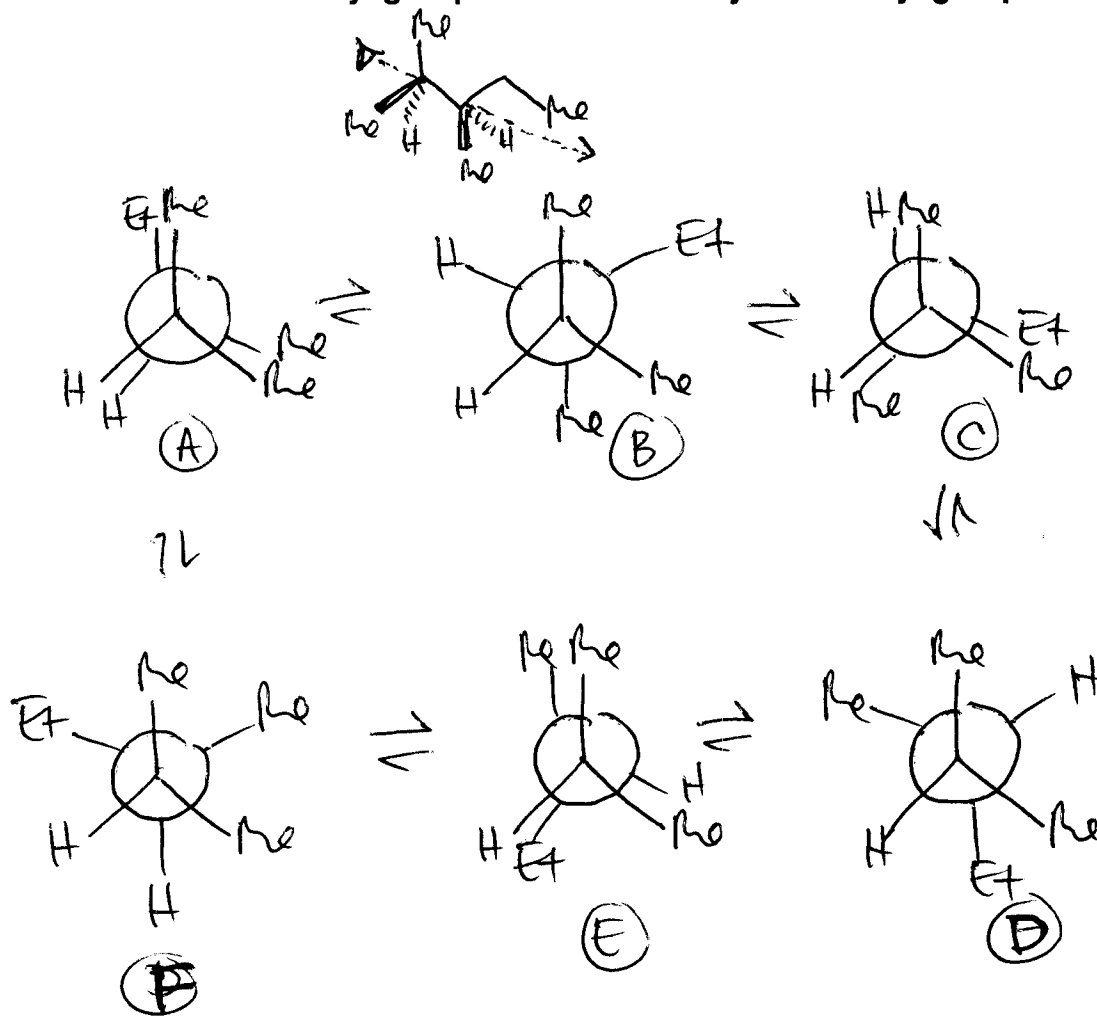Out of
20 pts.

Key

Problem Set #3, 5.12 Spring 2003
Due Monday, March 3, 4pm

1. a) Using Newman projections, draw **all of the staggered and eclipsed** conformers of 2,3-dimethylpentane with respect to rotation about the C2–C3 bond.
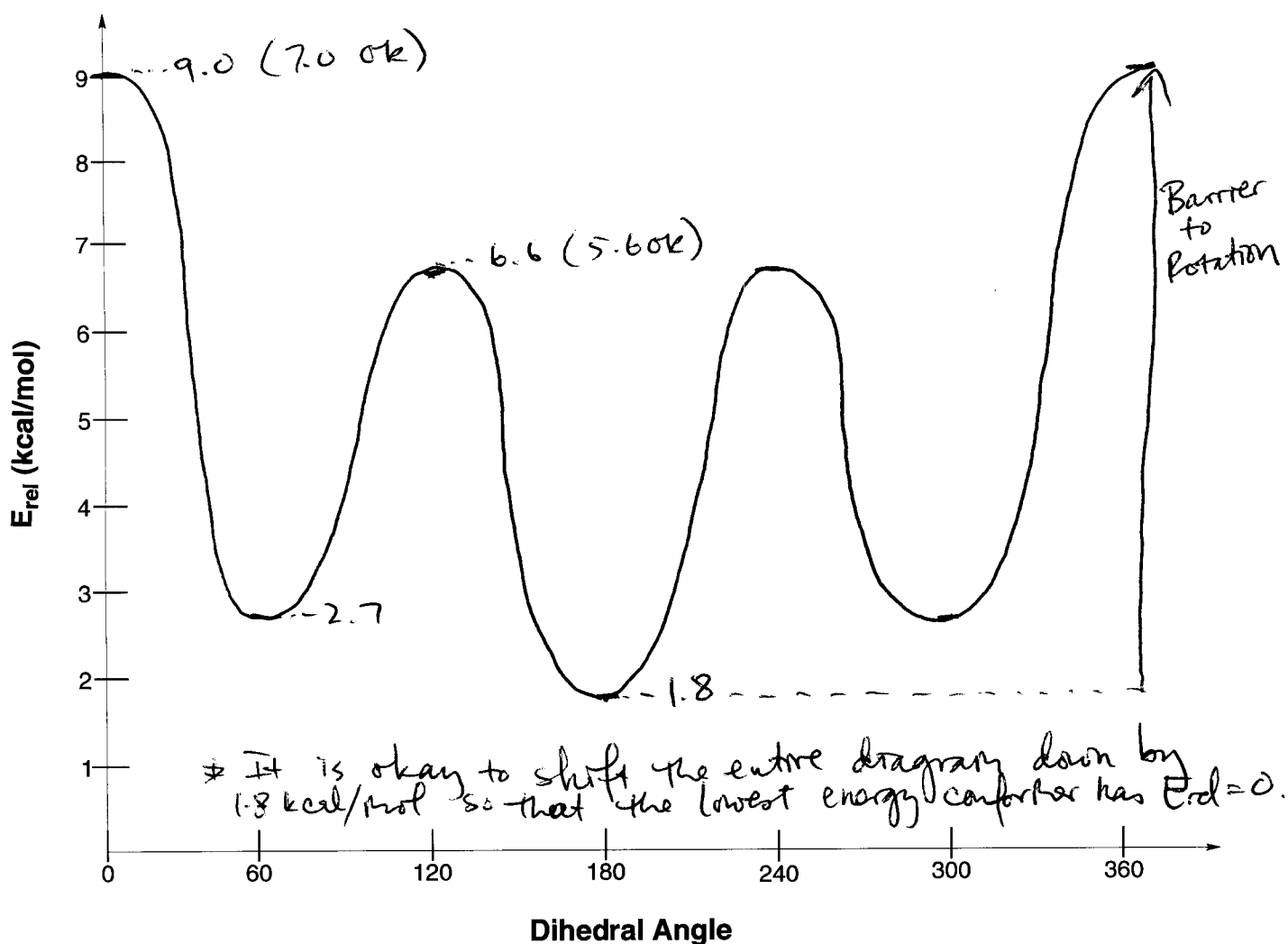
b) Assign the relative energies of each of the conformers in part **a**.
Hint: Assume that an ethyl group behaves similarly to a methyl group.

A : $E_{rel} = 4.0 + 4.0 + 1.0 = 9.0$ kcal/mol (7.0 ok)
B : $E_{rel} = 0.9 + 0.9 + 0.9 = 2.7$ kcal/mol
C : $E_{rel} = 4.0 + 1.3 + 1.3 = 6.6$ kcal/mol (5.6 ok)
D : $E_{rel} = 0.9 + 0.9 = 1.8$ kcal/mol
E : $E_{rel} = 4.0 + 1.3 + 1.3 = 6.6$ kcal/mol (5.6 ok)
F : $E_{rel} = 0.9 + 0.9 + 0.9 = 2.7$ kcal/mol

c) Starting with the highest energy eclipsed conformer, draw a potential energy diagram for a 360° rotation around the C2-C3 bond of 2,3-dimethylpentane.


Potential energy diagram with y-axis labeled E_{rel} (kcal/mol) ranging from 0 to 9, and x-axis labeled Dihedral Angle ranging from 0 to 360.

Annotations on the graph:
- ···9.0 (7.0 ok)
- ···6.6 (5.6 ok)
- ···2.7
- ···1.8 ·········
- Barrier to Rotation
- ✱ It is okay to shift the entire diagram down by 1.8 kcal/mol so that the lowest energy conformer has $E_{rel} = 0$.

d) What is the barrier to rotation around the C2-C3 bond of 2,3-dimethylpentane?

Barrier = 9.0 − 1.8 = 7.2 kcal/mol

(7.0 − 1.8 = 5.2 kcal/mol also ok)

2. You learned in lecture that cyclopentane prefers to adopt a low-energy envelope conformation. What you didn't learn is that mono-substituted cyclohexane derivatives favor the envelope that puts the substituent (X) at the "flap" of the envelope (**A**) rather than at the "base" (**B**).


A
(more stable)

B
(less stable)
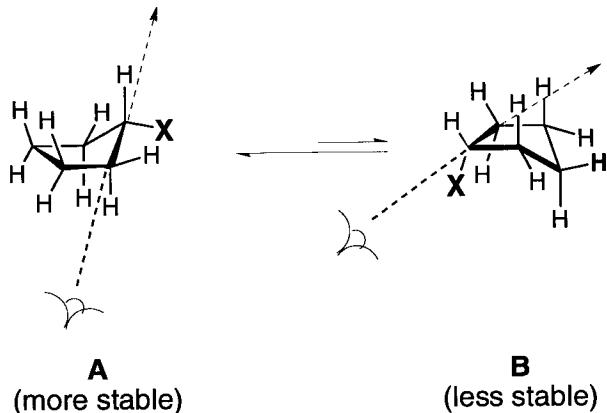
Draw Newman projections along the indicated bonds in **A** and **B**. Use these Newman projections to help you explain the energy difference between the two.

$\theta = \sim 60°$
(close to staggered)

$\theta = 0°$
(eclipsed!)
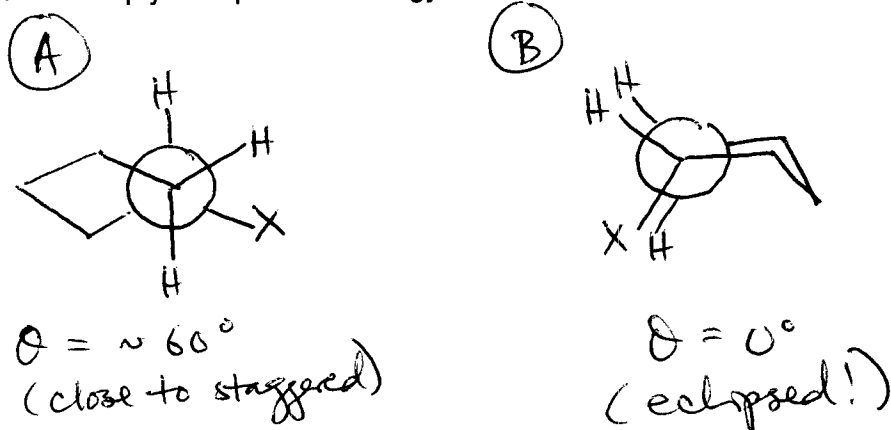
In Ⓐ, the substituent (x) is staggered relative to the H atoms on the adjacent carbons (no energy price to pay). In Ⓑ, the X is eclipsing a H atom on the adjacent carbon. It is reasonable to assume that an X/H - eclipsing interaction is more destabilizing than a H/H - eclipsing interaction. ⟶ Ⓑ higher in energy than Ⓐ.

3. For each of the following, draw both possible chair conformers, and circle the the one that is preferred.

a)

b)

c)
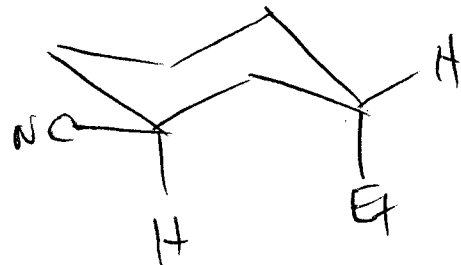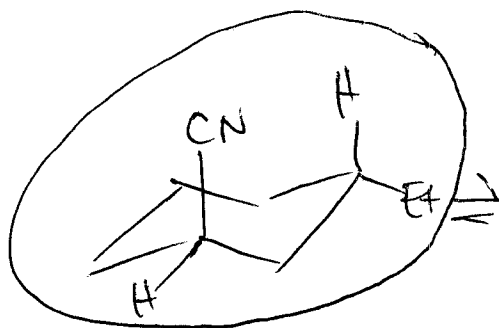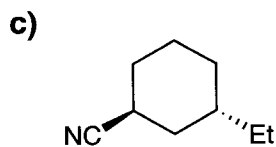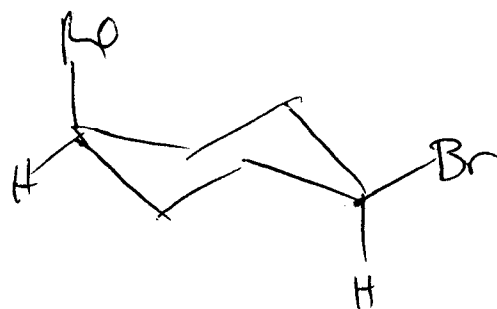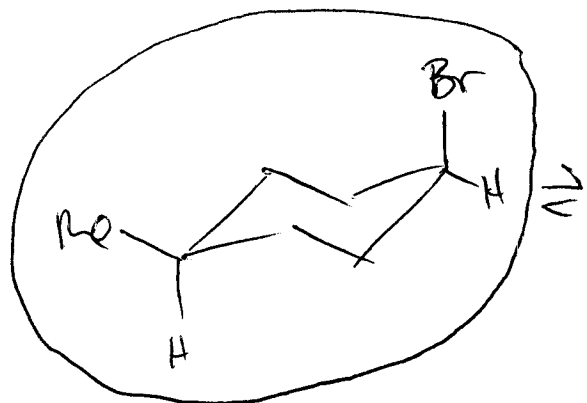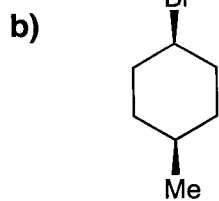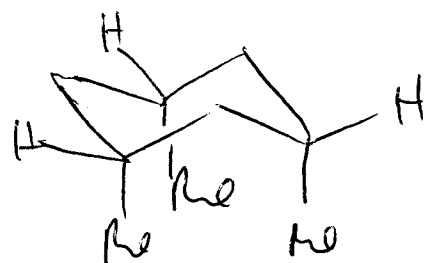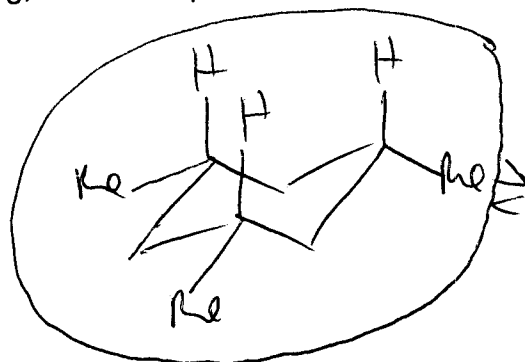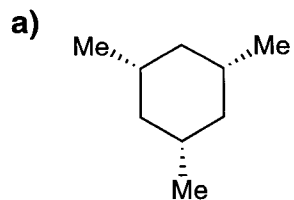
4. As you would expect based on A-values, *cis*-1-*tert*-butyl-4-methylcyclohexane prefers the conformation in which the *tert*-butyl group is equatorial **(eq 1)**. A related molecule, *cis*-5-*tert*-butyl-2-methyl-1,3-dioxane, prefers to put the *tert*-butyl group axial **(eq 2)**. Use what you know about the conformational analysis of cycloalkanes to explain this apparent contradiction.

preferred (moderate 1,3-diaxial) ⟶ ⇌ (severe 1,3-diaxial) **(eq 1)**

(moderate 1,3-diaxial) ⟶ ⇌ **preferred** (no 1,3-diaxial) **(eq 2)**
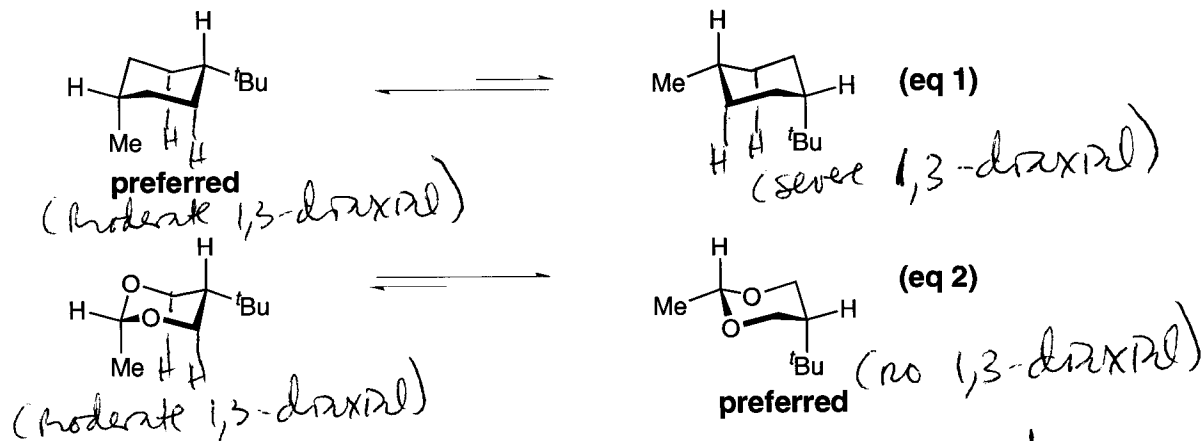
In equation 1, one of the major interactions that destabilizes the molecule on the right is 1,3-diaxial interactions between the t-butyl group and the axial Hs. Replacing the 1,3 carbons with oxygens results in a loss of 1,3-diaxial interactions with the t-Butyl. The 1,3-diaxial interactions with the axial methyl on the conformer on the left become more important, and the conformer on the right is favored.