

**HOMEWORK PROBLEMS: ALKANE AND CYCLOALKANE CONFORMATIONS**

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)

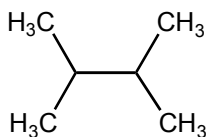
2-methylbutane (C2-C3 bond)	2,3-dimethylbutane (C2-C3 bond)
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3. For butane, what is the relative percentages of the most stable and least stable species with respect to each other?

4. For the compound HO-CH<sub>2</sub>-CH<sub>2</sub>-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 3). Why is the gauche conformer a higher percentage than predicted for this compound?

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.

6. Consider the molecule 2,3-dimethylbutane:



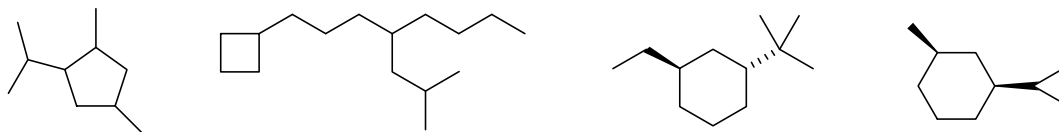
- Draw the eclipsed Newman projections for the conformations of this molecule.
- Draw the staggered Newman projections for the conformations of this molecule.
- Calculate the energy of each of the conformations/Newman projections you drew for **a.** and **b.** using the information provided below. For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

Steric interactions	Eclipsing (0°)	Staggered (60°)
H-H	1.0	0
CH <sub>3</sub> -H	1.4	0
CH <sub>3</sub> -CH <sub>3</sub>	2.5	0.9

Energies in kcal/mol

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.

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



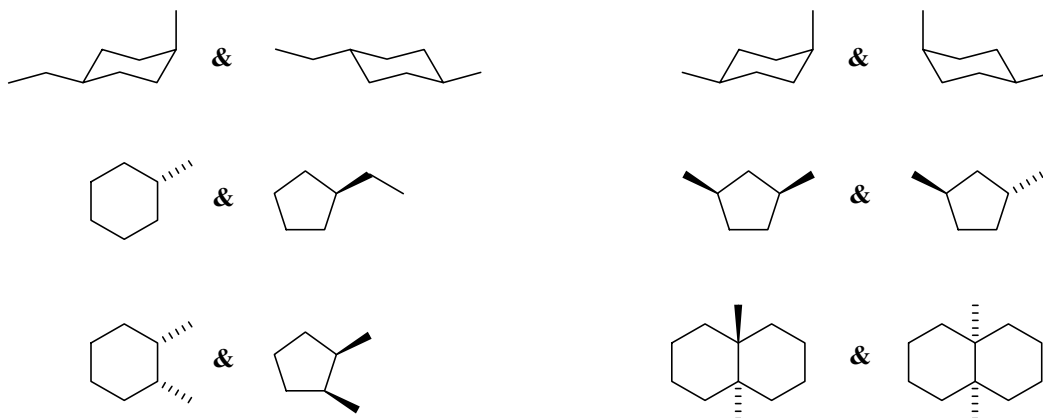
9. How many stereoisomers of 1-ethyl-2-methylcyclohexane are possible? How many stereoisomers of 1,2-diethylcyclohexane are possible? How many stereoisomers of 1,1-dimethylcyclohexane are possible? Draw all possible stereoisomers and name them for these three compounds (for this problem, you can draw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

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

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

12. Explain the increase in 1,3-diaxial strain energy in slide 32 of your notes 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?

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



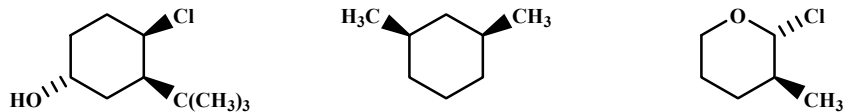
14. Draw the most stable chair conformation for each of the following cyclohexanes. Now, “flip” the ring and redraw the molecule in the higher energy form.

chlorocyclohexane  
trans-1-methyl-3-propylcyclohexane

cis-1-chloro-2-methylcyclohexane  
cis-1-tert-butyl-4-methylcyclohexane

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.

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 notes: 1,3-Diaxial interactions:  $\text{CH}_3\text{-OH} = 2.2$  kcal;  $\text{CH}_3\text{-Cl} = 2.4$  kcal;  $\text{CH}_3\text{-CH}_3 = 3.7$  kcal;  $\text{C}(\text{CH}_3)_3\text{-OH} = 4.4$  kcal. Gauche interactions:  $\text{CH}_3\text{-Cl} = 0.3$  kcal;  $\text{C}(\text{CH}_3)_3\text{-Cl} = 2.1$  kcal;  $\text{C}(\text{CH}_3)_3\text{-OH} = 2.5$  kcal.



17. Which compound below is more stable? Explain.



18. Draw all the possible isomers of dimethylcyclobutane, MF:  $\text{C}_6\text{H}_{12}$ . Two of the constitutional isomers you have drawn can exhibit stereoisomerism as well. Draw the two possible stereoisomers for each of these compounds.

19. Draw and name a constitutional isomer of methylcyclohexane.

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.

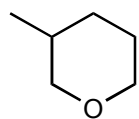
21. Consider the all *cis* isomer of 1,3,5-tribromo-2,4,6-trimethylcyclohexane.

- Draw the molecule as a skeletal structure.
- Draw a sawhorse representation of each of the two possible chair forms.
- Which chair conformation do you expect to be more stable? Briefly explain why.

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

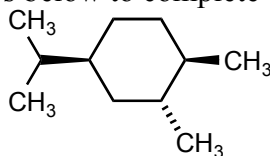
- Draw the molecule as a skeletal structure.
- Draw a sawhorse representation of each of the two possible chair forms.
- Given that a single  $\text{CH}_3\text{-CH}_3$  1,3 diaxial interaction has a cost of 15 kJ/mol, which chair conformation do you expect to be more stable? By how much?
- If you add 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.

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

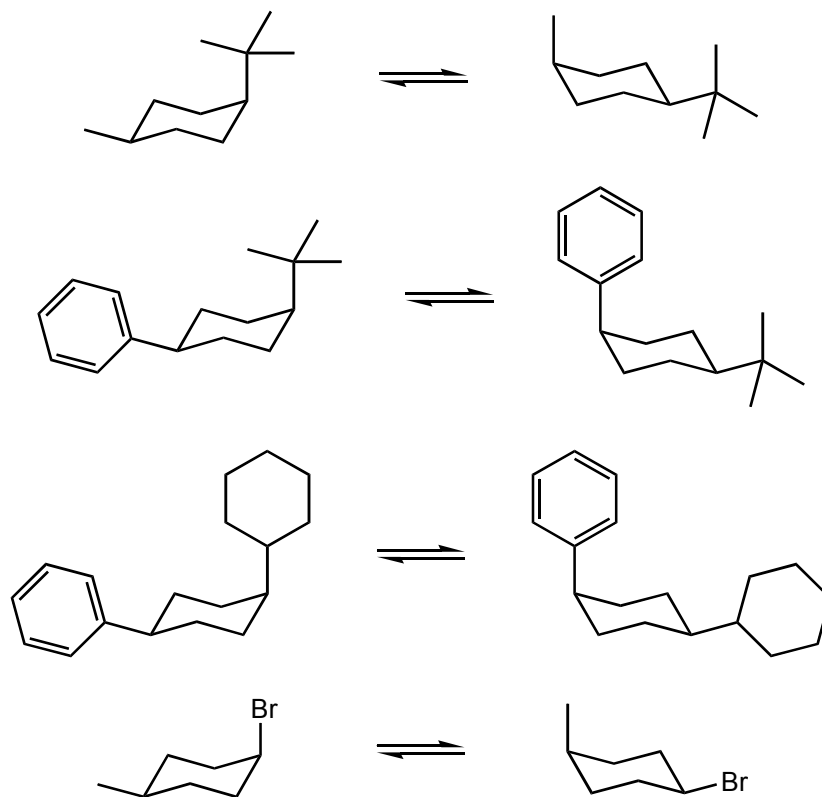
24. For the following molecule, perform a complete conformational analysis using the data provided in tables in the course notes. Follow the steps below to complete the analysis.



- Draw the two chair conformations possible for the compound.
- Calculate the energy difference between the two chair conformations.
- Estimate the ratio of most stable to least stable conformation for a sample of this compound at 25 °C.

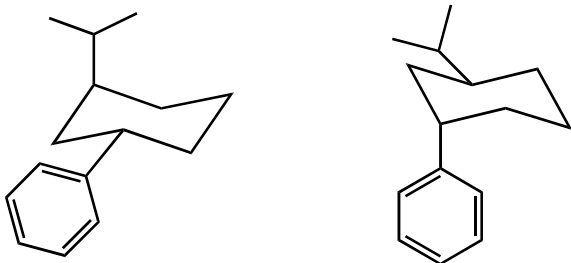
25. Draw a pair of substituted cyclobutane stereoisomers. Name them.

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

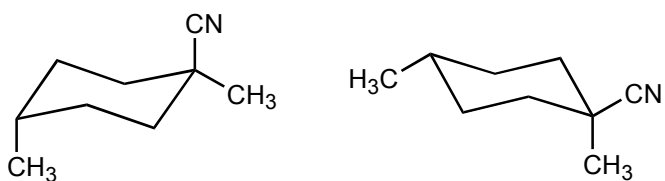


27. For the following pairs of cyclohexane chair conformations, circle the conformer that you expect to be more stable. Briefly explain your reasoning.

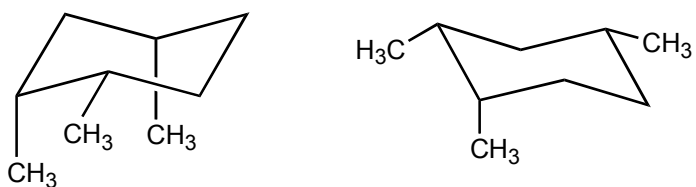
a.



b.



c.



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

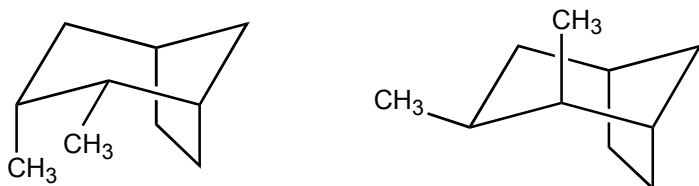
a.



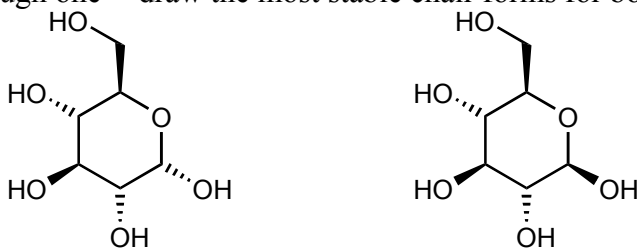
b.



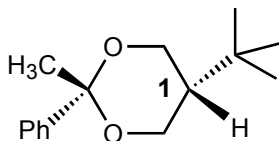
c.



d. A tough one -- draw the most stable chair forms for both and then compare their stability

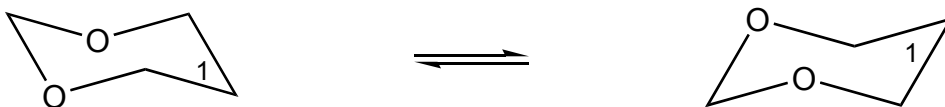


29. For the molecule below, follow the steps to perform a complete conformational analysis. Use the energy data provided in the course notes. Assume no distortion of the ring due to the oxygens, and assume no steric strain due to the electron pairs on oxygen.



Note:  $Ph = C_6H_5$  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 most stable to least stable conformation for a sample of this compound at 25 °C.

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

30. The energy of the boat conformation of cyclohexane is 7 kcal/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.

