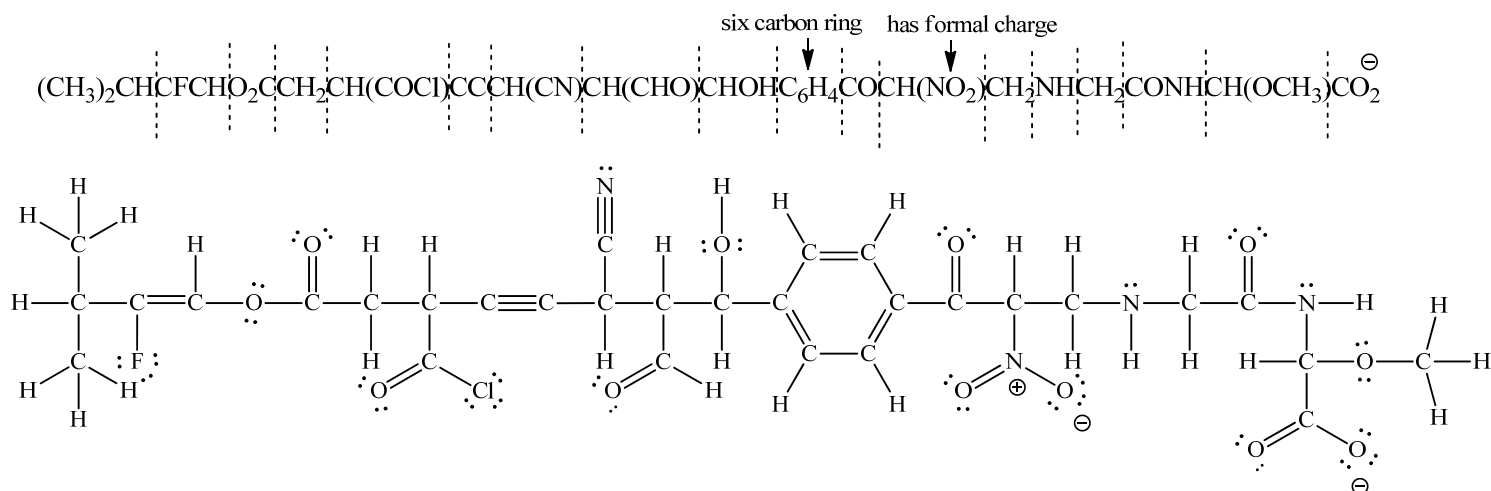


Problems	Points	Credit
1. Functional Group Nomenclature (1 large structure)	30	
2. Degrees of Unsaturation & Functional Groups (many different functional groups) or Various Nomenclature Terms	20	
3. 2D Structure (long string of atoms)	20	
4. Properties of Atoms, Logic Arguments of Organic Chemistry (ionization potential, Z_{eff} , radii, electronegativity, etc.)	15	
5. 3D Structure, Hybridization, Resonance, Angles, Shapes	30	
6. Cyclohexane Conformations (2 substituents), Newman Projections, K_{eq} calculation, Energy Diagram	30	
7. Chain Conformations, 360° rotations, Newman Projections, K_{eq} calculation, Energy Diagram	30	
8. Stereochemical Analysis	30	
9. Physical Properties, Forces of Interaction	15	
10. Resonance, Curved Arrows, Formal Charge, Polarity	15	
Total	235	

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.

3. 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 atom where present. Identify any functional groups by name (i.e. ketone, amide, etc.) (20 pts)



4. a. Ionization energy is the amount of energy required to steal an electron away from a substance (atom or compound). Provide an explanation differences in atomic ionization energy in a row (C vs. O) and in a column (O vs. S). (5 pts)

C +261	O +315
	S +239

It takes more energy to ionize an electron from oxygen than carbon because oxygen has a higher Z_{eff} ($=+6$) than carbon ($=+4$). It takes more energy to ionize an electron from oxygen than sulfur, even though they have the same Z_{eff} because the electron lost from sulfur is in the $n=3$ shell (farther away from the nucleus) where the attraction is weaker.

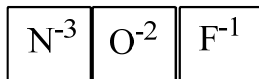
- b. Define electronegativity and provide an explanation for the differences in electronegativity in a row (C vs F) and in a column (F vs Cl). (5 pts)

C 2.5	F +4.0
	Cl +3.2

Electronegativity measures the attraction for electrons in bonds. A more electronegative element pulls the electrons closer to it and polarizes the bond with a partial negative charge on it and a partial positive charge on the other atom (like an O-H bond). A higher number means a stronger pull for the electrons. The reasons are the same as in the above explanation (Z_{eff} and distance from the nucleus).

- c. All 3 anions below have the same atomic configuration. Write that out. Match each anion structure with its radius and give a very brief explanation for your order. (5 pts)

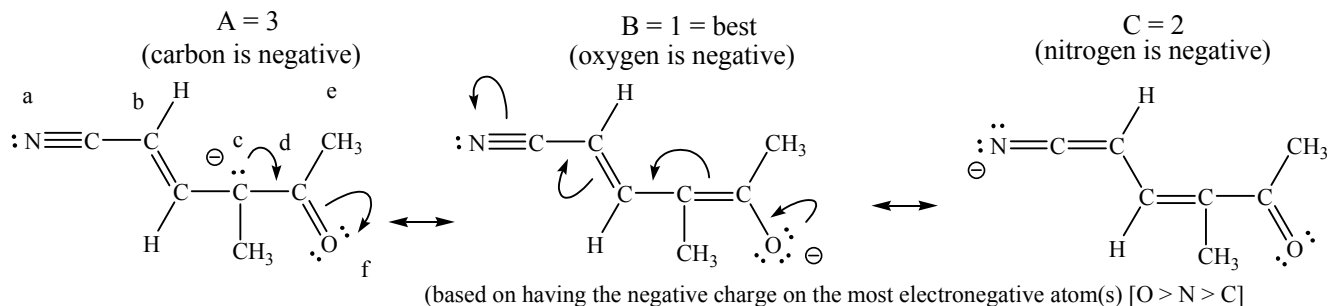
atomic configuration $1s^2, 2s^2, 2p^6$



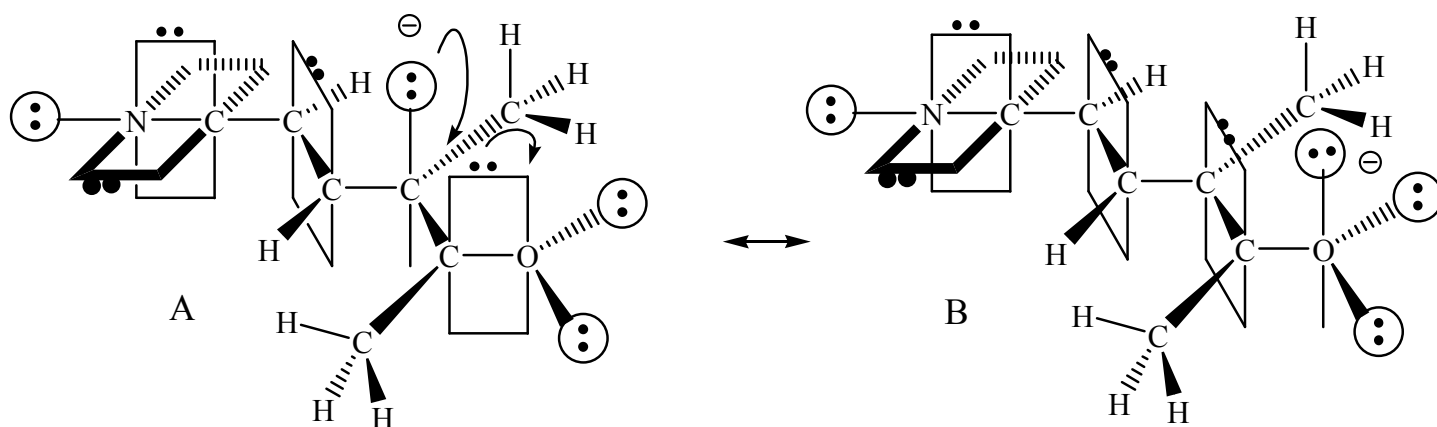
atomic radii: 132pm, 126pm, 119pm
 pm = picometer = 10^{-12} m

The more "extra" electrons an anion has the greater the electron/electron repulsion. The electron shell expands more when the charge is -3 than -2 and more when it is -2 than -1. So, N^{-3} has the largest radius, O^{-2} is in the middle and F^{-1} is the smallest radius. Also, F has a larger Z_{eff} than O than N which should contract the valence electron shell more. $\text{N}^{-3} = 132$ pm, $\text{O}^{-2} = 126$ pm and $\text{F}^{-1} = 119$ pm

5. First, draw two other **better** resonance structures than the one shown as two-dimensional representations. Include proper arrow conventions. Rank your structures from best (= 1) to poorest (= 3) with a very brief explanation. Draw a three-dimensional Lewis structure for the given representation and the best other resonance structure. Show sigma bonds as lines, wedges and dashes and the p orbitals in pi bonds as well as any orbitals holding lone pairs. Indicate any formal charge present and give the hybridization, bond angles and shape of each labeled nonhydrogen atom in the table below. Assume that all nonhydrogens atoms have full octets, unless a carbocation is written. (30 pts)



3D structure A and 3D best other



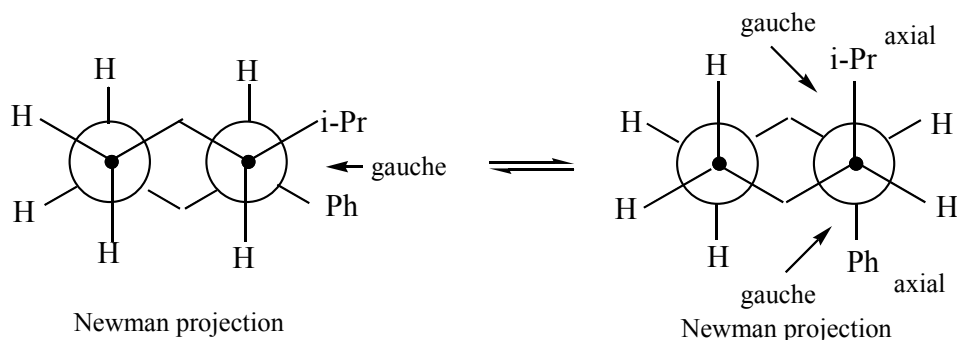
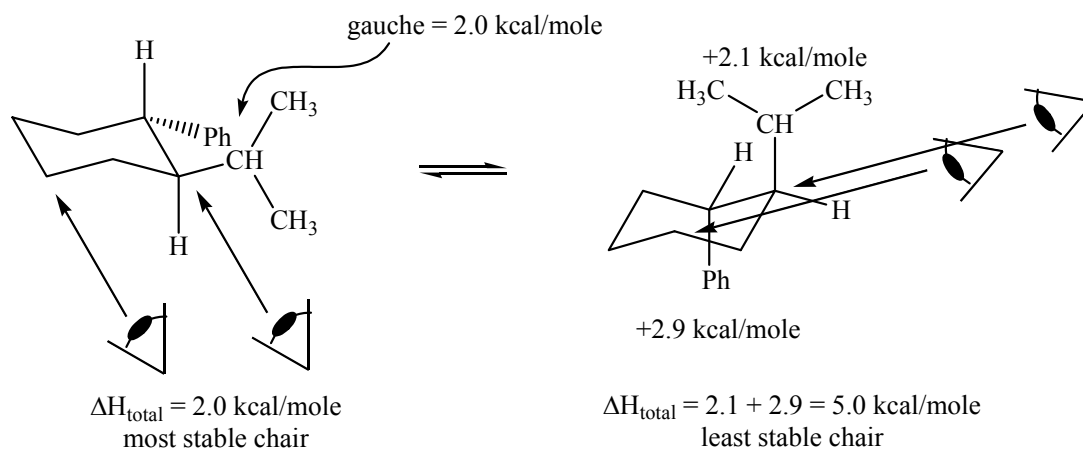
3D (A)

3D (best other)

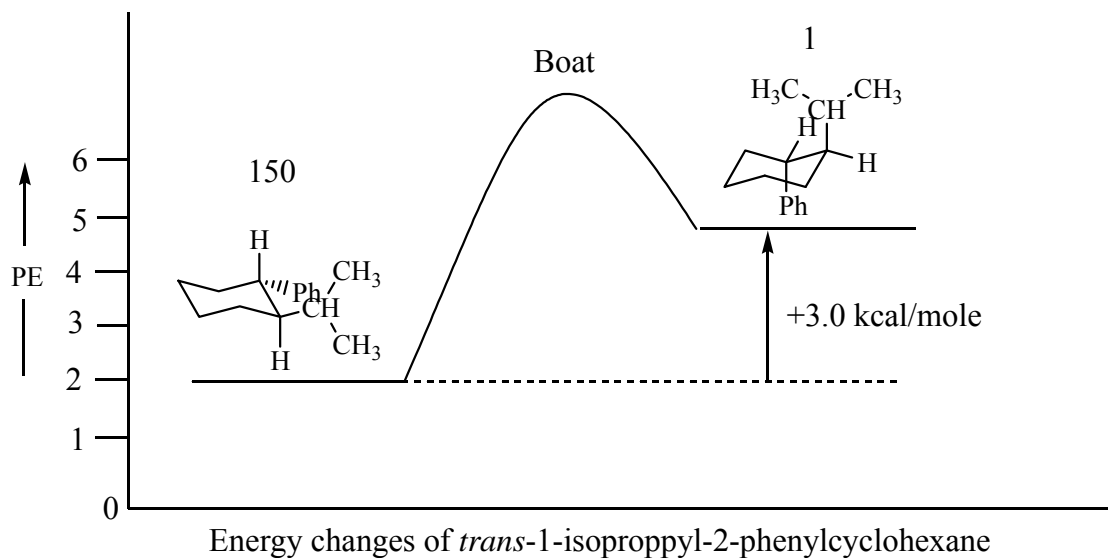
Use structure A to fill in the following table.

	Hybridization	Angles	Shape	# σ bonds	# π bonds	lone pairs
a	sp	180°	linear	1	2	1
b	sp ²	120°	trigonal planar	3	1	0
c	sp ²	120°	trigonal planar	3	0	1
d	sp ²	120°	trigonal planar	3	1	0
e	sp ³	109°	tetrahedral	4	0	0
f	sp ²	120°	trigonal planar	1	1	2

6. Draw all possible chair conformations of *trans*-1-isopropyl-2-phenylcyclohexane. Start with C₁ on the right side and count C₂ towards the back. Which conformation is more stable? Draw it first. Draw a Newman projection of each conformation using the C₁→C₂ and C₅→C₄ bonds to sight along. Point out any gauche interactions shown in your Newman projections. If the axial energy of an isopropyl group is 2.1 kcal/mole and 2.9 kcal for a phenyl group and an isopropyl/phenyl gauche interaction is 2.0 kcal/mole, what is the difference in energy between the chair conformations? What are the relative percents of each conformation (show work)? Sketch an energy diagram that shows how the energy changes from the conformational changes (start with low and go to high energy). (30 pts)

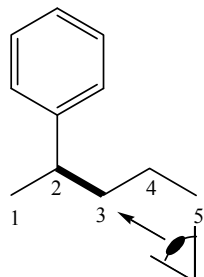


$$K = \frac{\text{chair 2}}{\text{chair 1}} = 10^{\frac{-\Delta G}{2.3RT}} = 10^{\frac{-(3000)}{1380}} = 10^{-2.17} = 0.00676 \approx \frac{1}{150}$$



7. Use a Newman projection of the C3→C2 bond of 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. Show all energy values by your structures. Plot the changes in energy in the graph diagram provided. Calculate and equilibrium constant between the lowest and highest energy conformations. Hint: Draw a 2D structure first and “bold” the bond viewed in your Newman projection, then decide your line of sight. (30 pts)

2D structure

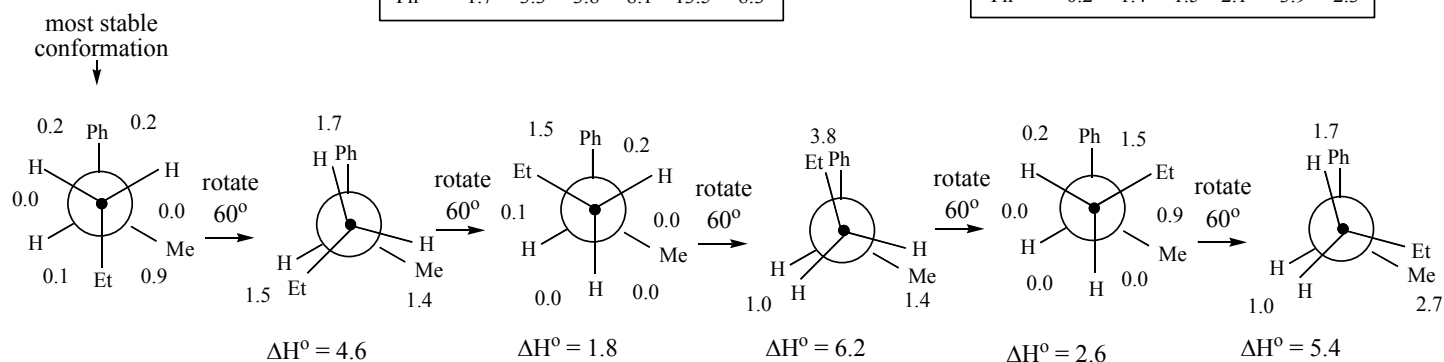


Approximate Eclipsing Energy Values (kcal/mole)						
	H	Me	Et	i-Pr	t-Bu	Ph
H	1.0	1.4	1.5	1.6	3.0	1.7
Me	1.4	2.5	2.7	3.0	8.5	3.3
Et	1.5	2.7	3.3	4.5	10.0	3.8
i-Pr	1.6	3.0	4.5	7.8	13.0	8.1
t-Bu	3.0	8.5	10.0	13.0	23.0	13.5
Ph	1.7	3.3	3.8	8.1	13.5	8.3

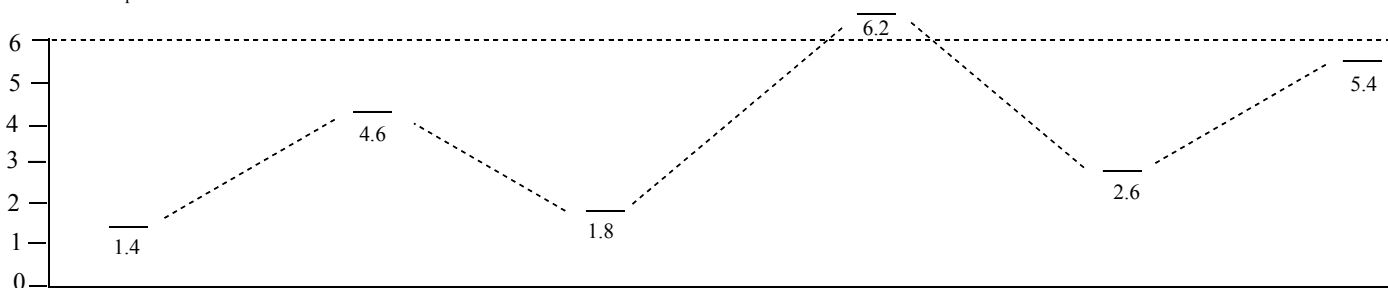
$$\Delta G \approx \Delta H$$

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

Approximate Gauche Energy Values (kcal/mole)						
	H	Me	Et	i-Pr	t-Bu	Ph
H	0	0	0.1	0.2	0.5	0.2
Me	0	0.8	0.9	1.1	2.7	1.4
Et	0.1	0.9	1.1	1.6	3.0	1.5
i-Pr	0.2	1.1	1.6	2.0	4.1	2.1
t-Bu	0.5	2.7	3.0	4.1	8.2	3.9
Ph	0.2	1.4	1.5	2.1	3.9	2.3

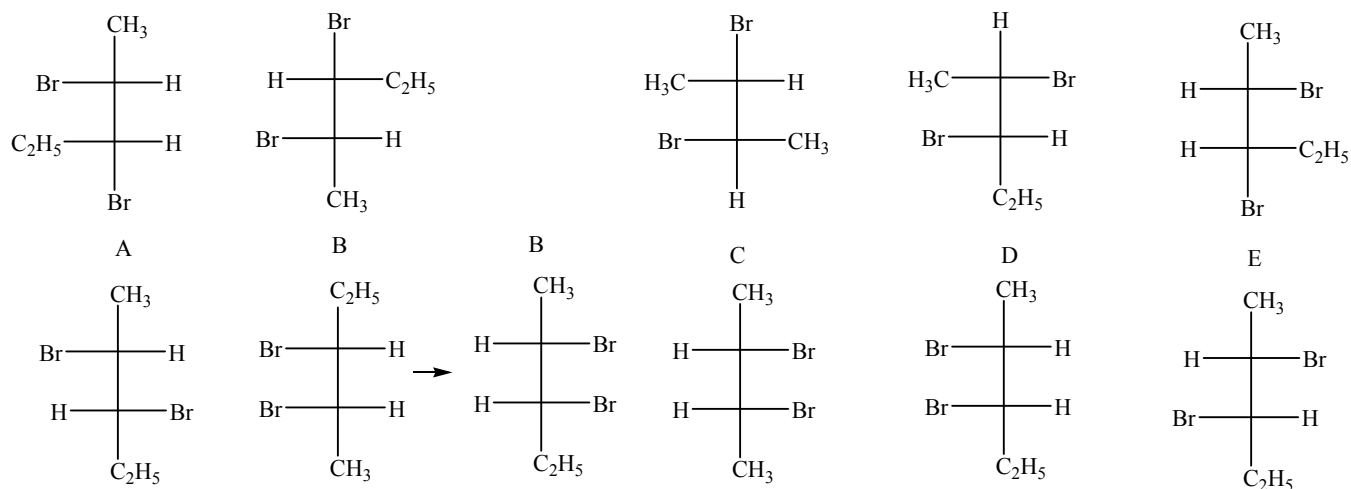


K_{eq} (lowest to highest) =



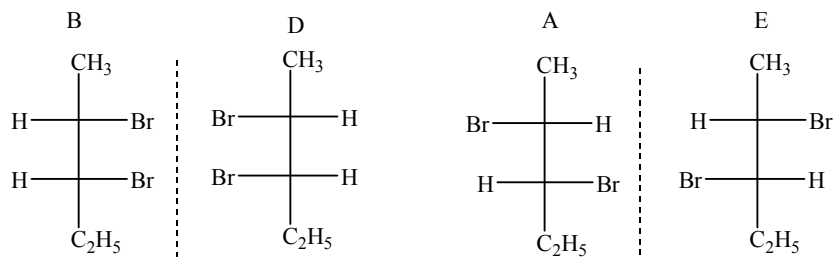
$$K = \frac{\text{conf. 4}}{\text{conf. 1}} = 10^{\frac{-\Delta G}{2.3RT}} = 10^{\frac{-(4800)}{1380}} = 10^{-3.47} = 0.00033 = \frac{1}{3000}$$

8. 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. (30 pts)



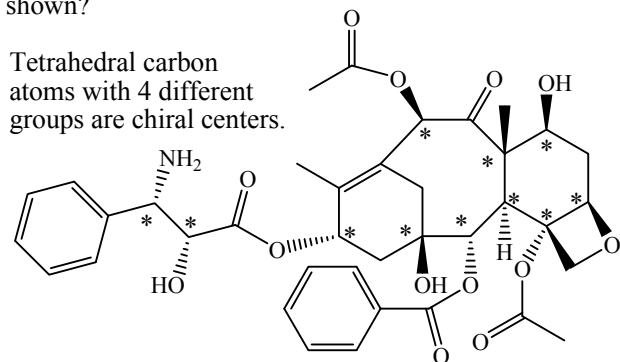
- a. Which are optically active?
 b. Which are meso?
 c. Which is not an isomer with the others?
 d. Which pairs are enantiomers?
 e. Which pairs are identical?
 f. Which pairs are diastereomers?
 g. Which pairs, when mixed in equal amounts will not rotate plane polarized light?
 h. Draw any missing stereoisomers of A.

<input type="checkbox"/> A	<input type="checkbox"/> B	<input type="checkbox"/> C	<input type="checkbox"/> D	<input type="checkbox"/> E					
A	B	<input type="checkbox"/> C	D	E					
A	B	<input type="checkbox"/> C	D	E					
AB	AC	AD	<input type="checkbox"/> AE	BC	<input type="checkbox"/> BD	BE	CD	CE	DE
AB	AC	AD	AE	BC	BD	BE	CD	CE	DE
<input type="checkbox"/> AB	AC	<input type="checkbox"/> AD	<input type="checkbox"/> AE	BC	<input type="checkbox"/> BD	<input type="checkbox"/> BE	CD	CE	<input type="checkbox"/> DE
AB	AC	AD	<input type="checkbox"/> AE	BC	<input type="checkbox"/> BD	BE	CD	CE	DE



None are missing

- j. Paclitaxel (discovered in the bark of a yew tree in 1971) is a potent chemotherapy medication used to treat several types of cancer, including ovarian cancer, breast cancer, lung cancer, Kaposi sarcoma, cervical cancer, and pancreatic cancer. Circle all chiral centers. How many stereoisomers are possible from the stereogenic centers shown?



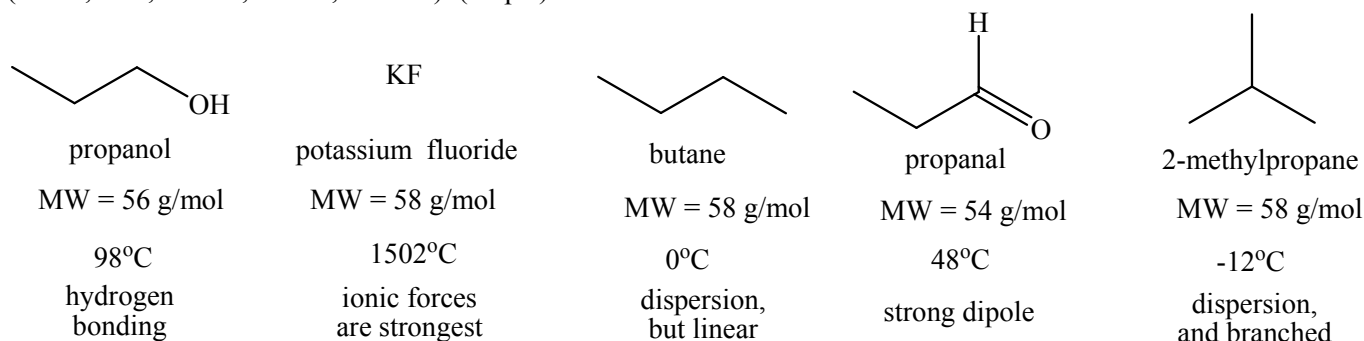
Maximum possible stereoisomers = $2^{11} = 2048$

The complete formula is $\text{C}_{38}\text{H}_{43}\text{NO}_{13}$
 What is the degree of unsaturation?
 Show your work.

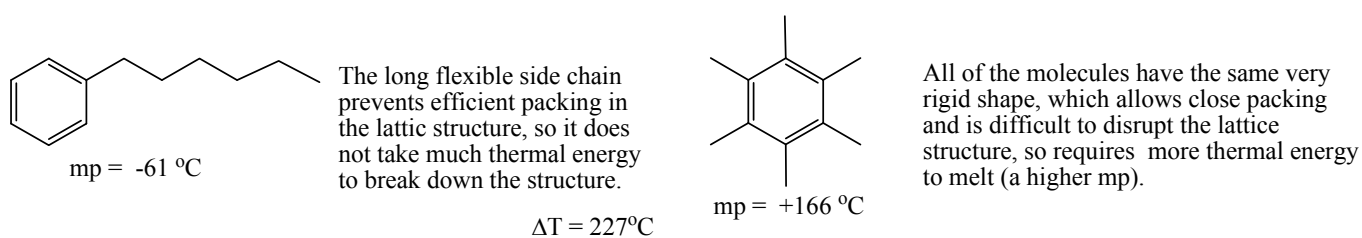
$$(2)(38) + 2 + 1 = 79$$

$$\frac{-43}{36 \div 2} = 18^\circ$$

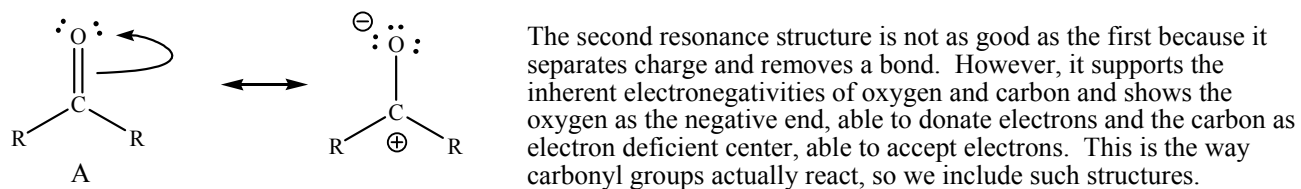
9. Match the given boiling points with the structures below and give a short reason for your answers. (-12°C, 0°C, +48°C, +98°C, 1502°C) (10 pts)



- b. Match the melting point with the isomers below and provide a brief explanation for the difference. (5 pts)



10. a. Resonance structures having fewer bonds and incomplete octets are considered of lesser importance. Yet, often they are drawn with functional groups having a carbonyl group (C=O). Show this extra resonance structure (include **ALL** lone pairs and proper resonance arrow conventions), and explain why it is considered “acceptable” for these groups. (5 pts)



- b. Indicate whether the changes made on A in each structure below (B and C) increase the importance of resonance or reduce its importance. Offer a very brief explanation. (10 pts)

