Course Chem 343 Lecturer Gellman (11am)

Day Wednesday Date 10/19/2011

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Review Session: Thursday, October 20
4-5 pm - HERE

Chapter 7: Ring Compounds & Stereochemistry of Organic Reactions

Recom. Problems: 1, 5, 6, 8-16, 19, 21, 23-37, 39-65.

Recall: Cycloalkanes

△ = cyclopropane
□ = cyclobutane
⬠ = cyclopentane
⋮
etc

General structure: 

- Consider Heats of Formation (ΔH_f°)
  - For linear alkanes, ($CH_3(CH_2)_nCH_3$) the ΔH_f° increases by ~5 kcal/mol per additional CH_2 unit.

What about cycloalkanes?

Cycloalkane	ΔH_f° (kcal/mol)
△	+4.2
□	+1.7
⬠	-3.7
⬡	-5.0
≥7 C's	-3.5 to -4.6

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Key observations of ΔH_f° for cycloalkanes:

1. Smallest rings seem to have some sort of internal destabilization relative to larger rings & linear alkanes
2. Cyclohexane is particularly stable (⬡)
3. Cyclopentane (⬠) and rings larger than 7 C's (≥7 C's) are slightly destabilized relative to linear alkanes.

SMALL RINGS: (3-4 membered rings)

- 2 sources of "internal strain" ("ring strain")
  1. Angle Strain
  2. Torsional Strain

1. Angle Strain:

Recall: for sp^3 carbon, ideal angle is 109.5°

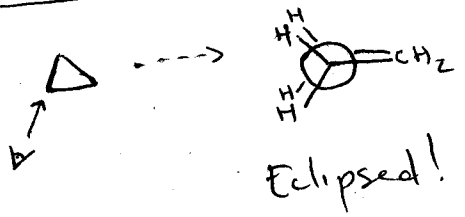
109.5° C ... vs. 60° 90° } Bond angles are much smaller than ideal bond angle

⇓

"Angle Strain"

---

2. Torsional Strain: Unavoidable eclipsing interactions



Eclipsed!

- 3 points (C's) define a plane, & thus the molecule is locked in an eclipsed conformation

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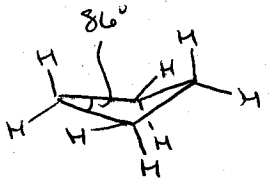
Internal Compromise - Example

Cyclobutane (□)

- Angle strain vs. Torsional strain
  - → If perfectly flat (as drawn on page), then all C-H bonds and C-C bonds will be eclipsed
  - ↓
  - to alleviate this, cyclobutane adopts a different (not planar) conformation

"Puckered" Conformation:



→ Bonds are no longer totally eclipsed!

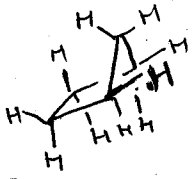
HOWEVER: Bonds in ring are smaller (90° → 86°)

Thus - Molecule takes on angle strain to relieve some torsional strain & minimize conformational energy.

Compromise in Cyclopentane (⬠)

108 in flat pentagon

Cyclopentane puckers to relieve torsional strain →



(C-Ĉ-C bond angles < 108°)

[Could avoid angle strain when flat, but instead puckers to alleviate torsional strain]

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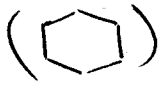
Cyclohexane: Special!



* ΔH_f° for CH_2 increment matches value for linear alkanes!

why? → In this case, the molecule can adopt a conformation that minimizes both angle strain and torsional strain!

Detailed Conformational Analysis

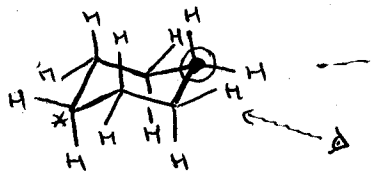
Flat Representation

120° → angle is larger than preferred bond angle for sp^3 carbons

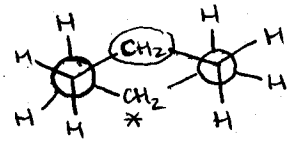
↳ puckering reduces both angle strain and torsional strain

Most stable conformation

"Chair Conformation"



(Newman Projection)



perfectly staggered!

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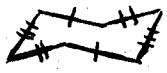
Chair Drawing Rules

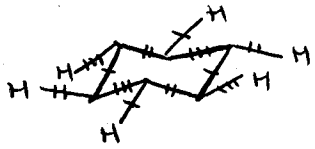
① C_6 ring is generated with 3 pairs of parallel lines



② onto this framework, each C has one H (or other bonding partner) drawn with vertical lines

"Axial" bonding positions

③ The other hydrogens (or bonding partners) are drawn with lines parallel to a specific ring bond.



"Equatorial" bonding positions

Equatorial bonds are parallel to the ring bonds to which they are <u>not</u> attached

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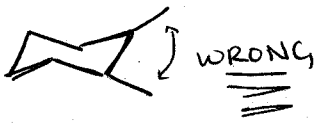
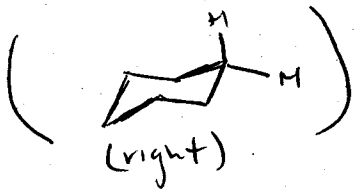
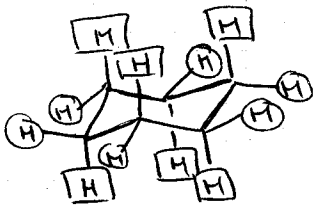
Graphical Nonsense (to be avoided)



these are neither axial nor equatorial & give no information (they are incorrect)



(right)



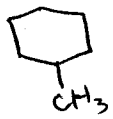
[H] - Axial H's are all identical to each other

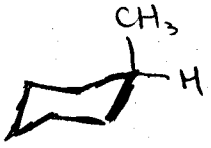
(H) - Equatorial H's are all identical to each other

[H] ≠ (H) Axial & Equatorial H's are not the same!

Equatorial vs. Axial Substituents

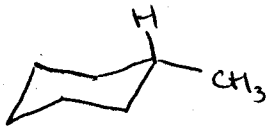
for:





Axial - CH_3

vs.



Equatorial - CH_3