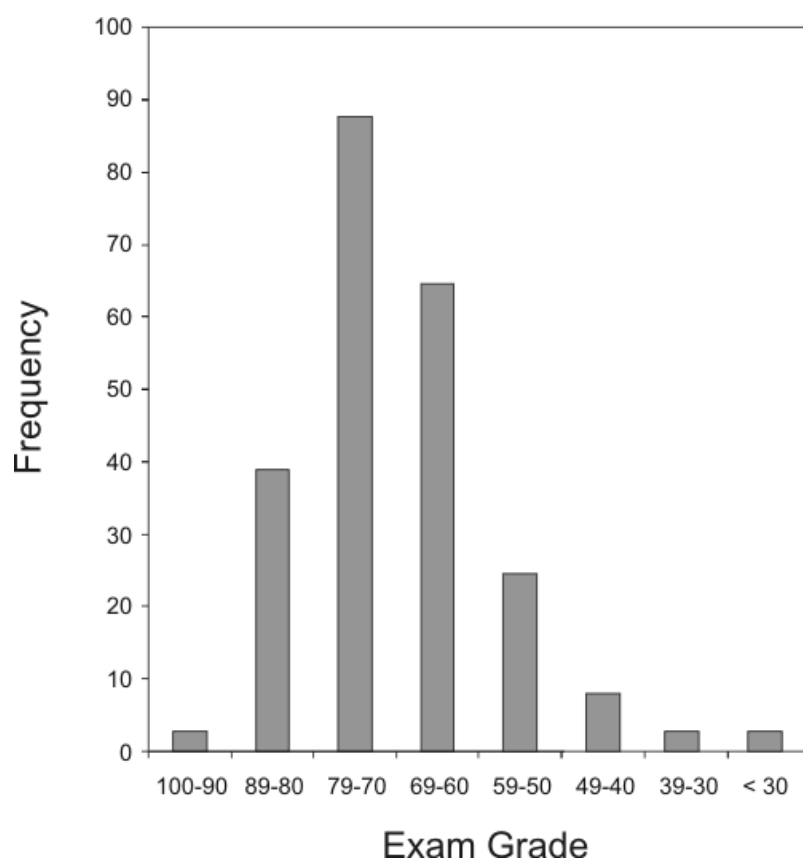


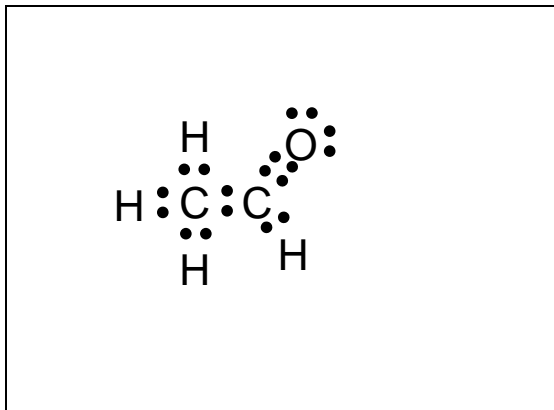
**Exam 1
Answer Key**

Exam 1 Mean: 69
Exam 1 Median: 72
Exam 1 St. Dev.: 12

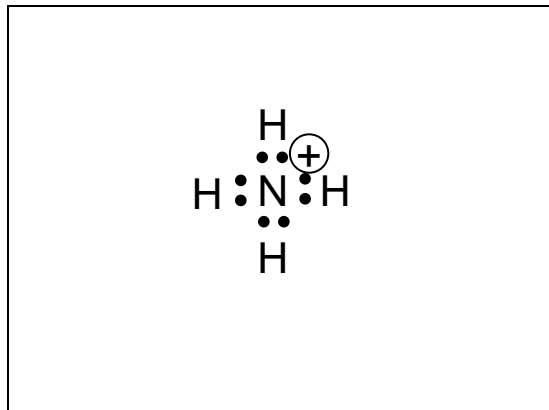


1. (12 pts) Draw Lewis dot structures for each of the molecules below. Draw all valence electrons as dots. If there is a formal charge on the molecule, draw it on the appropriate atom.

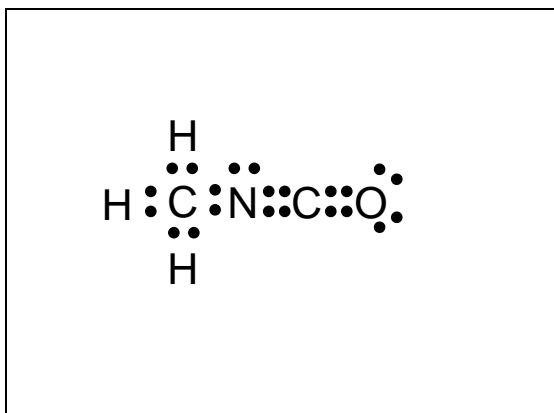
(a) acetaldehyde, CH_3CHO



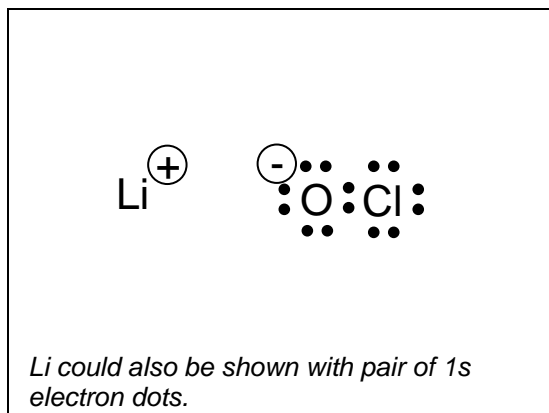
(b) ammonium cation, NH_4^+



(c) methylisocyanate, CH_3NCO



(d) lithium hypochlorite, LiOCl



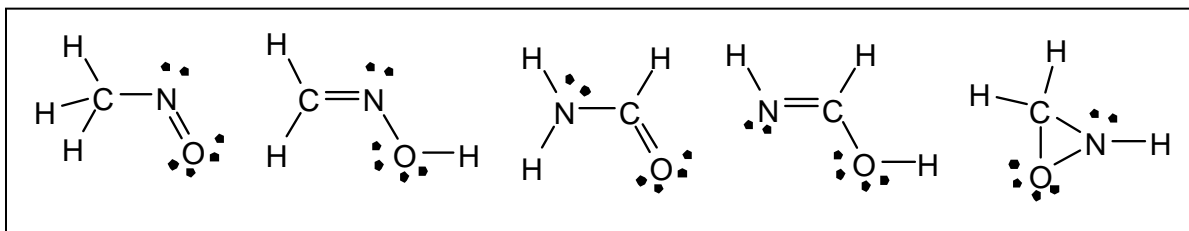
Rubric:

3 points each box.

-1 point for each missing or incorrectly assigned charge or electron pair.

Despite my warnings during the exam, a few of you still drew line-drawings instead of dots for these structures. The instructions were clear, however—we wanted dots. We gave each line drawing 1 point partial credit, as long as it was correct.

2. (6 pts) Draw Lewis dash-bond structures for two constitutional isomers with formula CH_3NO . Draw all atoms and lone pairs of electrons.

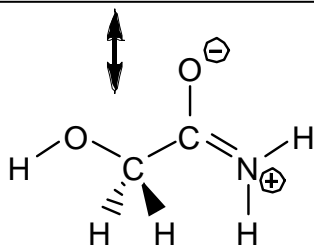
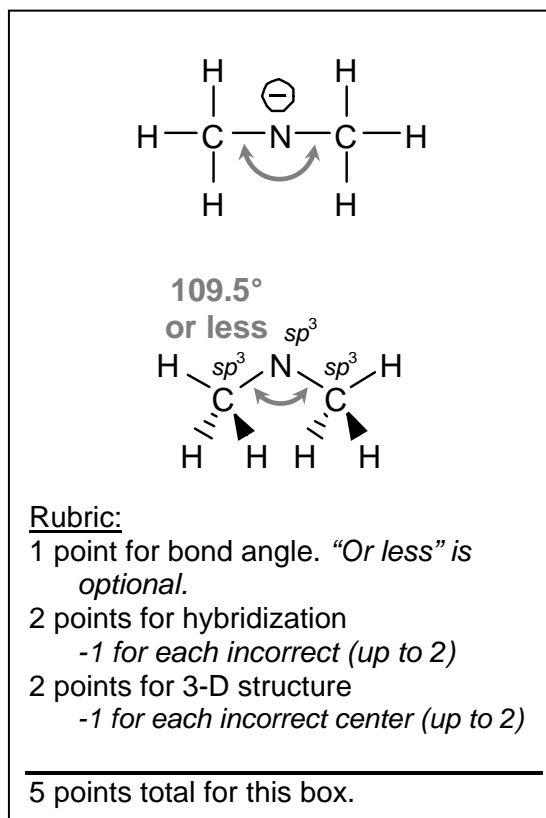
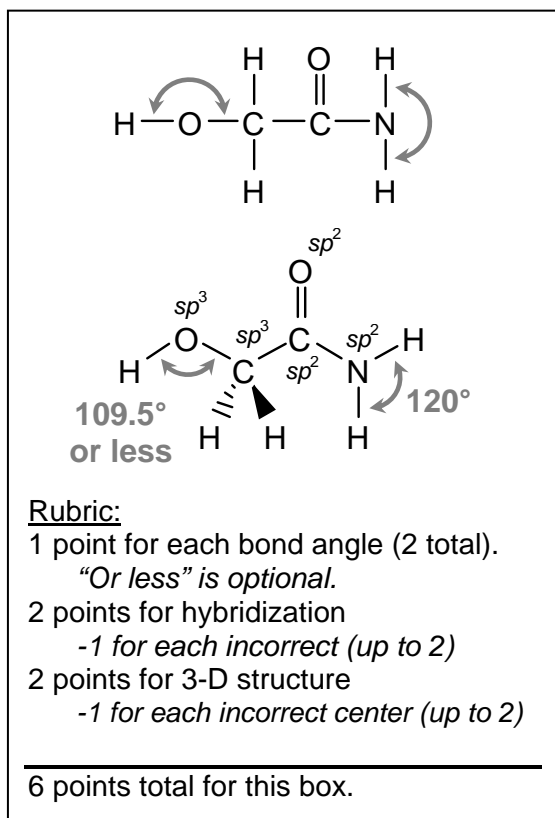


Rubric:

3 points each correct structure.

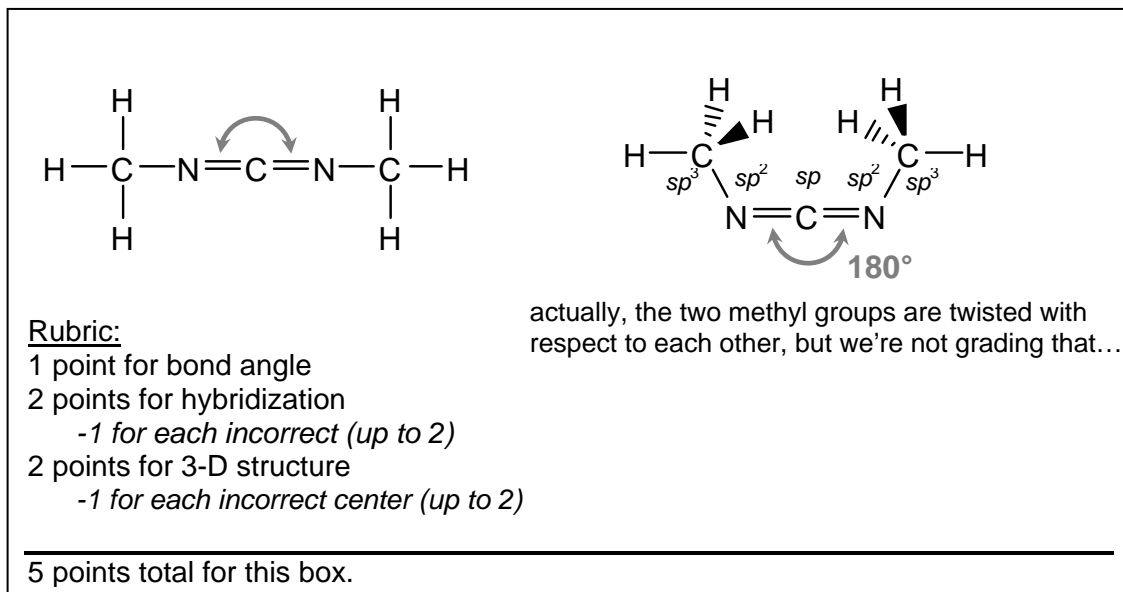
-1 point for each missing electron pair, dot, or bond.

3. (16 pts) For each of the Lewis structures drawn below, in the boxes provided:
- Draw Lewis wedge/dashed-bond structures that illustrate the three-dimensional structure of the molecule. Draw all atoms, but feel free to omit lone pairs.
 - Write the hybridization state on any atom heavier than hydrogen.
 - On your drawing, provide any bond angle indicated by curved arrows in the original Lewis structure.

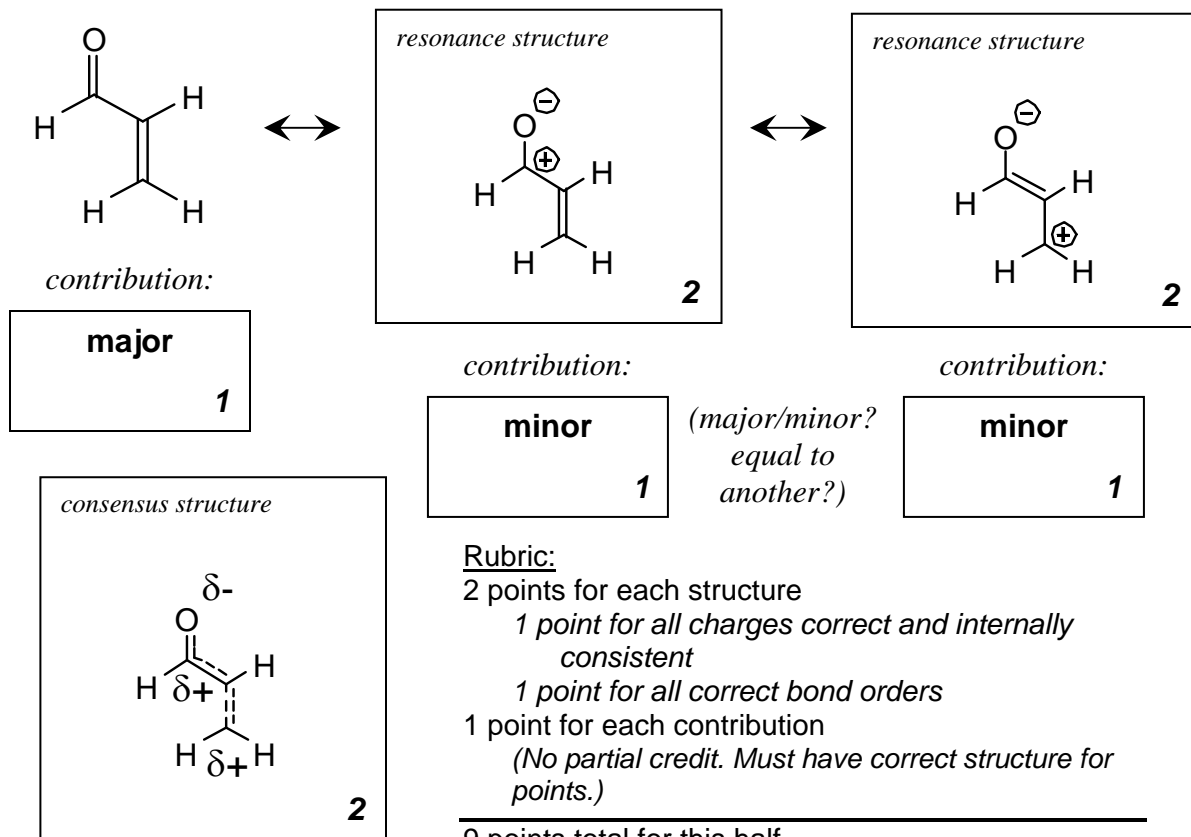


N is sp^2 -hybridized because of this resonance structure. This makes the bond angle 120° .

Why 109.5° "or less"? Remember that, in VSEPR, lone pairs are actually a little more repulsive than σ bonds. They squeeze the bond angle smaller.



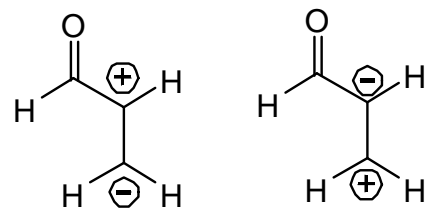
4. (18 pts) For each of the molecules on the left, draw as many Lewis dash-bond resonance structures as there are boxes. (Feel free to omit lone pairs and C-H's.) Then, below each structure, describe whether each would be a major or minor contributor, or equal in contribution with another resonance structure. Finally, draw a consensus structure that illustrates partial charges and multiple bonds.



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
 (No partial credit. Must have correct structure for points.)

9 points total for this half.

A number of you gave one of the two structures on the right as one of the resonance structures. There are no positive features to these resonance structures; they create charge on atoms that don't particularly want the charge, and they leave unfilled octets. So, we gave no credit for these structures.



Rubric:

2 points for each structure

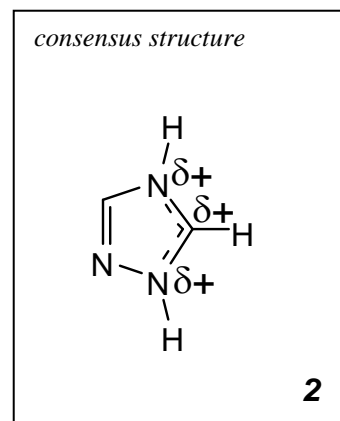
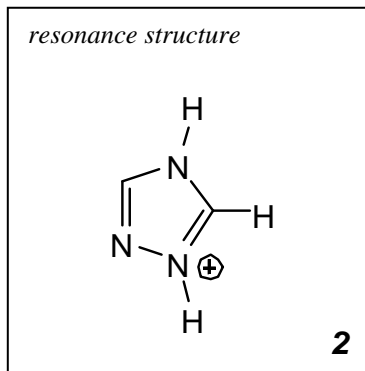
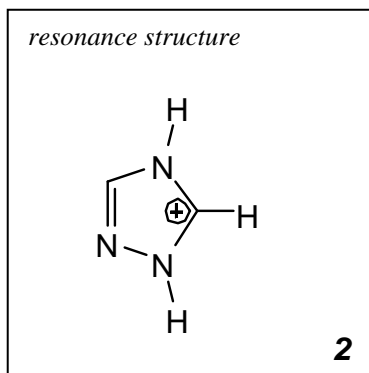
1 point for all charges correct and internally consistent

1 point for all correct bond orders

1 point for each contribution

(No partial credit. Must have correct structure for point. If "equal", must be clear what it's equal to.)

9 points total for this half.



contribution:

minor
or
equal **1**

(major/minor?
equal to
another?)

contribution:

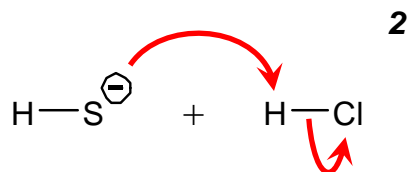
major
or
equal **1**

contribution:

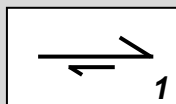
major
or
equal **1**

5. (18 pts) For each of the sets of molecules below:

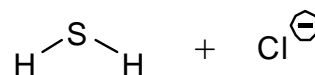
- Using “electron pushing” (with double-barbed arrows), show how the molecules on the left would react in an acid-base reaction to transfer a proton from one to the other.
- In the box on the right, draw the conjugate acid and base products of each reaction.
- In the middle, draw an equilibrium arrow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



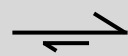
Cl is more electronegative than S, so it's happier with the charge. Equilibrium pushed to the right.



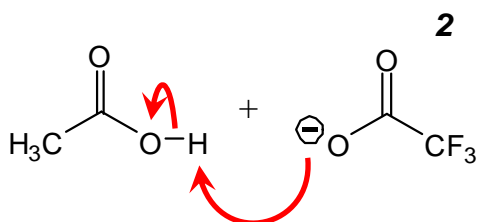
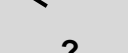
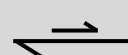
products



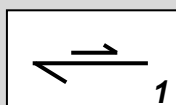
3



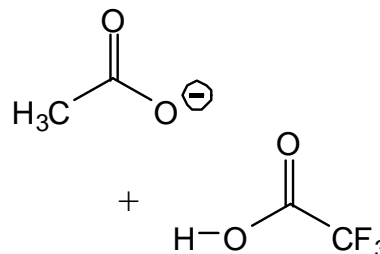
or



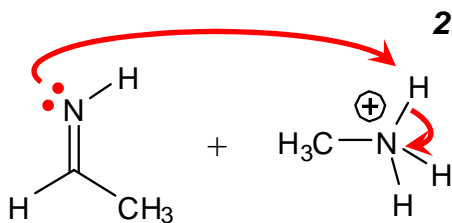
Inductive effect of electronegative F atoms stabilizes anion. So equilibrium to the left.



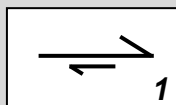
products



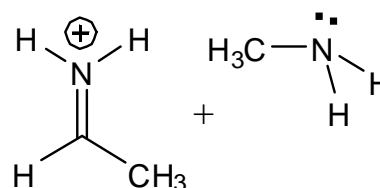
3



Cation product stabilized by resonance, but cation starting material is not.



products



3

Rubric: For each acid-base reaction,

2 points for electron pushing (one point each curved arrow).

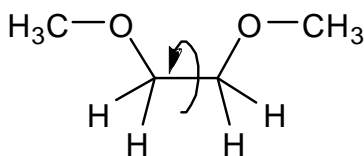
1 point total for the set of 2 arrows if you drew the lines in the correct place, but arrow heads were incorrect.

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.

6. (20 pts) For the molecule 1,2-dimethoxyethane (below):



(a) Draw Newman projections for the six conformers—three staggered and three eclipsed—accessed by rotation of the central C-C bond.

(b) Label which conformer you would expect to be most stable, and which you would expect to be least stable. If there are multiple conformations that are equally most or least stable, label them all.

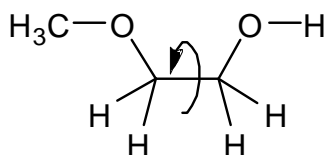
<p><i>Staggered conformers</i></p> <p>most stable</p>	<p><i>Rotating the back and keeping the front steady,</i></p>		<p>7</p>
<p><i>Eclipsed conformers</i></p>			<p>7</p>

Rubric: In each box,

2 points for each conformer.

1 point for each assignment of most/least stable. Must be exactly correct.

- (c) The most stable conformer of 2-methoxyethanol (below) is not the same as that of 1,2-dimethoxyethane, even though the two molecules differ only by a methyl group on one oxygen.



Draw the most stable conformer (or conformers, if there are multiple ones that are equally stable) of this molecule. Then, explain why this conformer is more stable than the one (or ones) you chose in part (b).

<p><i>Most stable conformer(s)</i></p> <p>(tie)</p> <p style="text-align: right;">4</p>
<p><i>Why different from (b)?</i></p> <p>Normally, the gauche conformer of the molecule would be slightly higher in energy than the anti conformer, due to steric interactions between the substituents. But in this case, the -OH group is <u>attracted</u> to the -OCH₃ by hydrogen bonding:</p> <p style="text-align: right;">2</p>

Rubric:

4 points for both stable conformers.

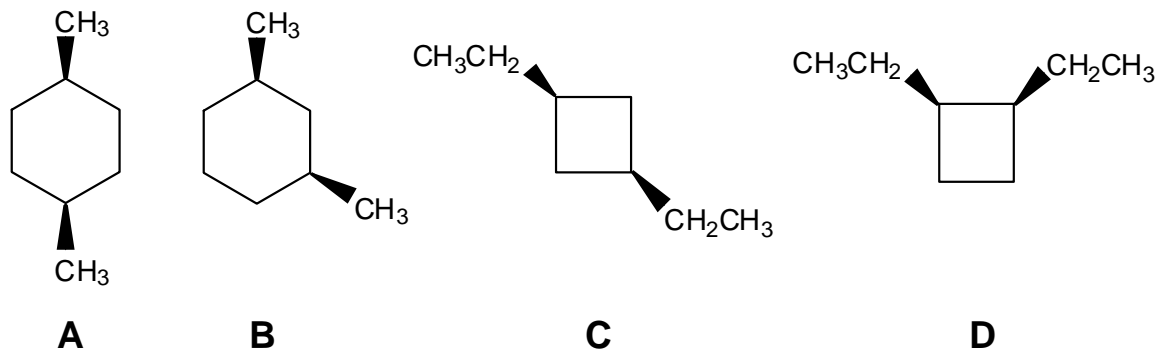
2 points partial if you draw only one.

0 points for other answers (e.g., all three staggered, one of the eclipsed ones).

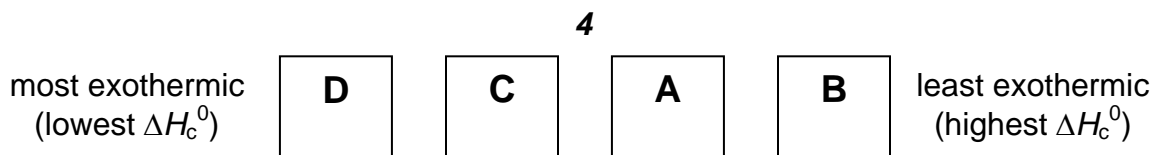
-1 for minor error (-CH₃ instead of -OCH₃, etc.).

2 points for "hydrogen bonding" anywhere in answer to "why".

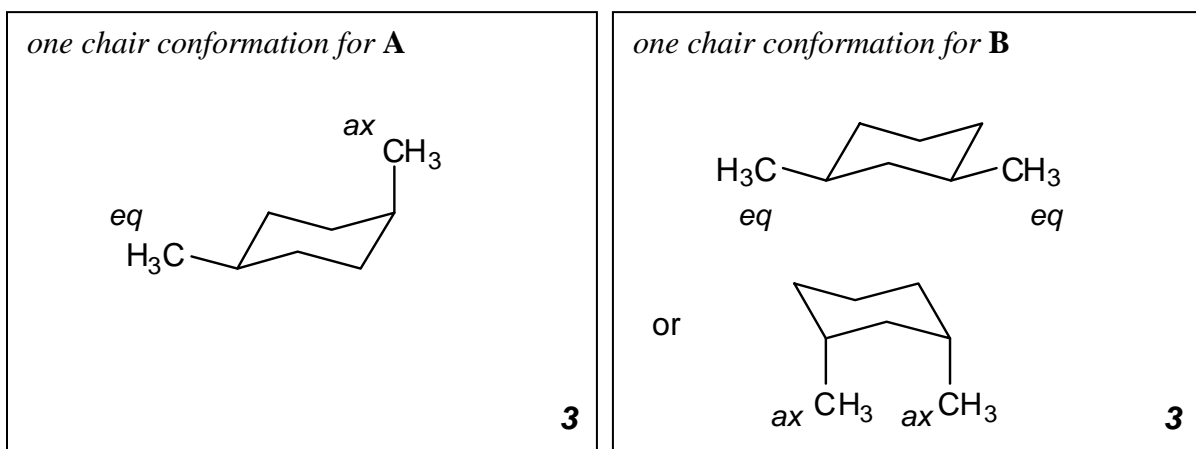
7. (10 pts) Each of the four isomers of C_8H_{16} shown below has its own heat of combustion (ΔH_c^0), corresponding to the enthalpy of burning one mole of the substance to CO_2 and H_2O . Combustion is exothermic, so $\Delta H_c^0 < 0$ for all four isomers.



- (a) In the boxes below, rank the molecules (**A-D**) in terms of their heats of combustion, from most exothermic to least exothermic.



- (b) For each of the substituted cyclohexanes **A** and **B**, draw one chair conformation. On each drawing, label each (non-hydrogen) ring substituent as axial (“ax”) or equatorial (“eq”).



Rubric:

1 point for each A-D in correct box.

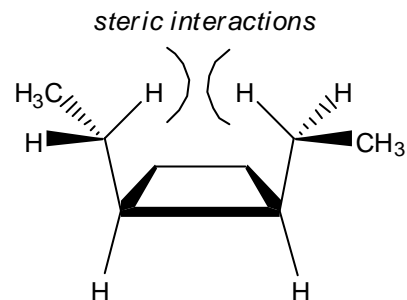
2 points for each conformer structure.

-1 point for errors that don't affect your answer (errors in drawing chair, etc.)

1 point for each structure's ax/eq assignment. You can get this point even if your structure is incorrect; just label ax/eq correctly on your structure.

This problem was really about strain and instability; the molecule that is most strained, that is least stable, will have the most energy bottled up inside of it and will combust to give off the most energy. So, asking “from most exothermic to least exothermic” is the same as asking “from least stable to most stable.”

The cyclobutane rings are really unstable; your book says they have ~27 kcal/mol of extra strain energy. So **C** and **D** will be the least stable of the four. But which of these two is worst? Cyclobutane is almost flat, resulting in eclipsing interaction between neighboring substituents. In **C**, none of the neighbors are sterically problematic, but in **D**, the two ethyl groups will repel one another. This should make **D** less stable than **C**.



So what about **A** and **B**? They have no ring strain, but what other sources of instability might distinguish these two? As the answer key shows, **A** has one equatorial and one axial methyl group, and no flipping of the chair will change this. By contrast, **B** has a conformation that allows both methyl groups to be equatorial, and presumably (because axial substituents are less stable than equatorial ones) the molecule will choose this conformation over the one in which both are axial. **A**'s one axial substituent should make it less stable than **B**, which has none.