Dr. Steven Pedersen October 3, 2017

Chemistry 3A
Midterm 1

Student name: ANSWER KEY

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

Student signature: _____

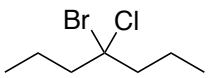
Problem 1	_____	(18 pts)
Problem 2	_____	(18 pts)
Problem 3	_____	(22 pts)
Problem 4	_____	(26 pts)
Problem 5	_____	(21 pts)
Problem 6	_____	(24 pts)
Problem 7	_____	(21 pts)
Total Points	_____	(150 pts)

No Calculators Allowed
No Molecular Models Allowed
Be Sure Your Exam has 9 Pages

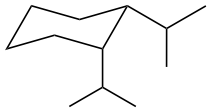
ALL ANSWERS MUST BE ON THE FRONT OF EACH PAGE. ANY ANSWERS ON THE BACK OF A PAGE WILL NOT BE CONSIDERED FOR GRADING.

1. There will be NO partial credit for this problem. Avoid careless errors by checking over your answers. (18 pts)

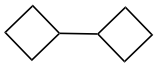
A. Provide a systematic (IUPAC) name for each of the following compounds. Use common nomenclature for any branched substituents.



4-bromo-4-chloroheptane
OR
4-chloro-4-bromoheptane



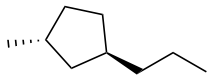
cis-1,2-diisopropylcyclohexane
OR
cis-1,6-diisopropylcyclohexane



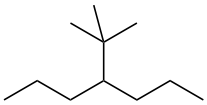
cyclobutylcyclobutane

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

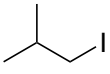
- *trans*-1-methyl-3-propylcyclopentane


OR


- 4-*tert*-butylheptane

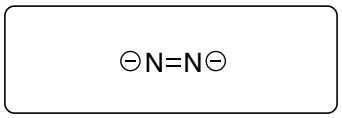


- isobutyliodide

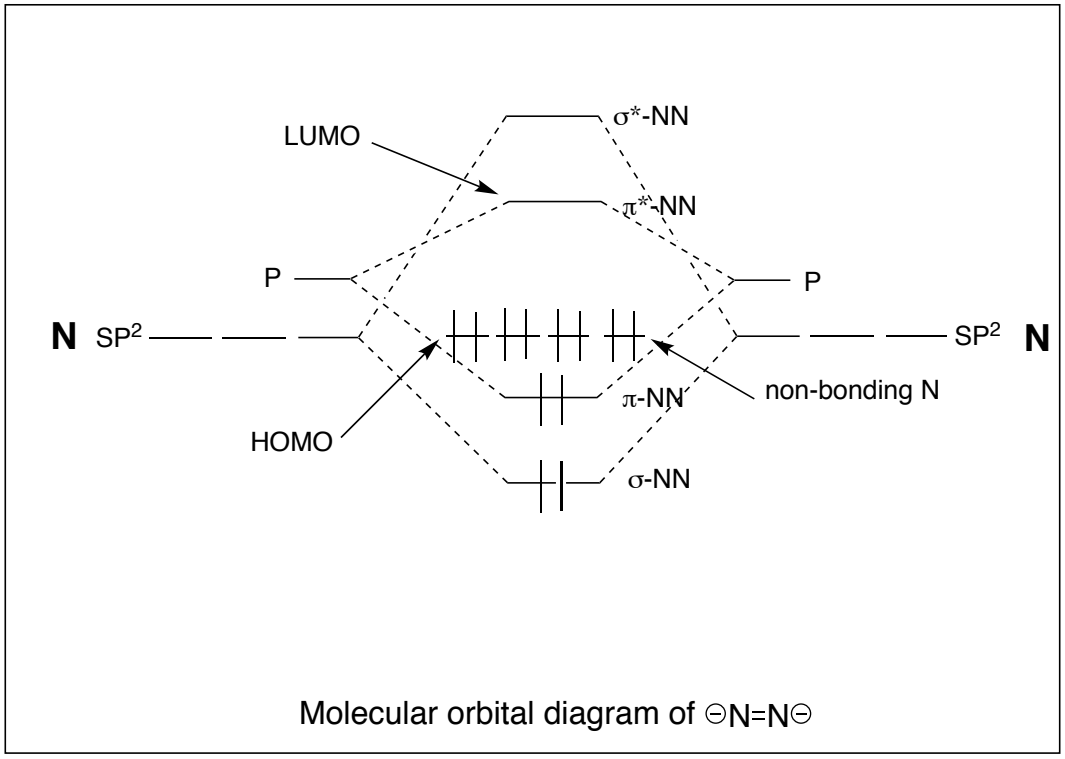


2. (18 pts)

A. Construct a molecular orbital diagram for the dianion shown below. Use the following guidelines and labeling schemes. Be sure to include everything asked for below in the "bullets".

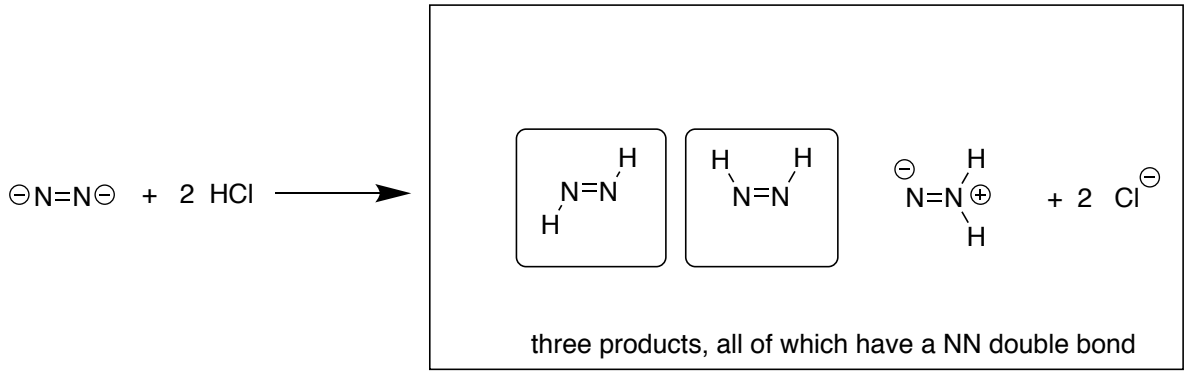


- Clearly indicate which orbitals are being combined to make molecular bonding orbitals.
- Label all the levels as σ, π, nb (non-bonding) etc.
- Fill in all of the electrons.
- Label the HOMO and LUMO



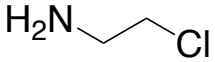
Molecular orbital diagram of ⊖N=N⊖

B. Reaction of the dianion in Part A with two equivalents of HCl can, in theory, yield three different products, two of which are stereoisomers. Show all three products below (Hint: all of the products have a NN double bond).



C. Circle the two stereosiomers in Part B. Wrong answers cancel right answers.

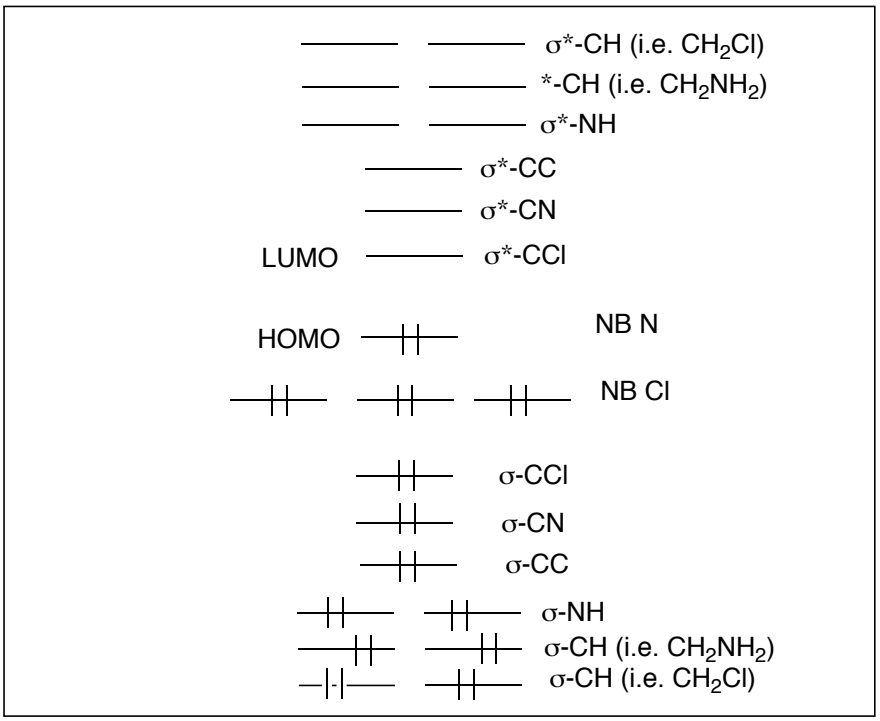
3. The compound shown below undergoes an intramolecular reaction to give a new compound(s). (22 points)



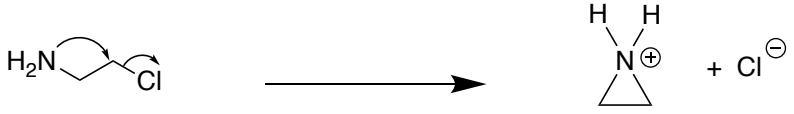
A. Draw the MO diagram for this compound. Part of the diagram has been started for you. Label all of the levels as σ, π, nb (i.e. non-bonding) etc. On your labels include the atoms involved.
On your handout there are bond strengths of various bonds AND an electronegativity chart. Be sure to use these when ordering your energy levels.

B. Fill in the electrons and label the HOMO and LUMO in your diagram.

MO Diagram of $H_2NCH_2CH_2Cl$

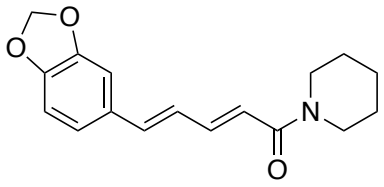


C. Intramolecular means "within the same molecule." In this case, the molecule contains a nucleophile and an electrophile. It will be clear from your MO diagram above which group within the molecule is the nucleophile and which group is the electrophile. Based on the MO diagram above and Frontier Molecular Orbital theory, use electron-pushing arrows to show how this compound undergoes an intramolecular reaction (i.e. within the same molecule) to form a new compound(s). Be sure to draw the product(s) of this reaction AND include any relevant charges. Your reaction and the product(s) shown MUST be consistent with YOUR MO diagram.



Use electron-pushing arrow(s) here to show how you arrived at the product(s) here

4. Capsaicin is the molecule responsible for the "heat" in chili peppers. (26 pts)



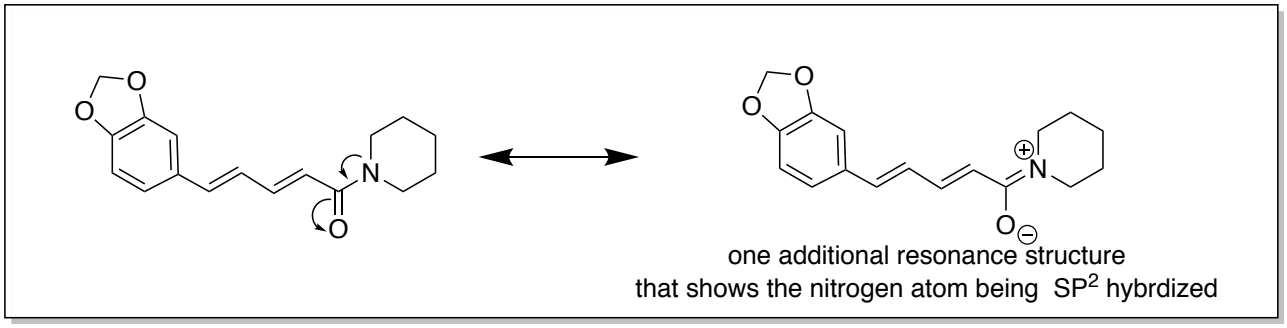
capsaicin

A. What is the molecular formula of capsaicin? Express your answer in the form C_xH_y followed by any other elements in alphabetical order.

$C_{17}H_{19}NO_3$

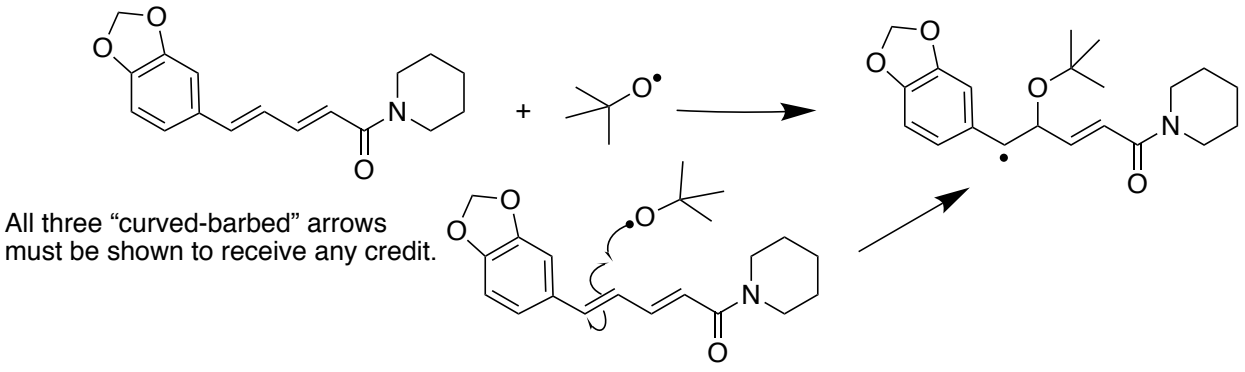
Answer the following questions using the structure shown at the top of the page.
B. Fill in the blank: capsaicin has _*12*_ SP^2 hybridized atoms.
C. Fill in the blank: capsaicin has _*9*_ SP^3 hybridized atoms.

D. Using electron-pushing arrows, draw one additional resonance structure of capsaicin THAT SHOWS THE NITROGEN ATOM BEING SP^2 HYBRIDIZED.



one additional resonance structure
that shows the nitrogen atom being SP^2 hybrdized

E. Add electron-pushing arrows that are consistent with the reaction shown.



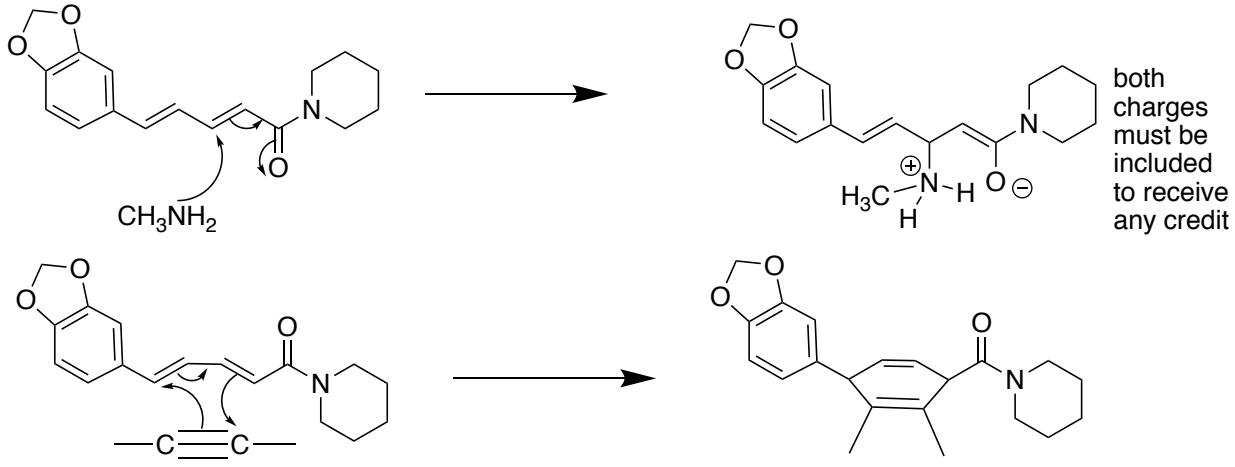
All three "curved-barbed" arrows must be shown to receive any credit.

F. The reaction in Question E is an example of: (circle one)

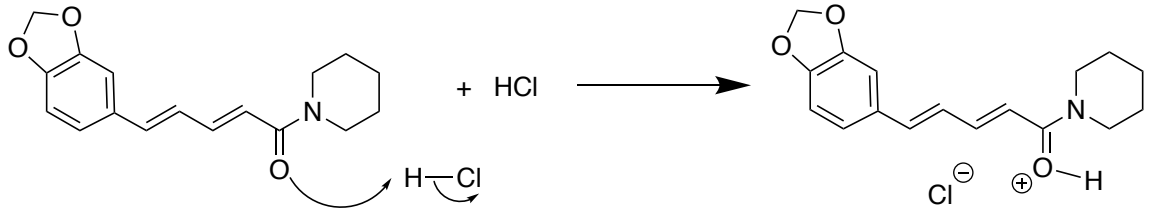
induction initiation propagation termination hyperconjugation

Continued on the next page

G. Based on the electron-pushing arrows provided, draw the product(s) from the following reactions. Be sure to show any relevant charges.

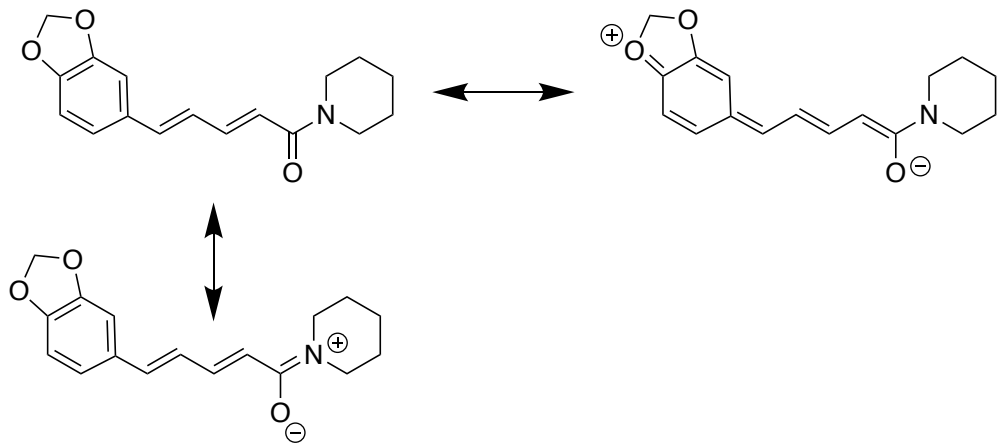


H. Which non-carbon atom in capsaicin is most likely to be protonated with HCl? Show the product of this protonation and provide electron-pushing arrows to show how you arrived at your answer. Below your reaction use some more DRAWINGS and a FEW WORDS to explain your choice relative to the other possibilities. NO CREDIT WILL BE GIVEN TO A CORRECT PRODUCT WITHOUT AN EXPLANATION.



We accepted many resonance structures of the one shown here.

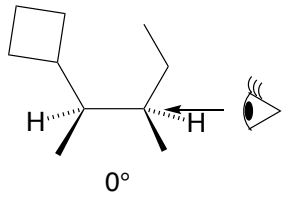
Explanation (do not write on the back of this page, it will NOT be graded):
Below are two additional resonance structures (there are many more) that clearly indicate the only non-carbon atom that will be protonated is the carbonyl oxygen (as shown in the above product).

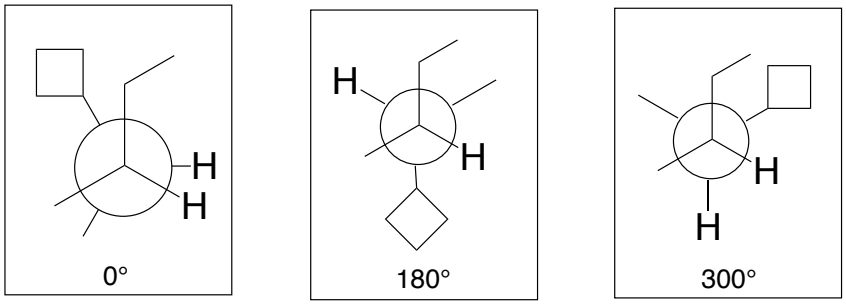


5. (21 pts)

A. Draw Newman projections of the three conformations asked for in the boxes. Note, the first Newman projection (i.e. 0°) will be of the bond-line structure shown. You must follow the instructions below:

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





Hold the front carbon constant and rotate the back carbon counterclockwise.

B. Order the relative energies of the three conformers in Part A from lowest energy to highest energy. Use the degree rotation to identify each conformer and place it in the appropriate box. No credit for the correct ranking will be given unless you provide a correct explanation for your assignments in the space below.

180°	300°	0°
Lowest Energy Conformer	"Inbetween" Energy Conformer	Highest Energy Conformer

Use the degree rotation in Part A to identify each conformer

Discuss your assignments below:

The highest energy conformer is the eclipsed structure at 0°. For alkanes, all eclipsed conformers are higher in energy than any staggered conformer.

For the two staggered conformers, the one at 180° is lower in energy than the one at 300°. This is due to the presence of two gauche interactions in the one at 180° (Me/Et, Me/Cyclobutyl) versus three gauche interactions in the one at 300° (Me/Me, Me/Et and Et/Cyclobutyl).

C. Provide an IUPAC name for the compound shown in Part A.

3-methyl-4-cyclobutylpentane OR: 4-cyclobutyl-3-methylpentane, 2-cyclobutyl-3-methylpentane, 3-methyl-2-cyclobutylpentane.

6. (24 pts)

A. In the box labeled “chair structure” draw the chair represented by the flat structure directly above it. Note that on the chair, one of the carbons is labeled with the number 1. This corresponds to the number 1 on the flat structure. It is important that the chair you draw matches the numbering on the flat structure. It is up to you to decide how to do that.

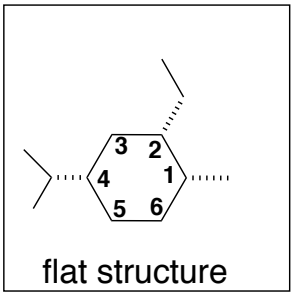
B. In the box labeled “ring-flipped chair structure” draw the ring-flipped conformer of the structure shown in the box labeled “chair structure.”

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.

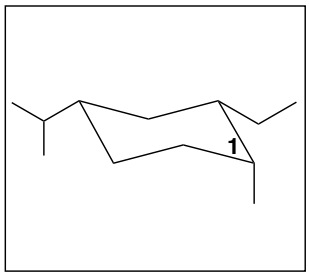
ALL CREDIT FOR THIS PART IS BASED ON SHOWING YOUR WORK!

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

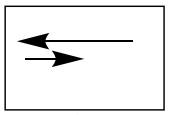
D. Based on your answer for ΔG, use arrows to indicate which side the equilibrium would favor.



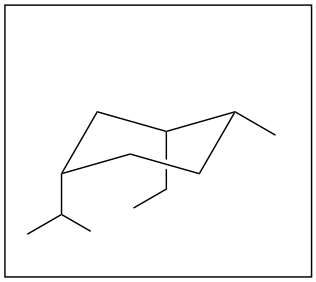
flat structure



chair structure



express the direction of K here



ring-flipped chair structure

Show your work for calculating ΔG here

Me(ax) to Me(eq) = -1.7

Et(eq) to Et(ax) = +1.75

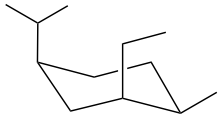
iPr(eq) to iPr(ax) = +2.2

Addiitonal 1,3-diaxial = +0.5

+2.75

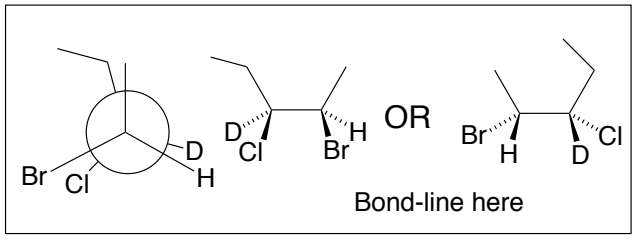
$\Delta G = 2.75$

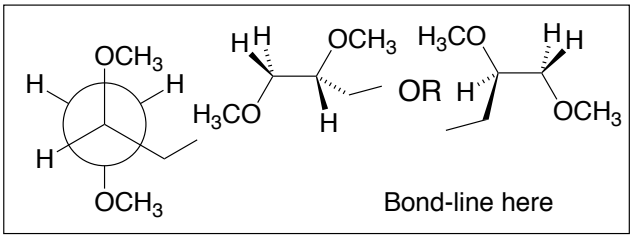
For this problem it does make a dfference, which side of the chair you place the ethyl group. The answer above is correct. The other possibility would have been to draw it like that shown below. If you put the ethyl group on the wrong side, you receive no points for that particular group. If your ring-flipped conformer was drawn correctly based on your first structure, you would have received full credit for the second chair.



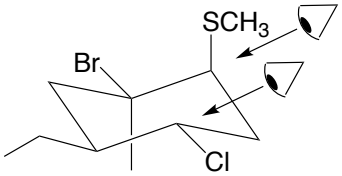
7. (21 points)

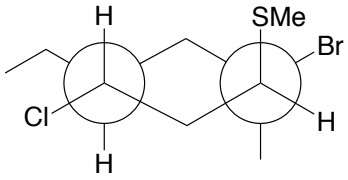
A. Draw the bond-line structure that exactly represents each Newman projection shown below. There is no partial credit so take your time.





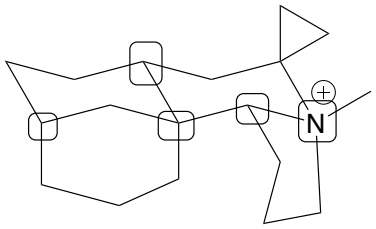
B. Draw a double-barrel Newman projection of the chair cyclohexane shown below. There is no partial credit so take your time.



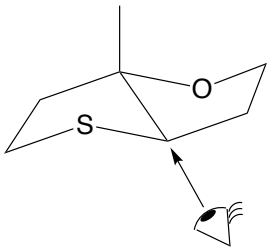


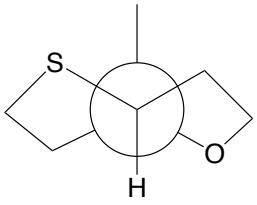
Double-barrel Newman Projection

C. 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.**



D. Draw a Newman projection of the bond-line structure shown. There is no partial credit so take your time.





Newman Projection Here

PROBLEMS A, B AND C STATE THERE IS NO PARTIAL CREDIT. THEREFORE, IF YOU ARE MISSING A GROUP (FOR EXAMPLE, YOU DREW A LINE BUT FORGOT TO ADD A HYDROGEN TO IT) THEN YOU RECEIVED NO POINTS.