1. Draw the most stable and least stable Newman projection for each of the following compounds when viewed down the indicated bond.

2-methylpropane (C1-C2 bond)
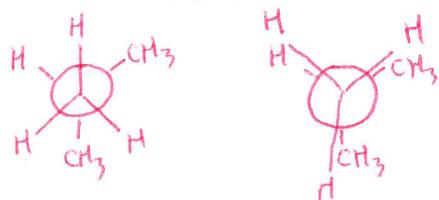
1,2-dichloroethane (C1-C2 bond)
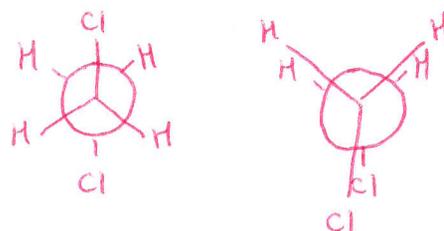
1-bromopropane (C1-C2 bond)
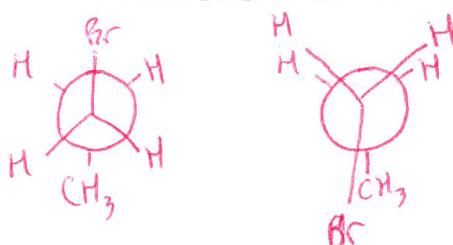
2,2-dimethylbutane (C2-C3 bond)
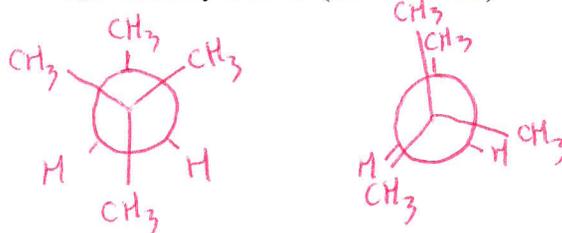
1-chloro-2-methylpropane (C1-C2 bond)
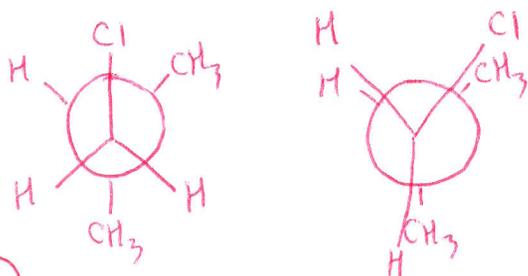
2,2-dimethylpentane (C3-C4 bond)
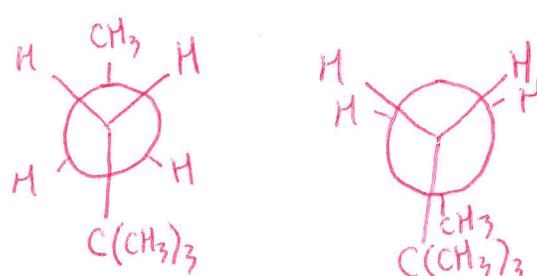
2. Sketch a graph of potential energy vs dihedral angle looking down the specified bond for the following alkanes. Include in your drawing the staggered and eclipsed Newman projections and relative energy differences. (use torsional and steric strain energy values from lecture/text)

2-methylbutane (C2-C3 bond)   2,3-dimethylbutane (C2-C3 bond)

0°   60°   120°   180°   240   300°

21 KJ/mol   3.8 KJ/mol   18 KJ/mol   3.8 KJ/mol   21 KJ/mol   7.6 KJ/mol

0°   60°   120°   180°   240°   300°

26 kJ/mol   11.4 kJ/mol   23 kJ/mol   7.6 kJ/mol   23 kJ/mol   11.4 kJ/mol
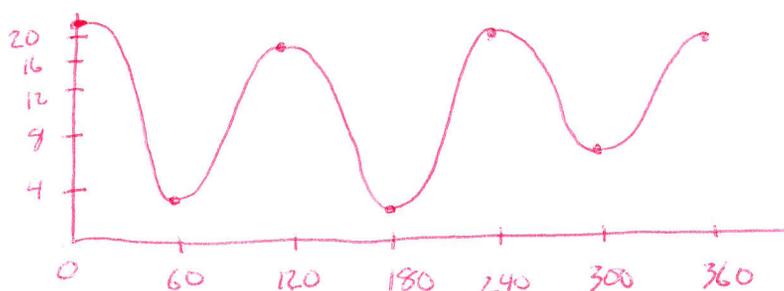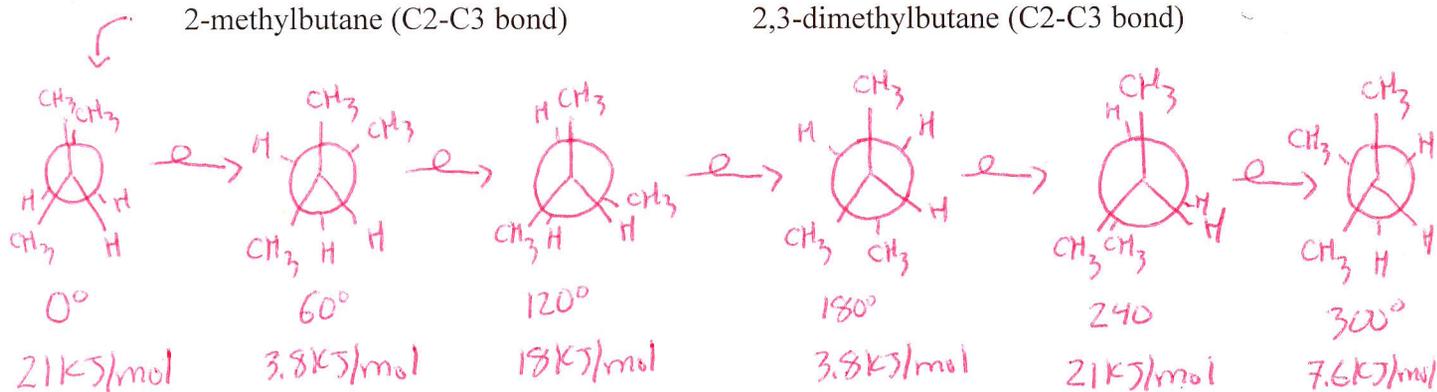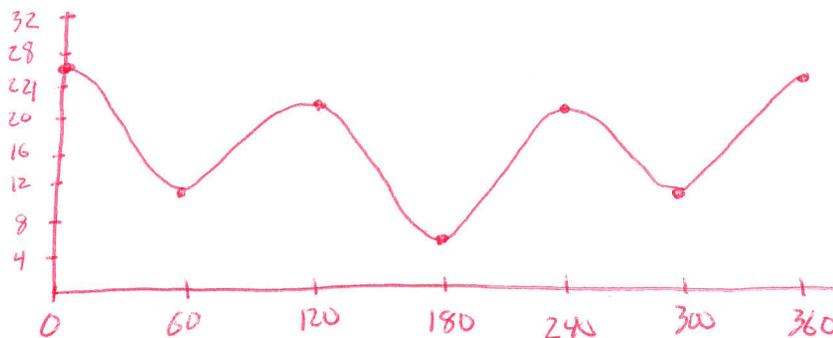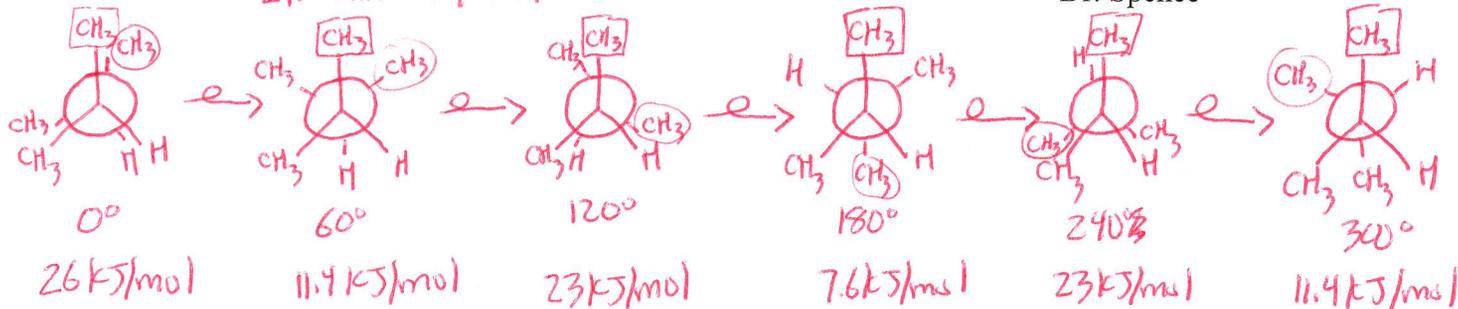
3. For butane, what is the relative percentages of the most stable and [least] stable species with respect to each other?
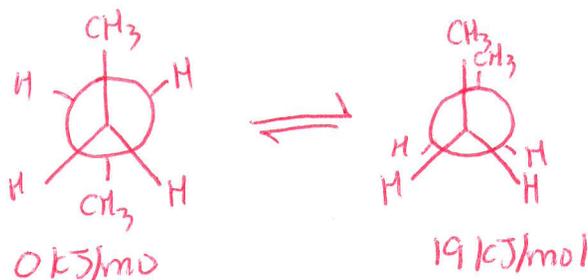
0 kJ/mol   19 kJ/mol

$$\Delta G = +19 \text{ kJ/mol} = 4.59 \text{ kcal/mol}$$

$$k = 10^{-(4.59/1.36)}$$

$$= 0.000422$$

least stable = 0.042%

most stable = 99.958%

4. For the compound $HO-CH_2-CH_2-OH$, the percentage of the gauche conformer is significantly higher than predicted based upon calculations between the anti and gauche conformers (like you did in problem 10). Why is the gauche conformer a higher percentage than predicted for this compound?

When it is gauche, this compound can intramolecularly H-bond, which provides favorable interactions not accounted for in calculation based on strain energy
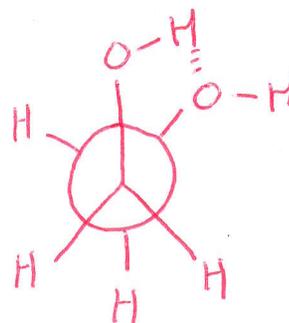
5. Sighting along the C2-C3 bond, draw all the possible staggered conformations (as Newman projections) of 3-methylpentane. Which is the lowest energy conformation? Draw a sawhorse projection of the lowest energy conformation of the entire molecule.
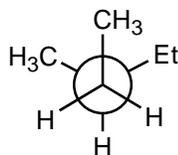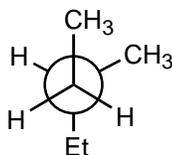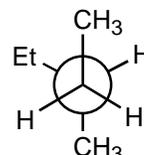

A   B   C

      A has two gauche interactions, while **B** and **C** each have only one. Between **B** and **C**, we can safely estimate that a methyl-ethyl gauche is slightly worse than a methyl-methyl gauche interaction. I'd rate **B** as the lowest energy conformation.

      For the last question, the answer is easy if we realize that skeletal drawings naturally put linear chains in their lowest energy conformations -- all anti-butane type conformations. Just add on the methyl!

**6.** Consider the molecule 2,3-dimethylbutane:
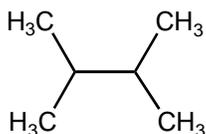
a. Draw the eclipsed Newman projections for the conformations of this molecule.

1 x H-H, 2 x CH$_3$-CH$_3$ 2 x CH$_3$-H, 1 x CH$_3$-CH$_3$ 2 x CH$_3$-H, 1 x CH$_3$-CH$_3$
1 + (2 x 2.5) = 6 kcal/mol   (2 x1.4) + 2.5 = 5.3 kcal/mol   (2 x1.4) + 2.5 = 5.3 kcal/mol
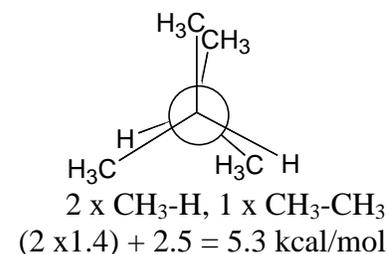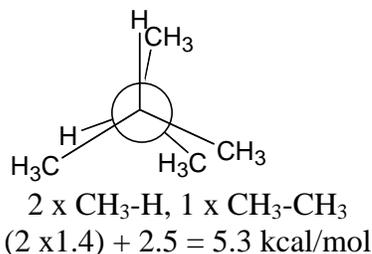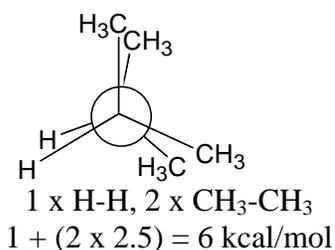
The second two are more stable than the first by 0.7 kcal/mol

b. Draw the staggered Newman projections for the conformations of this molecule.
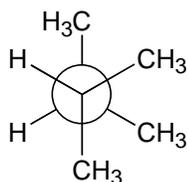
3 x CH$_3$-CH$_3$ gauche	2 x CH$_3$-CH$_3$ gauche	3 x CH$_3$-CH$_3$ gauche
3 x 0.9 = 2.7 kcal/mol	2 x 0.9 = 1.8 kcal/mol	3 x 0.9 = 2.7 kcal/mol

middle is most stable (by 0.9 kcal/mol of course!)

c. Calculate the energy of each of the conformations/Newman projections you drew for **a.** and **b.** using the information provided below. For each set, indicate which of the conformations is more stable?

   calculations done above

7. Consider the conformational isomers along the C1-C2 bond of 1-bromopropane. Draw all the distinct eclipsed and staggered conformations. For each, indicate the types of strain, if any, that you think may be incurred. Compare these conformers with their counterparts in our analysis of butane. For each pair of counterparts, indicate which you expect to be higher in energy, and briefly explain your reasoning.
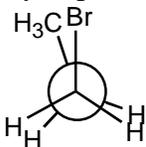
A	B	C	D
steric and torsional	steric	torsional	none
	like gauche butane		like anti butane
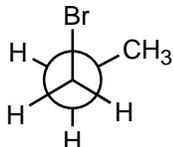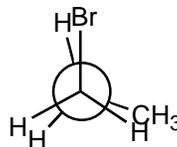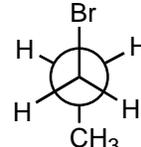
All the counterparts for butane simply have a methyl group where the bromine is. The bromine-carbon bond here is longer than the counterpart carbon-carbon bond in butane. Moreover, even though bromine is a bigger atom than carbon, it has no attached hydrogens like the methyl group does. As a result, the steric interactions should be less, and certainly the **A** and **B** conformers here should be lower in relative energy than the similar conformers in the butane case.

Ch 4 HW Set - Cycloalkanes

8. Provide the complete IUPAC name for each of the following compounds:

1-isopropyl-2,4-dimethylcyclopentane   trans-1-tertbutyl-3ethyl cyclohexane
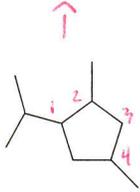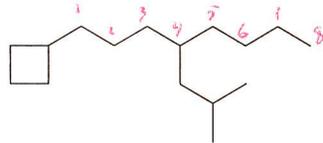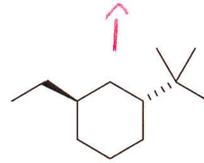
1-cyclobutyl-4-isobutyloctane   cis-1-cyclopropyl-3-methyl cyclohexane

9. How many stereoisomers of 1-ethyl-2-methylcyclohexane are possible? How many stereoisomers of 1,2-diethylcyclohexane are possible? How many stereoisomers of 1,1-dimethylcyclohexane are possible? Draw all possible stereoisomers and name them for these three compounds (for this problem, you can draw as flat hexagon instead of chair).

1-ethyl-2-methylcyclohexane

CIS   ,   CIS   ,   trans   ,   trans |4| (note the 2 cis are not the same! nor are the 2 trans - we'll see why later)

1,2-diethylcyclohexane

same!   ,   , |3|
CIS   trans (not the same)
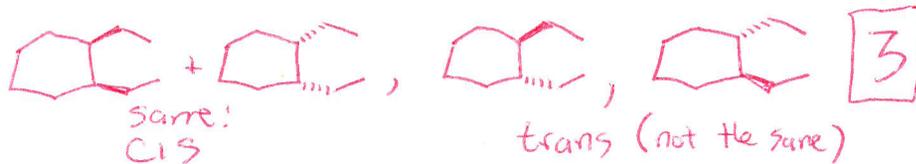
1,1-dimethylcyclohexane |1|

10. Draw the seven constitutional isomers of cycloalkanes with the molecule formula C_6H_{12}.

actually 12 possible
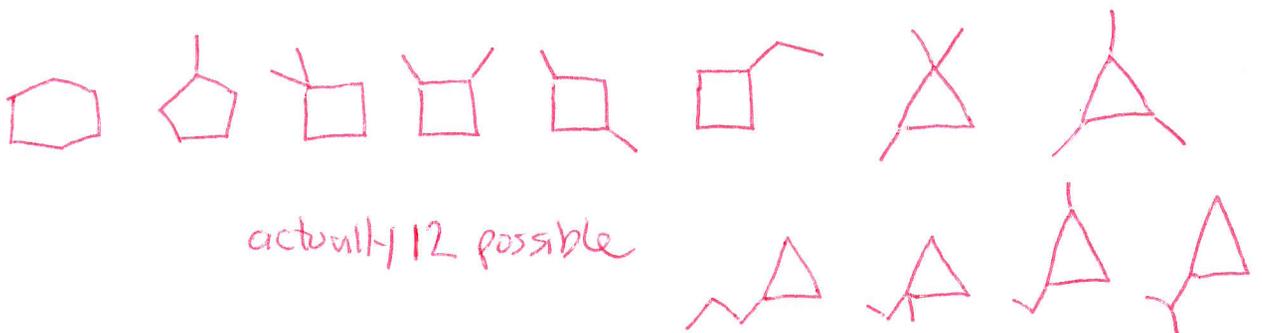
11. Approximately how much angle strain is present in cyclopropane? In cyclobutane?

total strain $E \cong 117.5$ kJ/mol

with 6 sets of eclipsing H-H interactions at 24 kJ/mol

so 117.5 kJ/mol $- 24$ kJ/mol $= 93.5$ kJ/mol angle strain

115 kJ/mol $- 32$ kJ/mol $= 83$ kJ/mol angle strain

12. Explain the increase in 1,3-diaxial strain energy in table 4.1 of your text as you go from methyl, to ethyl, to isopropyl, and finally tert-butyl. Why does the value only slightly increase until tert-butyl, which then dramatically increases in diaxial strain?
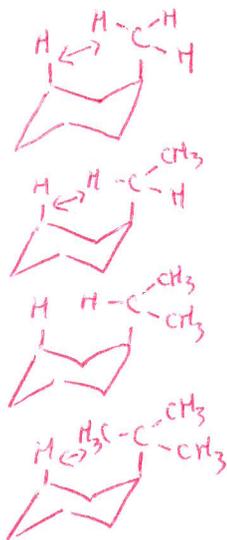
Changing methyl to ethyl or isopropyl, you can rotate the substituent so added carbon groups point away from other 1,3-diaxial hydrogens, resulting in only small increase of strain. You cannot do this for t-butyl, so you are forced to have steric strain between H & CH₃ dramatically raising energy.

13. For the following pairs of compounds, indicate whether they are constitutional isomers, stereoisomers, conformational isomers, or different compounds altogether.

stereo   cis   &   trans   &   conformational or same

constitutional   &   cis   &   trans   stereo

different (not isomers)   &   &   stereo

trans   cis
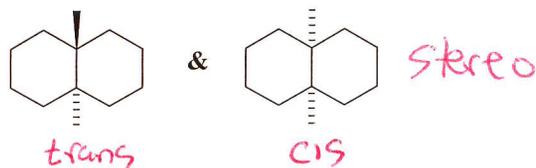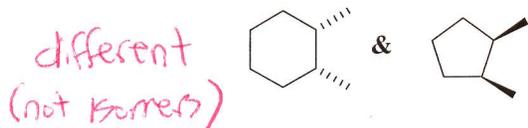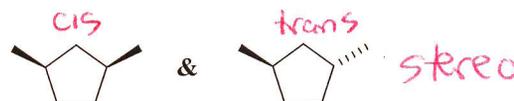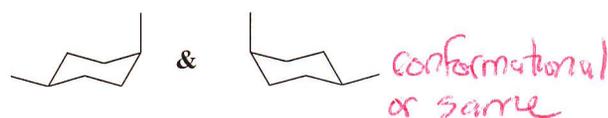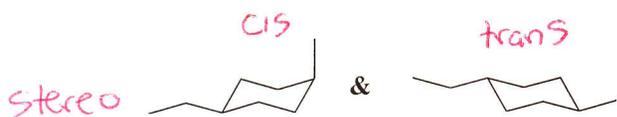
14. Draw the most stable chair conformation for each of the following cyclohexanes. Now, "flip" the ring and redraw the molecule in the higher energy form.

chlorocyclohexane

more stable
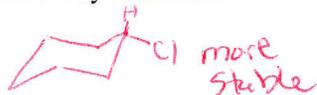
cis-1-chloro-2-methylcyclohexane

more stable
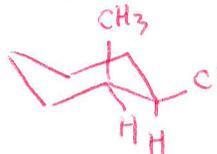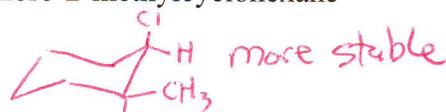
trans-1-methyl-3-propylcyclohexane


more stable
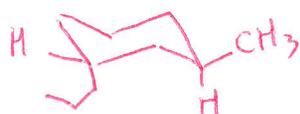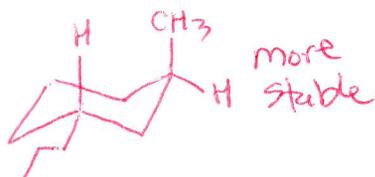
cis-1-tert-butyl-4-methylcyclohexane

more stable
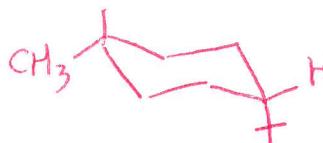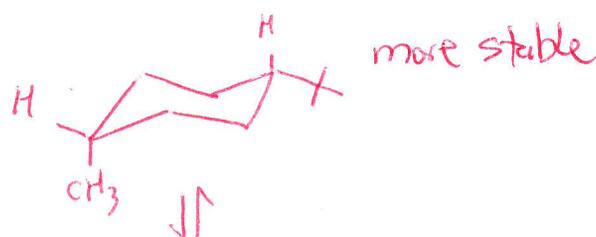
15. For your drawing of cis-1-chloro-2-methylcyclohexane, show the destabilizing 1,3-diaxial interactions present. Use the following values for 1,3-diaxial interactions to calculate the relative percentages of each conformer: each 1,3-diaxial Cl, H interaction = 0.25 kcal/mol, each 1,3-diaxial CH_3, H interaction = 0.9 kcal/mol.

A   ⇌   B
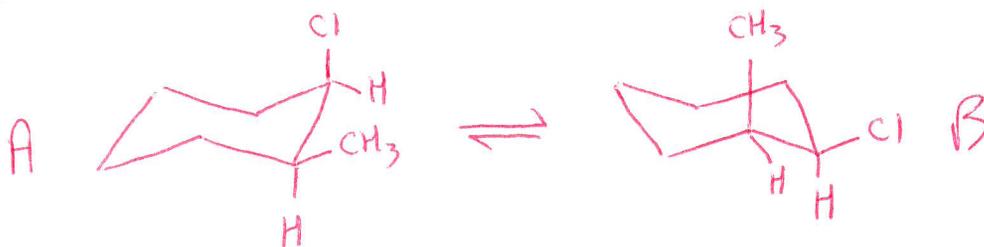
2 Cl-H 1,3 diaxial = 2 × 0.25 kcal/mol   2 CH_3-H 1,3 diaxial = 2 × 0.9 kcal/mol

1 gauche CH_3-Cl = ?   these two   1 gauche CH_3-Cl = ?
                                actually cancel
                                out for this
0.5 kcal/mol   calculation → I would provide values on exam

                                                          1.8 kcal/mol

ΔG = 1.3 kcal/mol   so 90% A , 10% B

K = 0.11

16. Convert the following cyclohexanes into their chair structures and calculate the total energy of both chair conformations. You will need the following values in addition to ones in your text: 1,3-Diaxial interactions: CH_3-OH = 2.2 kcal; CH_3-Cl = 2.4 kcal; CH_3-CH_3 = 3.7 kcal; $C(CH_3)_3-OH$ = 4.4 kcal. Gauche interactions: CH_3-Cl = 0.3 kcal; $C(CH_3)_3-Cl$ = 2.1 kcal; $C(CH_3)_3-OH$ = 2.5 kcal.


1

3.6 kcal/mol
(2*0.25 + 2*0.5 + 2.1)

7.5 kcal/mol
(2*2.7 + 2.1)

2

5.5 kcal/mol
(2*0.9 + 3.7)

0 kcal/mol

3

0.3 kcal/mol

1.4 kcal/mol
(0.9 + 2*0.25)
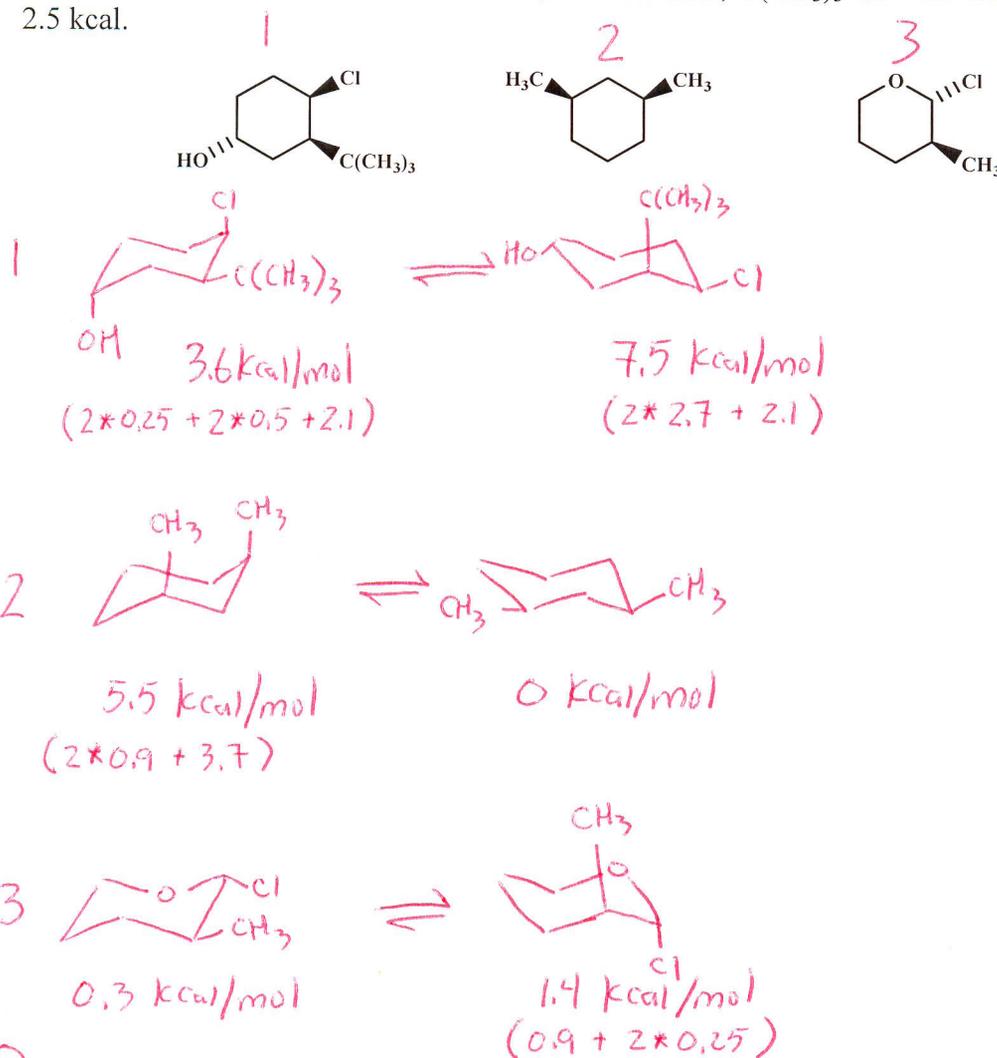
17. Which compound below is more stable? Explain.

less stable. Has 1,3 diaxial CH_3-H interactions not present in first structure
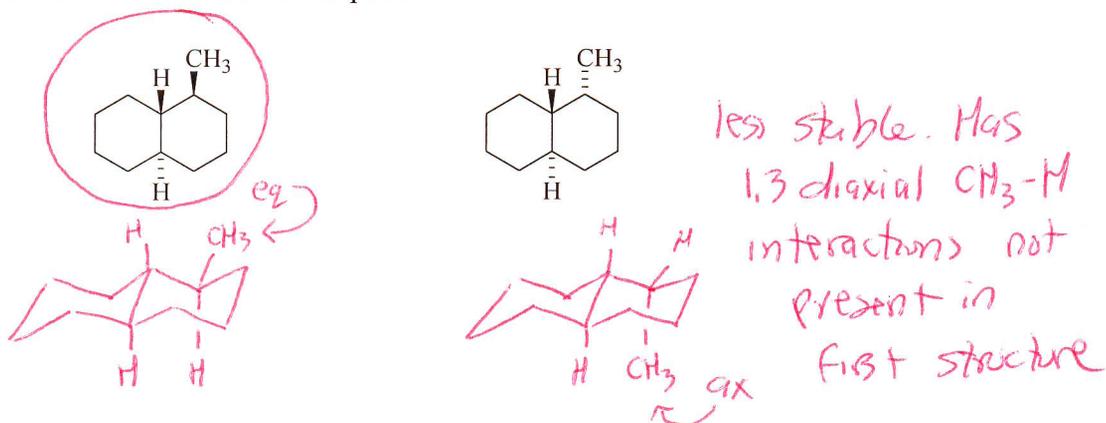
18. Draw all the possible isomers of dimethylcyclobutane, MF: C_6H_{12}. Two of the constitutional isomers you have drawn can exhibit stereoisomerism as well. Draw the two possible stereoisomers for each of these compounds.

cis   trans   cis   trans
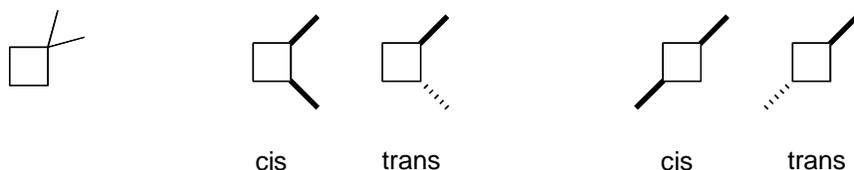
19. Draw and name a constitutional isomer of methylcyclohexane.

Here's one:

cycloheptane

20. Consider 1,3-dimethylcyclobutane. Do you expect the *trans* isomer or *cis* isomer to be more stable? Offer an explanation using the ideas of conformational analysis developed for cyclohexane.

First, we should draw the two possibilities as flat projections:

Now, we need to remember what we learned about cyclobutane conformations. Cyclobutanes usually adopt puckered conformations (increasing ring strain) in order to lessen the torsional strain from eclipsing interactions. When we draw the rings in these conformations, we create pseudo-axial and equatorial positions at each carbon. Similar to cyclohexane, having equatorial substituents creates less strain. As a result, we'd rather have the isomer that can place both the methyls in equatorial positions. That isomer is the *cis*-1,3-dimethylcyclobutane.

cis -- diequatorial   *trans* -- one axial, one equatorial

21. Consider the all *cis* isomer of 1,3,5-tribromo-2,4,6-trimethylcyclohexane.

a. Draw the molecule as a skeletal structure.

b. Draw a sawhorse representation of each of the two possible chair forms.

bromines equatorial
methyls axial

methyls equatorial
bromines axial
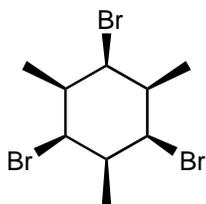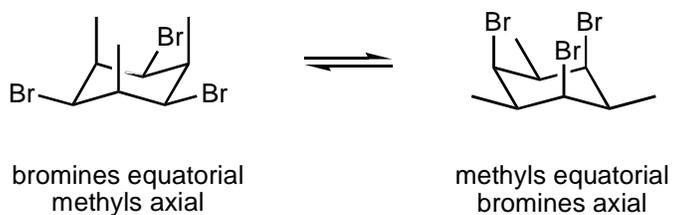
c. Which chair conformation do you expect to be more stable? Briefly explain why.

For the same kinds of arguments as above, the diaxial interactions between the bromines should be much less than between the methyl groups. Expect the second conformation (bromines axial) to be much more stable.

22. Consider the all *cis* isomer of 1-*tert*-butyl-2,4,6-trimethylcyclohexane.

a. Draw the molecule as a skeletal structure.
b.

b. Draw a sawhorse representation of each of the two possible chair forms.

A

B

t-butyl equatorial
methyls axial

methyls equatorial
t-butyl axial
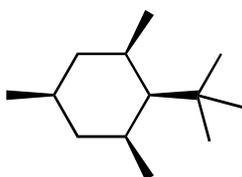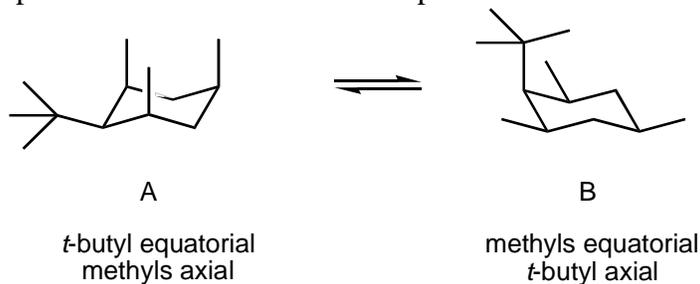
c. Given that a single CH_3-CH_3 1,3 diaxial interaction has a cost of 15 kJ/mol, which chair conformation do you expect to be more stable? By how much?

      A has 3 CH_3-CH_3 1,3 diaxial interactions for a total cost of 45 kJ/mol. **B** has only the *t*-butyl diaxial cost of 23 kJ/mol. **B** should be more stable by 22 kJ/mol.

d. If you add another *cis* methyl at carbon 3, how might this change the picture? Draw the chair forms and make a guess as to which is more stable. Explain your reasoning.

picture would now be modified to:

A   B
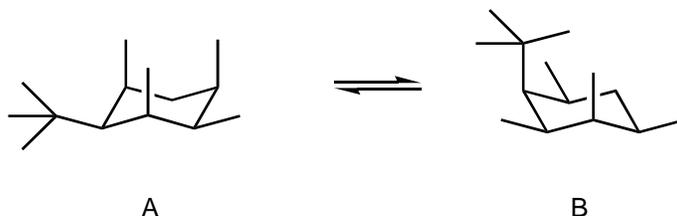
Energy cost for **A** is still 45 kJ/mol. The cost for **B** is now *t*-Bu-H at 11.5 + CH_3-H at 4 + whatever the cost of the *t*-Bu-CH_3 interaction is. If that interaction is greater than 30 kJ/mol, **A** would now be more stable than **B**. Knowing that CH_3-CH_3 costs 15 kJ/mol, it's a good guess that *t*-Bu-CH_3 is more than twice as much and greater than 30. I'd guess that **A** is now more stable.

23. Draw the two possible chair conformations for 3-methyltetrahydropyran (shown below). Indicate which is more stable. Estimate the relative populations of the two chair forms relative to those for methylcyclohexane.

3-methyltetrahydropyran

A   B
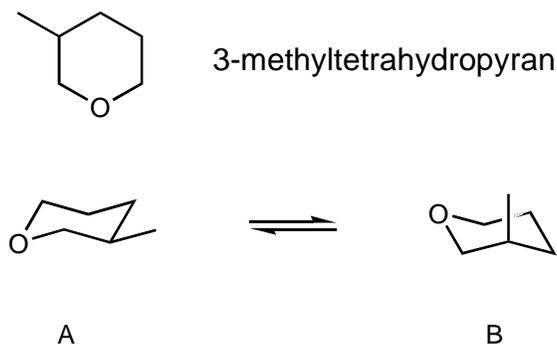
A, with the equatorial methyl, is more stable. Relative to methylcyclohexane, though, having the methyl axial does not cost as much energy. The oxygen has no attached hydrogens, so we have removed one of the diaxial interactions. The cost might be estimated as about 4-5 kJ/mol rather than 7.6 kJ/mol. (The assumption is that any interaction with a lone pair is a lot less than with the hydrogen.) An energy difference of 7.6 kJ/mol gives us a ratio of about 95% equatorial/5 % axial. Reducing that to 5 kJ/mol would give us a ratio of more like 85% equatorial/15% axial.

24. For the following molecule, perform a complete conformational analysis using the data provided in tables in the course packet (or in the book). Follow the steps below to complete the analysis.
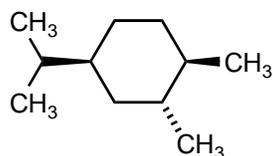
a. Draw the two chair conformations possible for the compound.
b. Calculate the energy difference between the two chair conformations.
c. Estimate the ratio of most stable to least stable conformation for a sample of this compound at 25 °C.

2 x 1,3 diaxial

CH_3-CH_3
gauche ($60°$)

1,2 disubstituted
2 x isopropyl-H 1,3 diaxial
1 x CH_3-CH_3 gauche

$(2 \times 1.1) + 0.9 = 3.1$ kcal/mol
more stable conformation

2 x 1,3 diaxial

anti -- 180°, no steric interactions

2 x 1,3 diaxial

4 x CH_3-CH_3 1,3 diaxial
no CH_3-CH_3 gauche, CH_3-CH_3 angle is 180°
isopropyl equatorial, no steric interactions

$4 \times 0.9 = 3.6$ kcal/mol
less stable conformation by 0.5 kcal/mol
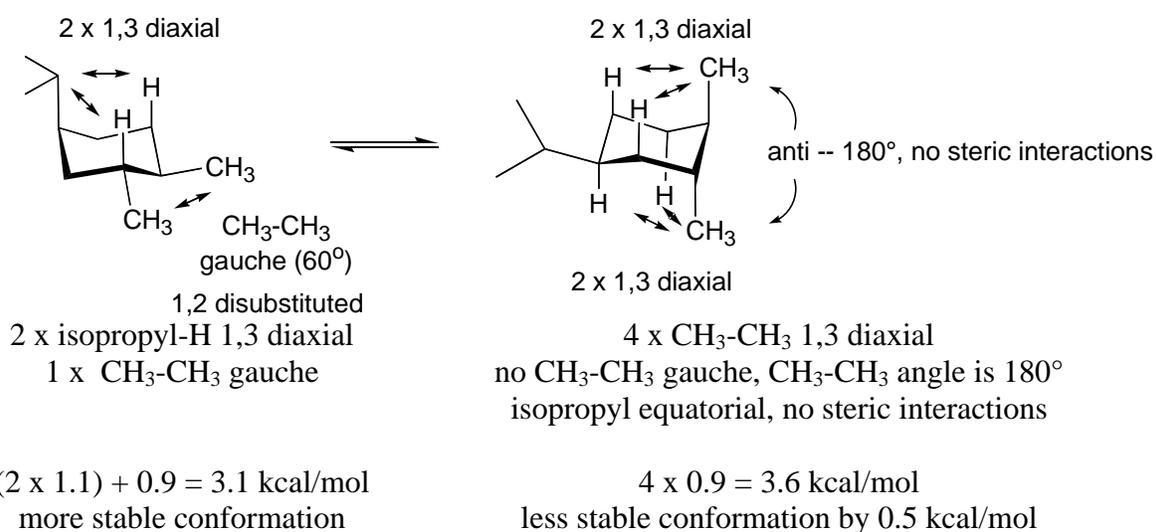
0.5 kcal/mol gives a ratio of about 70:30 (just estimate knowing that 0.65 is 75:25)

25. Draw a pair of substituted cyclobutane stereoisomers. Name them.

Here is one possibility:
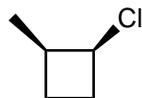
cis-1-chloro-2-methylcyclobutane
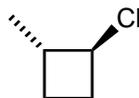
trans-1-chloro-2-methylcyclobutane

26. For the following pairs of cyclohexane chair conformations, circle the conformer that you expect to be more stable. Briefly explain your reasoning.
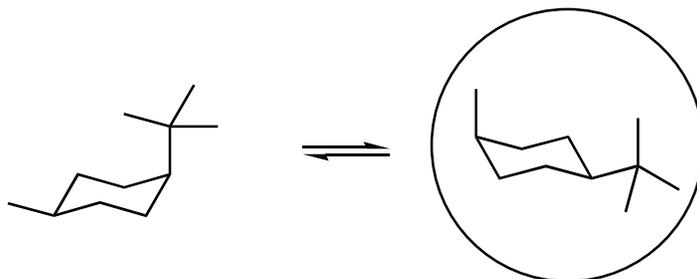

t-butyl is much bigger than methyl, more important to be equatorial.
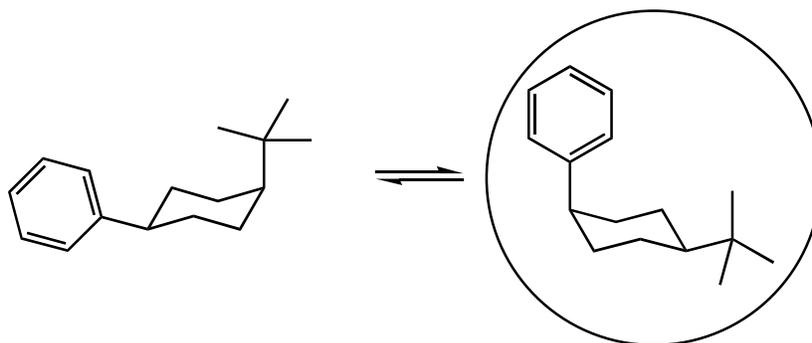
*t*-butyl is still bigger than phenyl, more important to be equatorial.
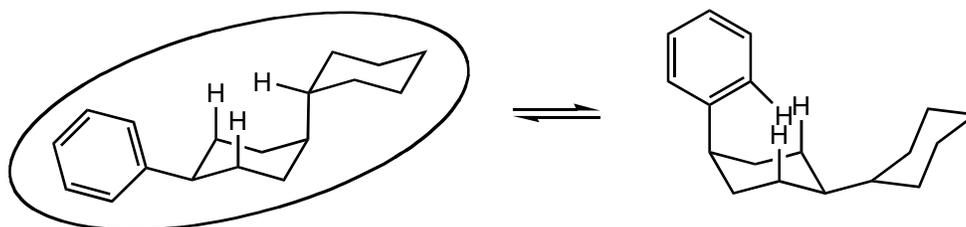
The cyclohexyl substituent can get out of the way -- the interaction isn't actually any worse than that of a methyl group. However, any orientation of the phenyl has atoms much closer. I've shown this arrangement, but even the 90° rotation of the phenyl ring has more problems than a methyl would.
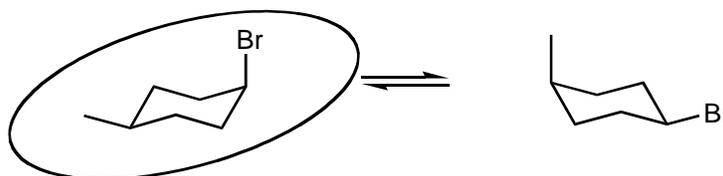
Bromine has no attached H's and it is attached to the ring via a longer bond. It will interact less with the diaxial H's and is better to have axial than the methyl would be.

27. For the following pairs of cyclohexane chair conformations, circle the conformer that you expect to be more stable. Briefly explain your reasoning.

a.
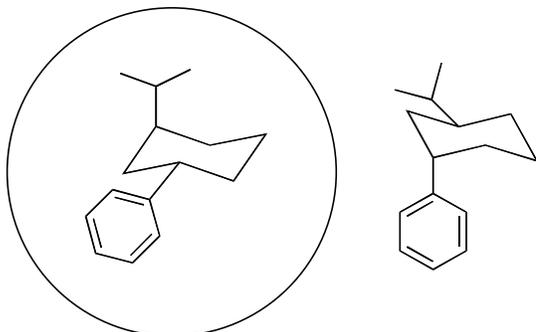
Biggest, most sterically demanding group ($-C_6H_5$) is equatorial. If you are unsure about which group, the benzene ring or the isopropyl, is sterically larger, see the table in the class packet: C_6H_5 has 1.5 kcal/mol (6.5 kJ) steric strain energy, isopropyl is only 0.95 kcal/mol (4 kJ).

b.
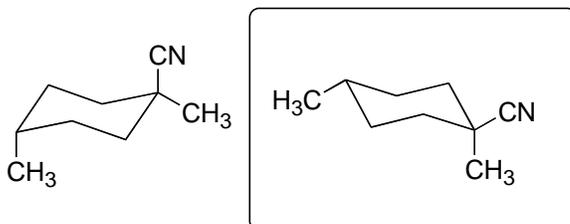
2 groups axial vs. only one group axial

c.
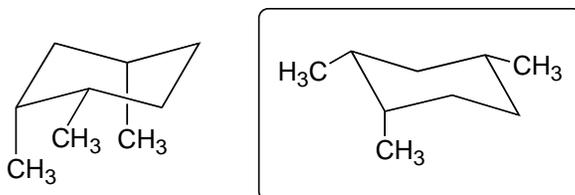
The first conformation has 2 CH_3 groups axial on the same side of the ring, leading to 2 CH_3-H diaxial interactions and also a very costly CH_3-CH_3 diaxial interaction (see problem 39 for an estimate). The second conformation has a single CH_3 group axial, which only leads to the 2 CH_3-H diaxial interactions. Note that both conformations also have a CH_3-CH_3 gauche interaction.

28. Identify the more stable conformation in each of the following pairs, and briefly explain your reasoning.

a.
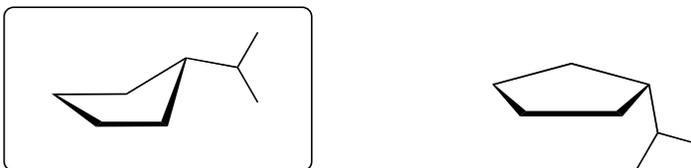
Ring is in preferred "envelope" conformation, which reduces all the eclipsing interactions around the ring and allows the isopropyl to adopt a psuedo-equatorial position.

b.
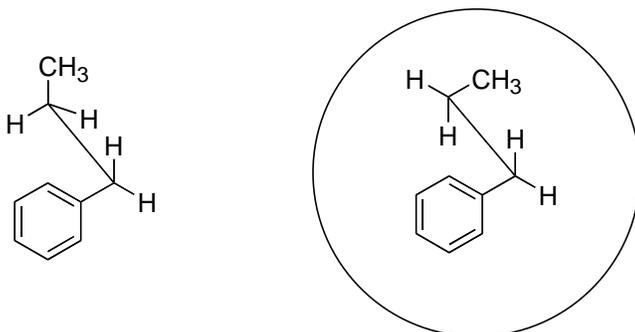
Good practice for working with different 3-D perspectives. The left conformation is eclipsed, while the right one is staggered, and in fact anti.

c.

2 CH$_3$-H diaxial interactions
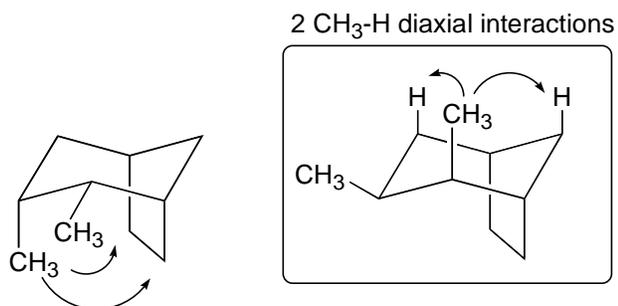
2 CH$_3$-CH$_2$ diaxial interactions

The CH$_3$-CH$_2$ diaxial interactions cost much more than the CH$_3$-H diaxial interactions.

d. A tough one -- draw the most stable chair forms for both and then compare their stability
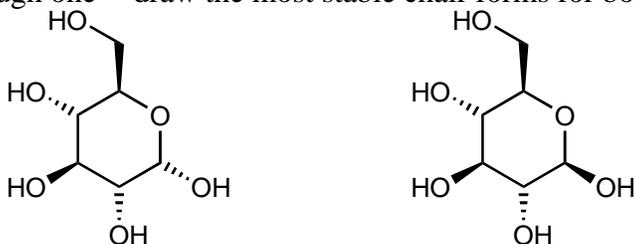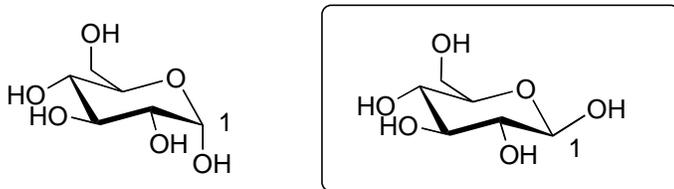
The -OH at carbon one is more stable when equatorial. All other groups are the same for both molecules.

29. For the molecule below, follow the steps to perform a complete conformational analysis. Use the energy data provided in the course handout packet. Assume no distortion of the ring due to the oxygens, and assume no steric strain due to the electron pairs on oxygen.
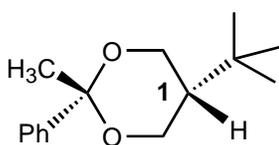
Note: Ph = C₆H₅ on Conformational Analysis Table in packet

a. Draw the two chair conformations possible for the compound. For convenience, fill in the appropriate substituents on the chairs below.
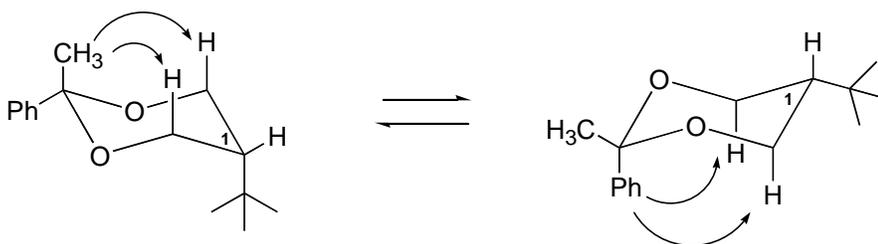
b. Calculate the energy difference between the two chair conformations drawn above.

c. Estimate the ratio of more stable to less stable conformation for a sample of this compound at 25 °C.

> Left: 2 (3.8) = 7.6 kJ/mol
> Right: 2 (6.5) = 13 kJ/mol
> Left is more stable by 5.4 kJ/mol, which we might estimate giving a 88:12 ratio of more stable:less stable.

d. Is there anything unusual about your findings above that may go against conventional wisdom in such conformational analyses? Explain briefly.

The preferred, lower energy conformation has the big *t*-butyl group in the axial position!? The reason is that no H's on the oxygen atoms means no 1,3 diaxial interactions. Crazy!

30. The energy of the boat conformation of cyclohexane is 7 kcal/mol (29 kJ/mol) higher than the chair conformation. Calculate the steric strain due to the H_a-H_b interaction in the boat using what you know about the other destabilizing interactions in this molecule. A model might be helpful here.
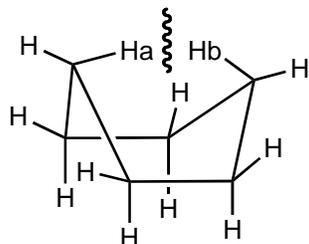
There are 4 H-H eclipsing interactions for the lower 4 H's (bottom of the boat): 4 x 1 kcal/mol (4 kJ/mol) = 4 kcal/mol (16 kJ/mol) for H-H eclipsing; therefore the H_a-H_b interaction costs 3 kcal/mol (13 kJ/mol).