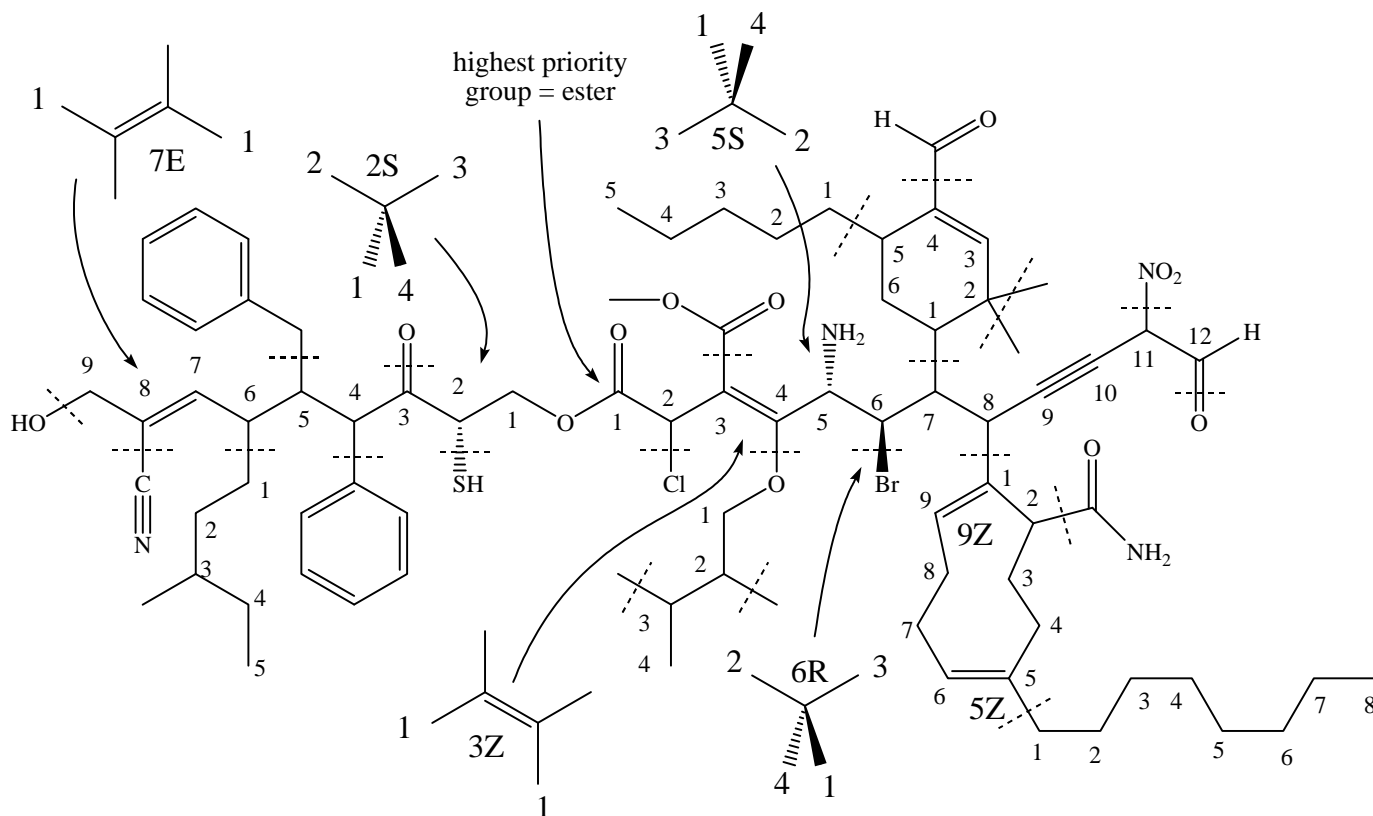


Problems	Points	Credit
1. Functional Group Nomenclature (1 large structure)	30	
2. Resonance, Formal Charge, Arrows	18	
3. Properties of Atoms, Logic Arguments of Organic Chemistry (ionization potential, Z_{eff} , radii, electronegativity, etc.)	20	
4. Types of Isomers, Degrees of Unsaturation	26	
5. Forces of Interaction and Physical Properties	24	
6. Cyclohexane Conformations, Newman Projections	30	
7. Newman Projections, Conformational Energies	25	
8. 3D Structure, Resonance, Hybridization, Angles, Shapes (1)	30	
9. Stereochemical Analysis	25	
10. 2D Lewis Structures (1)	20	
11. Functional Groups, Names, Degrees of Unsaturation or Special Types of Carbons and Substituents	21	
Total	269	

This is a long exam. It has been designed so that no one question will make or break you. The best strategy is to work steadily, starting with those problems you understand best. Make sure you show all of your work. Draw in any lone pairs of electrons, formal charge and curved arrows to show electron movement where appropriate. Do your best to show me what you know in the time available.

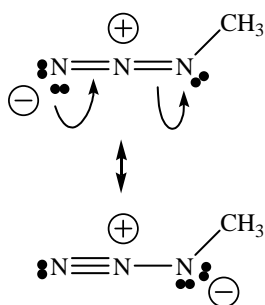
Excuses will always be there for you, opportunity won't.

1. Provide an acceptable name for the following molecule. Only specify R and S where shown as 3D. (30 pts)

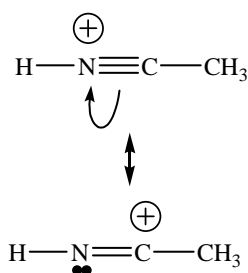


2S-mercapto-3-oxo-4-phenyl-5-benzyl-6-(3-methylpentyl)-8-cyano-9-hydroxynon-7E-enyl 2-chloro-3-methoxycarbonyl-4-(2,3-dimethylbutoxy)-5S-amino-6R-bromo-7-(2,2-dimethyl-4-formyl-5-pentylcyclohex-3-enyl)-8-(2-amido-5-octylcyclonona-5Z,9Z-dienyl)-11-nitro-12-oxododec-3Z-en-9-ynoate

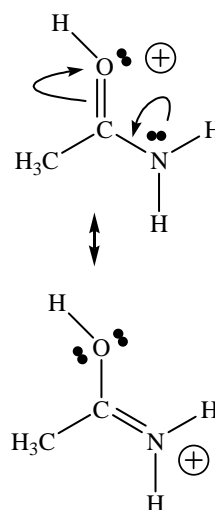
2. Indicate all formal charges present in the following structures. Assume all electrons are shown as lines or dots. If other reasonable resonance structures are possible, draw the best other resonance structure using the proper arrow conventions. Indicate which resonance structure is better or if they are equivalent. (18 pts)



Similar in stability, negative is on nitrogen in both resonance structures.



The first resonance structure is better because it has more bonds and full octets.



The second resonance structure is better because it has the positive charge on nitrogen rather than oxygen. Both resonance structures have an extra bond and full octets. There is an acceptable 3rd resonance structure with + on carbon, but it has fewer bonds and an incomplete octet.

3. a. Which atom has the higher first ionization potential and why? (Na or Cl) (20 pts)

Na and Cl are in the same row. Na has a Z_{eff} of +1 and Cl has a Z_{eff} of +7, so Cl will hold on to its electrons much tighter than Na and require more energy to strip an electron away. $\text{IP}_1(\text{Na}) = 118 \text{ kcal/mole}$ and $\text{IP}_1(\text{Cl}) = 300 \text{ kcal/mole}$

- b. Which neutral atom has the larger atomic radius and why? (Si or Ar)

Silicon and argon are in the same row. Si has a Z_{eff} of +4 and Ar has a Z_{eff} of +8, so Ar will hold on to its electrons much tighter than Si. This should contract the electron cloud making the radius of argon ($r_{\text{Ar}} = 70 \text{ pm}$) smaller than silicon ($r_{\text{Si}} = 110 \text{ pm}$).

- c. Which anion has the larger radius and why? (N^{3-} or O^{2-})

Both N^{3-} and O^{2-} are in the same row and have a full $n=2$ shell (full octets). Oxygen has Z_{eff} of +6 and N has a Z_{eff} of +5, so O will hold on to its electrons tighter than N. The radius of oxide ($r_{\text{O}^{2-}} = 126 \text{ pm}$) is smaller than nitride ($r_{\text{N}^{3-}} = 132 \text{ pm}$)

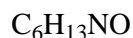
- d. Which cation has the larger radius and why? (Mg^{+2} or Al^{+3})

Both Mg^{+2} and Al^{+3} have lost all of their $n=3$ valence electrons and have a full $n=2$ shell (core electrons). Mg has Z_{eff} of +2 and Al has a Z_{eff} of +3, so Al will hold on to its electrons tighter than Mg. The radius of Al^{+3} ($r_{\text{Al}^{+3}} = 69 \text{ pm}$) should be smaller than Mg^{+2} ($r_{\text{Mg}^{+2}} = 86 \text{ pm}$).

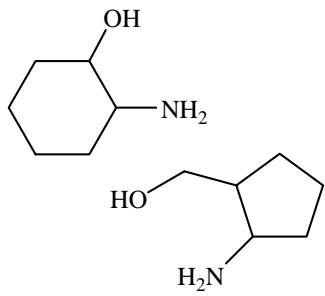
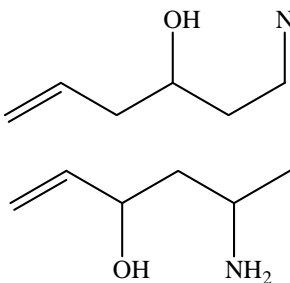
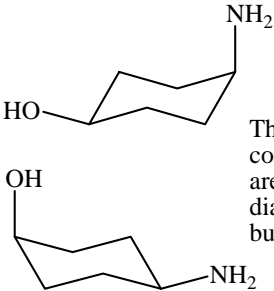
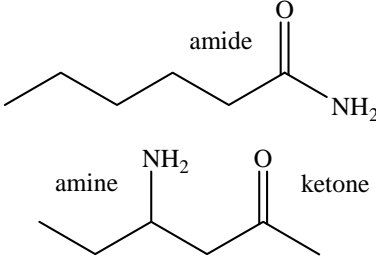
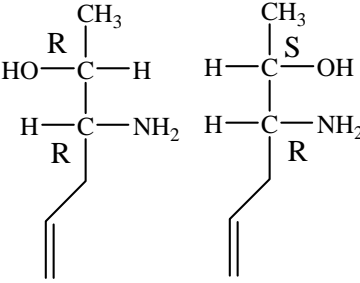
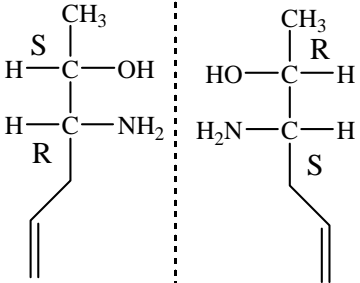
4. Use the formula $\text{C}_6\text{H}_{13}\text{NO}$ to draw examples for each type of isomerism indicated. This will require that you draw at least two structures in each box to show these differences. What is the degree of unsaturation? (26 pts)

$$\text{degree of unsaturation} = 2(6) + 2 + 1 = 15$$

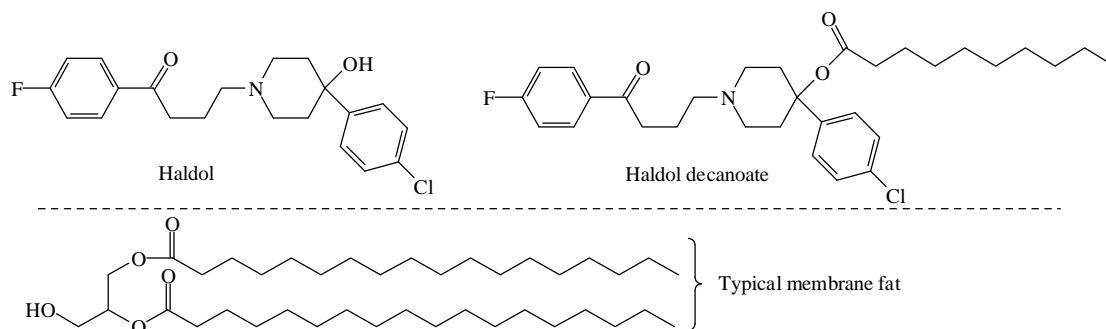
one pi bond or one ring



$$\frac{15 - 13}{2} = 1 \text{ degree}$$

 <p>skeletal isomers</p>	 <p>positional isomers</p>	 <p>conformational isomers</p> <p>These conformers are cis/trans diastereomers, but achiral.</p>
 <p>functional group isomers</p>	 <p>diastereomers</p>	 <p>enantiomers</p>

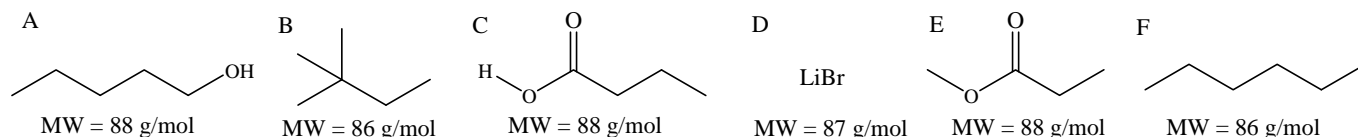
5. a. Haldol is a potent orally active central nervous system tranquilizer used in the treatment of psychoses. Peak plasma levels, when taken orally, are 2-6 hours (in the aqueous blood). Cell membranes, on the other hand, are composed largely of alkane-like fatty acid chains. A decanoate ester prodrug was prepared to increase Haldol's lifetime in the body. When injected intramuscularly its anti-psychotic activity lasted about 1 month. Provide an explanation for its longer lifetime. (12 pts)



Answer: The alcohol of Haldol makes it too water (blood) soluble and it is degraded as the blood passes through the liver by oxidizing enzymes, so it is excreted in the urine and/or feces. When the alcohol is esterified it is much less water (blood) soluble and gets stored in fatty tissue (membranes), where it is slowly released to the blood over a much longer time. Probably the ester is slowly hydrolyzed making it become more water soluble again, as the alcohol.

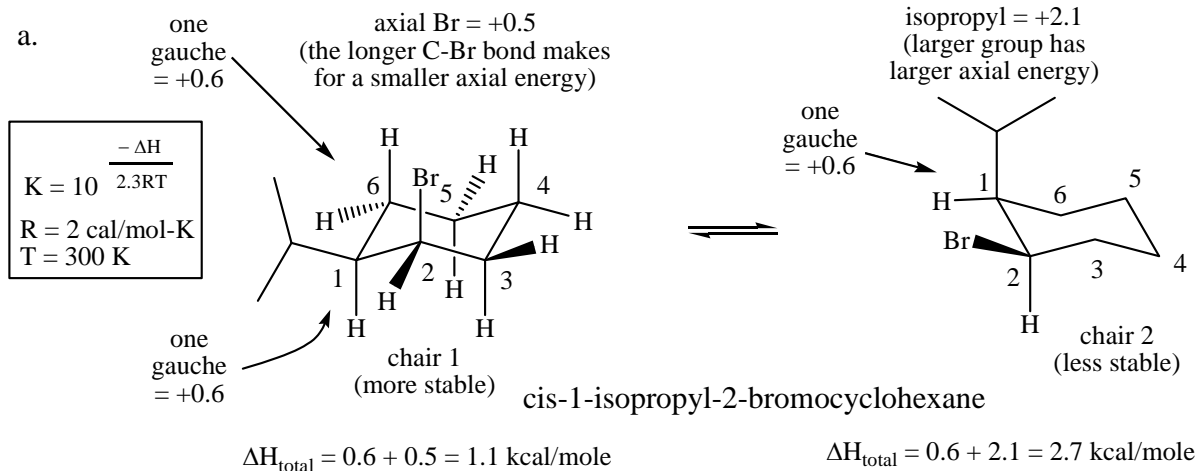
- b. Match the compounds with their boiling points with a brief explanation. (12 pts)

boiling points: 1265°C, 164°C, 138°C, 80°C, 69°C, 50°C



Answer: LiBr is ionic with very strong forces of interaction, so its boiling point is extremely high (+1265°C). Carboxylic acid, C, is next with both hydrogen bonding (OH) and strong polarity (C=O) and has boiling point of +164°C. Next is the alcohol, A, which has hydrogen bonding (OH) with boiling point of 138°C, followed by the ester, E, with polarity (C=O) and a boiling point of 80°C. Last are the two alkanes, having only dispersion forces. The linear hexane, F, has greater dispersion forces because more surface area of contact with its neighbors, boiling point = 69°C and the branched 2,2-dimethylbutane, B, has the lowest boiling point of 50°C, due to less contact surface area with its neighbor molecules because of the branches.

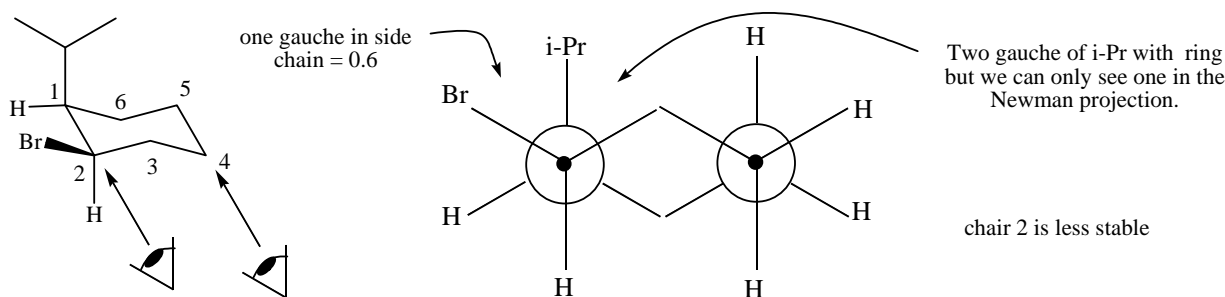
6. Draw all possible chair conformations of cis-1-isopropyl-2-bromocyclohexane. Make the left most ring carbon C1 and number towards the front. Show all axial and equatorial groups in the first chair. Which conformation is more stable? Provide a reason for your answer. Draw a Newman projections of the least stable conformation and the most stable conformation using the C₂→C₆ and C₃→C₄ bonds to sight along. Point out any gauche interactions shown in your Newman projection. If the axial energy of an isopropyl group is 2.1 kcal/mole and the axial energy of a bromo atom is 0.5 kcal/mole and a bromo/isopropyl gauche interaction is 0.6 kcal/mole, what is the ratio of the two conformations? Show your work. Sketch an energy diagram that shows how the energy changes with the conformational changes and estimate the ratio of the two conformations at equilibrium. (30 pts)



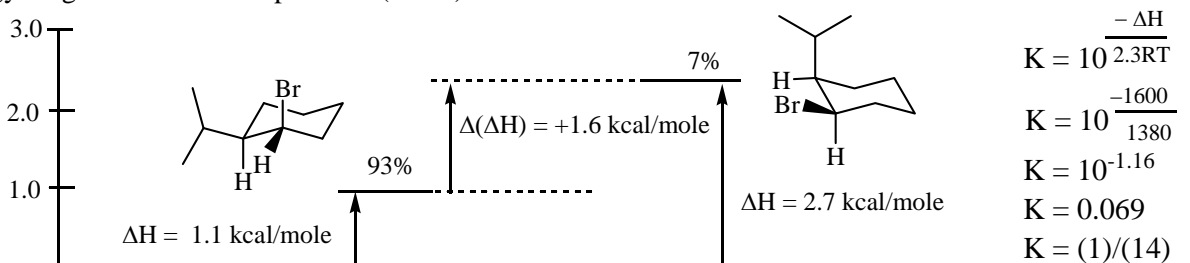
$$\Delta(\Delta H) = 2.7 - 1.1 = 1.6 \text{ kcal/mole}$$

larger group (higher axial energy) is axial in right structure so ΔH is positive and $K_{\text{eq}} < 1$.

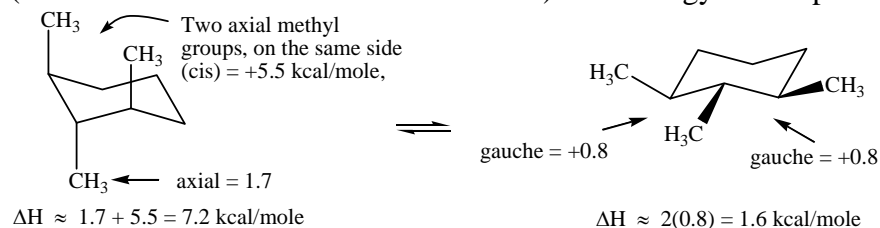
- b. Newman projection – least stable, point out any gauche interactions with the substituent(s)



- c. Energy diagram and relative percents ($K = ?$)



- d. Calculate an approximate ΔH difference between the two conformations. Use that value to estimate a K_{eq} . (Assume $R = 2 \text{ cal/mol-K}$ and $T = 300 \text{ K}$.) Use energy values provided in the box. Show your work.



The energy table is not shown here.

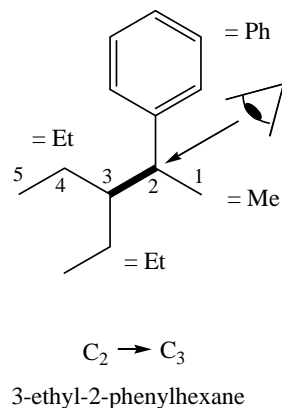
$$\Delta(\Delta H) = 1.6 - 7.2 = -5.6 \text{ kcal/mole}$$

$$K = 10^{\frac{-(-5600)}{1380}} = 10^{4.05} = 11,000 / 1$$

$$K = 1 / 10,000$$

7. Use a Newman projection of the C2→C3 bond of 3-ethyl-2-phenylpentane to **show the most stable conformation first**. Rotate through all of the eclipsed and staggered conformations. Using the energy values provided in the table below, calculate the relative energies of the different conformations. Plot the changes in energy in the graph diagram provided. Calculate a ratio of least stable to most stable based on ΔH values. Hint: Draw a 2D structure first and “bold” the bond viewed in your Newman projection, then decide your line of sight. (25 pts)

2D structure



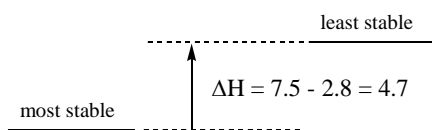
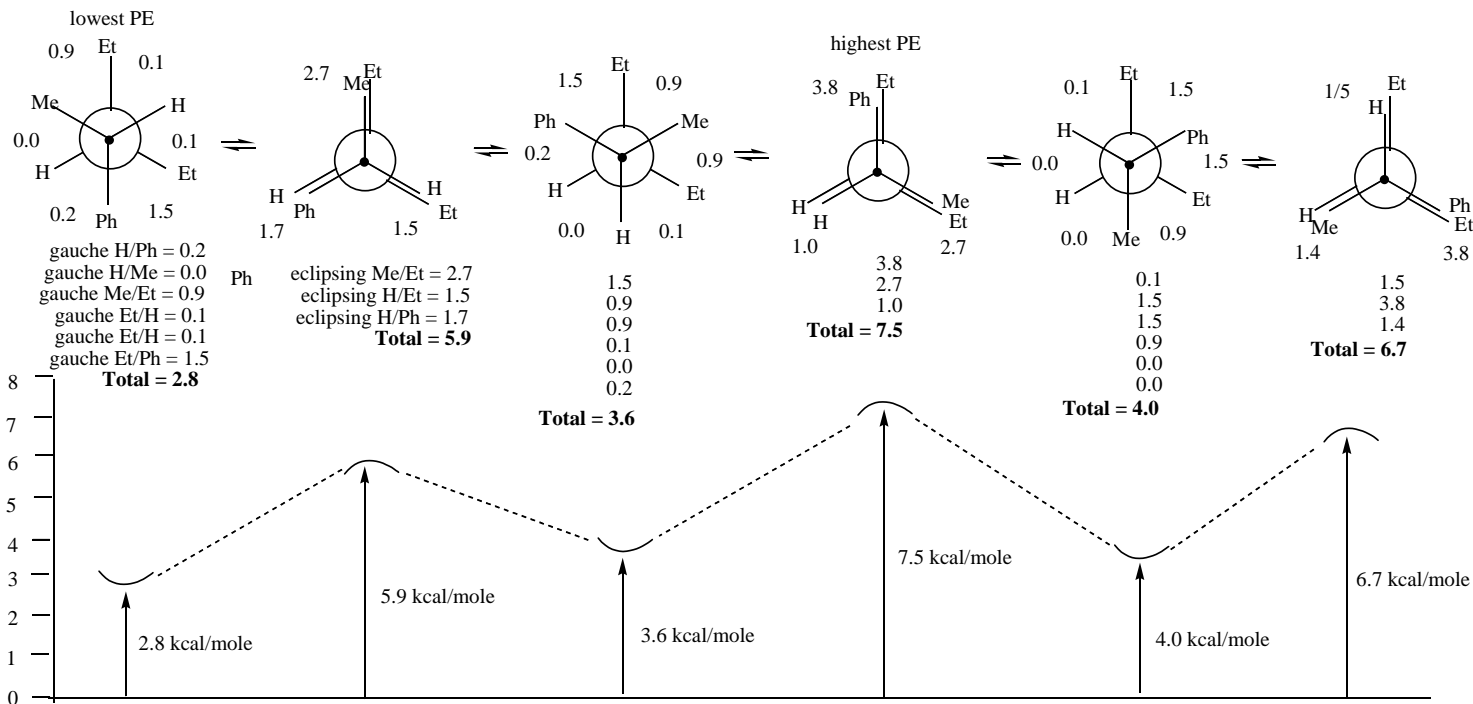
Approximate Eclipsing Energy Values (kcal/mole) Some were estimated by me.							
	H	Me	Et	i-Pr	t-Bu	Ph	Br
H	1.0	1.4	1.5	1.6	3.0	1.7	1.6
Me	1.4	2.5	2.7	3.0	8.5	3.3	2.8
Et	1.5	2.7	3.3	4.5	10.0	3.8	3.1
i-Pr	1.6	3.0	4.5	7.8	13.0	8.1	3.6
t-Bu	3.0	8.5	10.0	13.0	23.0	13.5	9.1
Ph	1.7	3.3	3.8	8.1	13.5	8.3	4.2
Br	1.6	2.8	3.1	3.6	9.1	4.2	3.0

$$\Delta G \approx \Delta H - \frac{\Delta H}{2.3RT}$$

$$K_{eq} = 10^{\frac{-\Delta H}{2.3RT}}$$

Approximate Gauche Energy Values (kcal/mole) Some were estimated by me.							
	H	Me	Et	i-Pr	t-Bu	Ph	Br
H	0	0	0.1	0.2	0.5	0.2	0.1
Me	0	0.8	0.9	1.1	2.7	1.4	1.0
Et	0.1	0.9	1.1	1.6	3.0	1.5	1.3
i-Pr	0.2	1.1	1.6	2.0	4.1	2.1	1.6
t-Bu	0.5	2.7	3.0	4.1	8.2	3.9	3.3
Ph	0.2	1.4	1.5	2.1	3.9	2.3	1.9
Br	0.1	1.0	1.3	1.6	3.3	1.9	1.1

Newman projections:

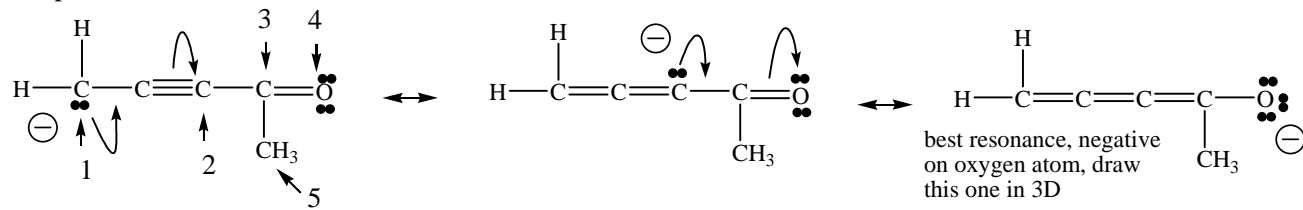


$$\Delta(\Delta H) = 7.5 - 2.8 = 4.7 \text{ kcal/mole}$$

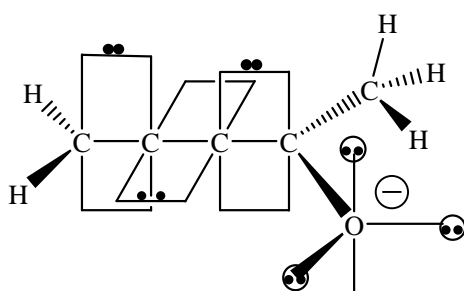
$$K_{eq} = 10^{\frac{-4700}{1380}}$$

$$K_{eq} = 10^{-3.40} = 0.00039 = 1 / 2500 = (\text{least}) / (\text{most})$$

8. Assume that all non-hydrogen atoms have a full octet, unless there is a positive charge on carbon. Draw a 2D Lewis structure for all reasonable resonance structures (include lone pairs and formal charge). Draw a 3D structure for the **best** resonance structure. Show bonds in front of the page as wedges, bonds in back of the page as dashed lines and bonds in the page as simple lines. Show orbitals and electrons for pi bonds and lone pairs with a circle around their electrons. Identify the hybridization, bond angles and descriptive shape for all numbered atoms.



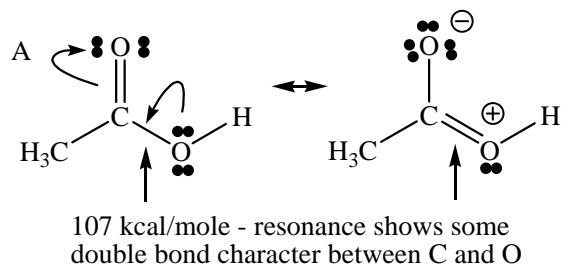
3D structure



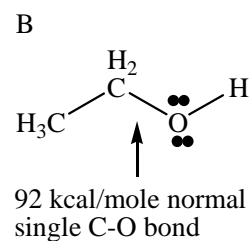
The best resonance has negative charge on the oxygen atom with the same number of pi bonds (3) in each of the resonance structures.

Atom	Shape	Hybridization	Bond Angles	# sigma bonds	# pi bonds	# lone pairs
1	trigonal planar	sp^2	120	3	1	0
2	linear	sp	180	2	2	0
3	trigonal planar	sp^2	120	3	1	0
4	trigonal planar	sp^2	120	1	0	3
5	tetrahedral	sp^3	109	4	0	0

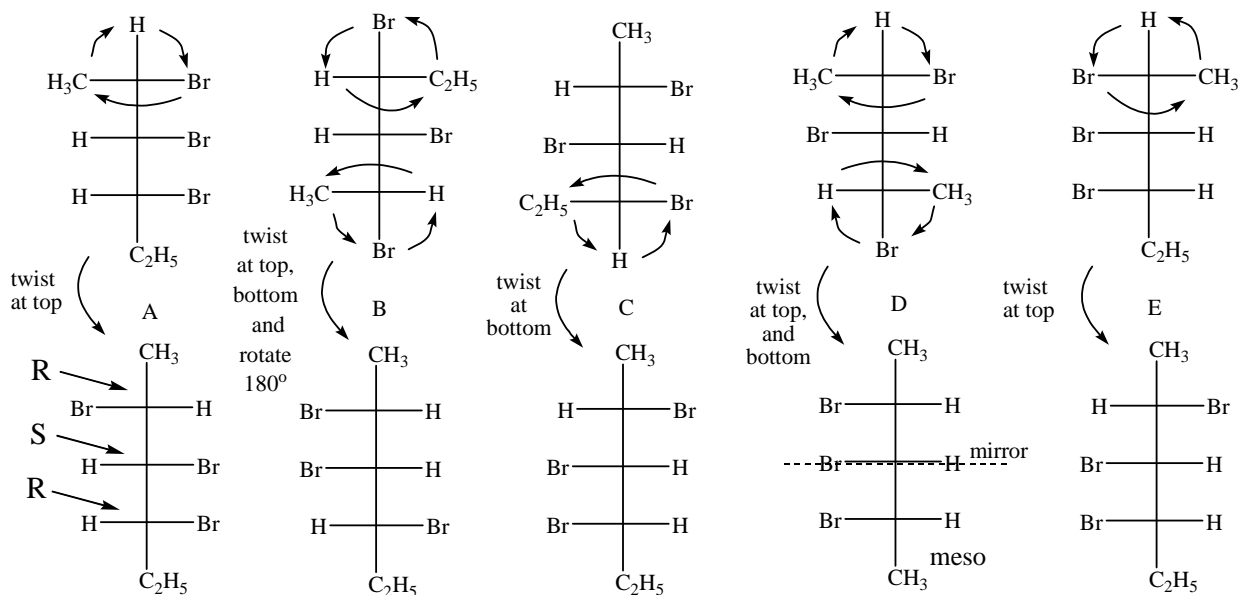
Explain the different C-O bond energies. Use structures in your explanation. Include any necessary lone pairs, formal charge, curved arrows, etc. What is the hybridization of "HO" oxygen in A and B?



The O_B-H of B is sp^3 , but O_A-H of A is sp^2 due to resonance with $C=O$ functionality. Look at the second resonance structure



9. For the following set of Fischer projections answer each of the questions below by circling the appropriate letter(s) or letter combination(s). Hint: Redraw the Fischer projections with the longest carbon chain in the vertical direction and having similar atoms in the top and bottom portion. Classify all chiral centers in the first structure as R or S absolute configuration. (25 pts)



a. Which are optically active?



b. Which are meso?



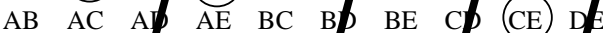
c. Which is not an isomer with the others?



d. Which pairs are enantiomers?



e. Which pairs are identical?



f. Which pairs are diastereomers?

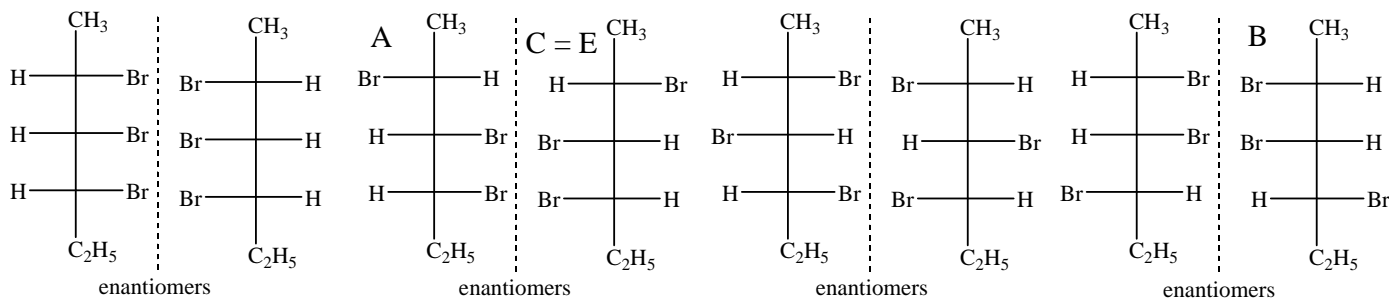


g. Which pairs, when mixed in equal amounts will not rotate plane polarized light?

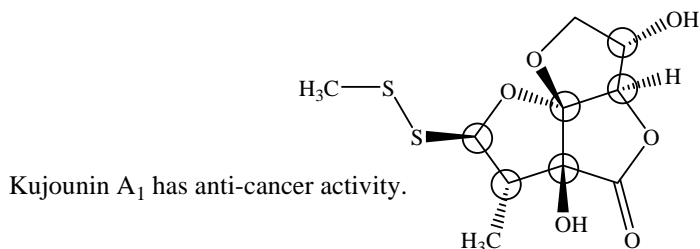


h. Draw any stereoisomers of 3-amino-2-butanol as Fischer projections, which are not shown above. If there are none, indicate this.

These are all of the stereoisomers.



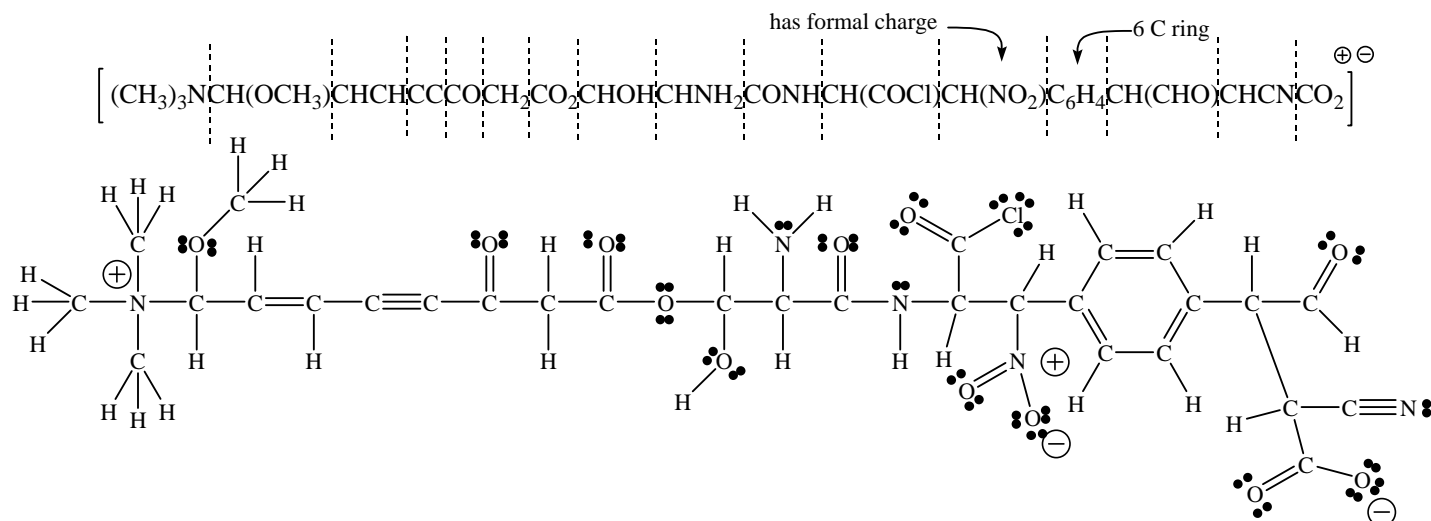
- i. In the most recent Organic Letters, 2018, 20, 28-31, three new sulfur compounds were isolated from welsh onion plant grown in Kyoto, Japan (only Kujounin A₁ is shown). Circle all of the chiral centers. How many stereoisomers are possible? Show work.



6 chiral centers

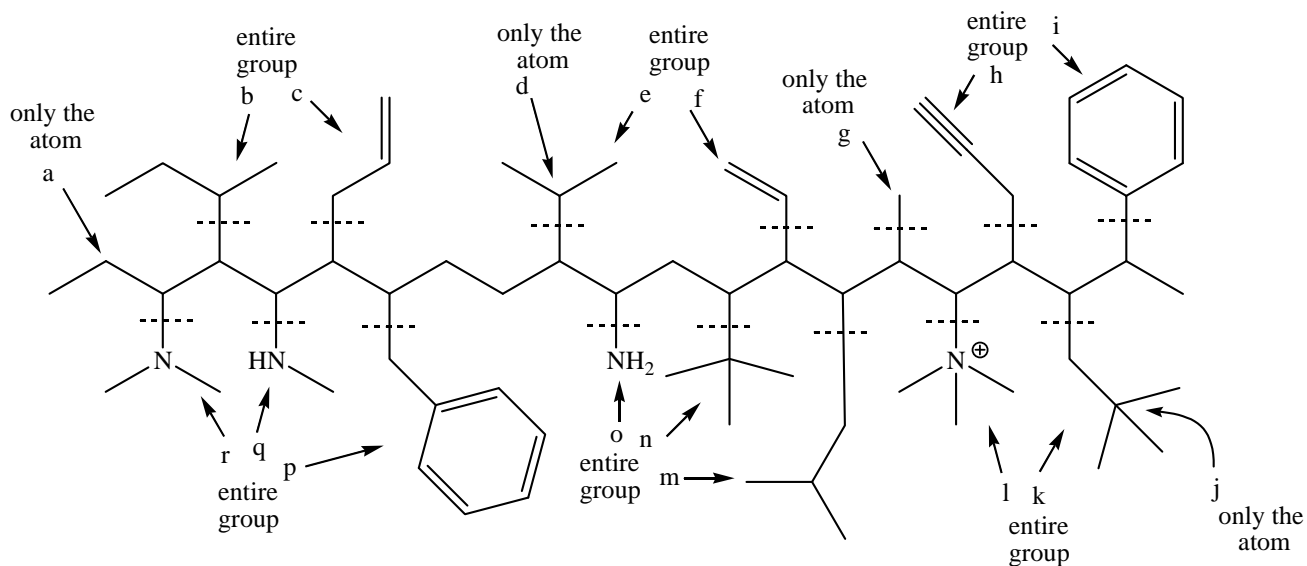
maximum stereoisomers = $2^6 = 64$

10. Draw an acceptable Lewis structure (2D) for the following formula. Show all single, double and triple bonds with one, two or three lines. Include all lone pairs of electrons as two dots. Include formal charge, if present at the atoms where present. (20 pts)



11. Match the arrows with the terms. Some arrows may be associated with more than one term. (21 pts)

- | | | | |
|-----------------------|-------------------------|----------------------------|--------------------------------------|
| 1. methyl <u>g</u> | 7. quarternary <u>j</u> | 13. vinyl <u>f</u> | 19. secondary amine <u>q</u> |
| 2. methylene <u>a</u> | 8. isopropyl <u>e</u> | 14. allyl <u>c</u> | 20. tertiary amine <u>r</u> |
| 3. methine <u>d</u> | 9. isobutyl <u>m</u> | 15. propargyl <u>h</u> | 21. quaternary ammonium ion <u>l</u> |
| 4. primary <u>g</u> | 10. sec-butyl <u>b</u> | 16. phenyl <u>i</u> | |
| 5. secondary <u>a</u> | 11. t-butyl <u>n</u> | 17. benzyl <u>p</u> | |
| 6. tertiary <u>d</u> | 12. neopentyl <u>k</u> | 18. primary amine <u>o</u> | |



Do more than just exist.