Strain: A rise in internal energy experienced by a molecule due to bond stretching, rotations, bending, or other "forced" changes in conformation.

Torsional strain: The strain due to eclipsing of bonds between neighboring atoms (resistance to twist/rotate).

Steric strain: the repulsive interaction that occurs when atoms are forced closer together than their atomic radii allow. It's the result of trying to force two atoms to occupy the same space.

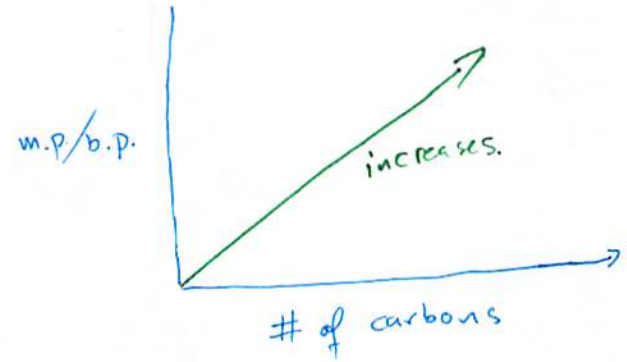
Angle strain: The repulsive interactions that occur when bond angles in a molecule deviate from the *ideal* bond angles.

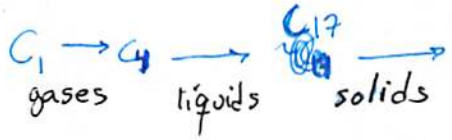
~~Cycloalkanes~~

Properties of Alkanes

Alkane		isomers
methane	CH_4	1
ethane	C_2H_6	1
propane	C_3H_8	1
butanes	C_4H_{10}	2
pentanes	C_5H_{12}	3
hexanes	C_6H_{14}	5
heptanes	C_7H_{16}	9
octanes	C_8H_{18}	18
nonanes	C_9H_{20}	35
decanes	$C_{10}H_{22}$	75
----		
eicosanes	$C_{20}H_{42}$	366,319

(C_nH_{2n+2})





- Within the same isomers, branching lowers mp/bp.
- Alkanes are water insoluble! (non-polar)

From Fossil fuels: natural gas
petroleum
coal

Petroleum is a mixture of hydrocarbons.

1. solvents
2. fuels
3. Raw materials for chemical synthesis.

-separated by fractional distillation in an oil refinery.

Combustion (your first reaction to know)

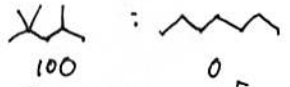
Very important

$$C_nH_{2n+2} + (xs)\,O_2 \xrightarrow[\text{(flame) heat}]{\Delta} n\,CO_2 + (n+1)\,H_2O + \text{Heat!}$$

Ex: n-octane $\Delta H_{rxn} = 1307.5$ kcal/mol

2,2,4-trimethylpentane (isooctane) $\Delta H_{rxn} = 1304.3$ kcal/mol

Octane rating in gasoline:
-pre-ignition rating in an engine



(not the amount of iso-octane in the gasoline)

100 ↑ no pre-ignition

0 ↖ lots of pre-ignition

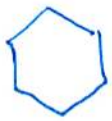
- Alkanes are not always linear or branched.

Cycloalkanes/Alicyclics: Aliphatic cmpds containing rings (ex. cycloalkanes, cycloalkyl halides, cycloalkyl alcohols, cyclic ethers, cycloalkenes, etc.)

cyclopropane C_3H_6

cyclobutane C_4H_8

cyclopentane C_5H_{10}



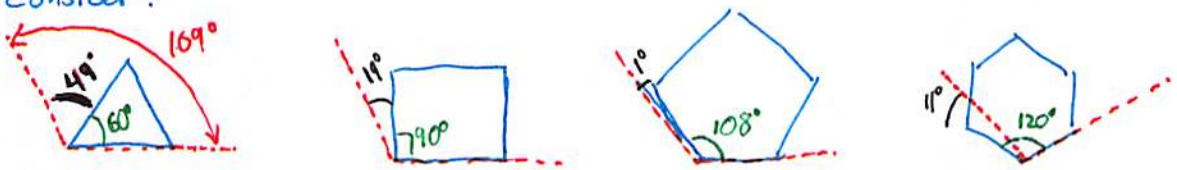
cyclohexane C_6H_{12} ← C_nH_{2n}

2 H's less than linear/branched alkanes = 1 degree of unsaturation.

Structural & bonding considerations.

sp^3 hybridized carbons are "happy" when all bonds (orbitals) are tetrahedral w/ 109° angles.

consider:



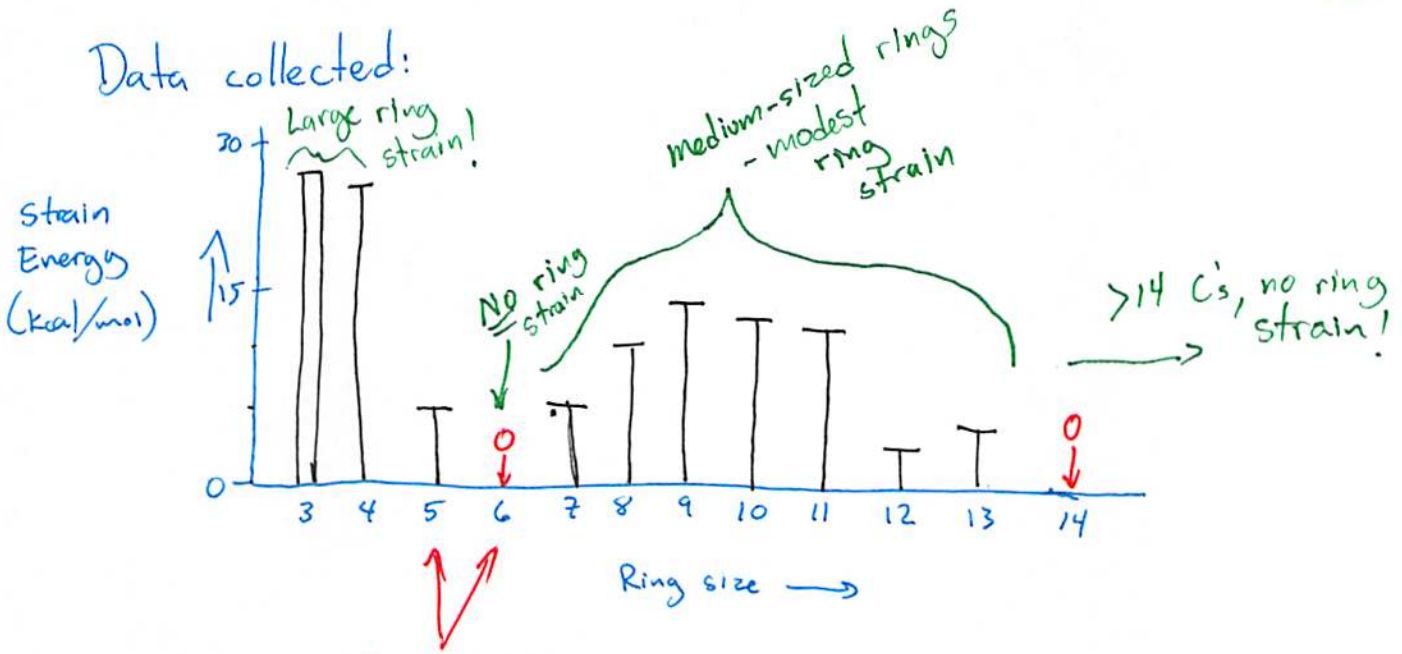
in 1885, von Baeyer proposed that small and large ring cmpds are unstable due to ring strain

if this statement is true, cyclopentane should be the most stable!
(the bond angle of 108° is closer to the tetrahedral value of 109°.

To test the hypothesis, measure the heat of combustion, using strain-free acyclic alkanes.

for the formula: $(CH_2)_n + \frac{3}{2} O_2 \xrightarrow{\Delta} n CO_2 + n H_2O +$ Heat

Data collected:

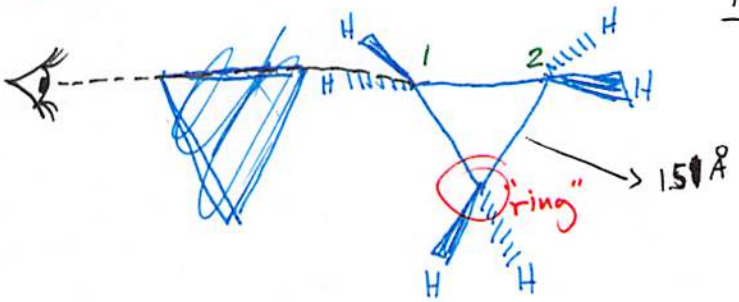


Major discrepancy in von Baeyer's hypothesis. WHY?

He assumed that all cycloalkanes were flat!

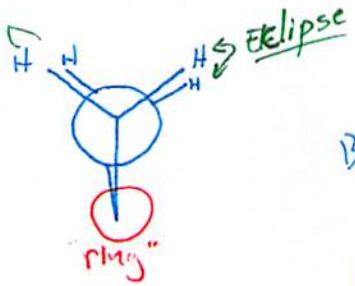
What do they look like in 3D?

1- Cyclopropane



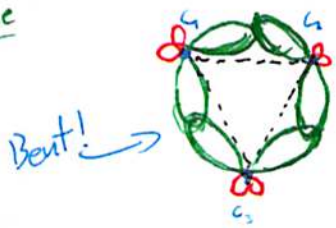
ONLY FLAT cycloalkane!
(only case wher Baeyer was right)

Newman Projection



All are eclipse interactions.

Orbitals



Orbital alignment is poor. Less overlap, means weaker bonds.

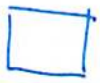
C-C bond in propane = 88 kcal/mol

C-C bond in cyclopropane = 61 kcal/mol

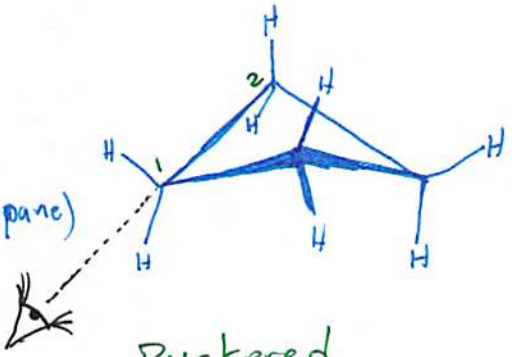
- weaker
- easier to break

Cyclobutane

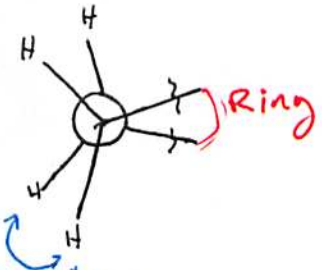
- Not flat
- Has enough carbons to allow twisting.



Less angle strain (than cyclopropane) but has more H atoms eclipsing each other



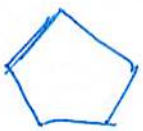
Puckered shape.



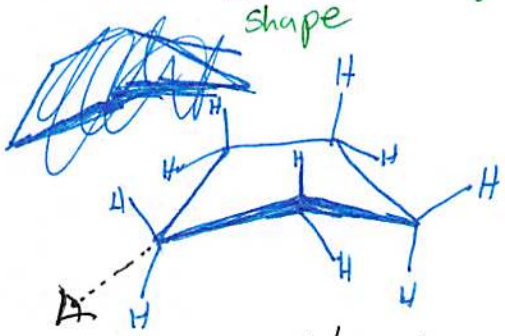
not quite a full eclipse or gauche.
- still contributes to torsional strain

Cyclopentane

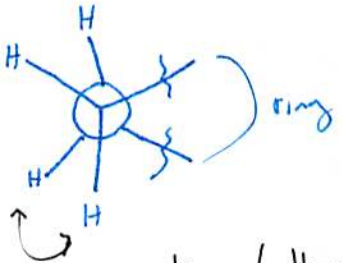
Baeyer thought that shouldn't have any strain, but it does! (way less than C3 & C4 though)



Puckered, envelope shape



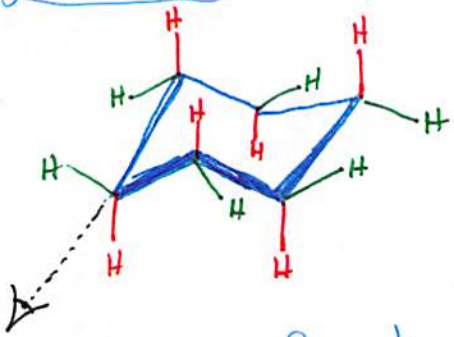
- Allows for less torsional strain, but a bit more ∡ strain



Less eclipsed than □, but not completely staggered.

Cyclohexane

⇒ A perfectly staggered conformation

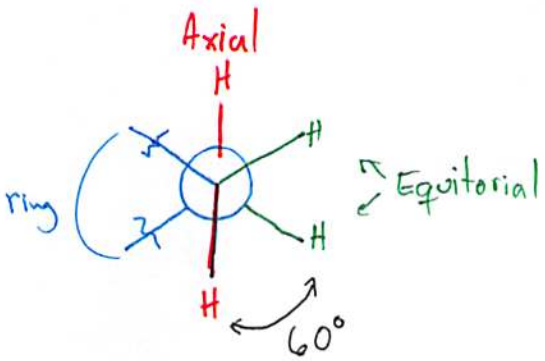


Chair conformation

Two sets of H's

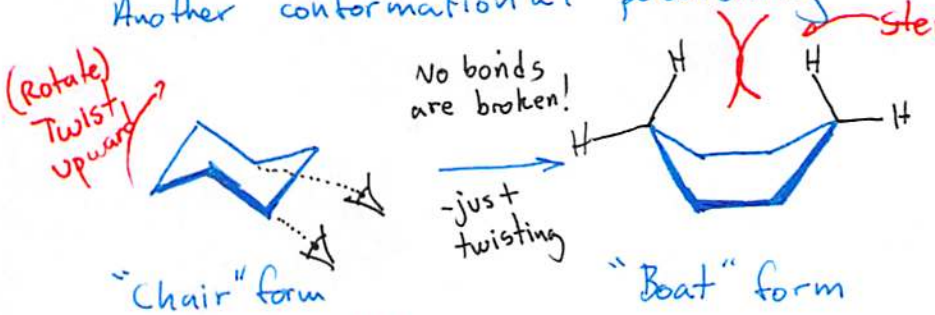
Axial

Equitorial



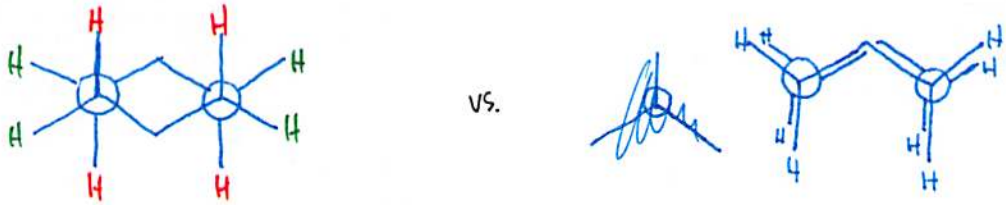
Perfectly staggered
- No strain!

Another conformational possibility:



"Chair" form — more stable

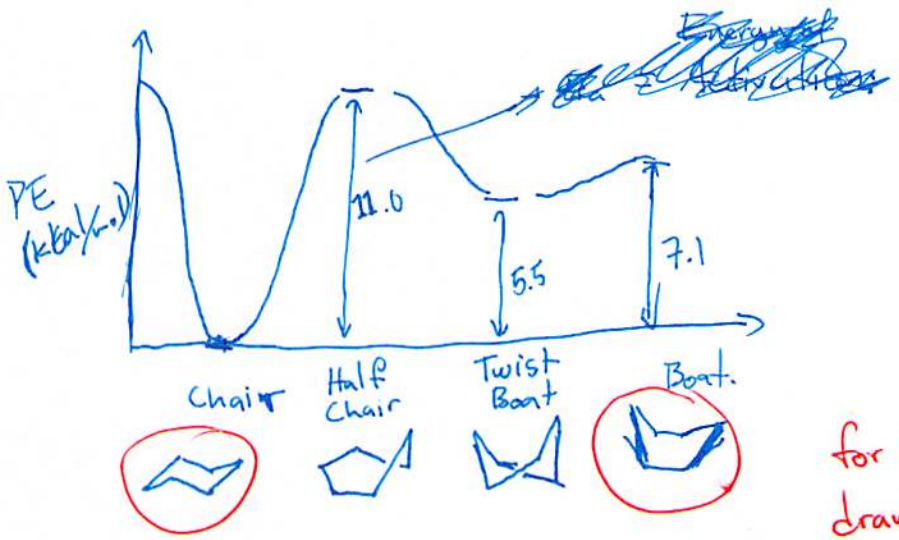
"Boat" form — Higher in energy by 7.1 kcal/mol



Eclipsed structures: No Bueno!

-Angle and torsional strain

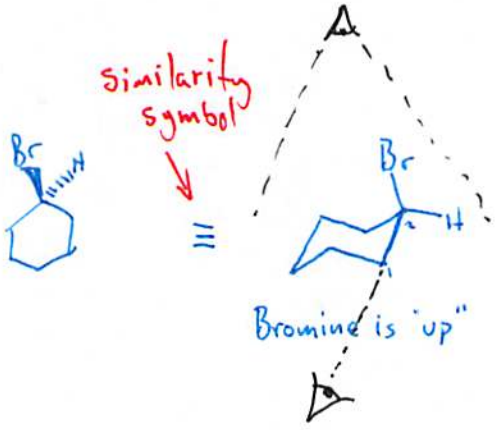
Twisting cyclohexane: Potential Energy Plot.

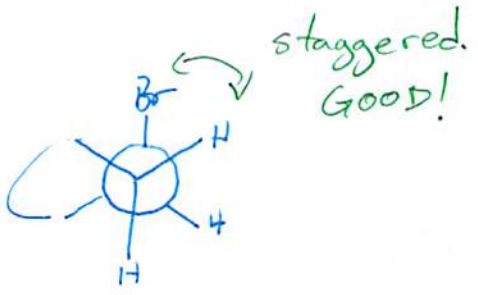


for simplicity, learn to draw cyclohexane like these two: chai & boat

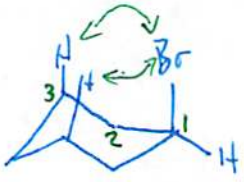
(but don't forget that twist-boat is lower in Energy than boat)

Introducing groups to cyclohexane: Bromocyclohexane.



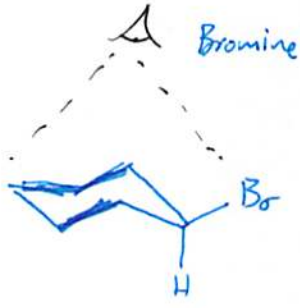


However: New interaction



Ring flip

(No bonds broken!)



1,3-Diaxial interaction!
- Energy penalty due to strain.

for Br. each is 0.25 kcal/mol

∴ 2(0.25) = 0.5 kcal/mol

- see Table in the Book! (p. 125, 8th Ed.)

- Staggered
- No 1,3-diaxial interaction

} lower in Energy!

The difference in 0.5 kcal/mol corresponds to a 2.3:1 ratio of equitorial Br : axial Br.

70% favored! 30%

How about multisubstituted hexane?