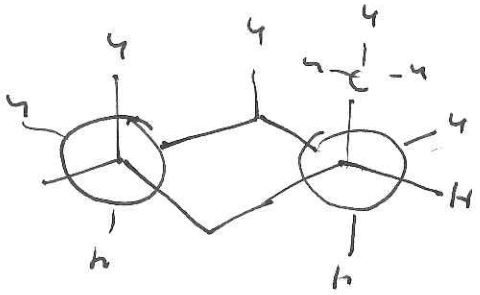
gauche butane

3.8 kJ/mol

(~ 0.9 kcal/mol)

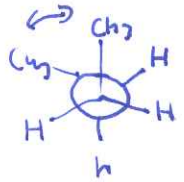


H site down 1-6 bond

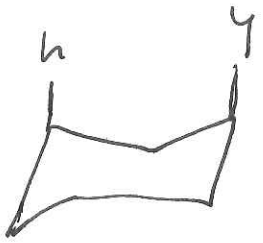


axial methyl cyclohexane

two gauche interactions = 7.6 kJ/mole steric strain (1.8 kcal/mol).



H site down 1-2 bond



The amount of 1,3 diaxial steric strain depends on the nature + size of the subst.

Y = CH_3

Y = tBu

Y = CN

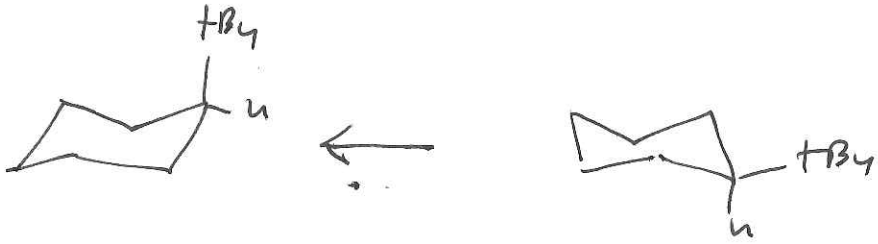
Y = Br, Cl

~~Y = I~~

	Strain of H–Y (1,3 diaxial)
Y = CH_3	3.8 kJ/mol (0.9 kcal/mol)
Y = tBu	11.4 kJ/mol (2.7 kcal/mol)
Y = CN	0.4 kJ/mol (0.1 kcal/mol
Y = Br, Cl	1.0 kJ/mol (0.25 kcal/mol)

Data refer to a single Y–H interaction and must be doubled to arrive at the amt of strain in a monosubst. cyclohexane

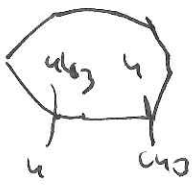
So for



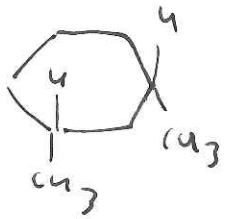
conformation with tBu equatorial estimated to be ~22 kJ/mol (5.4 kcal/mol) more stable than the axial form

~~Cis-trans~~ Disubstituted cyclohexanes : cis–trans isomers

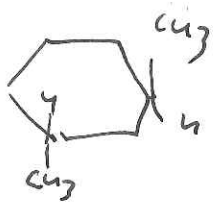
cis-1,2 dimethylcyclohex



trans-1,2, dimethyl cyclohexane



cis 1,3 DMC



trans 1,3 DMC