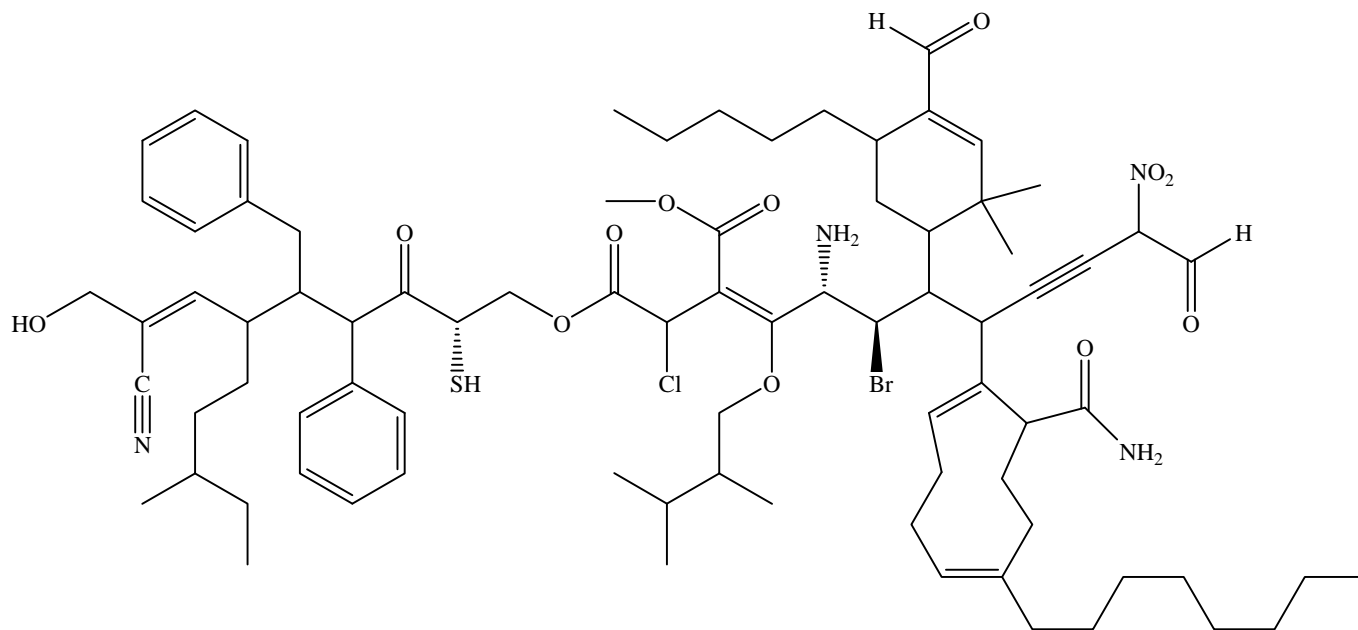


Problems	Points	Credit
1. Functional Group Nomenclature (1 large structure)	30	
2. Resonance, Formal Charge, Arrows	18	
3. Properties of Atoms, Logic Arguments of Organic Chemistry (ionization potential, $Z_{\text{eff}}$ , radii, electronegativity, etc.)	20	
4. Types of Isomers, Degrees of Unsaturation	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	

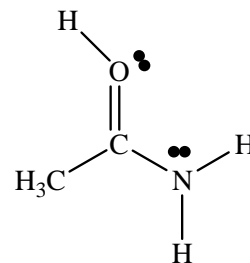
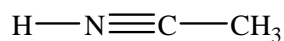
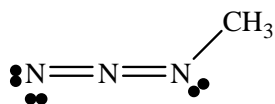
This is a long exam. It has been designed so that no one question will make or break you. The best strategy is to work steadily, starting with those problems you understand best. Make sure you show all of your work. Draw in any lone pairs of electrons, formal charge and curved arrows to show electron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



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)



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

(20 pts)

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

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

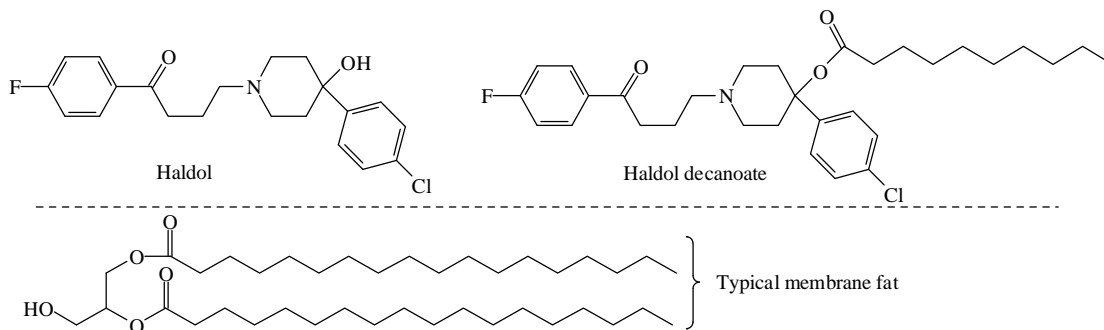
d. Which cation has the larger radius and why? ( $\text{Mg}^{+2}$  or  $\text{Al}^{+3}$ )

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)

skeletal isomers	positional isomers	conformational isomers
functional group isomers	diastereomers	enantiomers

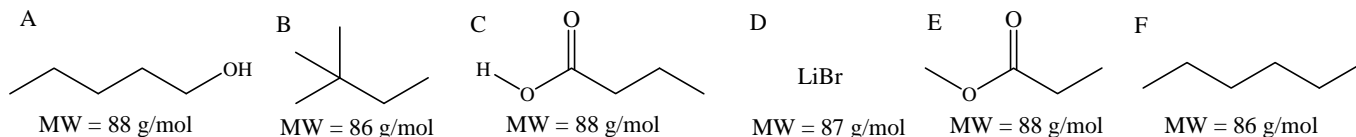
Degree of unsaturation (show work).

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)



- 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

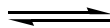


6. Draw all possible chair conformations of cis-1-isopropyl-2-bromocyclohexane. Make the left most ring carbon C1 and number towards the front. Show **all** axial and equatorial groups in the first chair. Which conformation is more stable? Provide a reason for your answer. Draw a Newman projections of the least stable conformation using the C<sub>2</sub>→C<sub>1</sub> and C<sub>4</sub>→C<sub>5</sub> 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)

a.

$$K = 10^{\frac{-\Delta G}{2.3RT}}$$

R = 2 cal/mol-K  
T = 300 K



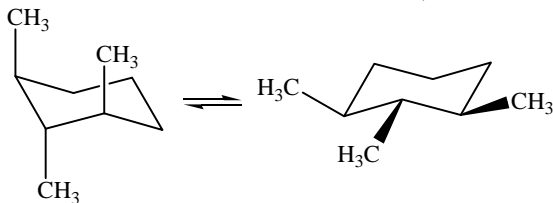
chair 1

chair 2

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

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

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



One axial methyl group = +1.7 kcal/mole,  
Two axial methyl groups, on the same side (cis) = +5.5 kcal/mole,  
Three axial methyl groups, on the same side = +12.9 kcal/mole and  
1,2 gauche methyl groups = 0.8 kcal/mole.

$\Delta H \approx$

$K_{eq} \approx$

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  $\Delta H$  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

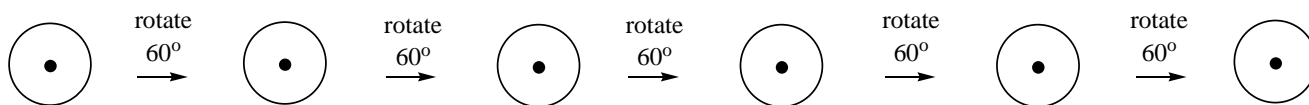
Approximate Eclipsing Energy Values (kcal/mole) Some were estimated by me.							
	H	Me	Et	i-Pr	t-Bu	Ph	Br
H	1.0	1.4	1.5	1.6	3.0	1.7	1.6
Me	1.4	2.5	2.7	3.0	8.5	3.3	2.8
Et	1.5	2.7	3.3	4.5	10.0	3.8	3.1
i-Pr	1.6	3.0	4.5	7.8	13.0	8.1	3.6
t-Bu	3.0	8.5	10.0	13.0	23.0	13.5	9.1
Ph	1.7	3.3	3.8	8.1	13.5	8.3	4.2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

$$\Delta G \approx \Delta H$$

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

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

most stable  
conformation  
↓



$\Delta H^\circ =$

$\Delta H^\circ =$

$\Delta H^\circ =$

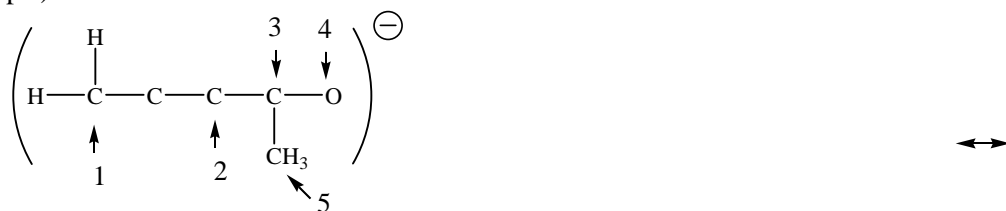
$\Delta H^\circ =$

$\Delta H^\circ =$

$\Delta H^\circ =$



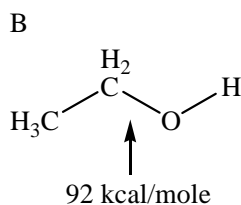
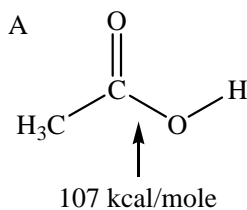
8. Assume that all non-hydrogen atoms have a full octet, unless there is a positive charge on carbon. Draw a 2D Lewis structure for all reasonable resonance structures (include lone pairs and formal charge). Draw a 3D structure for the **best** resonance structure. Show bonds in front of the page as 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. (30 pts)



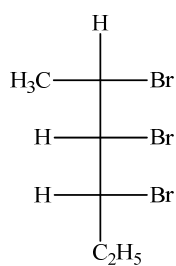
3D structure - Use the “best” resonance structure for the 3D structure and to fill in the following table.

Atom	Shape	Hybridization	Bond Angles	# sigma bonds	# pi bonds	# lone pairs
1						
2						
3						
4						
5						

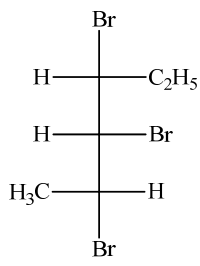
Explain the different C-O bond energies. Use structures in your explanation. Include any necessary lone pairs, formal charge, curved arrows, etc. What is the hybridization of “HO” oxygen in A and B?



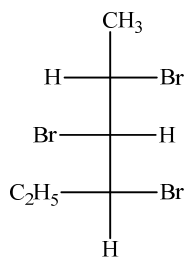
9. For the following set of Fischer projections answer each of the questions below by circling the appropriate letter(s) or letter combination(s). Hint: Redraw the Fischer projections with the longest carbon chain in the vertical direction and having similar atoms in the top and bottom portion. Classify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



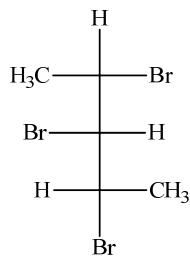
A



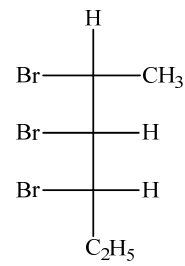
B



C



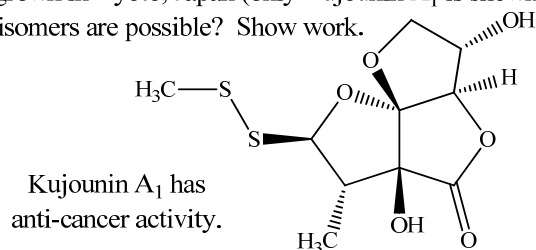
D



E

- a. Which are optically active?                    A    B    C    D    E
- b. Which are meso?                                A    B    C    D    E
- c. Which is not an isomer with the others?    A    B    C    D    E
- d. Which pairs are enantiomers?            AB   AC   AD   AE   BC   BD   BE   CD   CE   DE
- e. Which pairs are identical?                AB   AC   AD   AE   BC   BD   BE   CD   CE   DE
- f. Which pairs are diastereomers?            AB   AC   AD   AE   BC   BD   BE   CD   CE   DE
- g. Which pairs, when mixed in equal amounts will not rotate plane polarized light?    AB   AC   AD   AE   BC   BD   BE   CD   CE   DE
- h. Draw any stereoisomers, which are not shown above, as Fischer projections. If there are none, indicate this.

- 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 A<sub>1</sub> is shown). Circle all of the chiral centers. How many stereoisomers are possible? Show work.



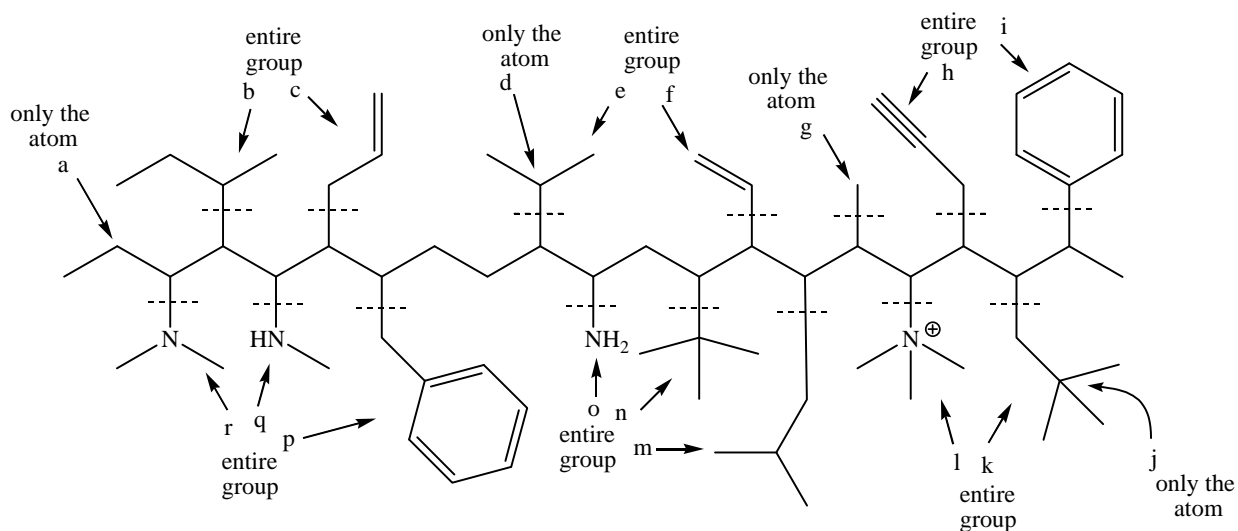


10. Draw an acceptable Lewis structure (2D) for the following formula. Show all single, double and triple bonds with one, two or three lines. Include all lone pairs of electrons as two dots. Include formal charge, if present at the atoms where present. (20 pts)



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

- |                    |                     |                         |                                   |
|--------------------|---------------------|-------------------------|-----------------------------------|
| 1. methyl _____    | 7. quaternary _____ | 13. vinyl _____         | 19. secondary amine _____         |
| 2. methylene _____ | 8. isopropyl _____  | 14. allyl _____         | 20. tertiary amine _____          |
| 3. methine _____   | 9. isobutyl _____   | 15. propargyl _____     | 21. quaternary ammonium ion _____ |
| 4. primary _____   | 10. sec-butyl _____ | 16. phenyl _____        |                                   |
| 5. secondary _____ | 11. t-butyl _____   | 17. benzyl _____        |                                   |
| 6. tertiary _____  | 12. neopentyl _____ | 18. primary amine _____ |                                   |



Do more than just exist.