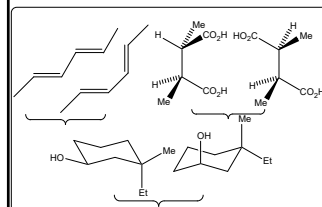


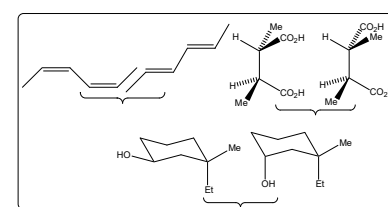
Conformational Analysis

Conformational analysis

- The different arrangements of the atoms in space that result from rotations of groups about single bonds are called **conformations** of the molecule.
- An analysis of the energy changes that a molecule undergoes as groups rotate about single bonds is called **conformational analysis**.



Different conformations



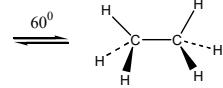
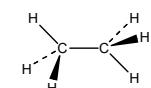
Different configurations

Conformations of ethane

Staggered conformation

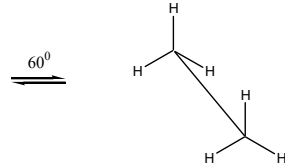
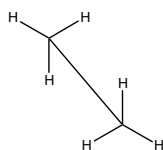
Eclipsed conformation

Wedge-and-dash structures



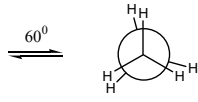
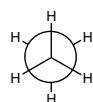
60°

Sawhorse projections



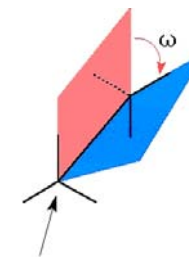
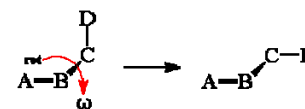
60°

Newman projections



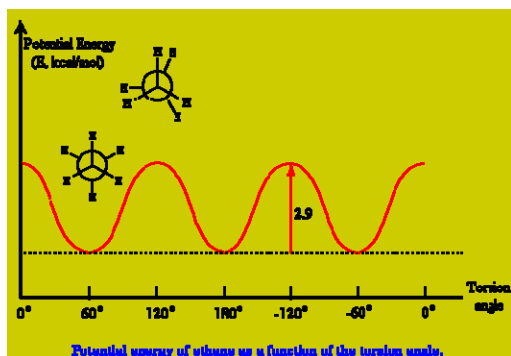
60°

Torsion or Dihedral angle



The single parameter to differentiate conformers is an angle between two planes that contain atoms ABC and BCD in themselves. This dihedral angle ω is called a "torsion" angle and is most frequently used for specification of the type of conformations.

Potential energy of ethane as function of torsion angles



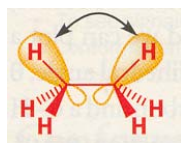
- staggered conformation has potential energy minimum
- eclipsed conformation has potential energy maximum
- staggered conformation is lower in energy than the eclipsed by 2.9 kcal/mole (12 kJ/mole)

Why is the eclipsed conformation higher in energy than the staggered conformation?

- The H-atoms are too small to get in each other's way-steric factors make up < 10% of the rotational barrier in ethane

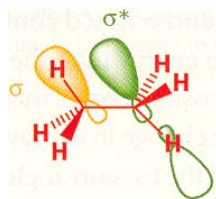
Torsional strain

Caused by repulsion of the bonding electrons of one substituent with the bonding electrons of a nearby substituent



filled orbitals repel

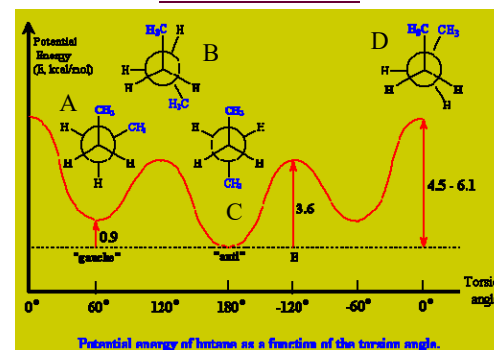
- Stabilizing interaction between filled C-H σ bond and empty C-H σ^* antibonding orbital



The real picture is probably a mixture of all 3 effects

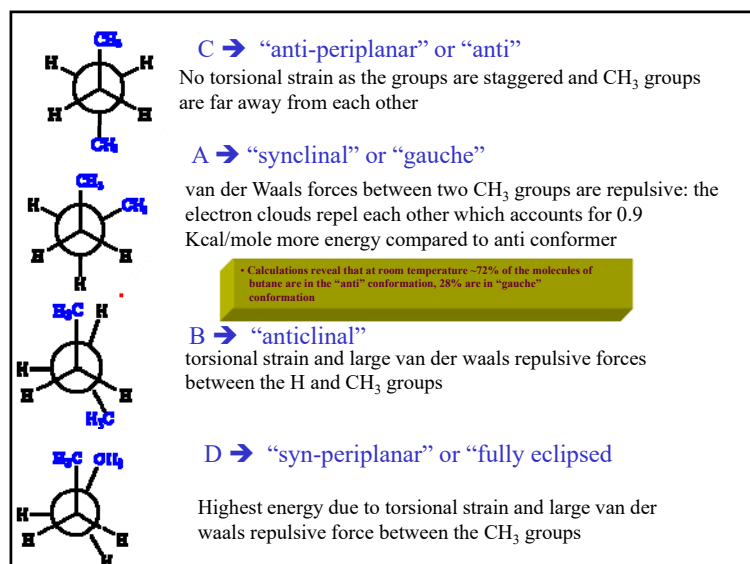
- The rotational barrier is (12 kJ/mol) small enough to allow the conformational isomers to interconvert million of times per second

Conformations of butane



Potential energy of butane as a function of torsion angle

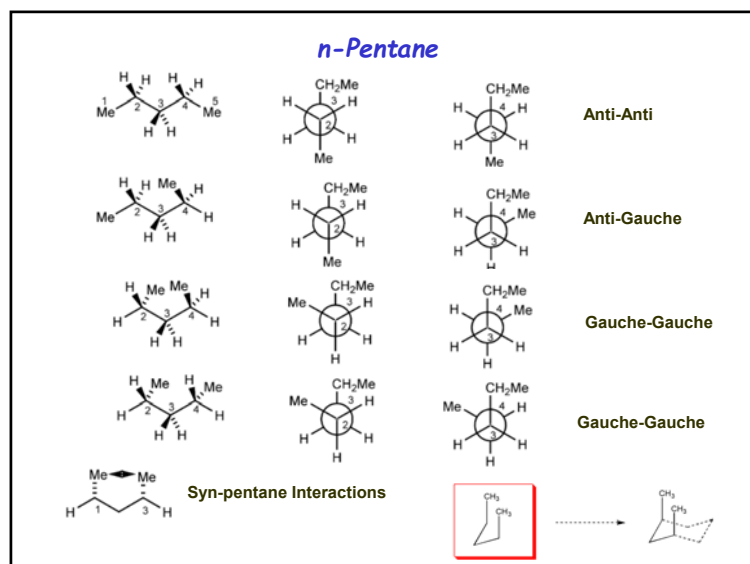
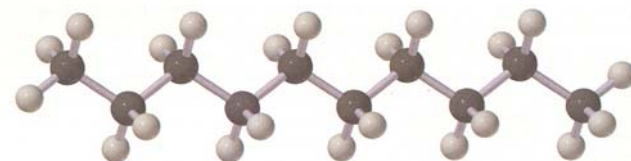
- A → "synclinal" or "gauche"
- B → "anticlinal"
- C → "anti-periplanar" or "anti"
- D → "syn-periplanar" or "fully eclipsed"



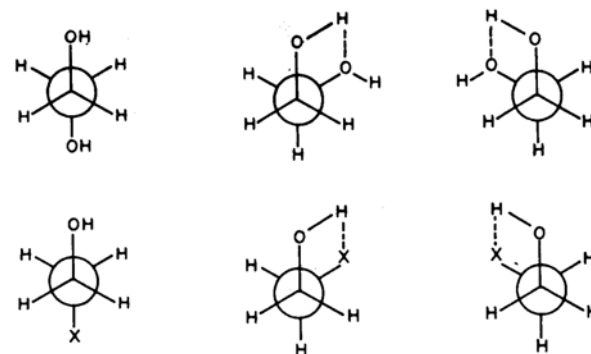
Conformations and Conformers

Butane can exist in an infinite number of **conformations** (6 most important have been considered), but has only 3 **conformers** (potential energy minima)-the two “gauche” conformations and the “anti” conformations

- The preference for a staggered conformation causes carbon chains to orient themselves in a **zig zag** fashion, see structure of decane

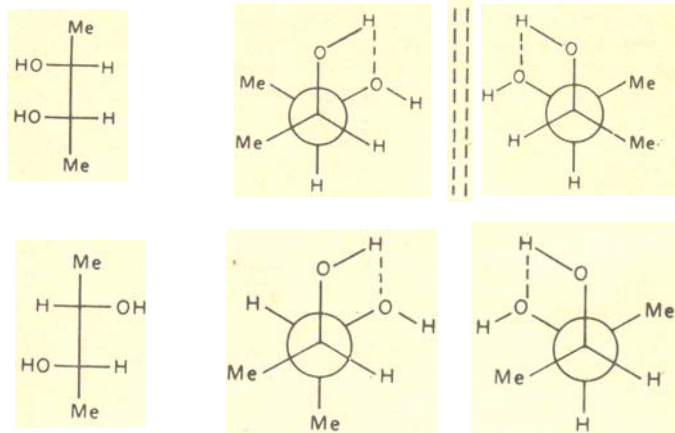


Conformation and hydrogen bonding



X = OH, NH₂, F, Cl, Br, OCH₃, NHCH₃, N(CH₃)₂ etc.

Conformation of butane-2,3-diols



Cycloalkanes



Is the energy per CH_2 is same in this series?

Is the energy per CH_2 is same in the straight chain alkanes?



Does the value of n has an effect on combustion energy per CH_2 ?

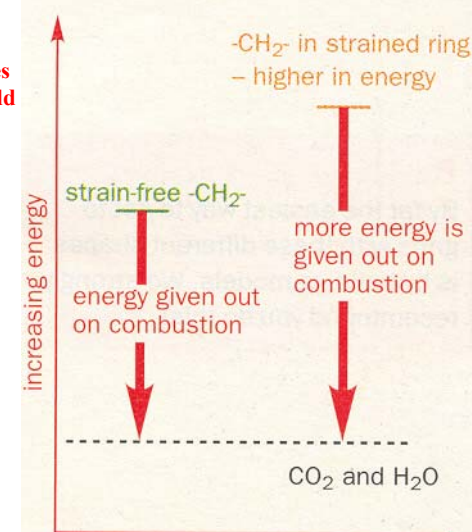
Heats of combustion for straight chain alkanes of formula
 $\text{CH}_3(\text{CH}_2)_n\text{CH}_3$

Straight chain alkanes	n	$-\Delta H_{\text{combustion}}$ kJ mol^{-1}	Difference kJ mol^{-1}
ethane	0	1560	-----
propane	1	2220	660
butane	2	2877	657
pentane	3	3536	659
hexane	4	4194	658
heptane	5	4853	659
octane	6	5511	658
nonane	7	6171	660
decane	8	6829	658
undecane	9	7487	658
dodecane	10	8148	661

• the difference between any two in series very nearly constant at around -660 kJ/mole (energy per CH_2)

Therefore in cycloalkanes heat of combustion should be $n \times 658.7 \text{ kJ/mole}$.

If there is some strain, more energy should given out on combustion



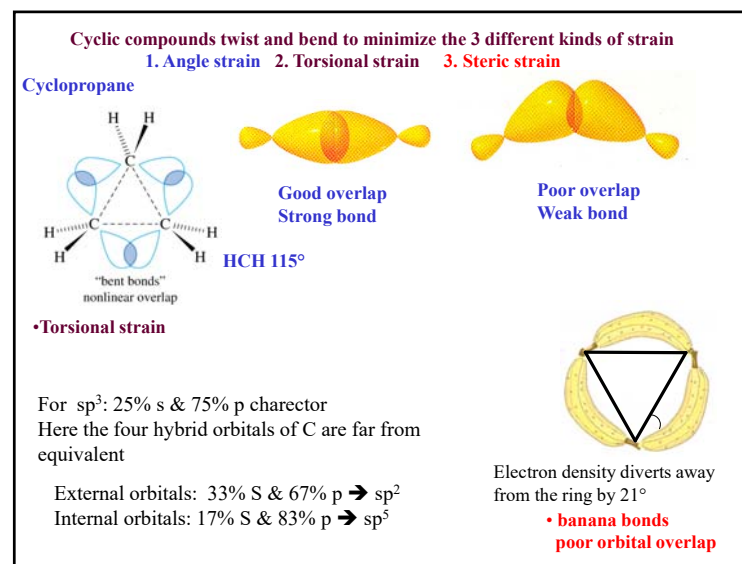
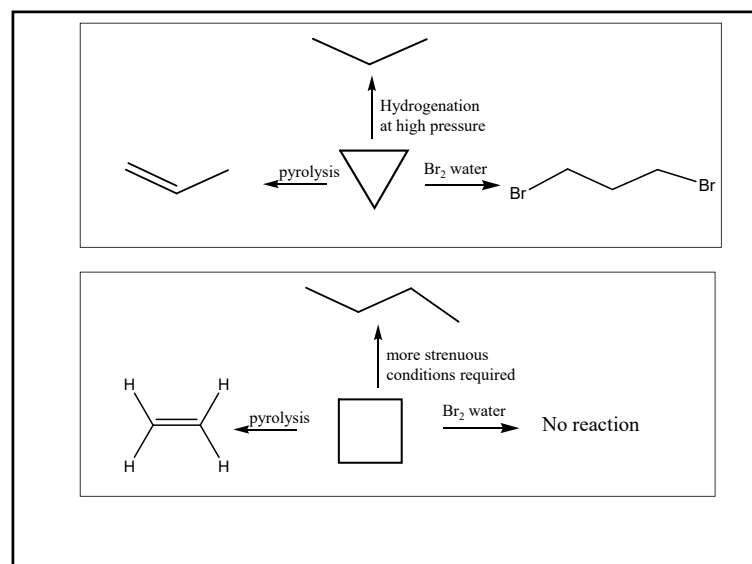
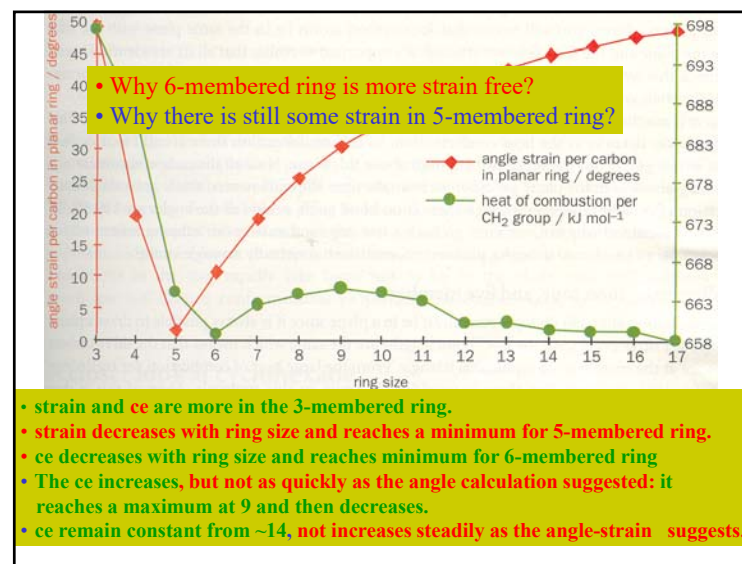
Cycloalkanes:

Ring strain

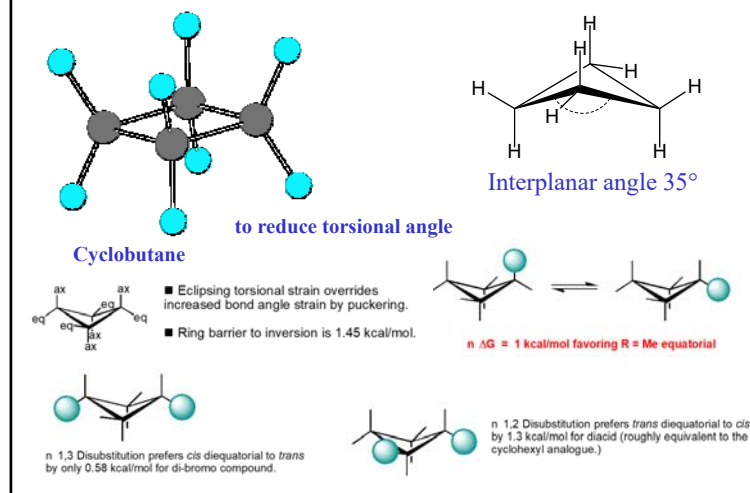
Ring	CH ₂ per CH ₂	Heat of combustion per CH ₂ group / kJ mol ⁻¹	Ideal angles	Deviation* from 109.5°
Cyclopropane	697	686	60°	49.5°
Cyclobutane	686	664	90°	19.5°
Cyclopentane	664	659	108°	1.5°
Cyclohexane	659	662.4	120°	-10.5°
Cycloheptane	662.4	663.8	128.5°	-19°
Cyclooctane	663.8	663.8	135°	-25.5°

* a measure of strain per C-atom

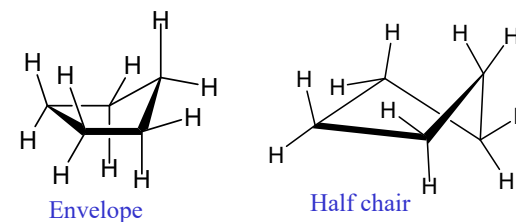
All internal angles 109.5°



Cyclobutane



Cyclopentane

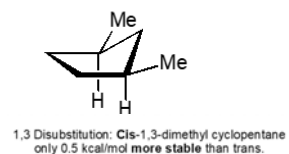
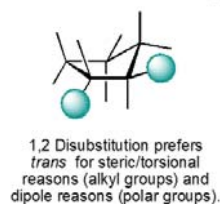
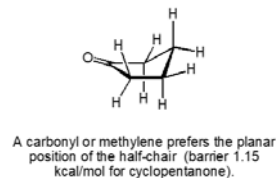
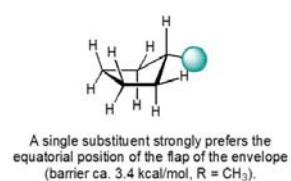


The energy difference is little

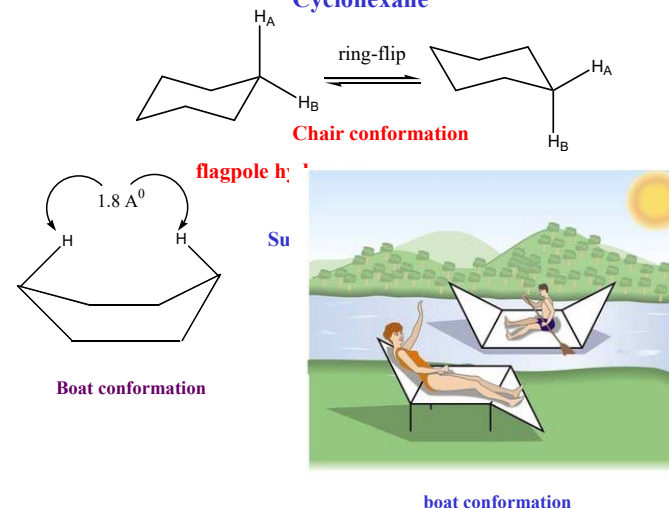
- one carbon atom is bent upwards
- The molecule is flexible and shifts conformation constantly
- Hence each of the carbons assume the pivotal position in rapid succession .
- The additional bond angle strain in this structure is more than compensated by the reduction in eclipsed hydrogens.
- With little torsional strain and angle strain, cyclopentane is as stable as cyclohexane.

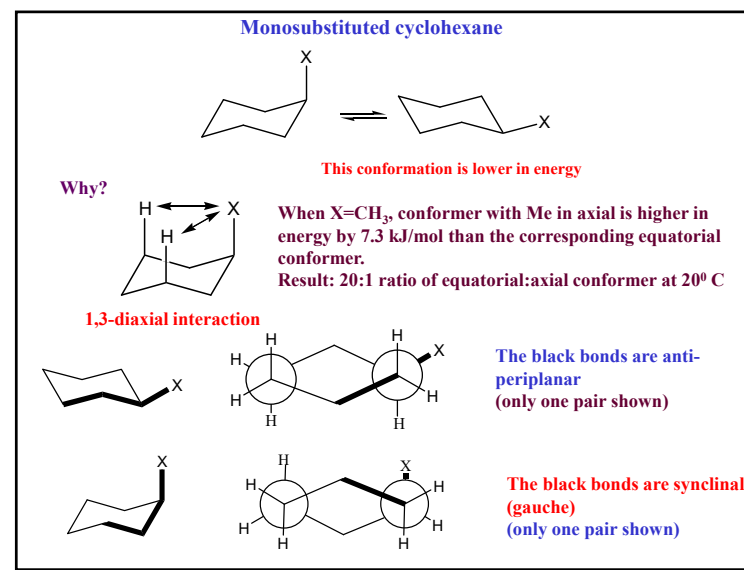
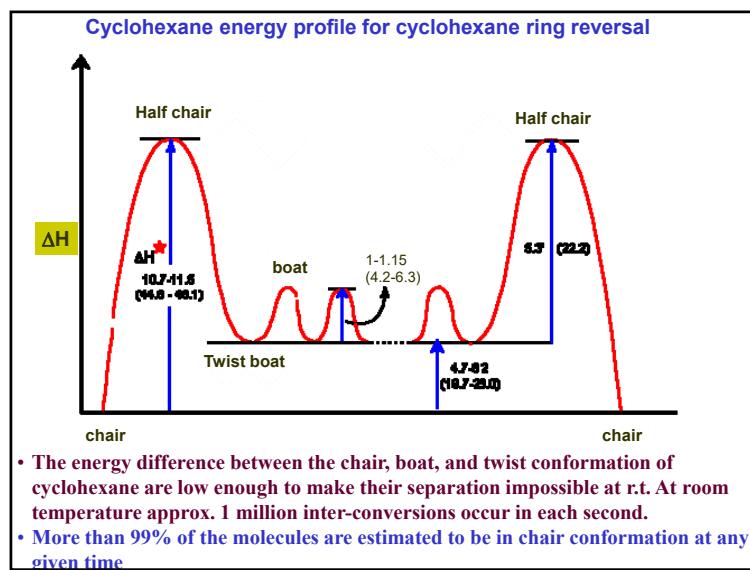
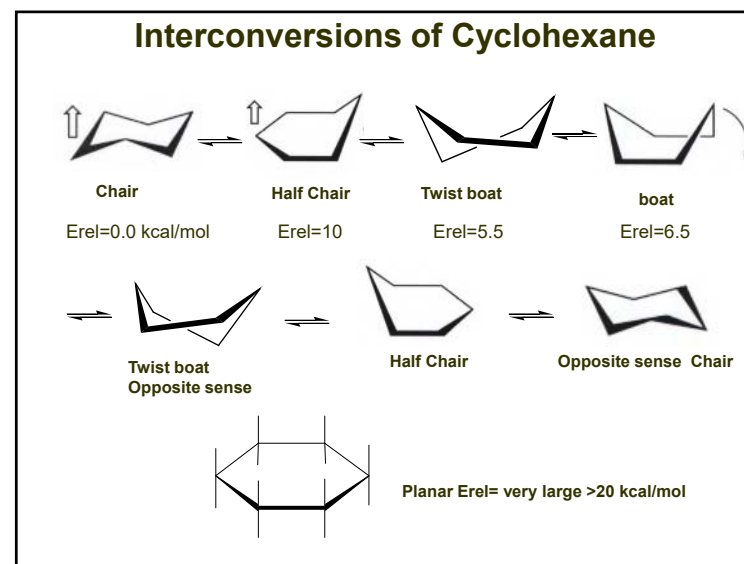
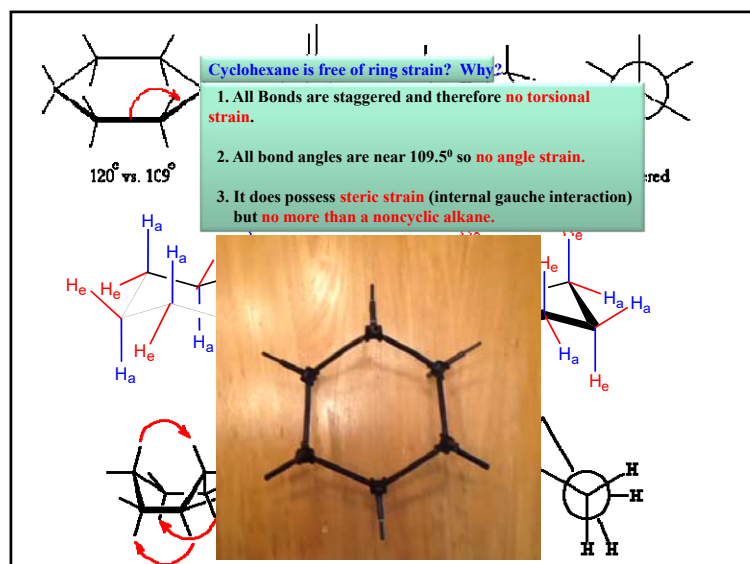
Cyclopentane

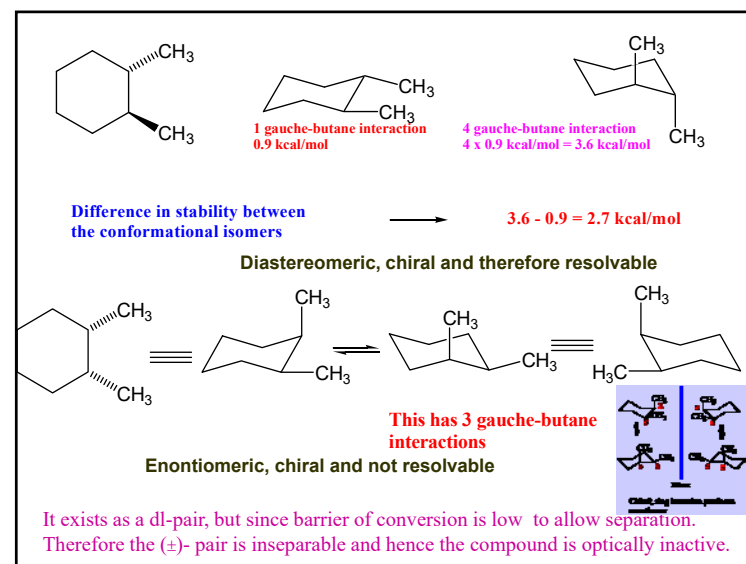
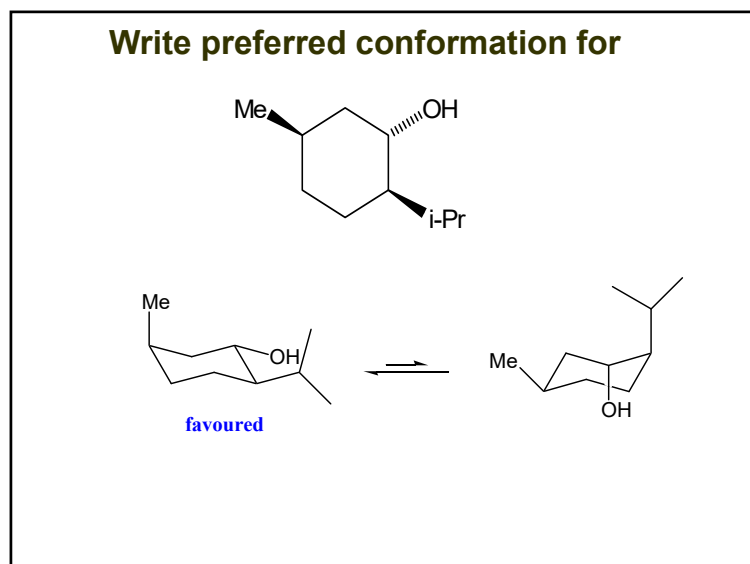
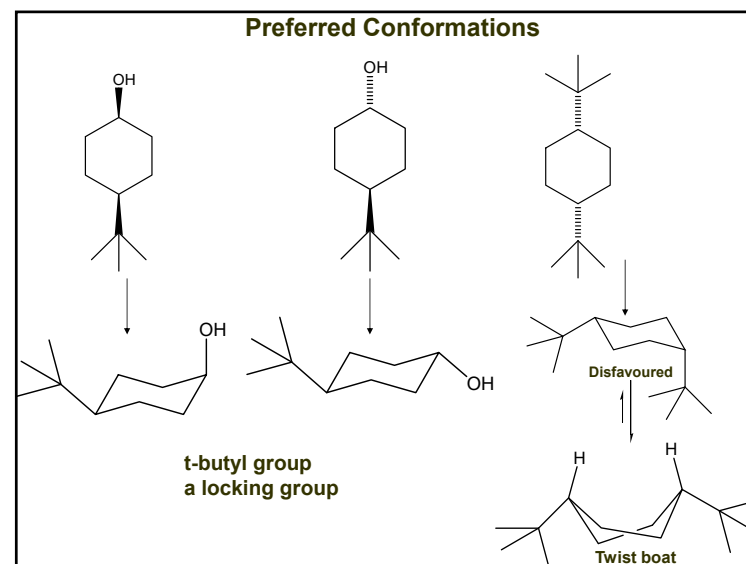
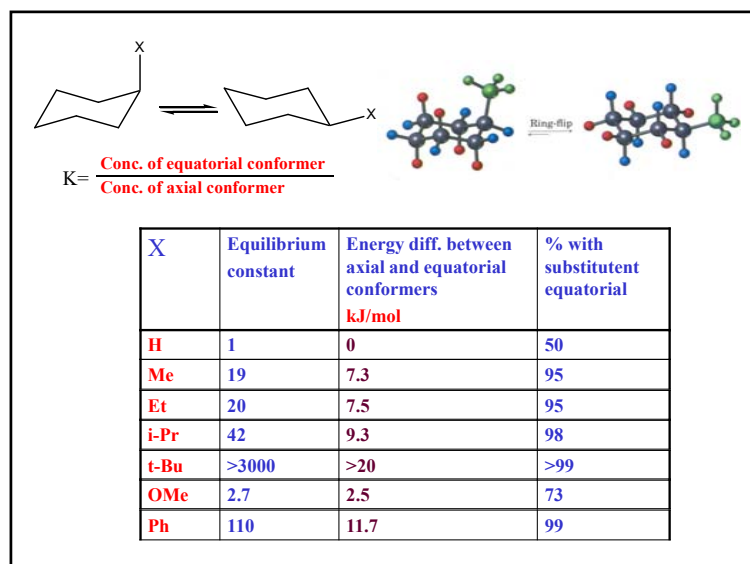
Since there is no "natural" conformation of cyclopentane, the ring conforms to minimize interactions of any substituents present.

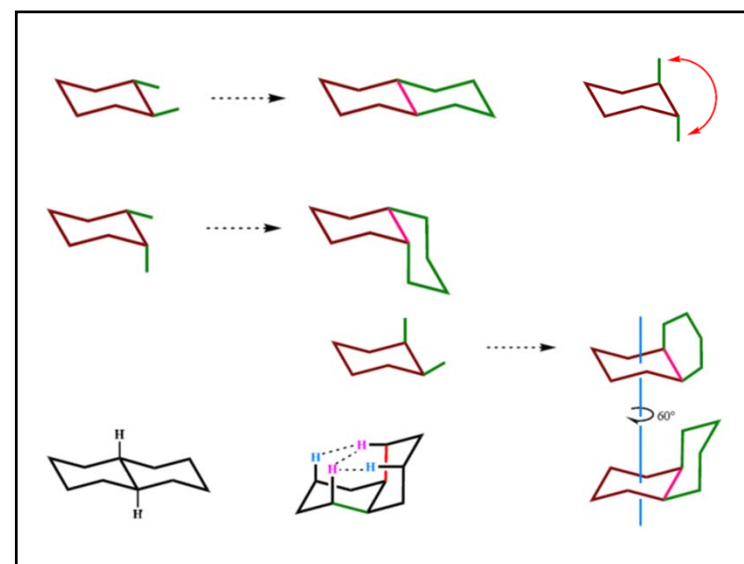
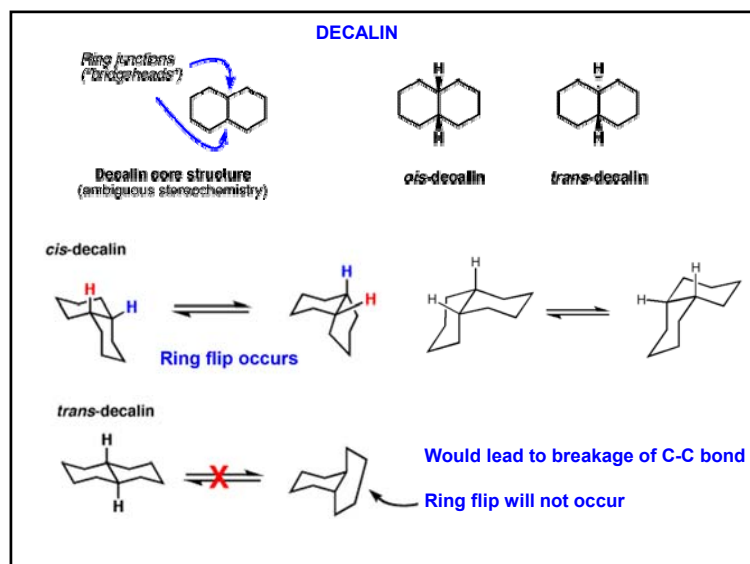
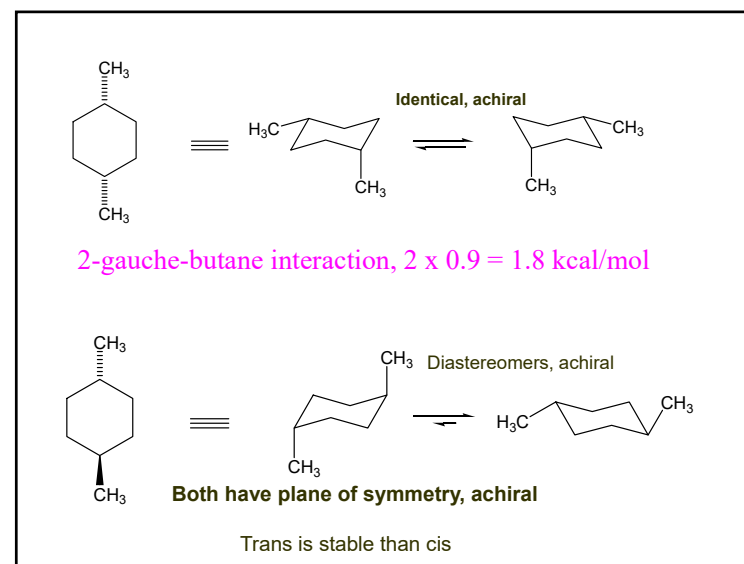
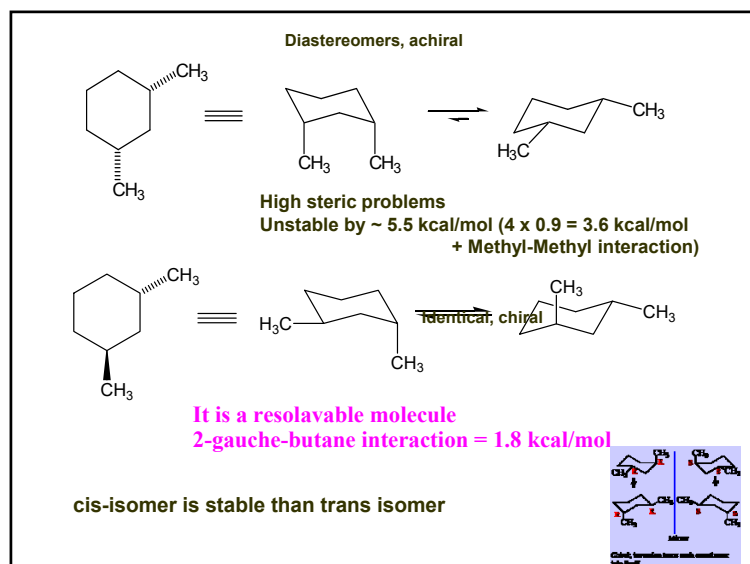


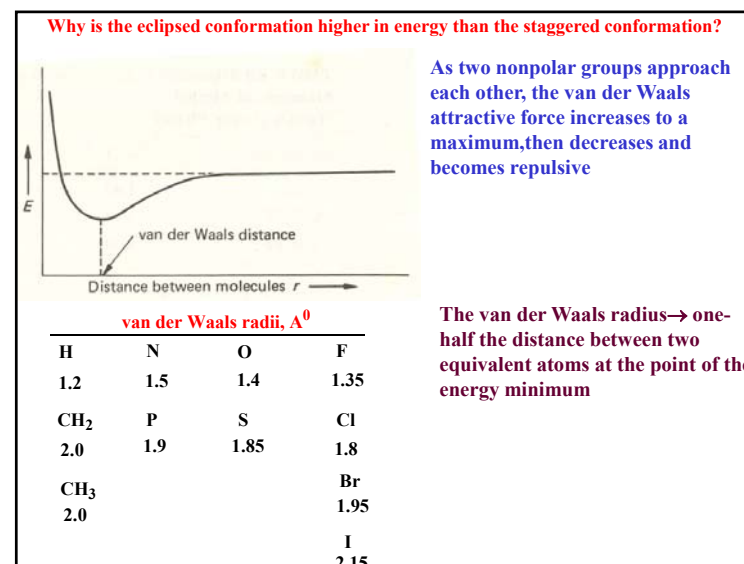
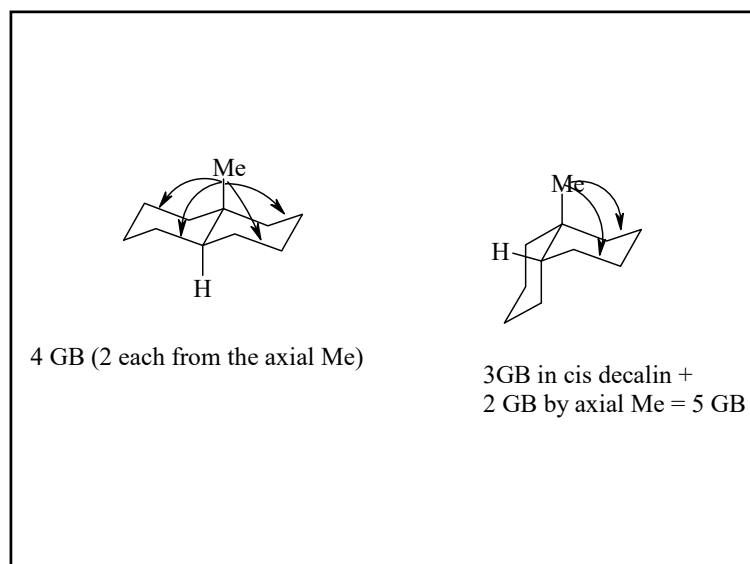
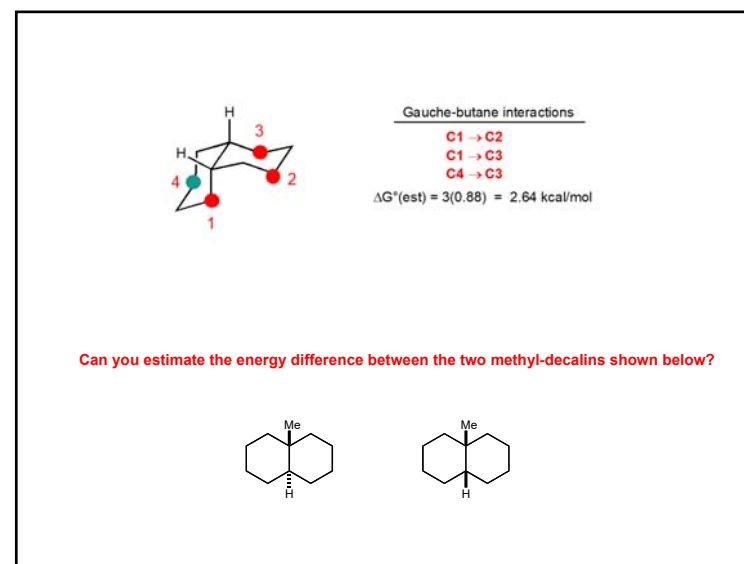
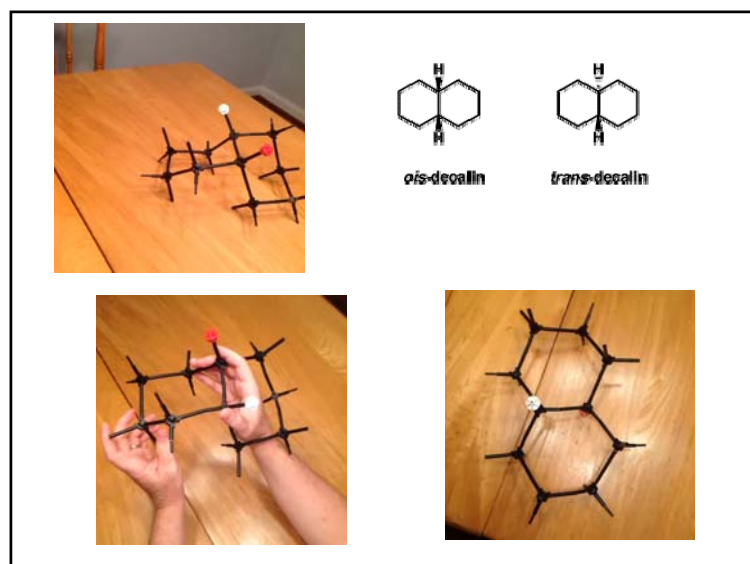
Cyclohexane



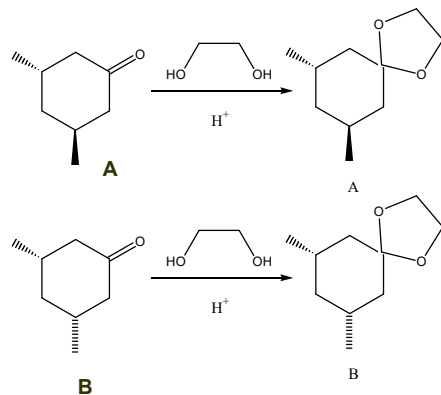




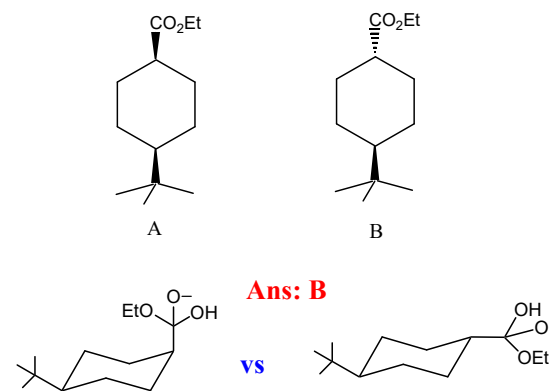




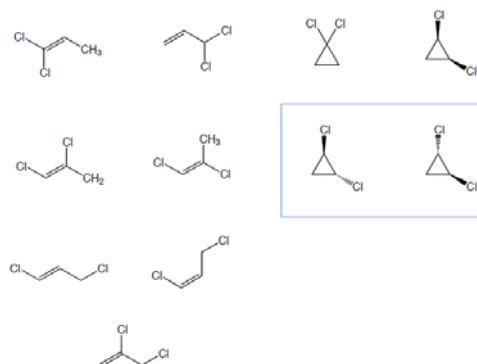
It is more difficult to form an acetal of compound A than of B.
Why?



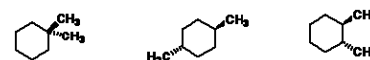
Which compound should saponify faster (A or B)?



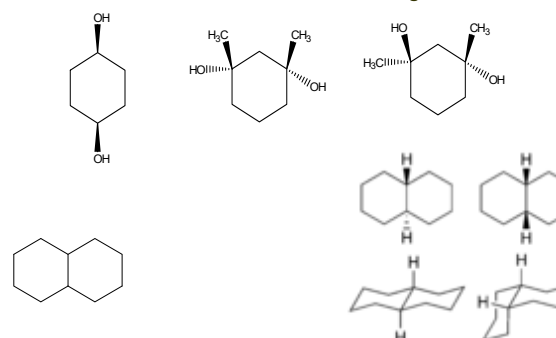
The Isomers of $\text{C}_3\text{H}_4\text{Cl}_2$



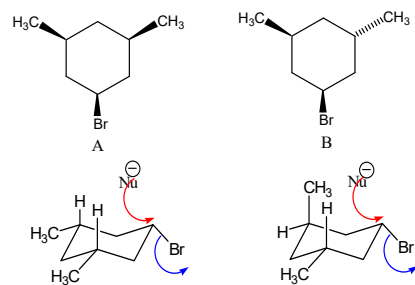
Order the following molecules in the order of their stability



Draw the stable conformers of following molecules

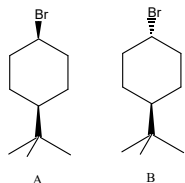


Q. Compound A reacts faster by the S_N2 mechanism than the compound B

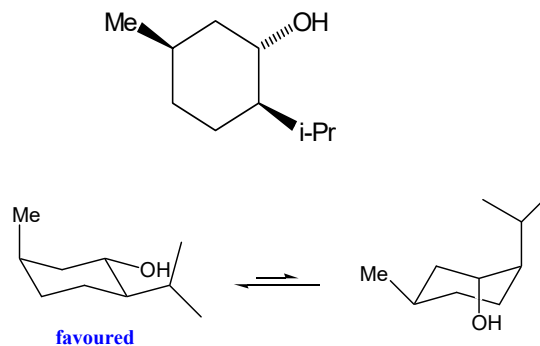


less hindered approach

Q. Compound A reacts faster by the S_N1 mechanism than compound B



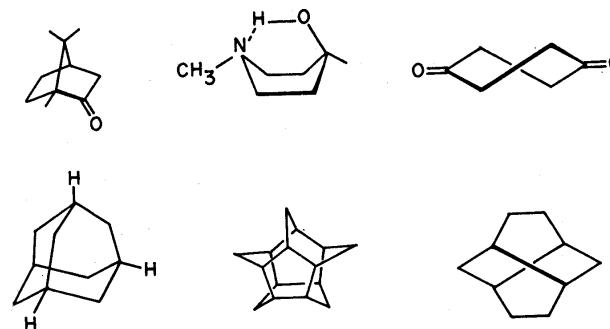
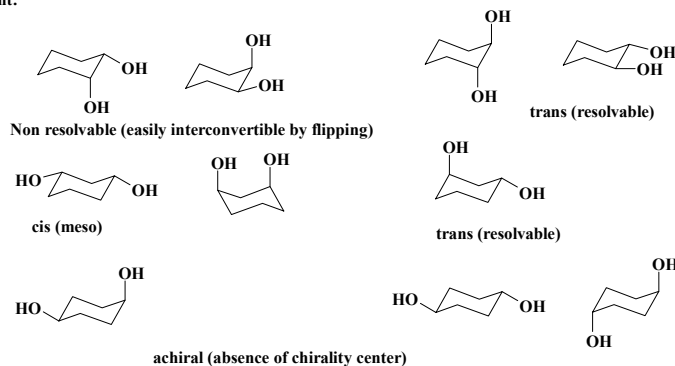
Write preferred conformation for



Problem: Which of the following compounds are resolvable, and which are non resolvable? Which are truly meso?

- a) cis-1,2-cyclohexane diol; b) trans-1,2-cyclohexane diol;
c) cis-1,3-cyclohexane diol; d) trans-1,3-cyclohexane diol;
e) cis-1,4-cyclohexane diol; f) trans-1,4-cyclohexane diol.

Hint:



Rigid molecules from cyclohexane conformers

