

CHEMISTRY 2500

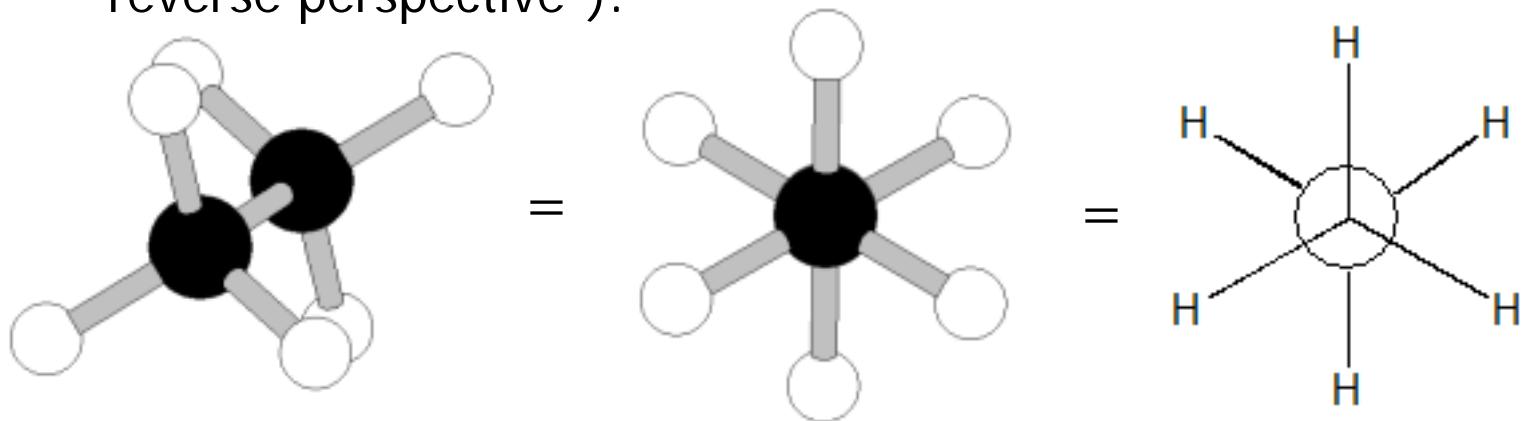
Topic #3: Conformations of Organic Molecules

Spring 2020

Dr. Susan Findlay

Newmann Projections

- One way to clearly show the arrangement of atoms around two adjacent tetrahedral atoms is to use a **Newmann projection**. In a Newmann projection, we are looking “along a bond” from one atom to another. The atom in front is represented by a dot and the atom behind represented by a large circle (in a kind of “reverse perspective”):

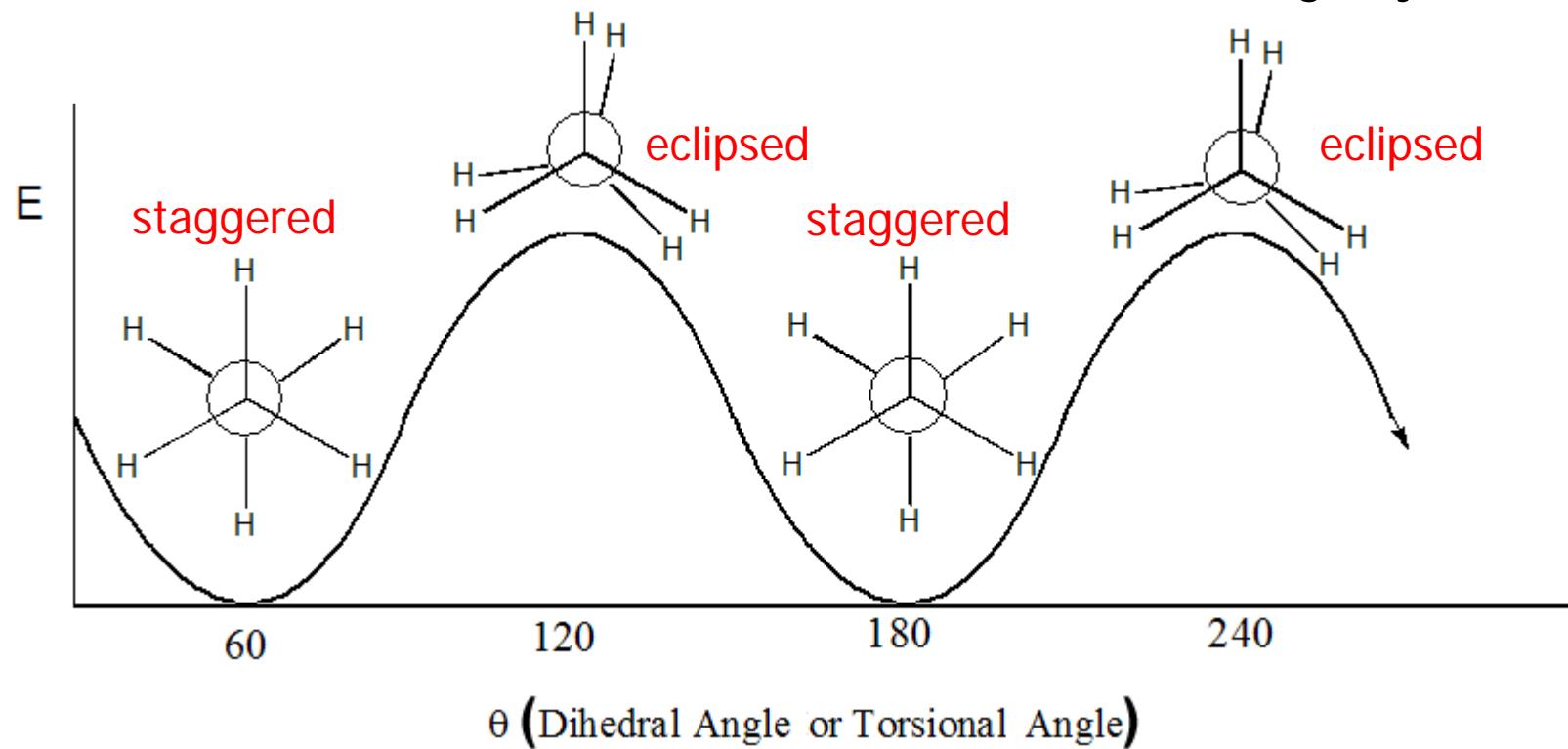


Newmann projection

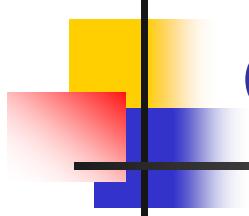
- Note that no dashed lines or wedges are used. It is understood that the atoms attached to the rear carbon (circle) are pointing away from us and those attached to the front carbon (dot) are pointing toward us.

Conformations of Ethane

- The two carbon atoms of ethane are connected by a single bond which is readily rotated, giving rise to different **conformers** (different spatial arrangements of atoms for the same molecule; conformers can be interconverted without breaking any bonds):



- Which conformer of ethane is favoured, staggered or eclipsed? Why?



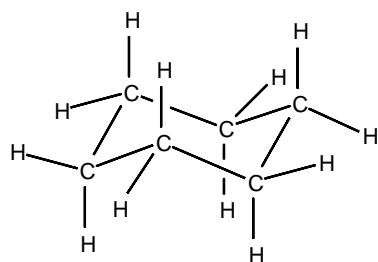
Conformations of Butane

- Imagine looking down the bond between the two central atoms of butane (the C2-C3 bond). Use Newmann projections to draw the four conformers:

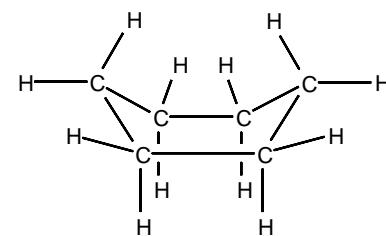
You will calculate the energies of these four conformers in lab. For now, rank them from lowest energy (most stable) to highest energy (least stable).

Conformations of Cyclohexane

- In general, it is preferable for groups to be spaced out as much as possible. Build a model of cyclohexane and compare the **chair** and **boat** conformations shown below. Note that you can do a “ring flip” to convert the molecule from one to the other and back again without breaking any bonds.



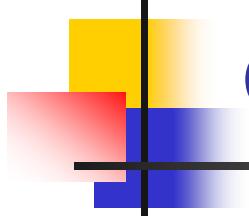
chair



boat

- Each carbon atom in the chair conformation has one axial group (directly above or below the ring) and one equatorial group (pointing out from the ring).

*Marks will be deducted for improperly drawn chairs. For guidance, see Ogilvie pp. 103-106.
Bonds to axial groups are vertical!*

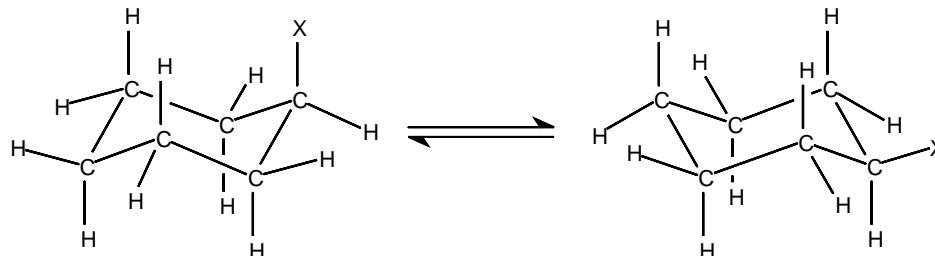


Conformations of Cyclohexane

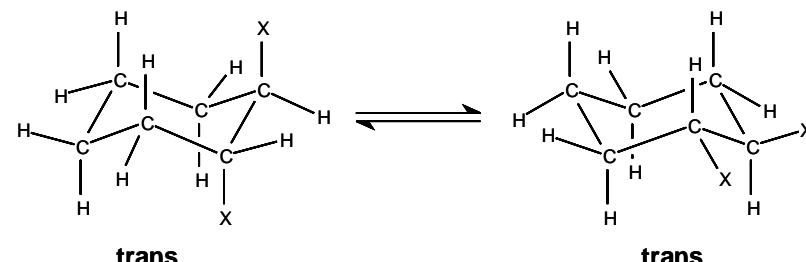
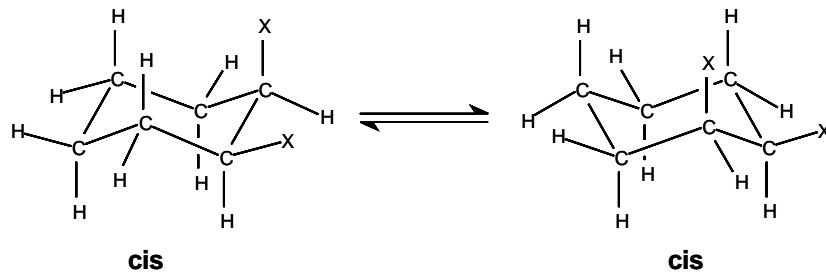
- The chair conformation of cyclohexane is more stable than the boat conformation. If we draw Newmann projections for opposite bonds (C1-C2 and C4-C5) of cyclohexane in each conformation, we can see why:
- There are many more eclipsed bonds in the boat than in the chair. The boat conformation also has what are known as **flagpole interactions** making it less stable:

Conformations of Substituted Cyclohexanes

- If we add a substituent to the cyclohexane, we can imagine putting it in either an axial or equatorial site. Note that it is possible to use a ring flip to move the group from axial to equatorial (and back again) without breaking any bonds.

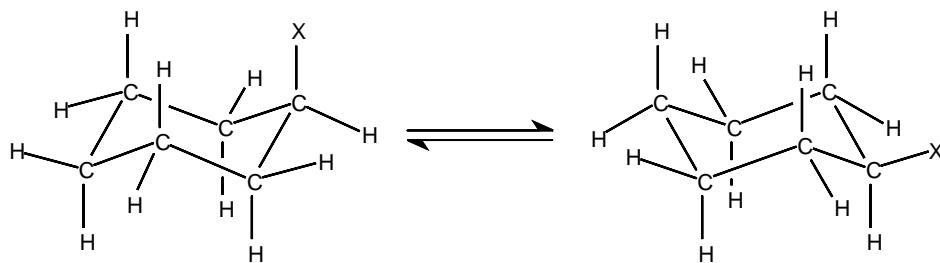


- Ring flips do not change relative positions of groups:



Conformations of Substituted Cyclohexanes

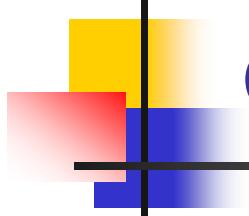
- The equatorial sites are less sterically hindered (more “open”) than the axial sites so it is preferable to put the larger groups in equatorial sites, leaving the axial sites for smaller groups (like H). This effect becomes more dramatic as X gets larger:



$$\Delta_r G^\circ = -RT \ln K$$

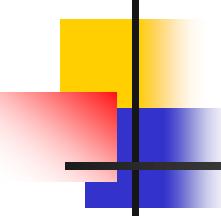
$$K = \frac{[\text{equatorial } X]}{[\text{axial } X]}$$

X	K	$\Delta_r G^\circ$ (kJ/mol)
H	1	0
CH ₃	19	-7.3
CH ₂ CH ₃	21	-7.5
C(CH ₃) ₃	3300	-20
F	1.7	-1.3
Cl	3	-2.7
Br	3	-2.7
I	2.3	-2.1



Conformations of Substituted Cyclohexanes

- For each of the following pairs of groups, rationalize why the second one listed favours the equatorial site more:
 - $-\text{CH}_3$ vs $-\text{C}(\text{CH}_3)_3$
 - $-\text{Cl}$ vs. $-\text{CH}_3$
 - $-\text{F}$ vs. $-\text{Cl}$
 - $-\text{I}$ vs. $-\text{Cl}$

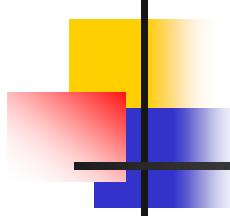


Conformations of Substituted Cyclohexanes

- When a substituted cyclohexane has multiple substituents, its best conformer will have the largest group equatorial. If there are multiple largest groups, try to put as many in equatorial sites as possible. It is particularly important to avoid 1,3-diaxial interactions.
- Find the most stable conformer for each of the following and identify each substituent as being axial or equatorial:
 - cis*-1,2-dimethylcyclohexane
 - trans*-1,2-dimethylcyclohexane

cis means the two groups are on the same side of the ring (CHEM 1000/2000)

trans means the two groups are on opposite sides of the ring (CHEM 1000/2000)



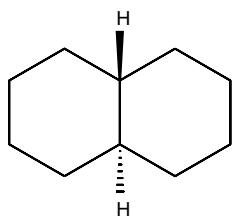
Conformations of Substituted Cyclohexanes

- *cis*-1,3-dimethylcyclohexane
- *trans*-1,3-dimethylcyclohexane

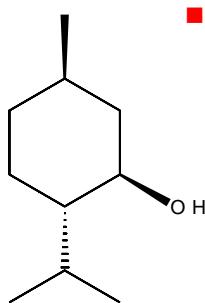
Conformations of Substituted Cyclohexanes

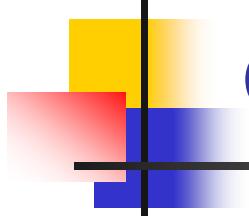
- *cis*-1-*t*-butyl-4-methylcyclohexane

- *trans*-decalin (*see left for structure*)



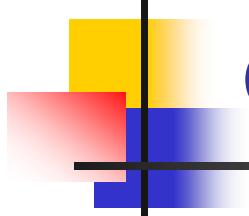
- menthol (*see left for structure; for practice, assign its proper name*)





Conformations of Other Cycloalkanes

- Six-membered rings such as cyclohexane are particularly common in nature because they have very little strain. Molecules become less stable if they have more strain. Strain can come from:
 - Angle strain (bond angles that are quite different from those predicted by VSEPR)
 - Torsional strain (eclipsed bonds)
 - Gauche interactions and 1,3-diaxial interactions (the two main factors favouring equatorial sites over axial sites for large substituents on cyclohexane rings)
- Build cyclopentane. Do you observe angle strain? Torsional strain? Find the most stable conformer. Hint: It's not flat.



Conformations of Other Cycloalkanes

- Build cyclobutane. Do you observe angle strain? Torsional strain? Find the most stable conformer. Hint: It's not flat.
- Build cyclopropane (if you can). Do you observe angle strain? Torsional strain? It can only be built flat.
- Considering the amount of strain, rank the four rings from most to least stable. Note that, because they form very quickly, three-membered rings are more common than you might expect...