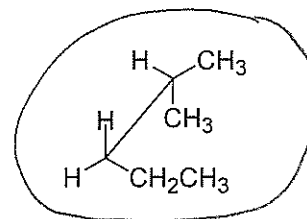
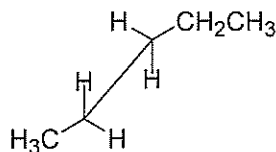
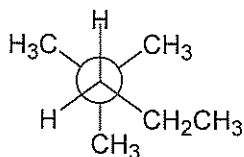
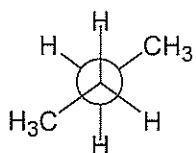


Key - Exam 2 Summer 2008
CHEM 3311

1. Circle the best answer for each of the following questions (20 pts).

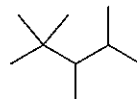
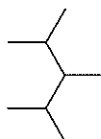
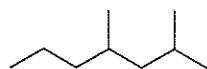
1a. Which of the following structures represents 2-methylpentane?



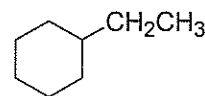
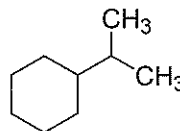
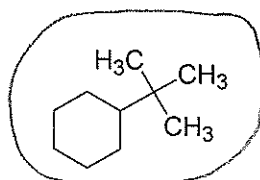
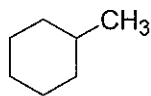
1b. Which of the following molecules has the most angle strain?



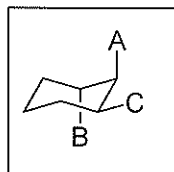
1c. Which of the following molecules is 2,2,4,4-tetramethylhexane?



1d. Which of the following monosubstituted cyclohexanes would exhibit the greatest preference for having the substituent in an equatorial position?



1e. What is the relationship of substituents A and B on this substituted cyclohexane?



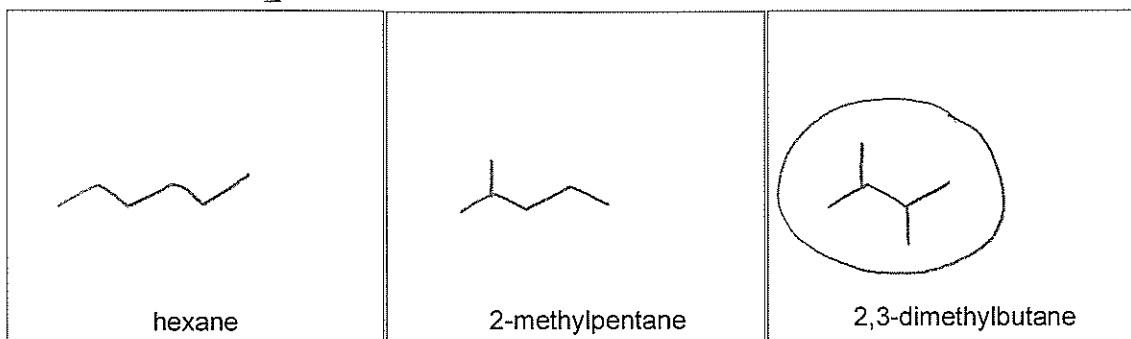
gauche

anti

eclipsed

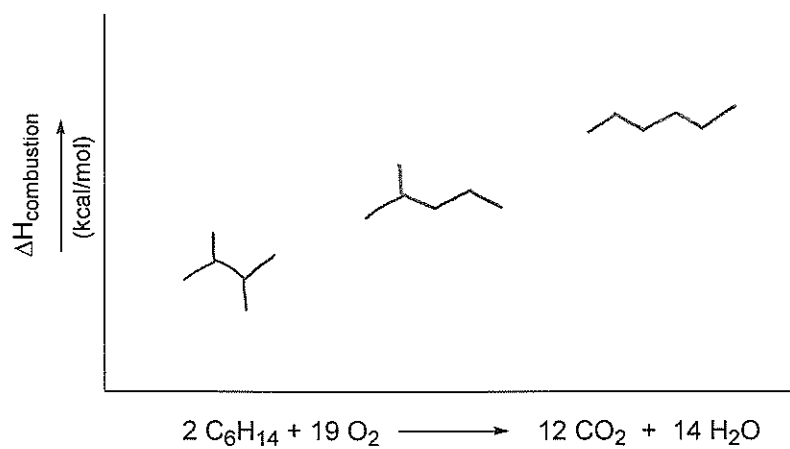
none of these choices

2a. Draw these three C₆H₁₄ constitutional isomers (6 pts):



2b. Put a circle around the compound with the lowest boiling point (3 pts).

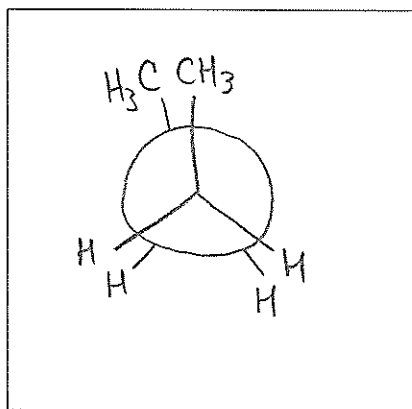
2c. Draw the three compounds on the potential energy diagram at the appropriate levels to correctly reflect their relative $\Delta H_{\text{combustion}}$ values (3 pts).



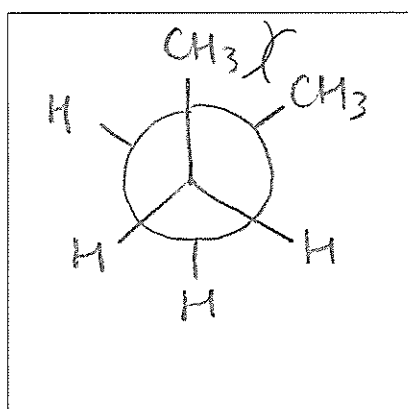
3a. In one or two sentences, explain the difference between torsional strain and Van der Waals strain. Support your answer by providing an example of each of these types of strain using correctly drawn Newman projections of appropriate conformations of butane.

Explanation (6 pts): Torsional strain arises from the eclipsing of bonds - bonding electrons approaching each other too closely cause repulsions that raise the potential energy of the molecule. Van der Waals strain is the result of repulsions due to non-bonded atoms getting too close to one another.

Examples to support explanation (6 pts):

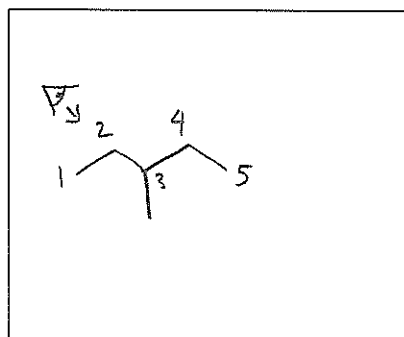


Newman projection to support torsional strain definition

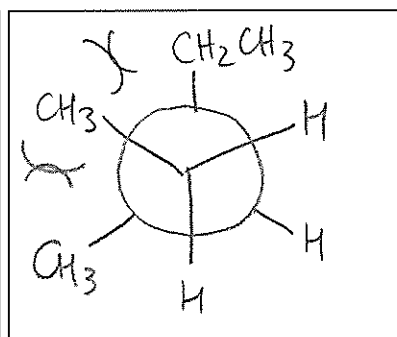


Newman projection to support Van der Waals strain definition

3b. Draw a bond-line structure for 3-methylpentane (2 pts). Then draw the **least stable staggered conformation** of 3-methylpentane looking down the C2-C3 bond (4 pts).

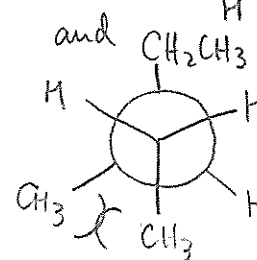
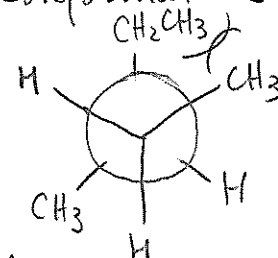


Bond-line drawing of 3-methylpentane



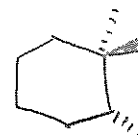
Newman projection of least stable staggered conformation of 3-methylpentane

The other two staggered conformations

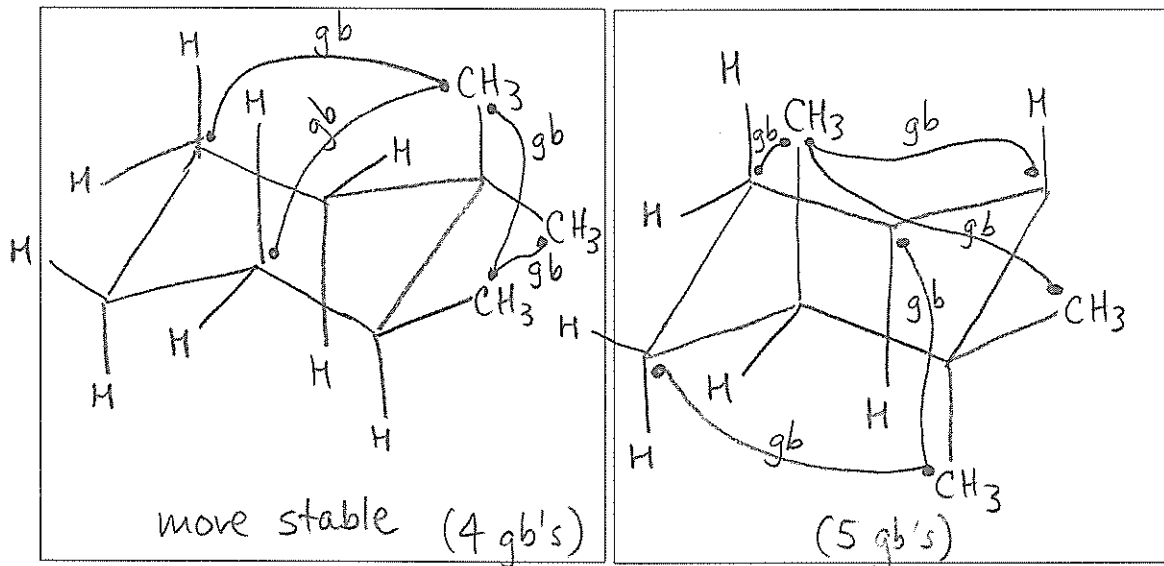


each have only one source of van der Waals strain.

4. The questions on this page involve the molecule 1,1,2-trimethylcyclohexane. Read the entire question before you start drawing so that you don't run out of room.



4a. Draw both chair conformations of 1,1,2-trimethylcyclohexane. Draw your chair structures neatly and in accordance with the guidelines shown in lecture and in the text. Show all axial and equatorial bonds and label every hydrogen on the ring. Points will be deducted for improperly or poorly drawn cyclohexanes (8 pts).



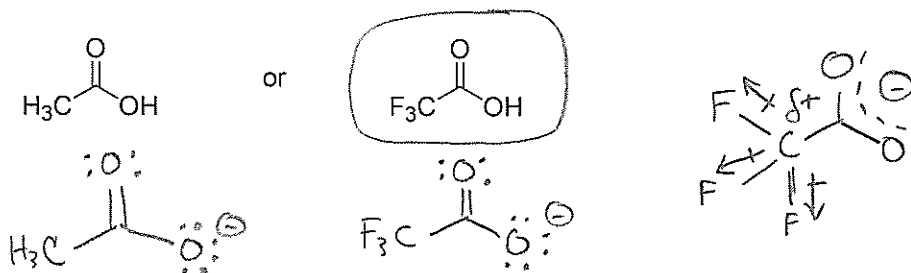
4b. In each conformation drawn above, clearly identify all sources of strain as shown in lecture (8 pts).

4c. Identify the **more stable** chair conformation of this molecule by labeling it clearly (2 pts).

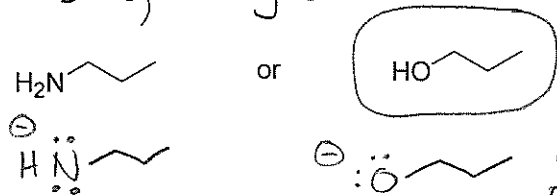
4d. Estimate the energy difference, in kcal/mol, between the two conformations of this molecule. Show how you arrived at your estimate (2 pts).

$$5 \text{ gb's} - 4 \text{ gb's} = 1 \text{ gb} = 0.8 \text{ kcal/mol}$$

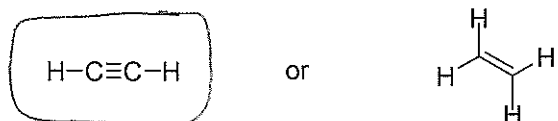
5a. In each of the following pairs of acids, circle the stronger acid (6 pts). Then, for **one of the pairs only**, provide an explanation to support your choice. Use words and properly drawn chemical structures in your explanation (4 pts).



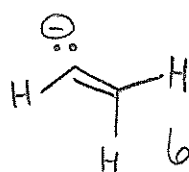
Both conjugate bases are stabilized by resonance. Conjugate base shown at right has additional stabilization via inductive electron withdrawal by the 3 F's, leaving δ^+ on C... δ^+ next to \ominus stabilizes the negative charge.



more stable conjugate base -
O more EN than N, electrons held more tightly (closer to nucleus)



more stable conjugate base - lone pair is in an sp orbital and thus is held more closely to nucleus (more s character, $\uparrow\downarrow$ closer to nucleus, stabilized by positive charge in nucleus)

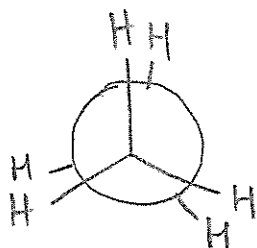


less stable conjugate base - lone pair in sp^2 orbital, farther from nucleus

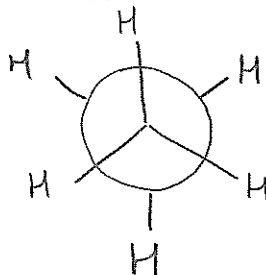
6. Ethane has two important conformations, eclipsed and staggered. In class, we discussed the fact that the energy difference between two structures often can be understood from two approaches: Structure A is stabilized in a way that Structure B is not, or Structure B is destabilized in a way that Structure A is not.

Provide an argument for each of the following two statements. Use both words and drawings, as needed, to support your arguments (12 pts).

Eclipsed ethane is destabilized relative to staggered ethane.



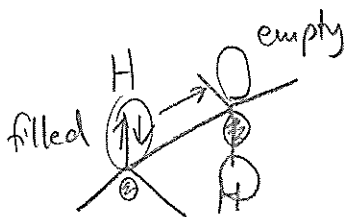
Torsional strain in eclipsed ethane raises the potential energy of this conformation.



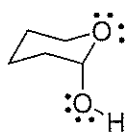
Staggered ethane does not have this destabilization.

Staggered ethane is stabilized relative to eclipsed ethane.

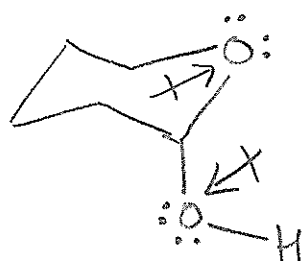
Staggered ethane experiences hyperconjugation, an interaction of filled and empty orbitals in adjacent bonds that lowers the energy of electrons. The orbitals involved are a $\text{CH } \sigma$ (filled) and a $\text{CH } \sigma^*$:



7. All the data we have seen in class suggest that substituents on six-membered rings such as cyclohexane prefer to occupy equatorial positions, when possible, to minimize strain. However, in molecules like the one shown below, the hydroxyl group shows a strong preference for an axial bond. This phenomenon is called the *anomeric effect* and at least two distinct arguments have been made to explain the observed preference. Propose an argument that explains why the hydroxyl group prefers to occupy an axial position in the compound shown here. Provide any structures or drawings that will help support your explanation. (*Hint: If there were no oxygen atom in the ring, the hydroxyl group would prefer an equatorial position.*) (8 pts)

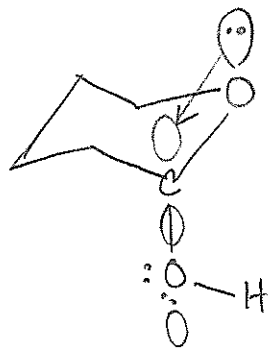


Two possible explanations:



When OH is in axial position, dipoles are aligned in such a way as to minimize potential energy, just like we saw in dipole-dipole intermolecular force

and/or hyperconjugation between a lone pair (a filled orbital) on O in the ring and a C-O σ^* (empty orbital)



(Drawing the exact shape of the C-O σ^* not so important as long as you get the general idea that hyperconjugation is involved.)