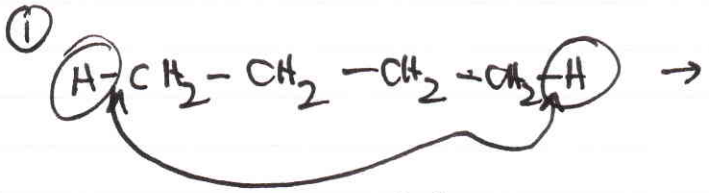
Lecture VII – Spring 2009 Chem 3331 02/10/2009

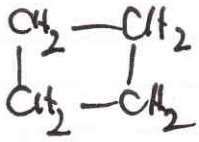
Last week, we talked about.
1. Alkanes
2. Nomenclature
3. Physical Properties
4. Sources
5. Conformational Analysis

Today:
1. Cycloalkanes
2. Nomenclature
3. Stability
4. Conformations
5. Cyclohexane conformations

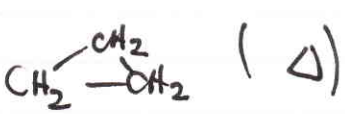
Many organic compounds are cyclic, including components of many biomolecules. We will start studying those compounds on the example of cycloalkanes:



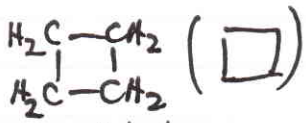
butane C_4H_{10}



cyclobutane C_4H_8



cyclopropane



cyclobutane

cyclopentane

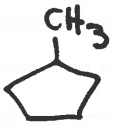
cyclohexane

General formula of cycloalkanes is C_nH_{2n} – two hydrogens had to go to close the cycle.

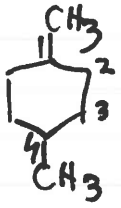
Their trends in physical properties parallel alkanes:
- nonpolar
- nonreactive
- insoluble in water
- their bps and mps increase with the number of carbons

(2) Nomenclature and Isomerism

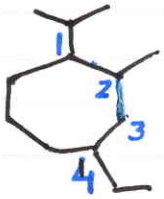
Pretty straight forward:



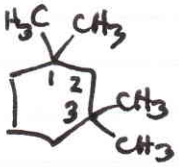
methylcyclopentane



1,4-dimethylcyclohexane



4-ethyl-1-isopropyl-2-methylcycloheptane

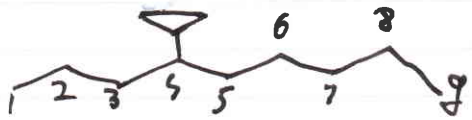


1,1,3,3-tetramethylcyclohexane

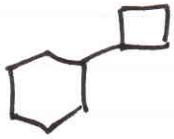
acyclic

But if your chain is longer than the number of atoms in your ring, the ring is treated as the substituent:

methylcyclopropane, but



4-cyclopropylnonane!

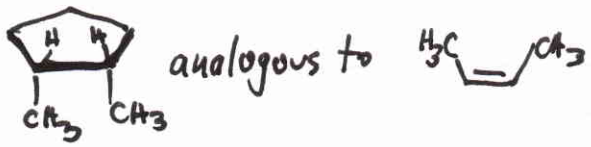


cyclobutylcyclohexane, NOT cyclohexylcyclobutane

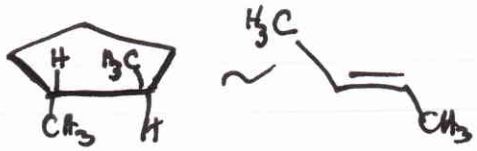
Rotation around single bond is normally free. But in a cyclic system, it would lead to ring twisting and could not be fully completed – RESTRICTED ROTATION!

Remember the case of double bond?

RESTRICTED ROTATION ⇒ STEREOISOMERS (cis/trans)



cis-1,2-dimethyl cyclopentane



trans-1,2-dimethyl cyclopentane

(3) Stabilities

Okay, so we take the ends of a chain:

and bring them together →

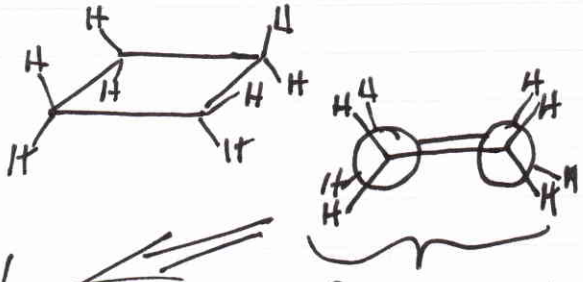
This cannot be equally easy for a small and for a large chain, can it?

Adolf von Baeyer (Nobel Prize, 1905):

Ring strain comes from the fact that carbons want to have 109.5° in their compounds, but small rings might not allow that.

internal angles of small polygons.

Additional problem is torsional strain:



torsional strain adds up in planar compounds!

fully eclipsed

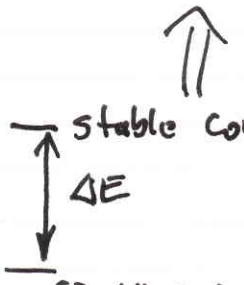
Now how do we determine these stabilities:
We burn the compound?

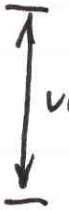
$+ \frac{3}{2} n O_2 \rightarrow$

$n CO_2 + n H_2O$

+ ENERGY → This is commonly divided by the number of CH_2 groups, to allow comparisons between different cycloalkanes.

this reference is  (unstrained long-chain open alkane)





ΔE (per CH_2) = 157 kcal mol^{-1} in long chain-alkane

ΔE (per CH_2)				
	166 kcal/mol	163	158.7	157

the difference between these numbers and 157 kcal/mol is ring strain!

9 kcal/mol	6	1.7	0

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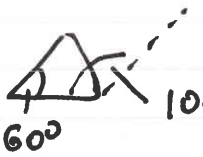
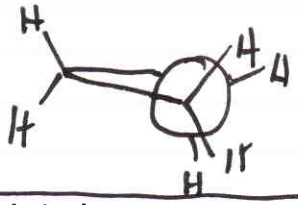
(4) Cyclopropane – very strained



large ring compression

Reactions that open Δ ring are very exothermic, since they release ~27 kcal mol^{-1}!

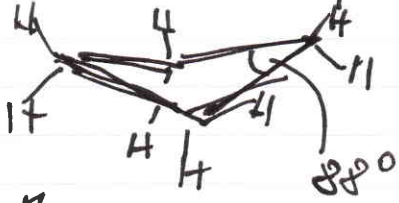
Torsional strain is a problem too:

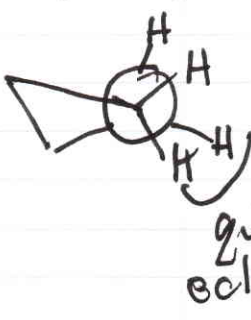


Cyclobutane

– torsional strain is relieved by some "puckering"

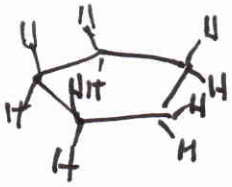
About as strained as cyclopropane, but this is spread out over 4 carbons, so overall the ring is more stable.



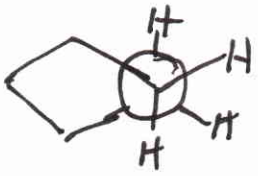


Cyclopentane

108° → virtually no angle strain here, but



⇒ planar structure would have too many eclipsing interactions ⇒ "puckering"



envelope-shaped

this kink is flexional

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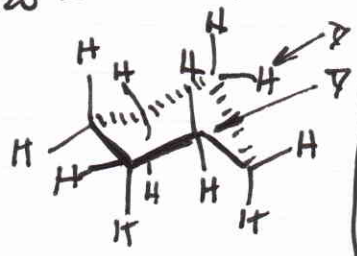
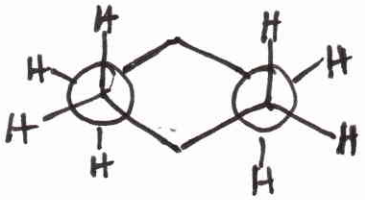
(5) Cyclohexane – has no ring strain

in a planar structure; but cyclohexane is not planar; by distorting from planarity, it can achieve 109.5° angles



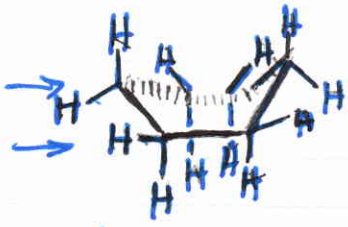
"chair" conformation
all carbons are ~~tetrahedral~~



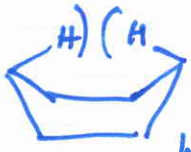
Chair conformation of cyclohexane

PRACTICE THIS WITH MODELS

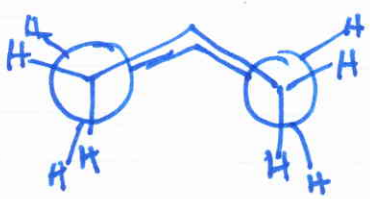
But there is another way to get to 109.5° angles:

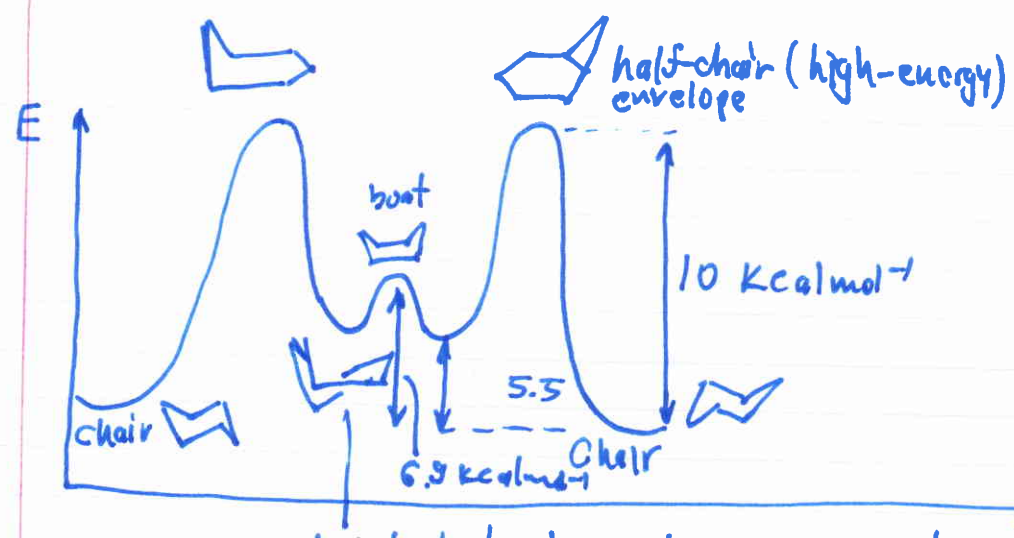


"boat" conformation, which looks good, until:

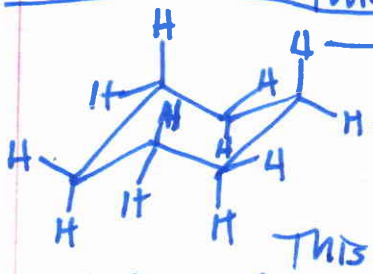


these "flagpole" hydrogens are pretty close to each other





twisted boat – relieves some torsional strain



4 — axial hydrogen (point straight up or down)

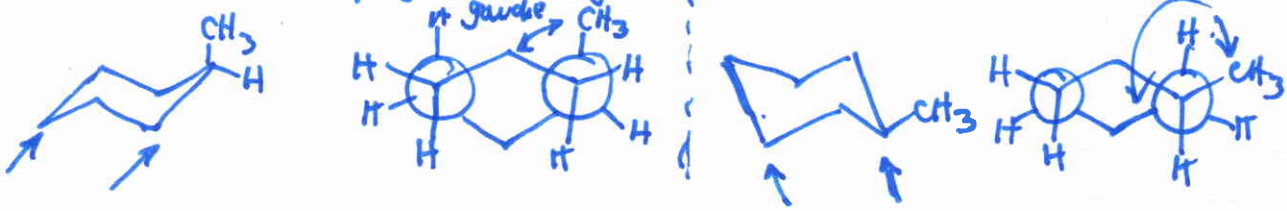
H — equatorial hydrogen (point up or down, but at an angle)

This becomes important as we start looking at substituted systems:

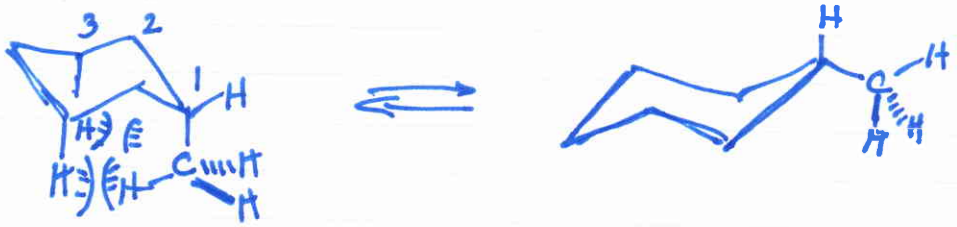
methyl is axial — methyl is equatorial

this process is known as ring-flip

Let's too Newman projections again:

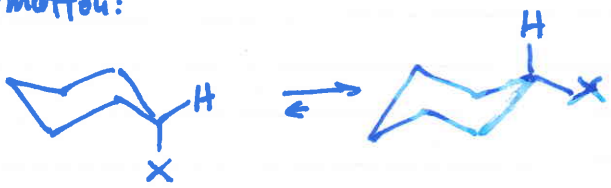


Equatorial methyl is more stable. And there is another reason:



1,3-diaxial strain

The larger the substituent, the more it will destabilize the axial conformation:



They all prefer to be equatorial, just not equally.

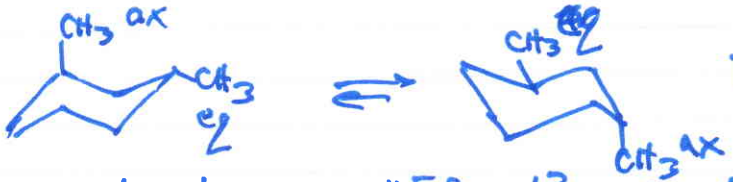
$-F$	0.2	kcal mol^{-1}
$-Cl$	0.5	" "
$-Br$	0.6	" "
$-OH$	1.0	" "
$-CN$	0.2	" "
$-CH_3$	1.8	" "
$-CH_2CH_3$	1.9	" "
$-CH(CH_3)_2$	2.1	" "
$-C(CH_3)_3$	5.4	" "

When we have two groups on cyclohexane, they would both prefer to be equatorial, if possible:

BETTER

This is cis-dimethyl cyclohexane

With trans, two conformations are the same:



THE SAME

If substituent are different? Well, if you can get them all equatorial—do that!

But if not, look at the table! The substituent with the higher number (larger size) will win and be equatorial:

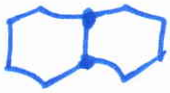
more stable

Isopropyl is equatorial!

t-Butyl group is so large that it is pretty much fixed in equatorial position:

What if we have two t-butyls?

Bicyclic Molecules - two or more rings together



fused - share a bond

bridged - share multiple atoms

spiro - share one atom (rare)

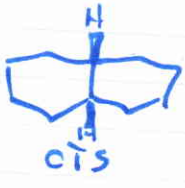
10 atoms total
2 rings
bicyclo[4.4.0]decane

How do we name these?
It's fun!

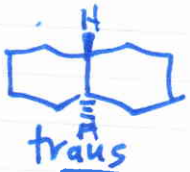
↓
Count the numbers of atoms in branches!

bicyclo[2.2.1]heptane

The only system you should worry about is decalin  !



or



Draw Newman projections! HOMEWORK: 3-34, 35, 37, 38, 42, 43