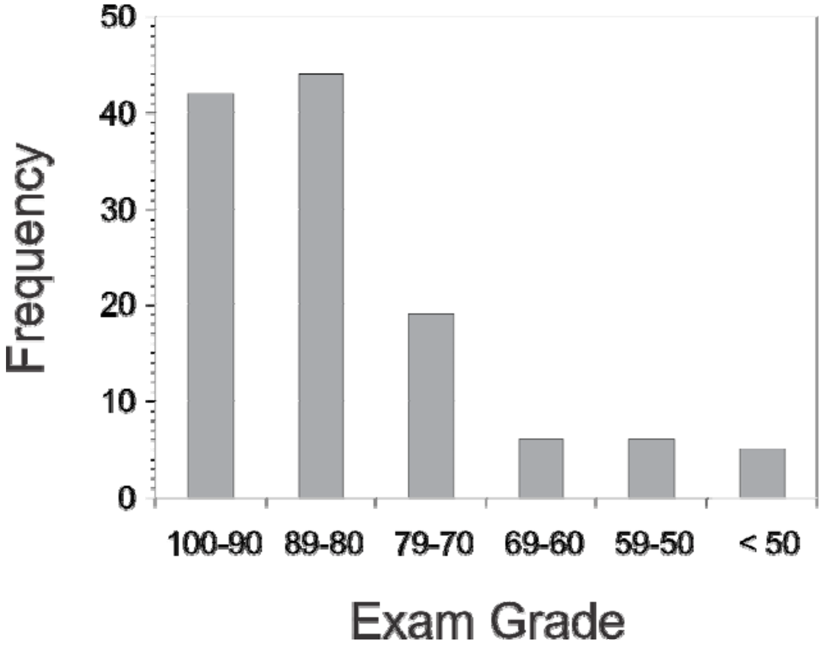
Chemistry 2301 Tuesday, July 1, 2014

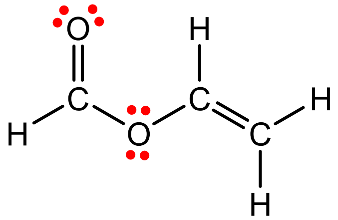
Exam 1
Answer Key

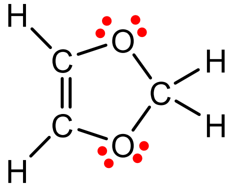
Exam 1 Mean:	81
Exam 1 Median:	83
Exam 1 St. Dev.:	14

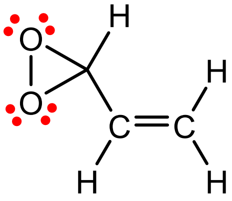


1. (6 pts) **Draw Lewis dash-bond structures** for two constitutional isomers that have molecular formula **$C_3H_4O_2$**, and that have **no formal charges** on any atom. Draw all atoms, bonds, and lone pairs of electrons. In each box, draw just one explicit structure; do not draw multiple resonance structures, and do not draw a resonance hybrid that is an average of multiple structures.

Lots of possible answers to this problem. Just a few examples:







Rubric:

3 points each correct structure (x 2, total of 6).

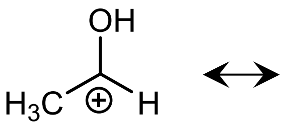
Structures that have formal charges, or that should have formal charges, receive no credit.

No partial credit for structures with an incorrect molecular formula.

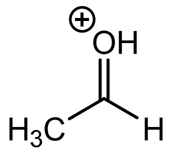
-1 point for each missing electron pair, dot, bond, or atom.

If you drew same structure twice (e.g., as resonance structures), or you drew stereoisomers instead of consititutional isomers, we gave you credit for one but not the other.

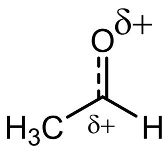
2. (15 pts) For each of the molecules on the left, draw as many of the best Lewis dash-bond resonance structures as there are boxes to put them in. (Feel free to omit lone pairs and C-H's, or draw them—your choice.) Then, below each resonance structure, describe whether each would be a major or minor contributor. Finally, draw a consensus structure that illustrates partial charges and multiple bonds.



resonance structure ②



consensus structure ②



contribution:

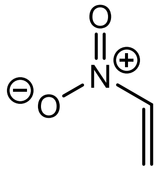
minor ①

(major/minor?)

contribution: **major** ①

meets criterion 3 (electronegativity), but fails 1 & 2 (octets and bonds)

fails criterion 3 (electronegativity), but meets 1 & 2 (octets and bonds)



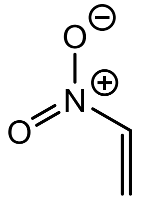
contribution:

major ①

(major/minor?)

↔

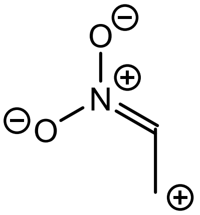
resonance structure ②



contribution: **major** ①

↔

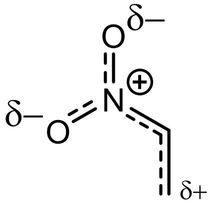
resonance structure ②



contribution: **minor** ①

The nitro- functional group is unusual, in that there isn't any way to draw it using the standard Lewis formalism without drawing at least one formal positive and one negative charge.

consensus structure ②



Rubric:

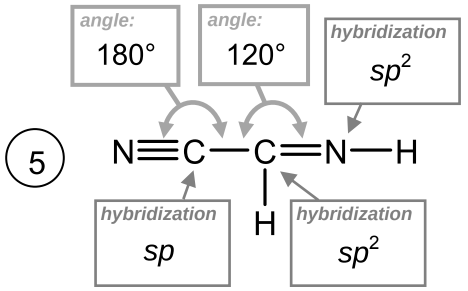
2 points for each structure.

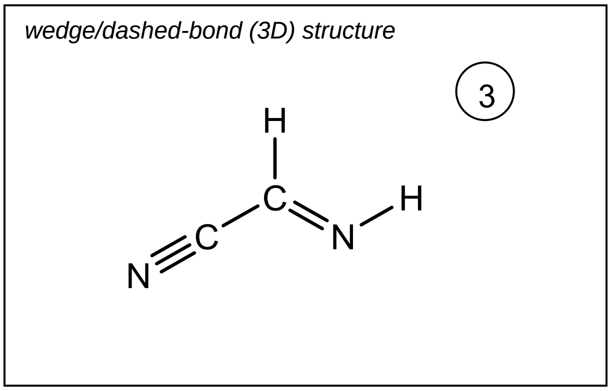
- *1 point for all charges correct and internally consistent*
- *1 point for all correct bond orders*

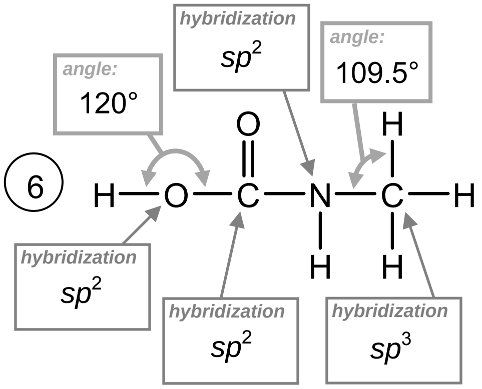
1 point for each contribution.

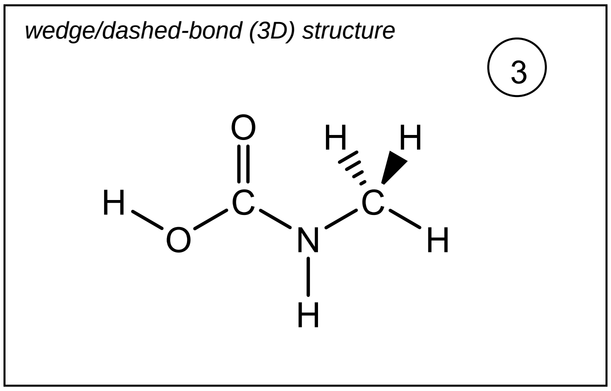
- *Just "major" and "minor" are enough. (No partial credit. Must have correct structure for point.)*

3. (17 pts) For each of the Lewis structures drawn below, in the boxes provided:
   - Draw Lewis wedge/dashed-bond structures that illustrate the most stable three-dimensional structure of the molecule. Draw all atoms, but feel free to omit lone pairs.
   - In the boxes provided, write the hybridization state for any atom heavier than hydrogen.
   - In the boxes provided, give any bond angle indicated by curved arrows in the original Lewis structure.





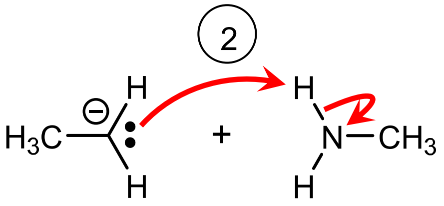




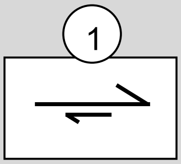
Why are the O and N in the second structure *sp*^{2}-hybridized? They certainly look, at first glance, as if they should be *sp*^{3}-hybridized; the O has two σ bonds and two lone pairs, and the N has three σ bonds and one lone pair, and hybridization math says that would normally mean *sp*^{3}. But in class, I explained that there is an important exception to *sp*^{3} hybridization. If an ostensibly *sp*^{3} center (i) has at least one lone pair, and (ii) is adjacent to a multiple bond, the center will re-hybridize *sp*^{2} and put a lone pair into a *p* orbital. Both the O and the N meet these criteria, so they end up *sp*^{2}-hybridized.

<u>Rubric:</u>
1 point for each bond angle and hybridization.
3 points for each 3-D structure.
-1 for each incorrect center or bond rotation (up to 3).

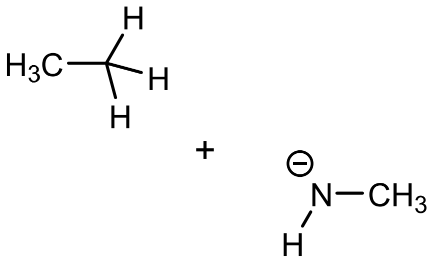
4. (18 pts) For each of the sets of molecules below:
   - Using "electron pushing" (with double-barbed arrows), show how the molecules on the left would react in an acid-base reaction to transfer a proton from one to the other.
   - In the box on the right, draw the conjugate acid and base products of each reaction.
   - In the middle, draw an equilibrium arrow that shows whether you feel the acid-base equilibrium would lie on the left or the right.

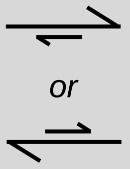


N is more electronegative than C, so it's accommodates the negative charge better. Equilibrium pushed to the right.

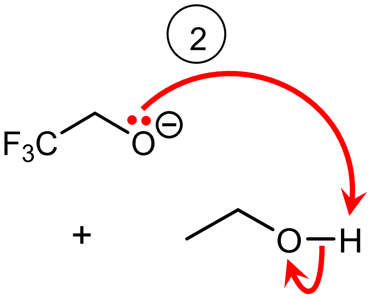


products ③

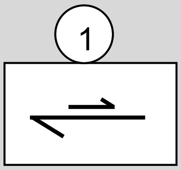




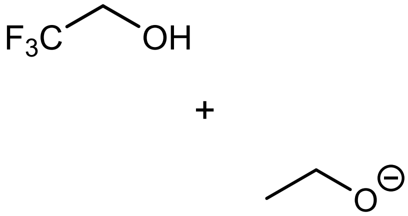
?

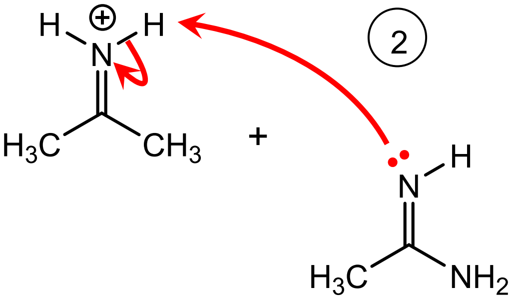


Starting anion is stabilized by inductive effect of electron-withdrawing fluorine groups, but product anion is not. Equilibrium favors starting anion.

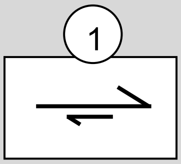


products ③

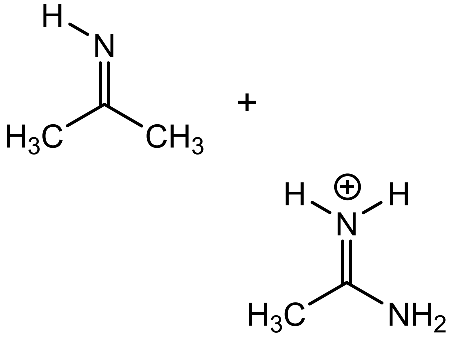




Product cation is stabilized by resonance (with multiple major resonance structures) more than reactant.



products ③

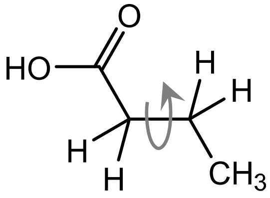


Rubric: For each acid-base reaction,

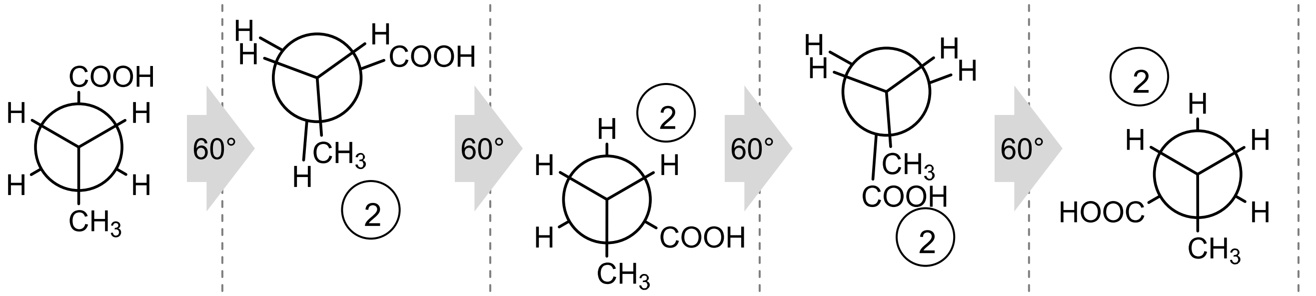
- 2 points for electron pushing (one point each curved arrow).
  - *1 point total for the set of 2 arrows if you drew the lines in the correct place, but arrow heads were incorrect.*
  - *You can start arrow from a lone pair or from a negative charge sign (if available).*
- 1 point for equilibrium arrow direction.
- 3 points for each set of products. Structures must be correct.
  - *2 points partial for one of two products correct.*

5. (26 pts) Butanoic acid (**BA**, drawn at right), is free to rotate about its C2-C3 bond, as shown.

   (a) Starting from the Newman projection I've drawn below, draw four more Newman projections that would be encountered by twisting the central C-C bond in 60° steps. Then, indicate whether each Newman projection represents a ***gauche***, an ***anti***, or an ***eclipsed*** conformer by circling one answer.



BA



gauche	***gauche***	[✓ ***gauche***] ①	***gauche***	[✓ ***gauche***] ①
or	*or*	*or*	*or*	*or*
[✓ ***anti***] ①	***anti***	***anti***	***anti***	***anti***
or	*or*	*or*	*or*	*or*
eclipsed	[✓ ***eclipsed***] ①	***eclipsed***	[✓ ***eclipsed***] ①	***eclipsed***
?	*?*	*?*	*?*	*?*

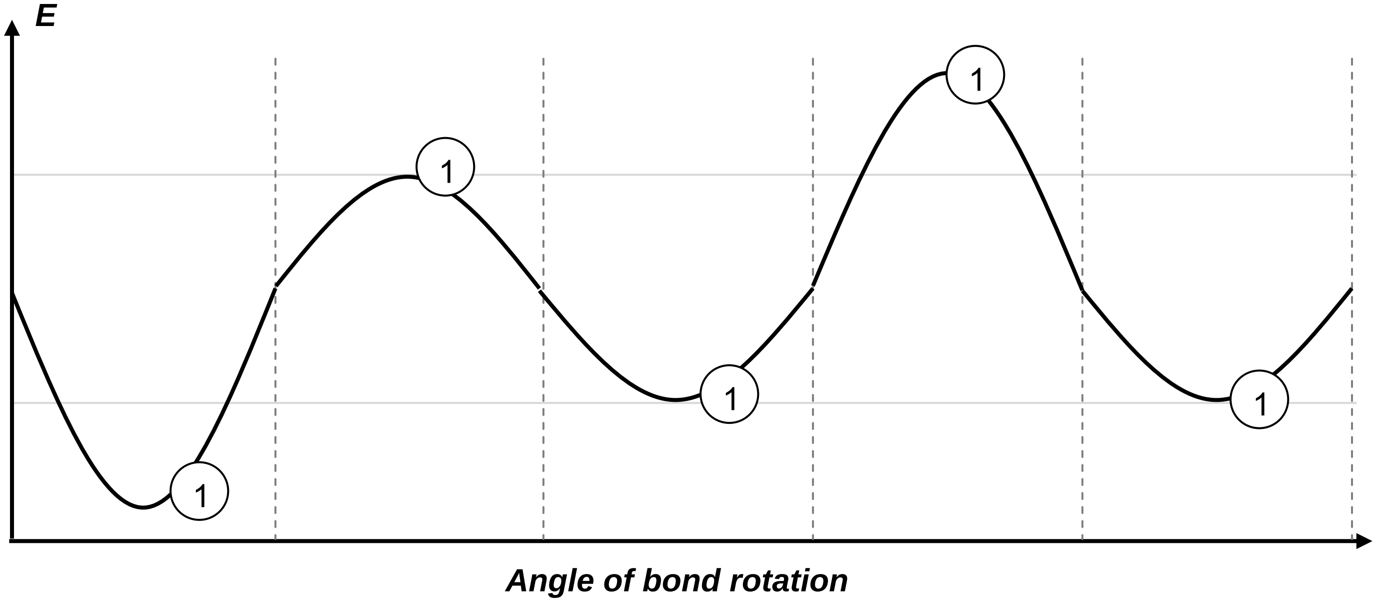
I've rotated the back group clockwise, but you could rotate either the front or the back group, either clockwise or counter-clockwise.

Rubric: No partial credit for incorrect answers, but:

- If you made a mistake in rotating, but everything after the mistake is correct, you receive credit for the correct answers.

- Your circled answers were graded assuming your Newman projections were correct. So if you made a mistake in a Newman projection, but assigned it the correct *gauche/anti/eclipsed* label, you received credit.

(b) What would be the relative energies of the five conformers above? In the space below, draw one continuous potential energy curve that illustrates these energies, in the same order as shown above.



Rubric:

1 point for drawing initial anti state with lowest-energy well.
1 point for drawing first eclipsed state as a hump, but not the highest.
1 point for drawing first gauche state as a higher-energy well.
1 point for drawing totally eclipsed state as the highest-energy hump.
1 point for second gauche state identical to first gauche state.

(c) What is the name of the functional group in **BA** (the molecule from the previous page)?

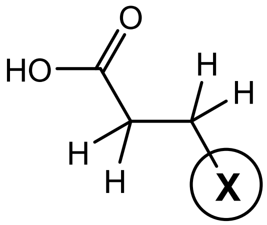
carboxylic acid ②

(d) Within 1 pKa unit, what is the pK_a of **BA**?

2.5 ②

(any answer between 1 and 4, inclusive, counts)

(e) If **BA** had a group other than a $-CH_3$ on the right, how would that affect the energy difference between the eclipsed and anti conformers? For this problem, we'll define "ΔE" as the energy difference between the "totally eclipsed" and anti conformers, such that



$$\Delta E = [E(\textit{totally eclipsed}) - E(\textit{anti})].$$

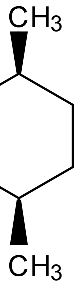
If **X** = $-C(CH_3)_3$ ("*tert*-butyl"), would

ΔE\{**X** = $-C(CH_3)_3$\} be [✓ ***greater than***] ②, ***less than*** *or* ***equal to*** ΔE\{**BA**\} ?

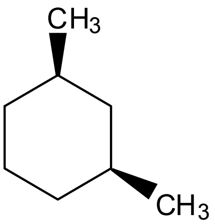
If **X** = -OH, would

ΔE\{**X** = -OH\} be ***greater than***, [✓ ***less than***] ② *or* ***equal to*** ΔE\{**BA**\} ?

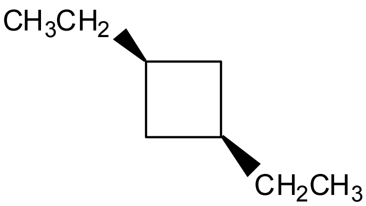
6. (18 pts) This problem deals with the following four isomers of C_8H_{16}:



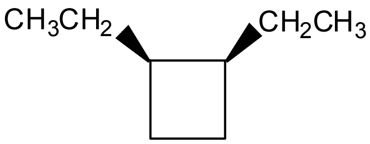
A



B



C



D

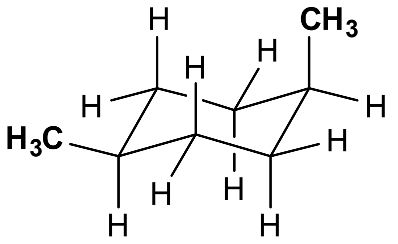
(a) Are these cycloalkanes [✓ ***cis-***] ② or ***trans-*** substituted? (Circle one.)

"*cis*" means "same side" or "same face". All of these are functionalized on the same (top) face, so they are *cis*-substituted.

(b) For each of the molecules **A** and **B**, draw the most stable chair conformation. Include all hydrogens on the cyclohexane ring, but you can abbreviate the methyl groups as “-CH_3”.

most stable chair conformation for **A**

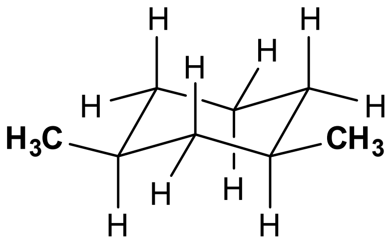
③



You can put the methyl groups on any carbons, as long as they are across from each other (1,4), and on either face (top or bottom), as long as they are on the same face.

most stable chair conformation for **B**

③



Similar comments to left: Substituents can be on any two carbons, as long as they are 2 away from each other (1,3), and on either face (top or bottom), as long as they are on the same face.

Rubric:

3 points for each chair in part (b).

1 point partial for drawing a chair. Any chair.

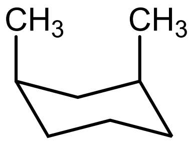
1 point partial for drawing every hydrogen correctly. Every hydrogen must be identifiable as axial/equatorial.

1 point partial for drawing both methyls correctly.

(c) Which of the two cyclohexanes—**A** or **B**—would have the *least* stable chair conformation? What would it look like?

least stable chair conformation

③



Rubric:

3 points for an obviously 1,3-diaxial chair. No partial credit.

(d) Which of these two molecules is more stable, **A** or [✓ **B**]? (Circle one.) ②

In molecule **B**, both groups are equatorial in the most stable chair conformer. In molecule **A**, there is always one group axial.

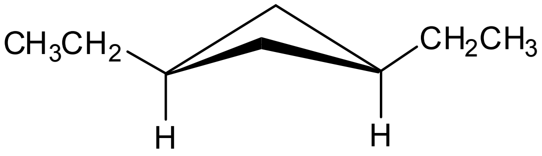
(e) Each of the isomers **A**-**D** has its own heat of combustion (ΔH_c^0), which is the amount of energy given off when the molecule is burned to CO_2 and H_2O. Combustion is always exothermic, so ΔH_c^0 is always negative. In the boxes below, rank the molecules (**A**-**D**) in terms of their heats of combustion, from most exothermic to least exothermic.

most exothermic (most negative ΔH_c^0)	**D**	**C**	**A**	**B**	least exothermic (least negative ΔH_c^0)
(least stable)					**(most stable)**

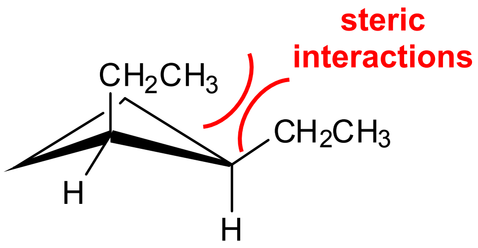
④

The heat of combustion is a measure of molecule stability; the more exothermic combustion is, the more energy the molecule gives off when it burns, the more energy the molecule had bottled up inside of it at the beginning—and the less stable the molecule is. So, the least stable molecule will have the most exothermic ΔH_c^0, and the most stable will have the least exothermic ΔH_c^0.

In this problem, the two cyclobutanes are going to be less stable than the two cyclohexanes, because of ring strain (25 kcal/mol or so). Out of cyclobutanes **C** and **D**, cyclobutane **D** is going to have additional steric interactions between the two adjacent ethyl groups, whereas the ethyl groups in **C** are across from each other:



molecule **C**



molecule **D**

This means **D** is least stable, followed by **C**, then **A** then **B**.

Rubric:

4 points for boxes in (d).

- *2 points partial for (C and D) before (A and B).*
- *1 point partial for D before C.*
- *1 point partial for A before B.*
- *2 points partial for **perfectly** reverse order (B-A-C-D). No other partial credit in this case.*