Course CH 343 Lecturer Sam Gellman

Day Friday 1:20 Date 10/21/11

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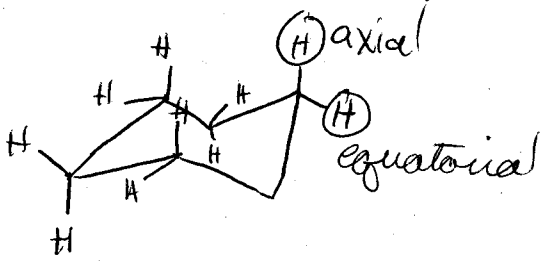
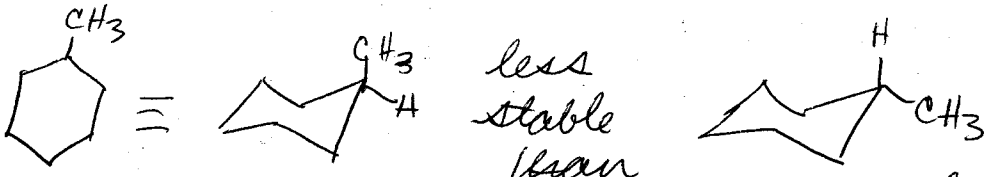
Recall: Chair conformation of cyclohexane



w/a substituent



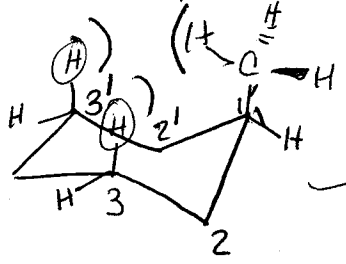
axial methyl

equatorial methyl

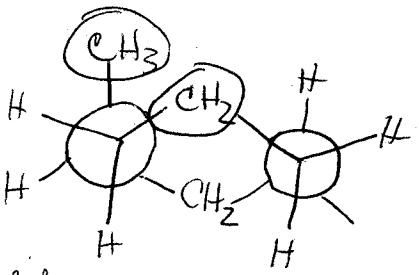
~1.8 Kcal/mol

- Axial methyl conformation has higher internal energy because of internal steric repulsions

"1,3-diaxial interactions" • numbering indicates relative spacing



Newman projection



- like gauche butane - one of two 1,3-diaxial interactions

Course CH 343 Lecturer Dawn Gilman

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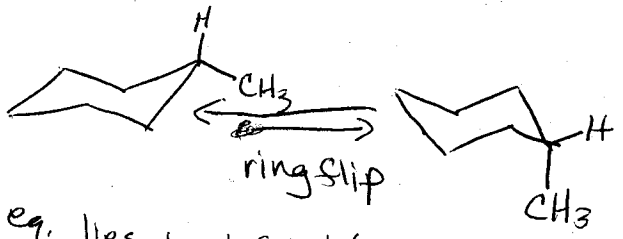
1) Where is the other 1,3-diaxial interaction?
2) Draw the Newman projection for equatorial sub. methyl conf.

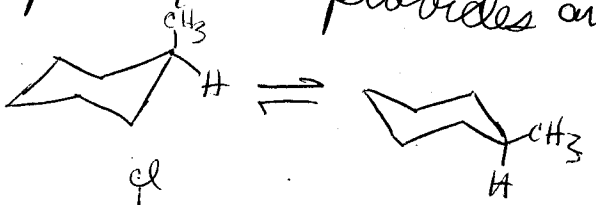
- Cyclohexane has 2 chair conformations. If you convert from one to the other, each axial H goes to equatorial, and vice versa



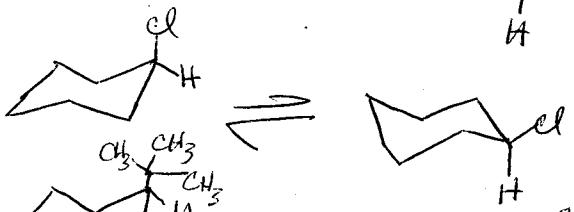
Chair conf. interconversion

eq. lies to left b/c eq. is more stable

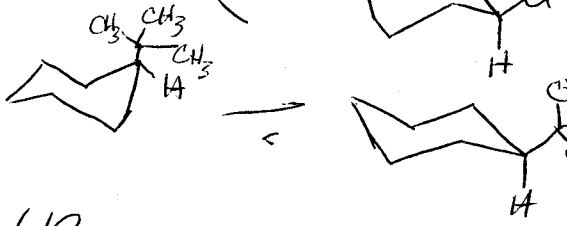
Note: position of conf. equilibrium for monosubstituted cyclohexanes provides an index of substituent size.



ΔH
-1.8 kcal/mol



-0.4 kcal/mol



-5 kcal/mol

• t-butyl is BIG!

• t-Bu cyclohexane is effectively "locked" into one of two chair conformations.

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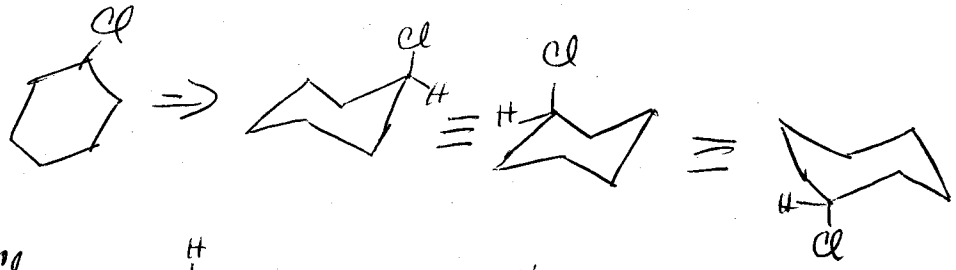
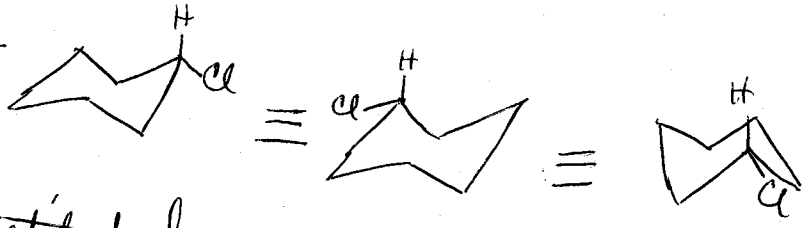
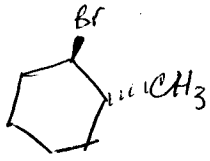
Note: Must be able to recognize when different drawings represent the same molecule.

Consider ax ~~eq~~ 

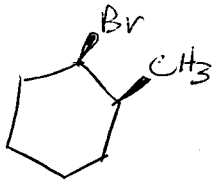
eq ≡ 

Disubstituted cyclohexanes



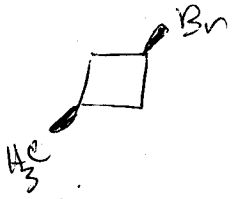
trans

vs

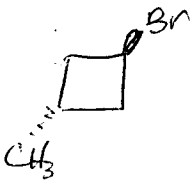


cis

- This is general for rings



cis



trans

We must understand how cis/trans is manifested in chair conformations

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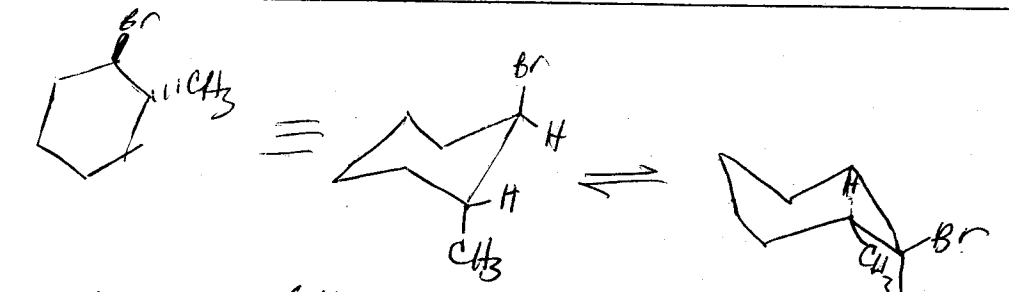
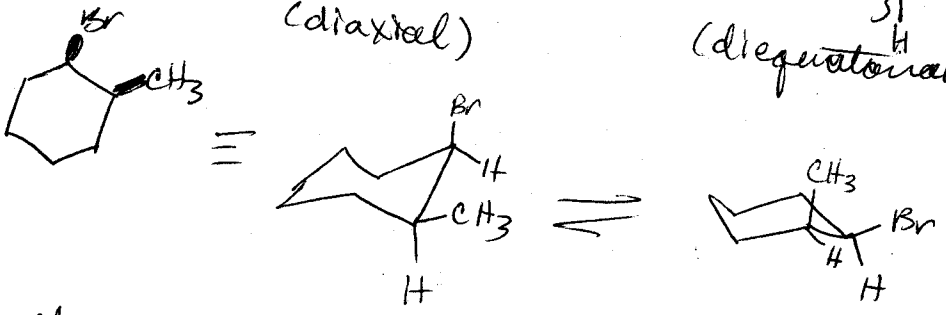


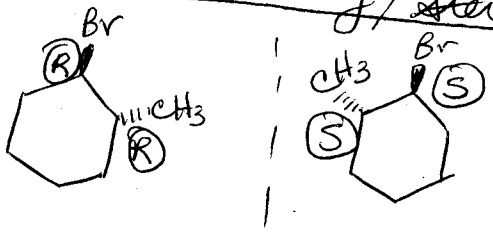
(diaxial) (diequatorial)



You fill in 1,3 + 1,4 - disubstitution cases

Wedges & dashes do not correlate D axial + equatorial!

Stereochemistry / ~~Stereoisomerism~~

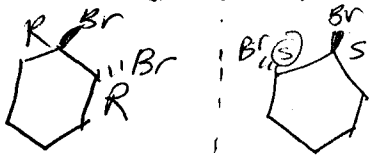


enantiomers

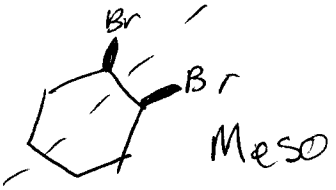
cis - another pair of enantiomers

Cis vs trans

⇒ diastereomers



enantiomers



Meso

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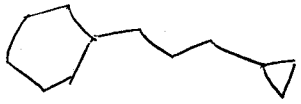
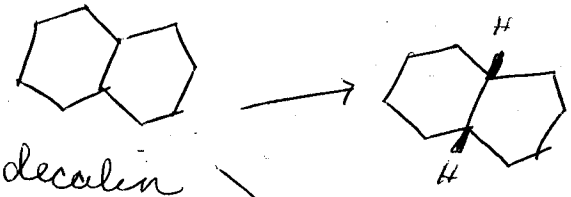
Molecules w/ ≥ 2 rings...

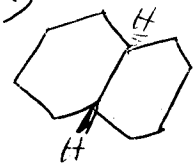


Share 1 atom or more.

Share two atoms (i.e. 1 bond) ⇒ "fused rings"



decalin → cis-decalin ("cis ring fusion")

decalin → 

trans decalin ("trans ring fusion")