Dr. Steven Pedersen October 3, 2016

Chemistry 3A
Midterm 1

Student name: Answer Key

Student ID: _____ (Also include your SID in the top left corner of each page)

Student signature: _____

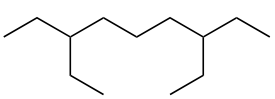
Problem 1	_____	(22 pts)
Problem 2	_____	(18 pts)
Problem 3	_____	(16 pts)
Problem 4	_____	(20 pts)
Problem 5	_____	(18 pts)
Problem 6	_____	(18 pts)
Problem 7	_____	(18 pts)
Problem 8	_____	(20 pts)
Total Points	_____	(150 pts)

No Calculators Allowed
No Molecular Models Allowed
Be Sure Your Exam has 10 Pages

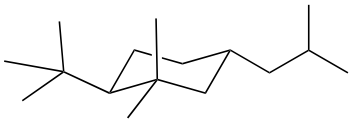
ALL ANSWERS MUST BE ON THE FRONT OF EACH PAGE. ANY ANSWERS ON THE BACK OF A PAGE WILL NOT BE CONSIDERED FOR GRADING.

1. There will be NO partial credit for this problem. Avoid careless errors by checking over your answers. (22 pts)

A. Provide a systematic (IUPAC) name for each of the following compounds. Use common nomenclature for any branched substituents.

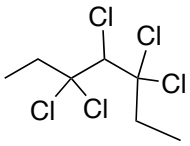


3,7-diethylnonane



trans-2-*tert*-butyl-5-isobutyl-1,1-dimethylcyclohexane

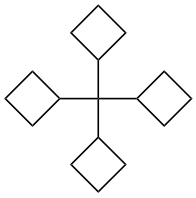
there are many other possible names, but all must have a trans in front of them



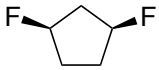
3,3,4,5,5-pentachloroheptane

B. Draw a structure for each of the following names. For cycloalkanes use flat rings. For all others use bond-line notation.

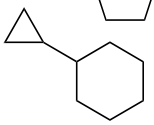
- tetracyclobutylmethane



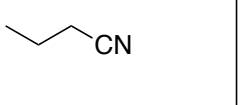
- *cis*-1,3-difluorocyclopentane



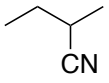
- cyclopropylcyclohexane



C. Based on the information provided, draw structures for the names given in the blank boxes.

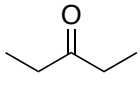


propylcyanide

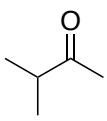


sec-butylcyanide

Provide a Structure



diethylketone



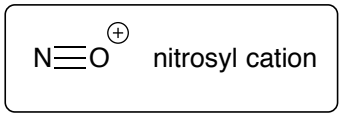
isopropylmethylketone

Provide a Structure

As mentioned in class, if your bond to the CN group is not conclusively shown going to the carbon, you received no credit for this problem.

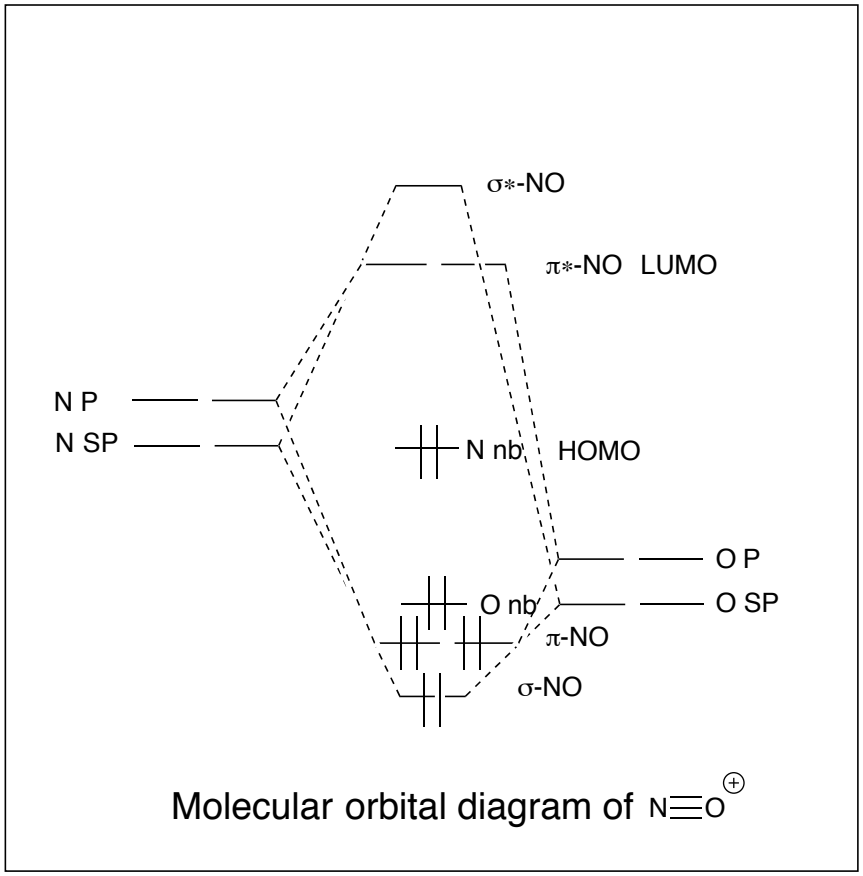
2. (18 pts)

A. The major contributing resonance structure for the nitrosyl cation is shown below. Construct a molecular orbital diagram for this compound (specifically for this resonance contributor) using the following guidelines and labeling schemes. BE SURE TO INCLUDE EVERYTHING ASKED FOR BELOW.

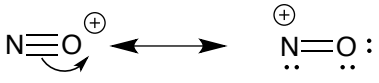


- Clearly indicate which orbitals are being combined to make molecular bonding orbitals.
- Label all the levels as σ, π, nb (non-bonding) etc. For non-bonding levels be sure to label which atom it is associated with.
- Fill in all of the electrons.
- Label the HOMO and LUMO

  Hint: All bonds, σ or π, will be lower in energy than any non-bonding levels, filled or unfilled.

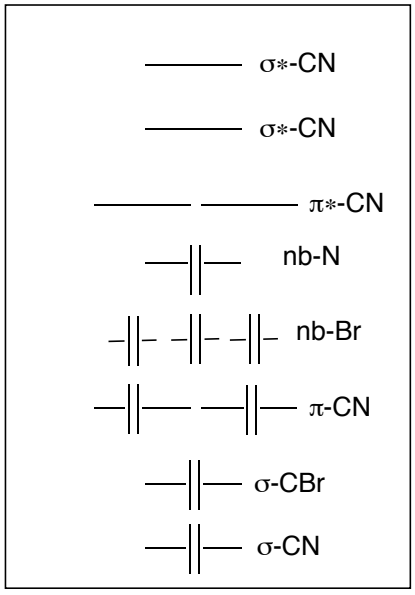


B. Show the other resonance structure for the nitrosyl cation. You must include all lone pairs of electrons and any relevant charges. You must also use an electron-pushing arrow(s) to indicate how you arrived at the other structure.

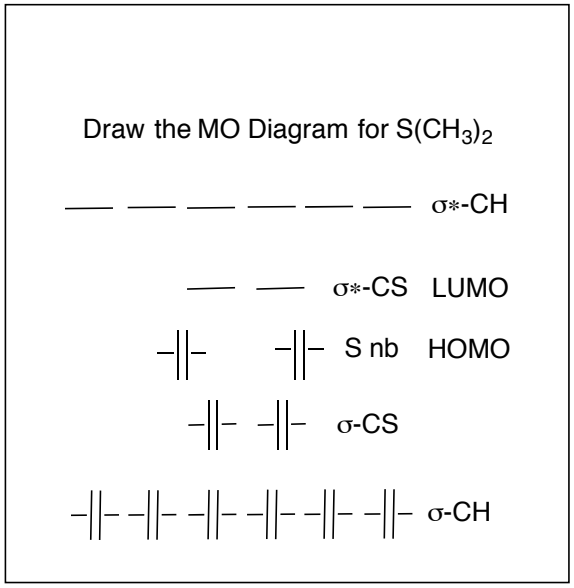


3. Cyanogen bromide (BrCN) is used to cleave peptides and proteins specifically at sites that contain methionine residues (an amino acid). The following questions are related to this reaction. (16 points)

A. The MO diagram for cyanogen bromide is provided below. Next to this is an empty box. Draw the MO diagram for dimethylsulfide ($S(CH_3)_2$) in this box. Label all of the levels as σ, π, nb (non-bonding) etc. For any non-bonding level(s) be sure to label which atom it is associated with. Fill in the electrons and label the HOMO and LUMO.

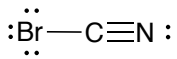


Electrophile

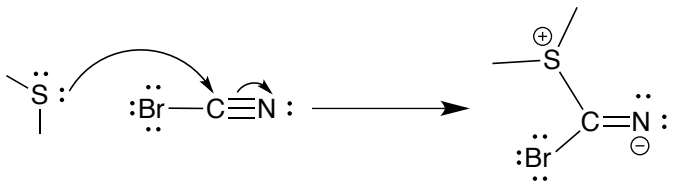


Nucleophile

B. Based on the MO diagram shown in Part A, draw the structure of cyanogen bromide showing all bonds and lone pairs of electrons.

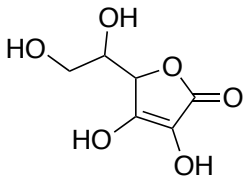


C. The methionine residue mentioned in the introduction to this problem has a $RSCH_3$ group (the nucleophile) that reacts with cyanogen bromide (the electrophile). Dimethylsulfide behaves similarly. Based on the MO diagrams in Part A and Frontier Molecular Orbital theory, use electron-pushing arrows to show how dimethylsulfide reacts with cyanogen bromide. Be sure to draw the product of this reaction AND include any relevant charges. Your reaction and the product shown MUST be consistent with your MO diagrams.



If your product was missing any relevant charges, you received no credit for part C.

4. Vitamin C (also known as ascorbic acid) is an important cofactor in many enzyme processes and is often touted as a means of "fighting" off the common cold (whether it helps or not is an ongoing debate). All of the questions below relate to Vitamin C. (20 points)

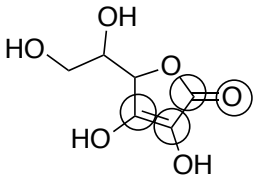


Vitamin C

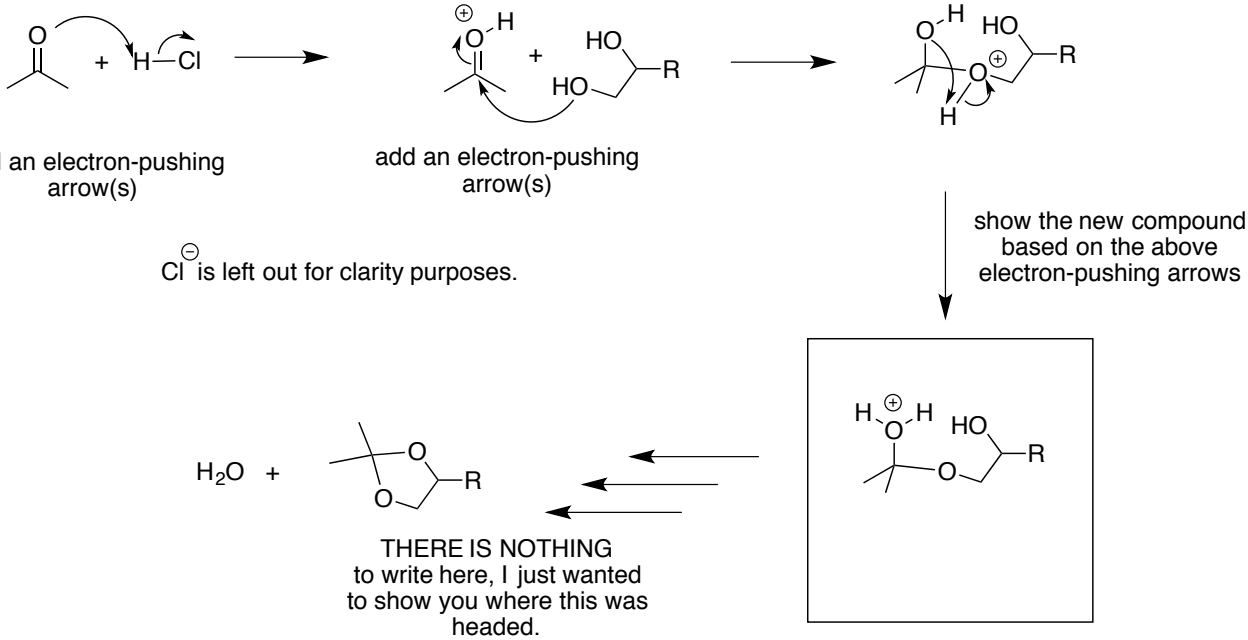
A. What is the molecular formula of Vitamin C? Express your answer in the form $C_xH_yO_z$

$C_6H_8O_6$

B. On the structure below, circle all SP^2 atoms. Wrong answers cancel right answers.

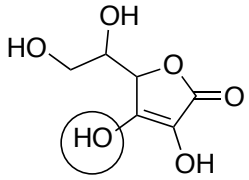


C. Complete the following mechanistic scheme that shows a few steps involved in "protecting" two of the four alcohol groups in Vitamin C. Note that the ring portion of Vitamin C has been designated R. Also, the chloride ion that balances the positive charge after the first step has been left out for clarity purposes. In the first two steps you will add electron-pushing arrows to indicate how the new structure is arrived at and in last equation you will draw a new structure based on the electron-pushing arrows that are provided.



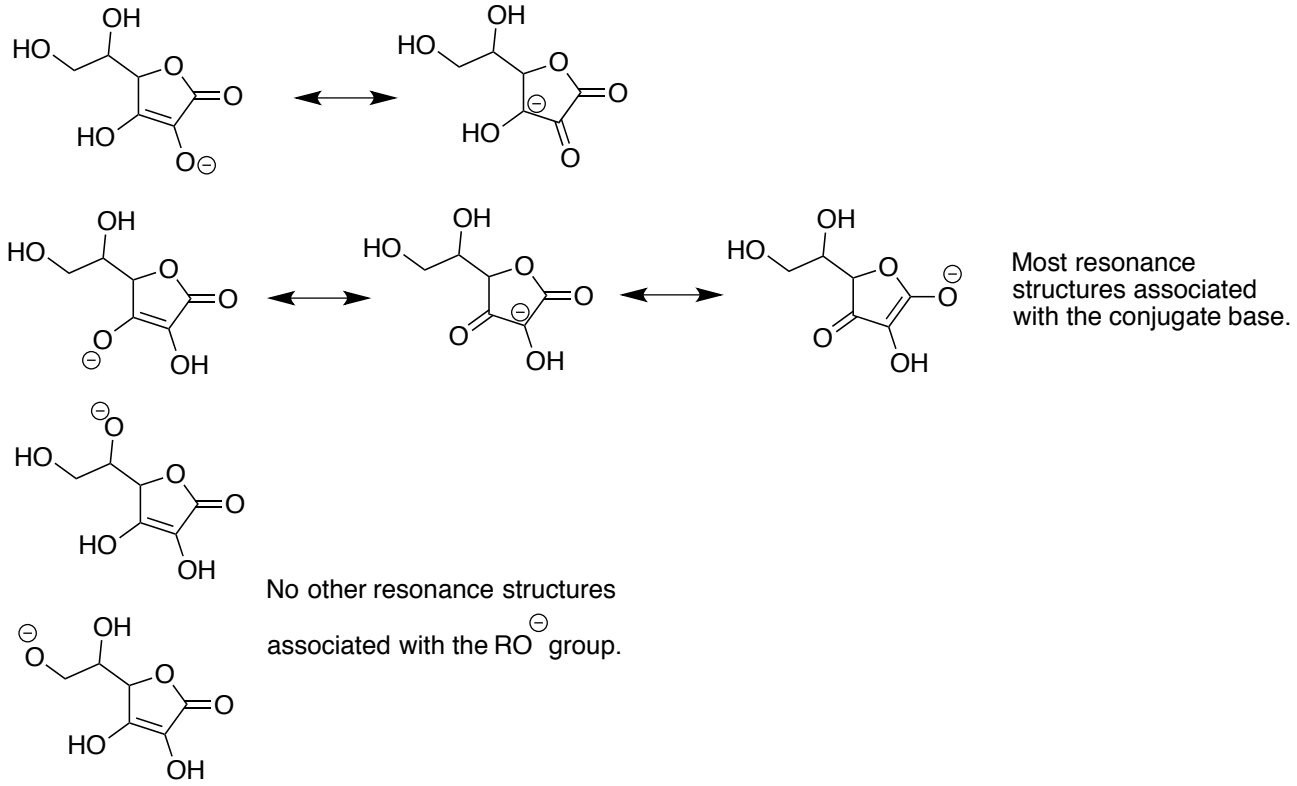
Problem 4 continued on the next page.

D. Which one of the four hydroxyl protons (i.e. the OH groups) in Vitamin C is most acidic? Circle it on the drawing below and provide a brief explanation using words and drawings. Your explanation must relate to the other possible hydroxyl protons. No credit for the correctly circled hydroxyl group if no explanation or a wrong explanation is provided.



You will not need this whole space!

As can be seen below, the conjugate base of the hydroxyl group circled above will have the most resonance structures. Therefore, this will be the most stable conjugate base of the four possible conjuagate bases which means the acid it comes from will be the most acidic.

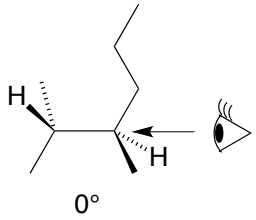


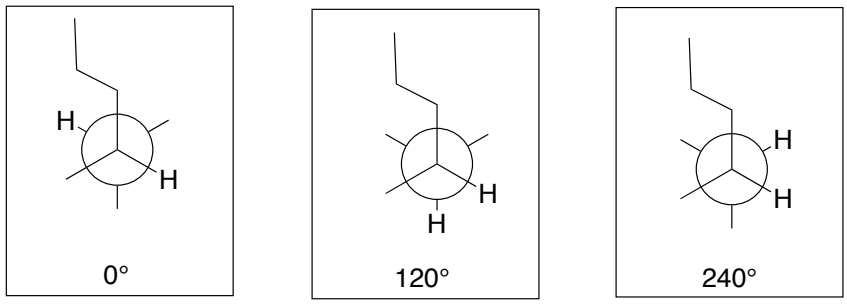
You needed to have drawn several CORRECT resonance structures to receive most of the credit for this problem. If you only showed resonance structures for the most stable conjugate base and didn't show how the other conjugate bases did not have as many resonance structures, you did not receive full credit.

5. (18 pts)

A. Draw Newman projections of the three staggered conformations of the compound shown below. You must follow the instructions below:

- Hold the front carbon constant
- Rotate the back carbon counterclockwise.





Three staggered conformers, holding the front atom constant and rotating the back carbon counterclockwise.

B. Order the relative energies of the three staggered conformers in Part A from lowest energy to highest energy. Use the degree rotation to identify each compound and place it in the appropriate box. Justify your ranking by discussing the interactions found in each conformer. No credit for the correct ranking will be given unless the interactions within each conformer are discussed.

0°	240°	120°
Lowest Energy Conformer	"Inbetween" Energy Conformer	Highest Energy Conformer

Use the degree rotation in Part A to identify each conformer.

Discuss the interactions below:

0° has a: Me/Me and Me/Pr

120° has a: Me/Me, Me/Pr and Me/Pr

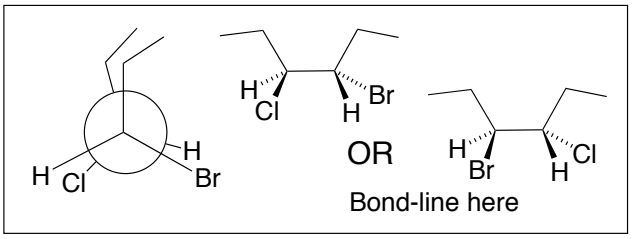
240° has a: Me/Me, Me/Me and Me/Pr

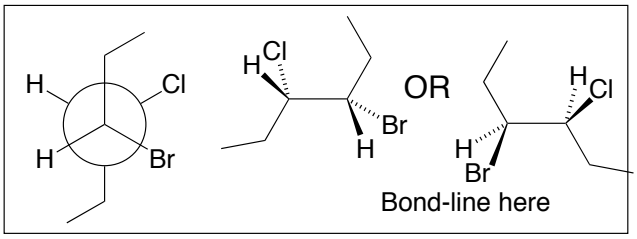
C. Circle the correct answer to the following statement. For an acyclic alkane, the lowest energy eclipsed conformation will be lower in energy than the highest energy staggered conformation.

TRUE FALSE

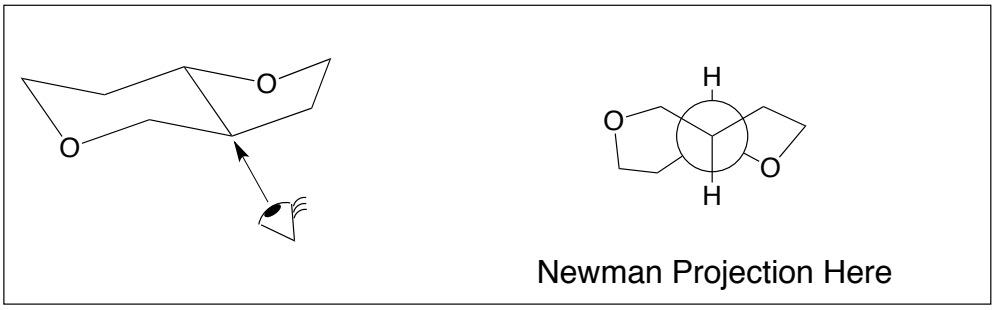
6. (18 pts)

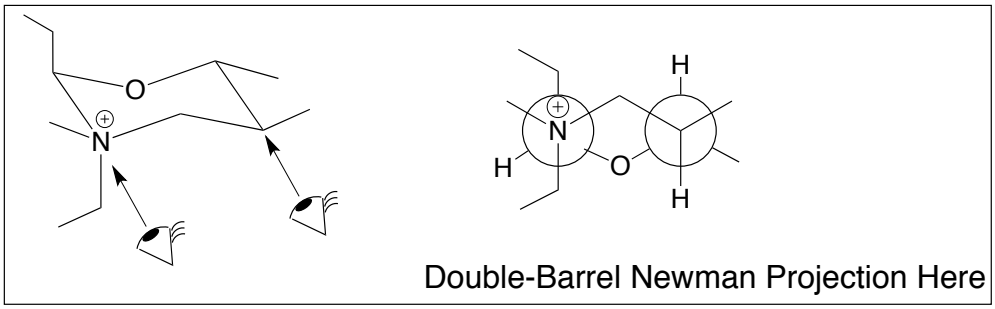
A. Draw the bond-line structures that exactly represent the Newman projections shown below. There is no partial credit. ***If one substituent is incorrectly drawn, the entire structure is incorrect.***



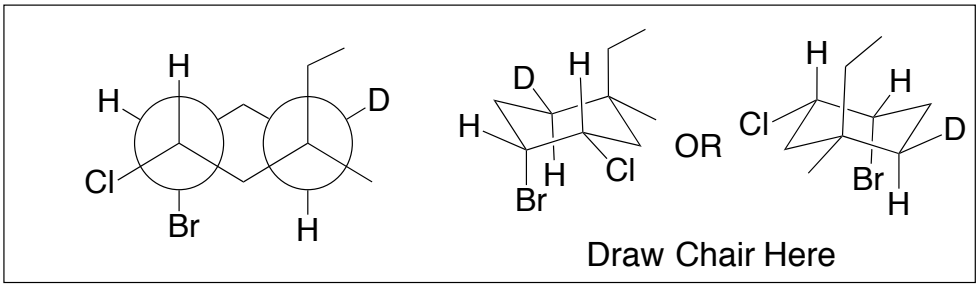


B. Draw Newman projections that represent the following compounds looking down the bond(s) indicated. Be sure and show all hydrogen atoms that are directly attached to the two carbon atoms making up each bond in question. There is no partial credit. ***If one substituent is incorrectly drawn, the entire structure is incorrect.***





C. Draw the chair conformation that is represented by the following Newman projection.



7. (18 pts)

A. In the box on the left draw a chair for the 1,2,3-trimethylcyclohexane isomer shown directly above the box.

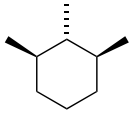
B. In the box labeled "ring-flipped chair structure" draw the ring-flipped conformer of the structure you drew in the first box.

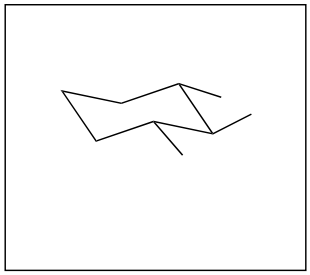
C. Using the values from the Table on your handout AND the following information (there might or might not be more information than you need) calculate ΔG for this equilibrium. Clearly show your work in the appropriately labeled box. Place your final numerical value in the box labeled ΔG =.

- Assume every additional gauche interaction between ANY two substituents is worth 0.9 kcal/mole.
- Assume every additional 1,3-diaxial interaction between ANY two substituents is worth 0.5 kcal/mole.

You will receive no credit for Part C if you do not show your work!

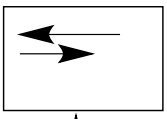
D. Based on your answer for ΔG, use arrows to indicate which side the equilibrium would favor.



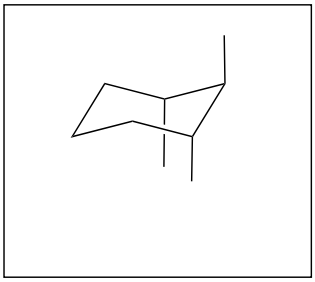


draw a chair structure of the isomer of 1,2,3-trimethyl-cyclohexane shown above the box

ΔG = + 3.8



express the direction of K here



ring-flipped chair structure

Show your work for calculating ΔG here

3 Me_{eq} to 3 Me_{ax} = 3 x 1.7 = 5.1

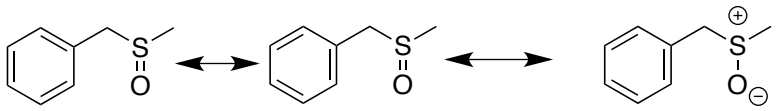
2 additional gauche interactions relieved = -1.8

1 additional 1,3-diaxial interaction = 0.5

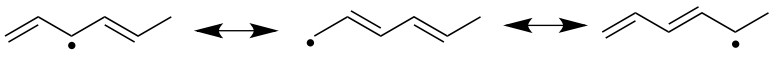
+ 3.8

8. (20 pts)

A. Draw additional REASONABLE and VALID resonance structures for the compounds shown below. Do not draw more resonance structures than asked for.

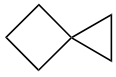


Two addtional resonance structures.



Two addtional resonance structures.

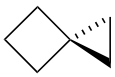
B. Some people call the compound below "The Goldfish Molecule." Based on what you know about the structure of this compound, use a few words and a structure to indicate why this is not an accurate depiction of a fish.



The Goldfish Molecule?

A goldfish, along with other fish have their tails in the same plane as their dorsal fin (i.e. coplanar). The molecule actually has a set of perpendicular rings as shown below. There are other ways to describe this, which we accepted when it made sense.

Your answer must have included a structure like the one shown below to receive credit.



What structure actually looks like.

C. If one is inclined to anthropomorphize molecules, which marine animal better represents the compound shown in Question B?

Examples include a whale or a dolphin. There are other possible answers. The main theme is that it has to be an animal that has its fluke (i.e. back tail fin) perpendicular to its dorsal fin. There are other ways to describe this, which we accepted when it made sense.

D. On the compound shown, circle all bridgehead atoms. Be sure that your circle only includes one atom (not including hydrogen atoms). Wrong answers cancel right answers.