Course CH 343 Lecturer Sam Gellman

Day Wednesday 1:20 Date 10/19/11

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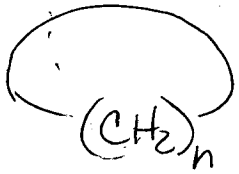
Chap 7 - Cyclic molecules + Stereochemistry of organic rxn

* Rec. Probs: 1, 5, 6, 8-16, 19, 21, 23-37, 39-65

Cycloalkanes

△ cyclopropane · 5+6 membered rings are really common

□



Recall: Heats of Formation (ΔH_f°)

Benchmark: linear alkanes

$CH_3(CH_2)_n CH_3$ ⇒ incremental ΔH_f° per CH_2 = -5.0 kcal/mol

· Energetically favorable to form from elements

Cycloalkanes

	ΔH_f° per CH_2	
△	+4.2	} unfavorable to form from elements
□	+1.7	
⬠	-3.7	
⬡	-5.0	← same as linear alkanes
>7 C's	-3.5 to -4.6	

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Observations

1) Smallest rings (△ + □) have some destabilization relative to larger rings or linear alkanes - "internal strain"

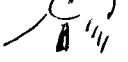
2) Cyclohexanes is unique (matches linear alkanes)

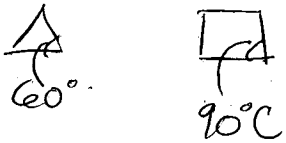
3) ⬠ ≥ 7 C's - modest destabilization relative to linear alkanes

Explanations

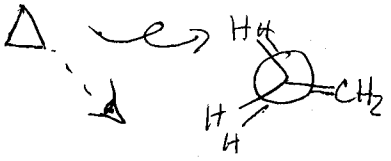
1) △ or □ - 2 sources of internal strain

- Angle strain

Recall: sp^3 C  109.5°

Consider: 

- Torsional strain

 Totally eclipsed!

- Internal compromises between sources of strain (angle + torsional.

Consider:

• Perfectly flat would also be perfectly eclipsed!

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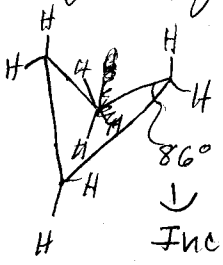
Result: molecule is not going to stay flat - deforms from perfectly flat ("pucker"); relieves some torsional strain

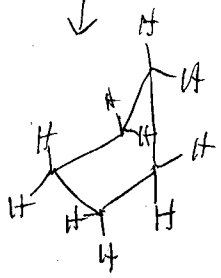


↓ Inc in angle strain

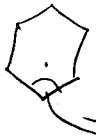
Compromise in cyclopentane

"Flat" - max. eclipsing

"envelope" shape ↓ puckered



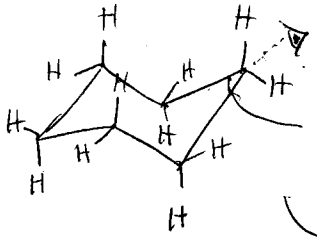
Recall:



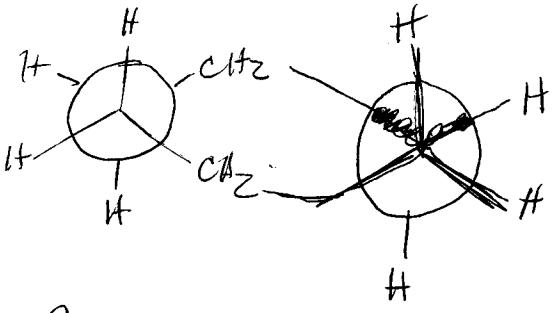
is "perfect"

120° for flat cyclohexane

Cyclohexane's most stable form: Chair conformation



• No angle strain or ~~torsional~~ strain!



2 C-C bonds are parallel

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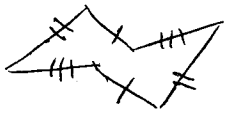
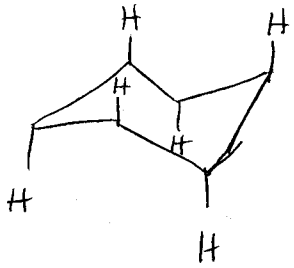
Rules for cyclohexane chair drawing

1. C-C bonds form 3 pairs of parallel lines

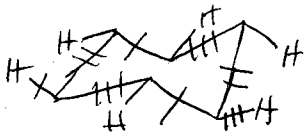


2. Each carbon has one H indicated a/a vertical line



"axial" positions (ax.)

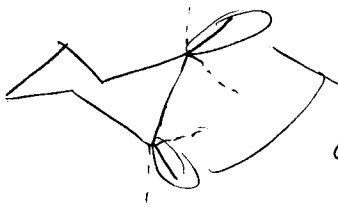
3. Another H on each C is "to the side"



"Equatorial" positions (eq.)

Each eq C-H bond is parallel to a pair of C-C bonds of the ring that are not directly attached.

Nonsense



not axial or equatorial !!

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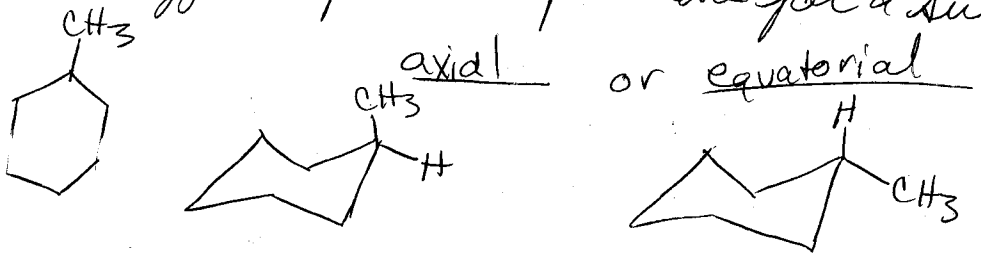
Equivalency: all axial H's are equivalent to each other in cyclohexane all equatorial H's are equivalent to each other

BUT axial is different from equatorial!!

Thus, different possible positions for a substituent



- Axial CH_3 is less stable than eq. CH_3