Name: _____

(Print your name)

Chem 2010

Spring, 2019

Midterm 1

PERIODIC TABLE OF THE ELEMENTS

PERIOD \ GROUP	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIIIB	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	1 1.008 **H** HYDROGEN																	2 4.0026 **He** HELIUM
2	3 6.94 **Li** LITHIUM	4 9.0122 **Be** BERYLLIUM											5 10.81 **B** BORON	6 12.011 **C** CARBON	7 14.007 **N** NITROGEN	8 15.999 **O** OXYGEN	9 18.998 **F** FLUORINE	10 20.180 **Ne** NEON
3	11 22.990 **Na** SODIUM	12 24.305 **Mg** MAGNESIUM											13 26.982 **Al** ALUMINIUM	14 28.085 **Si** SILICON	15 30.974 **P** PHOSPHORUS	16 32.06 **S** SULPHUR	17 35.45 **Cl** CHLORINE	18 39.948 **Ar** ARGON
4	19 39.098 **K** POTASSIUM	20 40.078 **Ca** CALCIUM	21 44.956 **Sc** SCANDIUM	22 47.867 **Ti** TITANIUM	23 50.942 **V** VANADIUM	24 51.996 **Cr** CHROMIUM	25 54.938 **Mn** MANGANESE	26 55.845 **Fe** IRON	27 58.933 **Co** COBALT	28 58.693 **Ni** NICKEL	29 63.546 **Cu** COPPER	30 65.38 **Zn** ZINC	31 69.723 **Ga** GALLIUM	32 72.64 **Ge** GERMANIUM	33 74.922 **As** ARSENIC	34 78.971 **Se** SELENIUM	35 79.904 **Br** BROMINE	36 83.798 **Kr** KRYPTON
5	37 85.468 **Rb** RUBIDIUM	38 87.62 **Sr** STRONTIUM	39 88.906 **Y** YTTRIUM	40 91.224 **Zr** ZIRCONIUM	41 92.906 **Nb** NIOBIUM	42 95.95 **Mo** MOLYBDENUM	43 (98) **Tc** TECHNETIUM	44 101.07 **Ru** RUTHENIUM	45 102.91 **Rh** RHODIUM	46 106.42 **Pd** PALLADIUM	47 107.87 **Ag** SILVER	48 112.41 **Cd** CADMIUM	49 114.82 **In** INDIUM	50 118.71 **Sn** TIN	51 121.76 **Sb** ANTIMONY	52 127.60 **Te** TELLURIUM	53 126.90 **I** IODINE	54 131.29 **Xe** XENON
6	55 132.91 **Cs** CAESIUM	56 137.33 **Ba** BARIUM	57-71 **La-Lu** Lanthanide	72 178.49 **Hf** HAFNIUM	73 180.95 **Ta** TANTALUM	74 183.84 **W** TUNGSTEN	75 186.21 **Re** RHENIUM	76 190.23 **Os** OSMIUM	77 192.22 **Ir** IRIDIUM	78 195.08 **Pt** PLATINUM	79 196.97 **Au** GOLD	80 200.59 **Hg** MERCURY	81 204.38 **Tl** THALLIUM	82 207.2 **Pb** LEAD	83 208.98 **Bi** BISMUTH	84 (209) **Po** POLONIUM	85 (210) **At** ASTATINE	86 (222) **Rn** RADON
7	87 (223) **Fr** FRANCIUM	88 (226) **Ra** RADIUM	89-103 **Ac-Lr** Actinide	104 (267) **Rf** RUTHERFORDIUM	105 (268) **Db** DUBNIUM	106 (271) **Sg** SEABORGIUM	107 (272) **Bh** BOHRIUM	108 (277) **Hs** HASSIUM	109 (276) **Mt** MEITNERIUM	110 (281) **Ds** DARMSTADTIUM	111 (280) **Rg** ROENTGENIUM	112 (285) **Cn** COPERNICIUM	113 (285) **Nh** NIHONIUM	114 (287) **Fl** FLEROVIUM	115 (289) **Mc** MOSCOVIUM	116 (291) **Lv** LIVERMORIUM	117 (294) **Ts** TENNESSINE	118 (294) **Og** OGANESSON

GROUP NUMBERS IUPAC RECOMMENDATION (1985) / GROUP NUMBERS CHEMICAL ABSTRACT SERVICE (1986)

ATOMIC NUMBER — SYMBOL — RELATIVE ATOMIC MASS (1) — ELEMENT NAME

Example: 13 IIIA / 13 IIA — 5 10.811 **B** BORON

LANTHANIDE

57 138.91 **La** LANTHANUM	58 140.12 **Ce** CERIUM	59 140.91 **Pr** PRASEODYMIUM	60 144.24 **Nd** NEODYMIUM	61 (145) **Pm** PROMETHIUM	62 150.36 **Sm** SAMARIUM	63 151.96 **Eu** EUROPIUM	64 157.25 **Gd** GADOLINIUM	65 158.93 **Tb** TERBIUM	66 162.50 **Dy** DYSPROSIUM	67 164.93 **Ho** HOLMIUM	68 167.26 **Er** ERBIUM	69 168.93 **Tm** THULIUM	70 173.05 **Yb** YTTERBIUM	71 174.97 **Lu** LUTETIUM

ACTINIDE

89 (227) **Ac** ACTINIUM	90 232.04 **Th** THORIUM	91 231.04 **Pa** PROTACTINIUM	92 238.03 **U** URANIUM	93 (237) **Np** NEPTUNIUM	94 (244) **Pu** PLUTONIUM	95 (243) **Am** AMERICIUM	96 (247) **Cm** CURIUM	97 (247) **Bk** BERKELIUM	98 (251) **Cf** CALIFORNIUM	99 (252) **Es** EINSTEINIUM	100 (257) **Fm** FERMIUM	101 (258) **Md** MENDELEVIUM	102 (259) **No** NOBELIUM	103 (262) **Lr** LAWRENCIUM

www.periodni.com

(1) Atomic weights of the elements 2013, Pure Appl. Chem., **88**, 265-291 (2016)

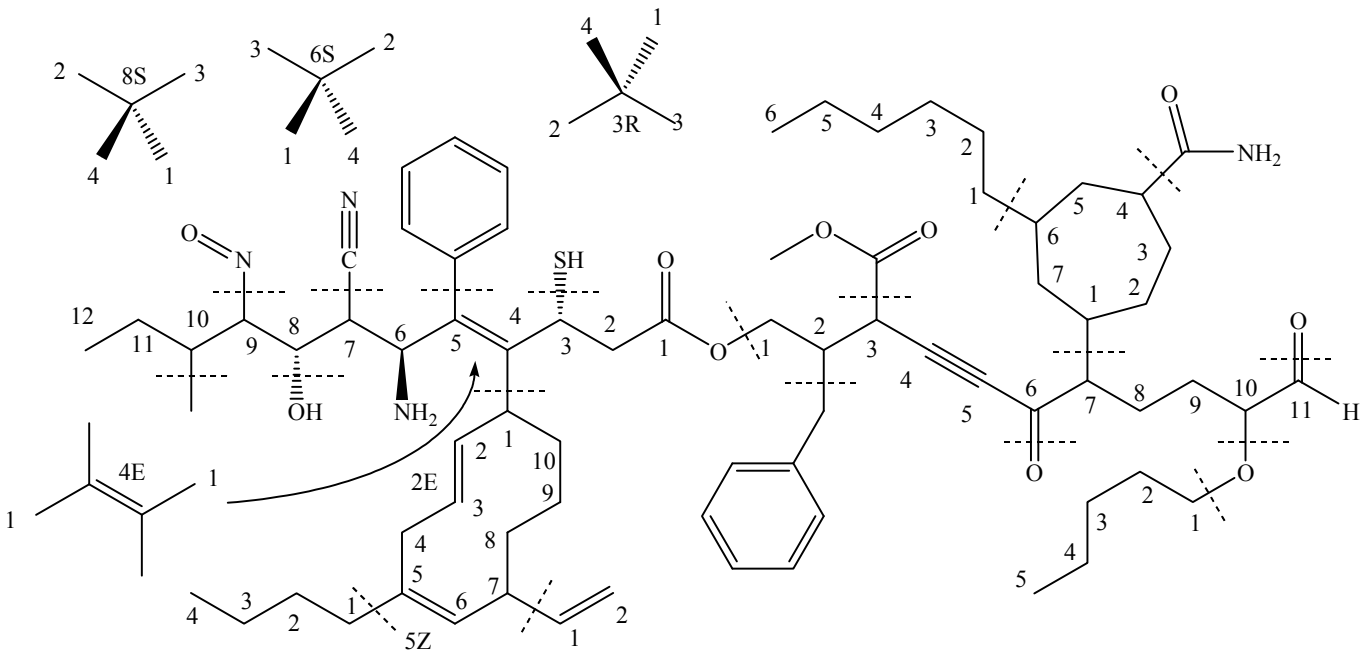
Chem 2010 Midterm 1
Spring, 2019
Beauchamp Name _____

Problems	Points	Credit
1. Functional Group Nomenclature (1 large structure)	30	
2. Lewis Structures, Resonance, Formal Charge	20	
3. Cyclohexane Conformations, 2 substituents, Newman Projections, Relative Energies, K_{eq} Calculation	32	
4. Newman Projections, Conformational Energies, K_{eq} Calculation	30	
5. Stereochemical Analysis	30	
6. 2D Resonance Structures, 3D Structure, Hybridization, Angles, Shapes, Explain bond energies	32	
7. Types of isomers from a given formula	26	
8. Draw a long 2D structure and identify functional groups	26	
9. Physical Properties	26	
Total	252	

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.

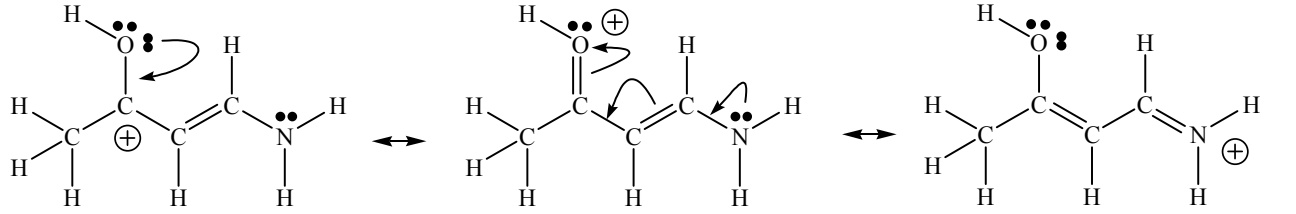
"Yesterday I was clever, so I wanted to change the world. Today I am wise, so I am changing myself."
— Rumi

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



2-benzyl-3-methoxycarbonyl-6,11-dioxo-7-(4-amido-6-hexyl-cycloheptyl)-10-pentoxyundec-4-ynyl (3R,4E,6S,8S)-3-mercapto-4-(5-butyl-7-ethenylcyclodeca-2E,5Z-dienyl)-5-phenyl-6-amino-7-cyano-8-hydroxy-9-nitroso-10-methyldodec-4-enoate

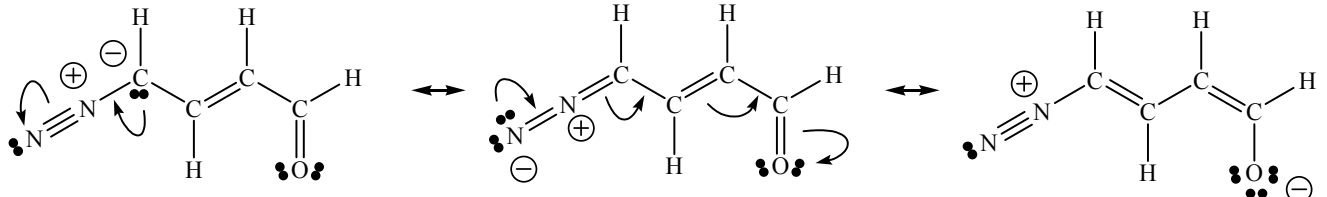
2. Indicate all formal charges present in the following structures. Assume all electrons are shown as lines or dots. Draw 2 better resonance structures using the proper arrow conventions. Order the resonance structures from best (=1) to worst (=3). (20 pts)



3, one less bond, incomplete octet on carbon

2, an extra bond, full octets but + on oxygen, less willing to share electrons than nitrogen

best = 1, an extra bond, full octets and + on nitrogen, more willing to share electrons than oxygen

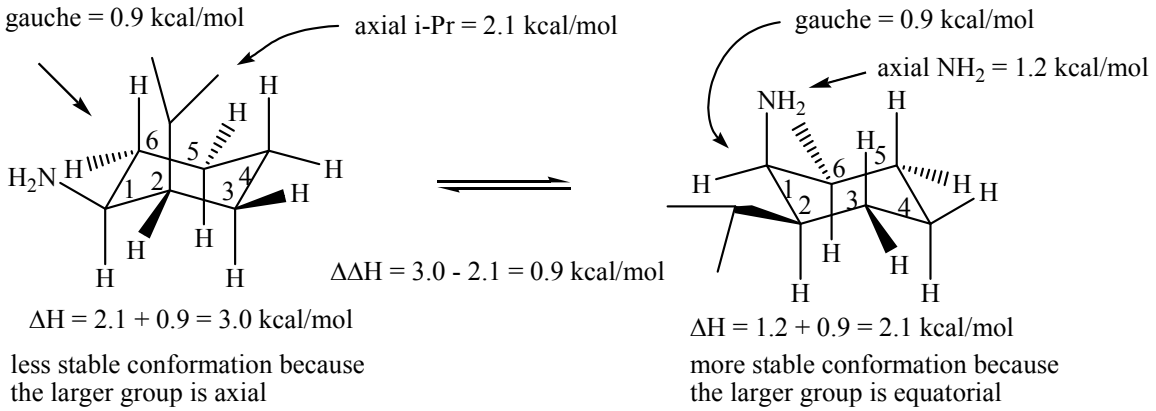


#3 same number of bonds and ⊖ is on carbon, that's OK, but less electronegative than nitrogen and oxygen

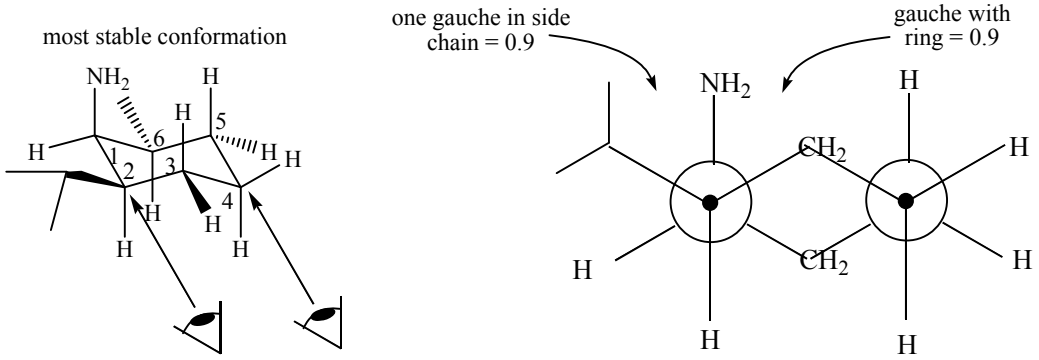
#2 same number of bonds and ⊖ is on nitrogen, middle electronegative, better than carbon

#1 same number of bonds and ⊖ is on oxygen, more electronegative, better than carbon or nitrogen

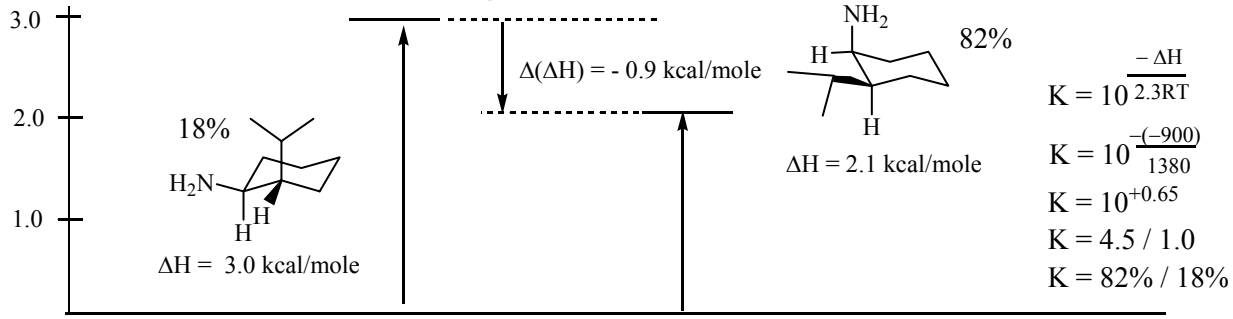
3. Draw all possible chair conformations of cis-1- amino-2-isopropyllcyclohexane. Make the left most ring carbon C1 and number towards the front. Show **all** axial and equatorial groups in the first chair. Which conformation is more stable? Provide a reason for your answer. Draw a Newman projections of the most stable conformation using the $C_2 \rightarrow C_1$ and $C_4 \rightarrow C_5$ bonds to sight along. Point out any gauche interactions shown in your Newman projection. If the axial energy of a isopropyl group is 2.1 kcal/mole and the axial energy of amino group is 1.2 kcal/mole and a isopropyl/amino gauche interaction is 0.9 kcal/mole, what is the ratio of the two conformations at equilibrium? Show your work. Sketch an energy diagram that shows how the energy changes (higher to lower) with the conformational changes. (14 pts, 32 pts total)



b. Newman projection ($C_2 \rightarrow C_1$ and $C_4 \rightarrow C_5$) – most stable, point out any gauche interactions with the substituent(s) (6 pts)



c. Energy diagram and relative percents (K_{eq} = ?) (6 pts)



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

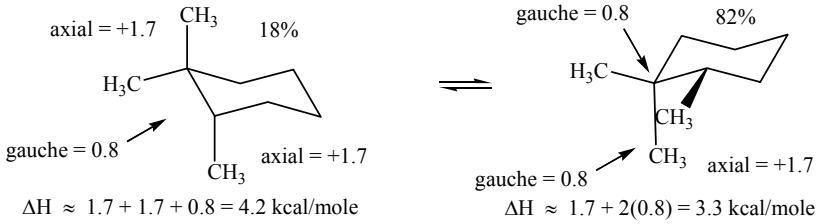
$$K = 10^{\frac{-(-900)}{1380}}$$

$$K = 10^{+0.65}$$

$$K = 4.5 / 1.0$$

$$K = 82\% / 18\%$$

d. Calculate an approximate ΔH 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. (6 pts)



The energy table is not shown here.

$\Delta(\Delta H) = 4.2 - 3.3 = - 0.9$ kcal/mole

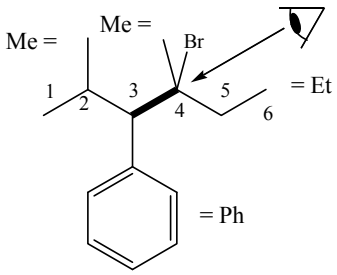
$$K = 10^{\frac{-(+900)}{1380}} = 10^{-0.65} = 0.22 = 1 / 4.5$$

4. Use a Newman projection of the C4→C3 bond of 2,4-dimethyl-3-phenyl-4-bromohexane to **show the most stable conformation first**. Rotate through all of the eclipsed and staggered conformations. Using the energy values provided in the tables 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. (30 pts)

2D Structure (4 pts, provided at cost of points)

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	(1.2)
Me	1.4	2.5	2.7	3.0	8.5	3.3	2.0
Et	1.5	2.7	3.3	4.0	10.0	3.8	2.4
i-Pr	1.6	(3.0)	(4.0)	7.8	13.0	8.1	(2.7)
t-Bu	3.0	8.5	10.0	13.0	23.0	13.5	7.5
Ph	1.7	(3.3)	(3.8)	8.1	13.5	8.3	(3.0)
Br	1.2	2.0	2.4	2.7	7.5	3.0	2.2



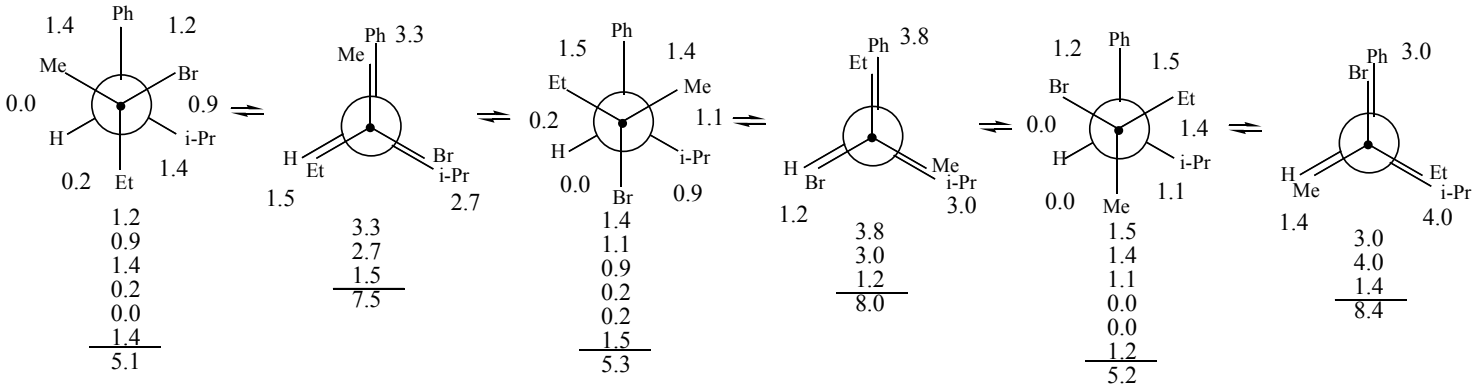
$\Delta G \approx \Delta H$

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

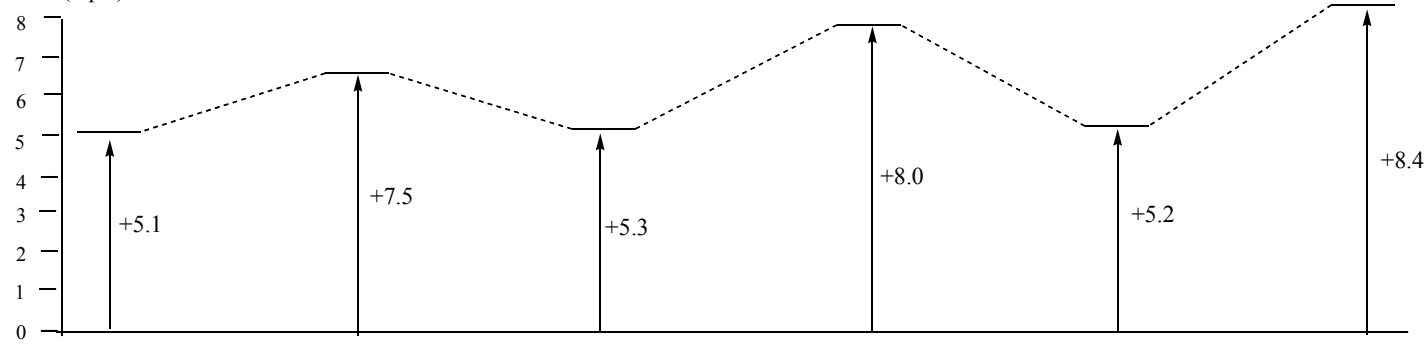
Approximate Gauche Energy Values (kcal/mole)
Some were estimated by me.

	H	Me	Et	i-Pr	t-Bu	Ph	Br
H	0	(0)	(0.2)	0.3	0.7	0.4	(0.0)
Me	0	0.8	0.9	1.1	2.7	1.4	0.6
Et	0.2	0.9	1.1	1.4	3.0	1.5	0.7
i-Pr	0.3	(1.1)	(1.4)	2.0	4.1	2.1	(0.9)
t-Bu	0.7	2.7	3.0	4.1	8.2	3.9	2.4
Ph	0.4	(1.4)	(1.5)	2.1	3.9	2.3	(1.2)
Br	0.0	0.6	0.7	0.9	2.4	1.2	0.8

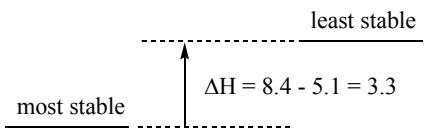
Newman projections (show work, 18 pts):
lowest PE



PE (4 pts)



K_{eq} calculation (4 pts)

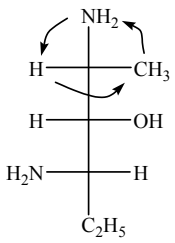


$\Delta(\Delta H) = 8.4 - 5.1 = 3.3$ kcal/mole

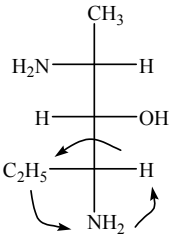
$K_{eq} = 10^{\frac{-3300}{1380}}$

$K_{eq} = 10^{-2.4} = 0.0041 = 1 / 240 = (\text{least}) / (\text{most})$

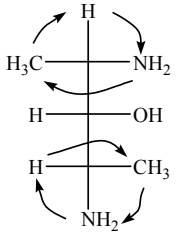
5. Use the following set of Fischer projections to answer each of the questions below by circling the appropriate letter(s) or letter combination(s). Hint: Redraw the Fischer projections with the longest carbon chain in the vertical direction and having similar atoms in the top and bottom portion. Classify all chiral centers in the first structure as R or S absolute configuration. (30 pts)



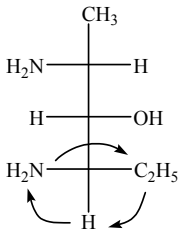
A
(R/S, 3 pts)



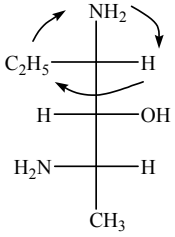
B



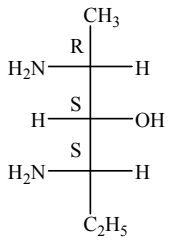
C

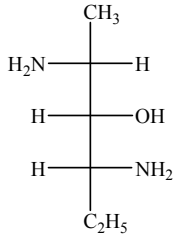


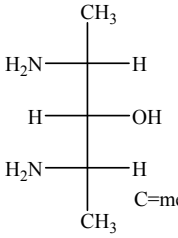
D



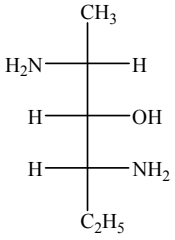
E

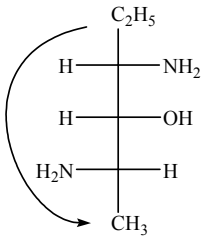


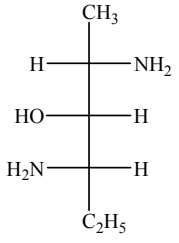




C=meso







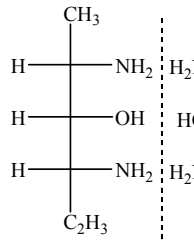
a. Which are optically active?
b. Which are meso?
c. Which is not an isomer with the others?
d. Which pairs are enantiomers?
e. Which pairs are identical?
f. Which pairs are diastereomers?
g. Which pairs, when mixed in equal amounts will not rotate plane polarized light?

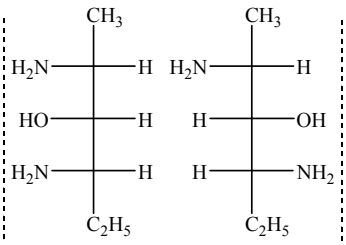
(15 pts)

a.	(A)	(B)	C	(D)	(E)					
b.	A	B	(C)	D	E					
c.	A	B	(C)	D	E					
d.	AB	AC	AD	AE	BC	BD	(BE)	CD	CE	(DE)
e.	AB	AC	AD	AE	BC	(BD)	BE	CD	CE	DE
f.	(AB)	AC	(AD)	(AE)	BC	BD	BE	CD	CE	DE
g.	AB	AC	AD	AE	BC	BD	(BE)	CD	CE	(DE)

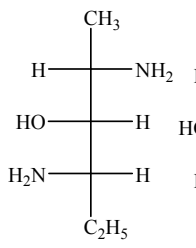
h. Draw any stereoisomers of 2,4-diaminohexan-3-ol as Fischer projections, which are not shown above. If there are none, indicate this. (5 pts)

B = D



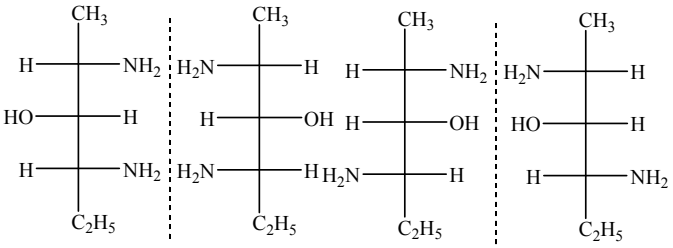


E

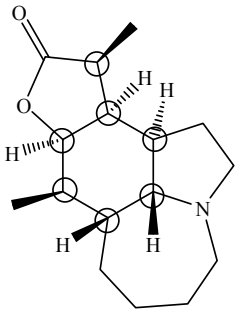


3 chiral centers = 2^3 possible stereoisomers = 8

A



i. Stenine is an antitussive (anti cough) alkaloid isolated from Stenoma moths. A recent article in Org. Lett. 2019, 21, 18-21 published a synthesis. Circle all of the chiral centers. How many stereoisomers are possible? Show work. (5 pts)



Stenine

chiral centers = 7

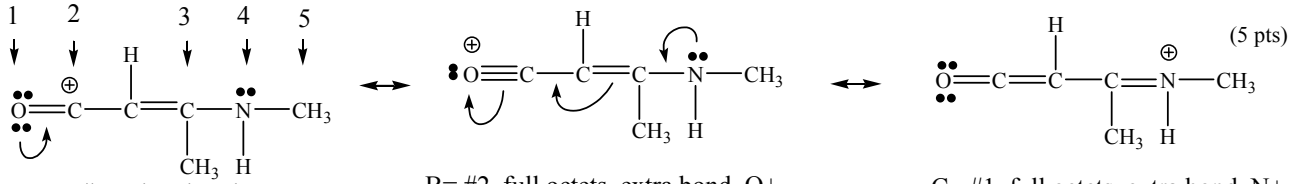
possible stereoisomers $2^7 = 128$

j. What is the degree of unsaturation? Show work. (2 pts)

$C_{13}H_{11}BrClFN_2O_2$

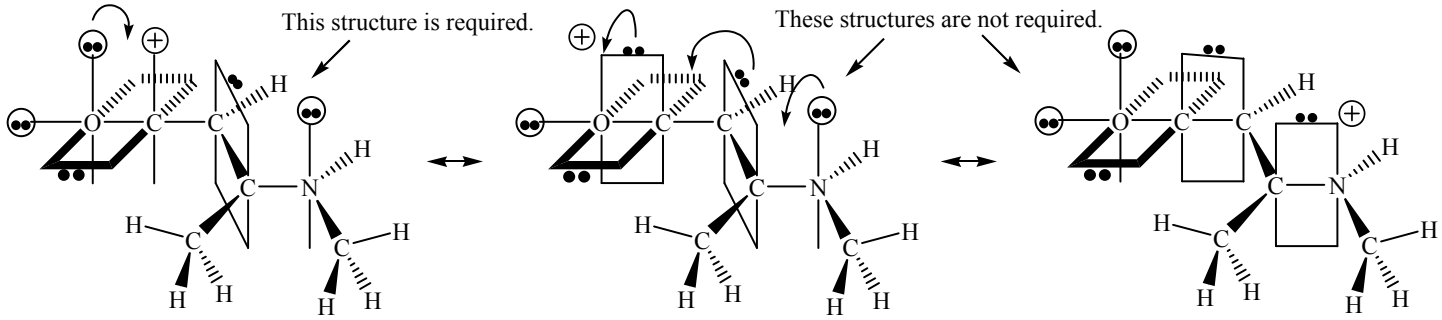
2(13) + 2 + 2 = 30
- 14
16 ÷ 2 = 8 degrees

6. Assume all nonhydrogen atoms have full octets except when + carbon is shown. Add in any necessary lone pairs and use proper curved arrows. Draw two additional "**better**" 2D resonance structures of the given structure. Which structure(s) is(are) best and why? Draw a 3D structure **for the given 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 for pi bonds and lone pairs along with their electrons. Identify the hybridization, bond angles and descriptive shape for all numbered atoms in the **given** structure. (32 pts)



A = #3, 1 less bond, C+ B= #2, full octets, extra bond, O+ C= #1, full octets, extra bond, N+

3D structure of A (13 pts)

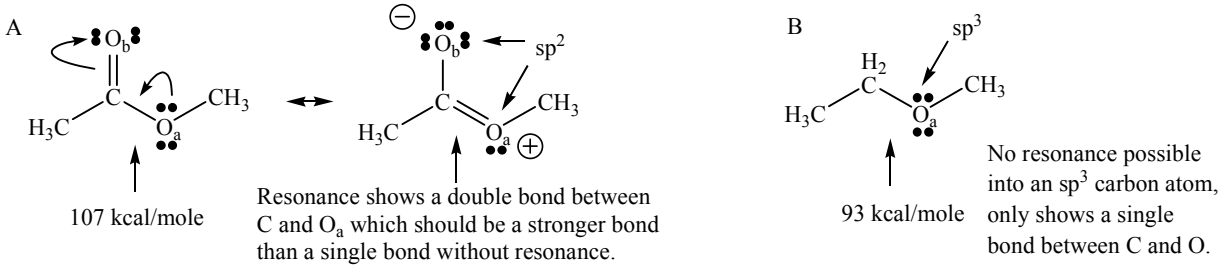


A = #3, 1 less bond, C+ B= #2, full octets, extra bond, O+ C= #1, full octets, extra bond, N+

Use the given (first) Lewis structure to answer this part. (10 pts)

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

Explain the different C-O_a bond energies. Use structures in your explanation. Include any necessary lone pairs, formal charge, curved arrows, etc. What are the hybridizations of the oxygen atom in A and B? (4 pts)



7. Use the formula $C_5H_8Br_2$ 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)

<table>
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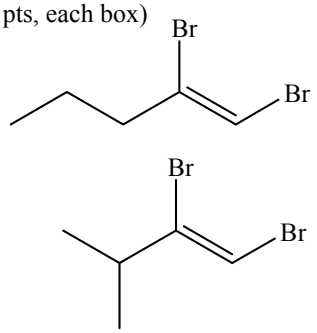
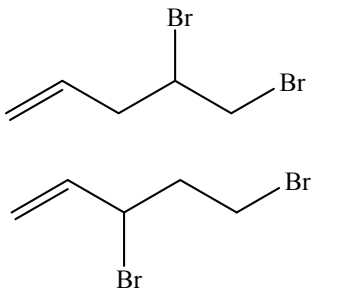
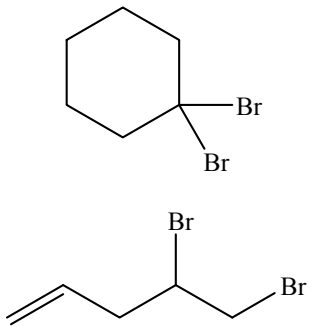
<td>(4 pts, each box)
 
skeletal isomers</td>
<td> 
positional isomers</td>
<td> 
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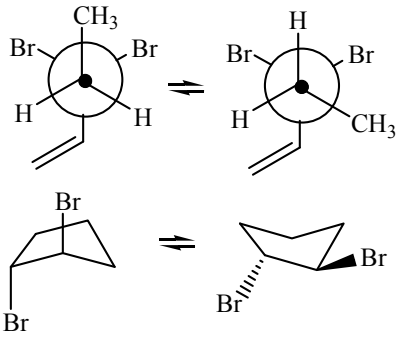
<td> 
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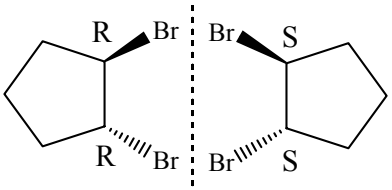
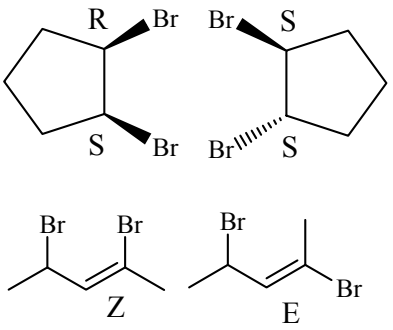
<td> 
R/S not required
enantiomers</td>
<td> 
diasteromers</td>
</tr>
</table>

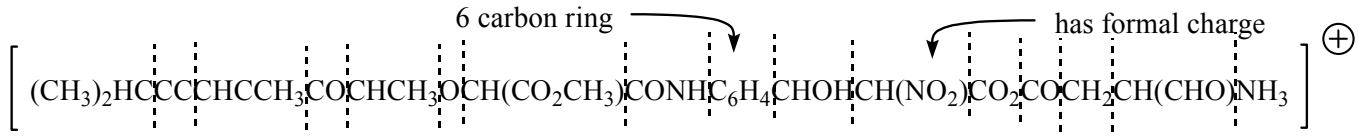
Degree of unsaturation calculation.

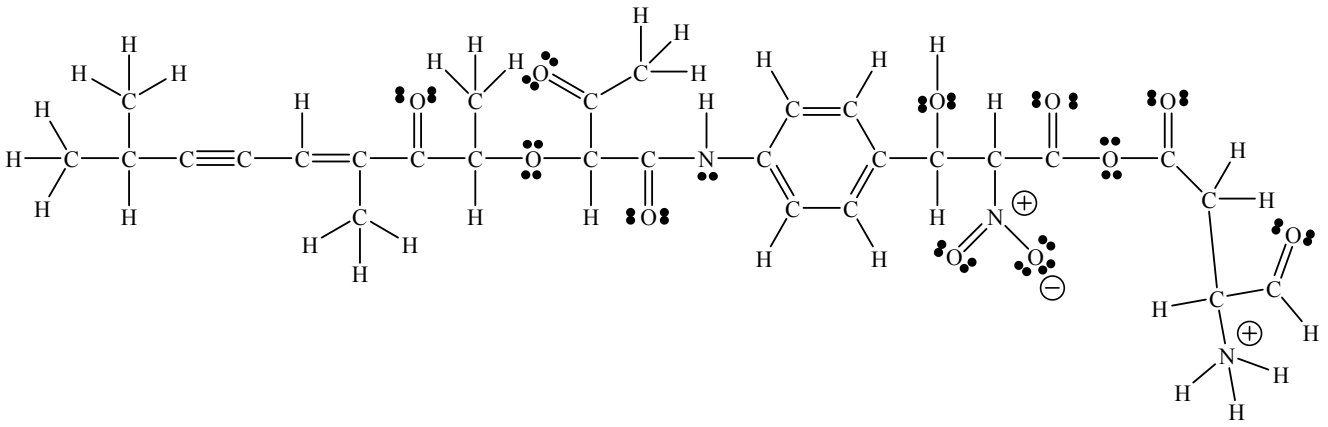
$C_5H_8Br_2$ $\quad 2(5) + 2 = 12$

$\qquad\qquad\qquad\quad - 10$

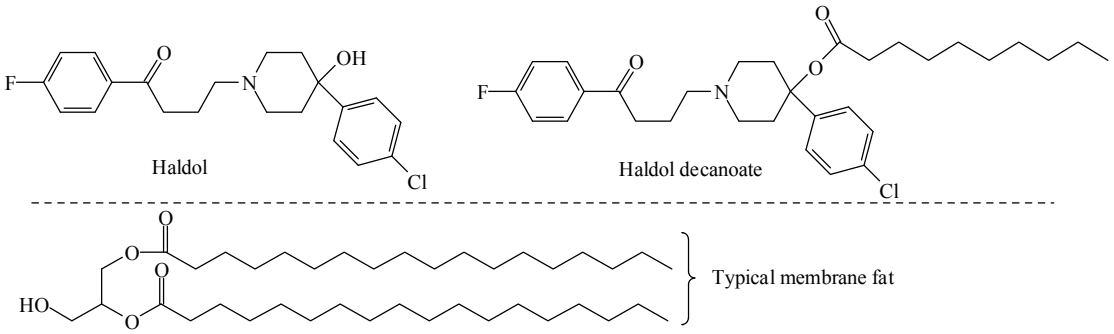
$\qquad\qquad\qquad = 2 \div 2 = 1$ degreee unsaturation (= pi bond or a ring)

8. Draw a 2D structure that includes the listed functional groups. Write the functional group name by its appearance in your 2D structure. Calculate the degree of unsaturation for the given formula. (26 pts)





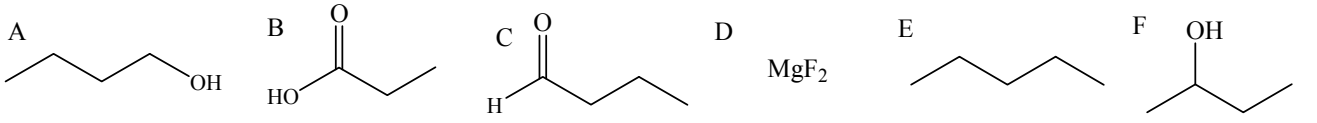
9. a. Haldol is a potent orally active central nervous system tranquilizer used in the treatment of psychoses. Peak plasma levels, when taken orally, are 2-6 hours (in the aqueous blood). Cell membranes, on the other hand, are composed largely of alkane-like fatty acid chains. A decanoate ester prodrug 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)



The alcohol "O-H" 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 rapidly 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, 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. (10 pts)

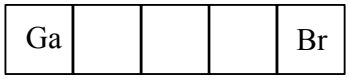
boiling points: 2260°C, 141°C, 118°C, 99°C, 75°C, 36°C



MW = 72 g/mol | MW = 74 g/mol | MW = 72 g/mol | MW = 62 g/mol | MW = 72 g/mol | MW = 72 g/mol

MgF_2 (D = 2260°) is ionic and has a super high boiling point to break down the very strong lattice structure. The carboxylic acid (B = 141°) has hydrogen bonding and a polar C=O bond which interact together to make the second highest boiling point. The straight chain alcohol (A = 118°) can get closer to the neighbor molecules than the branched alcohol (F = 99°), so it boils a little higher. The aldehyde (C = 75°) has polarity in the C=O bond, but no hydrogen bonding, so it has a little lower boiling point than the alcohols. The alkane (E = 36°) only has dispersion forces, and is the lowest boiling compound in this group since they are all about the same size.

c. Which atom has the higher first ionization potential and why? (Ga or Br) (3 pts)



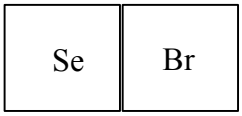
Z_{eff} = +3 Z_{eff} = +7

Br has a higher ionization potential than Ga

Gallium (#31)and bromine (#35) are in the same n=4 row and shielded by the first 3 shells of electrons (28 electrons). The higher Z_{eff} of bromine means that it will hold onto the valence electron much tighter and require more energy to ionize one of its electrons (has a higher ionization potential). IP_1 (Br) = 273 kcal/mol) > IP_1(Ga) = 138 kcal/mol

d. Which neutral atom has the larger atomic radius and why? (Se or Br) (3 pts)

Z_{eff} = +6 Z_{eff} = +7



Selenium (#34) and bromine (#35) are in the same n=4 row and shielded by the first 3 shells of electrons (28 electrons). The higher Z_{eff} of bromine means that it will hold onto the valence electron much tighter and contract the valence electron shell more and have a smaller radius than selenium.

r_{Br} = 94 pm, r_{Se} = 103 pm (pm = 10^{-12} m)

"Action is the foundational key to all success." — Pablo Picasso