Chem 201 Midterm
Spring, 2018

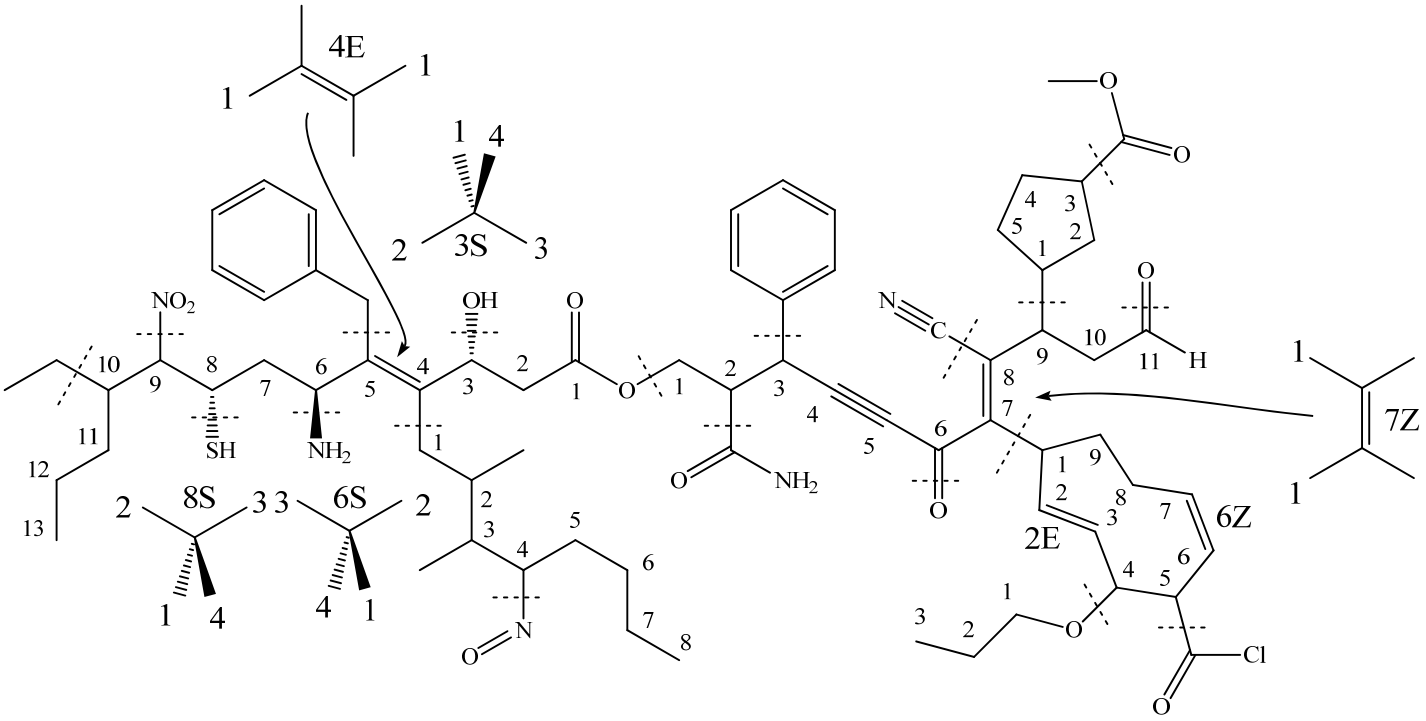
Beauchamp Name _____KEY_____

Problems	Points	Credit
1. Functional Group Nomenclature (1 large structure)	30	
2. Resonance, Formal Charge, Arrows	18	
3. Cyclohexane Conformations, Newman Projections	30	
4. Newman Projections, Conformational Energies	25	
5. Stereochemical Analysis	30	
6. 3D Structure, Resonance, Hybridization, Angles, Shapes (1)	30	
7. 2D Lewis Structures (1, large)	20	
8. Functional Groups, Names or Types of Isomers or Special Types of Carbons and Substituents, Degrees of Unsaturation	25	
9. Forces of Interaction and Physical Properties	20	
10. Properties of Atoms, (ionization potential, Z_{eff}, radii, electronegativity), Logic Arguments of Organic Chemistry (inductive, resonance, steric)	30	
Total	258	

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.

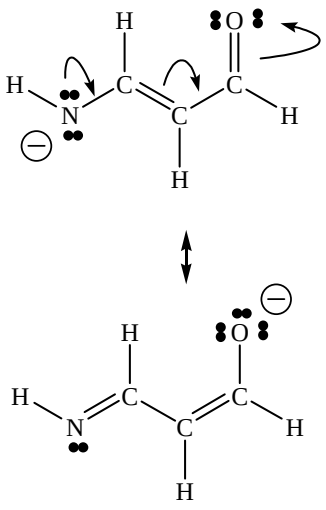
I have no special talent. I am only passionately curious. Albert Einstein

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

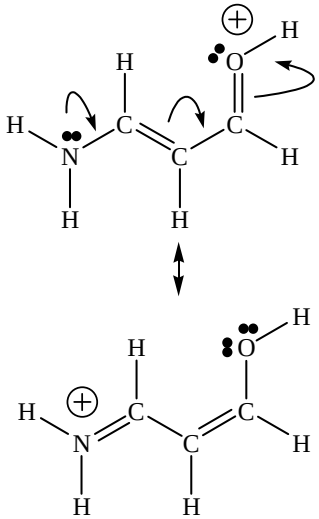


2-amido-3-phenyl-6,11-dioxo-7-(4-propoxy-5-chlorocarbonylcyclonona-2E,6Z-dienyl)-8-cyano-9-(3-methoxycarbonylcyclopentyl)undec-7Z-en-4-ynyl 3S-hydroxy-4-(2,3-dimethyl-4-nitrosooctyl)-5-benzyl-6S-amino-8S-mercapto-9-nitro-10-ethyltridec-4E-enoate

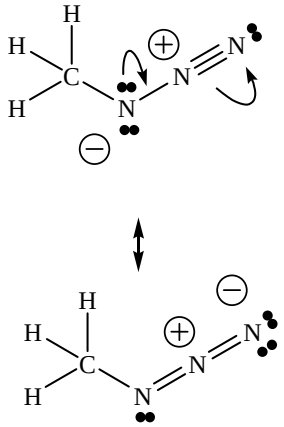
2. Indicate all formal charges present in the following structures. Assume all electrons are shown as lines or dots. If other reasonable resonance structures are possible, draw the best other resonance structure using the proper arrow conventions. Indicate which resonance structure is better or if they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



better resonance, negative charge is on oxygen, same number of bonds



better resonance, positive charge is on nitrogen, same number of bonds



similar resonance structures, both have minus charge on nitrogen, same number of bonds

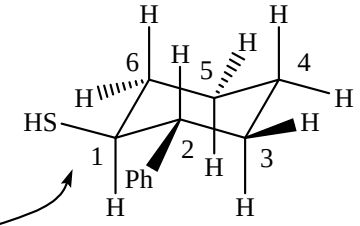
3. Draw all possible chair conformations of trans-1- mercapto-2-phenyllcyclohexane. The axial energy of the thiol group is 1.2 kcal/mole and axial energy of phenyl is 2.9 kcal/mole. The gauche energy of thiol/phenyl is 1.1 kcal/mole. Make the left most ring carbon C_1 and number towards the front. Show **all** axial and equatorial groups in the first chair. Which conformation is more stable? Provide a reason for your answer. Draw a Newman projection 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 of the substituents shown in your Newman projection. What is the ratio of the two conformations at equilibrium? Show your work. Sketch an energy diagram that shows how the energy changes (lower to higher) with the conformational changes and estimate the ratio of the two conformations at equilibrium. (30 pts)

a.

trans-1- mercapto-2-phenylcyclohexane

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

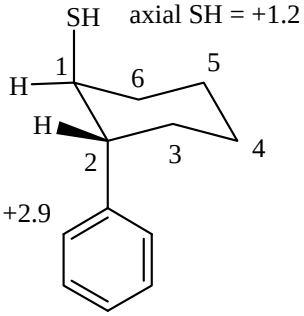
R = 2 cal/mol-K
T = 300 K



one gauche = +1.1

chair 1
(more stable no axial groups, only 1 gauche)

ΔH_{total} = 1.1 kcal/mole

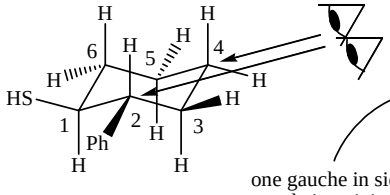


chair 2
(less stable, 2 axial groups)

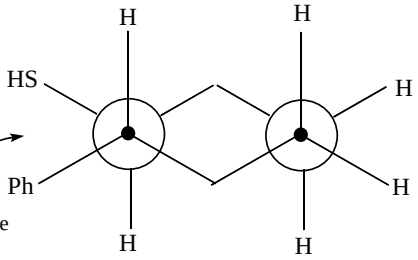
ΔH_{total} = 1.2 + 2.9 = 4.1 kcal/mole

$\Delta(\Delta H)$ = 4.1 - 1.1 = 3.0 kcal/mole
axial groups are less stable so ΔH is positive and $K_{eq} < 1$.

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)

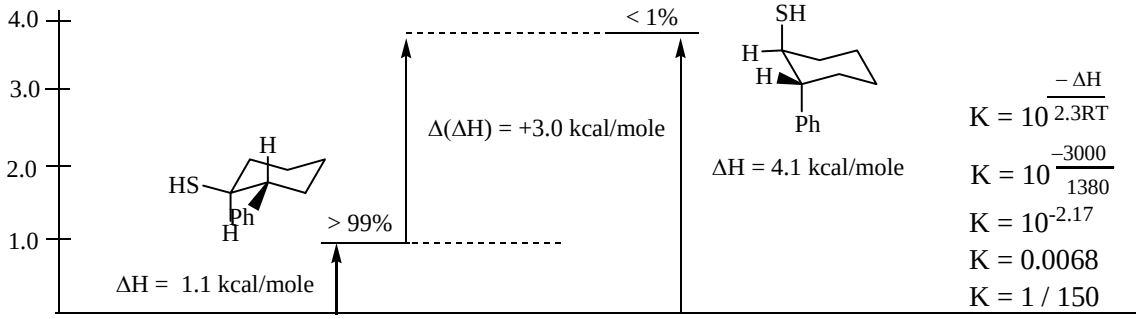


one gauche in side chain = 1.1



chair 1 is more stable

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



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

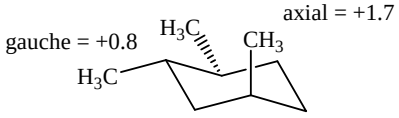
$K = 10^{\frac{-3000}{1380}}$

$K = 10^{-2.17}$

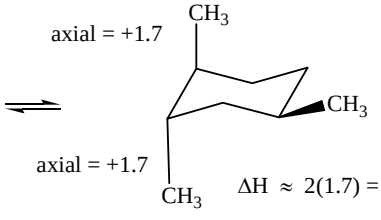
K = 0.0068

K = 1 / 150

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.



$\Delta H \approx 1.7 + 0.8 = 2.5$ kcal/mole



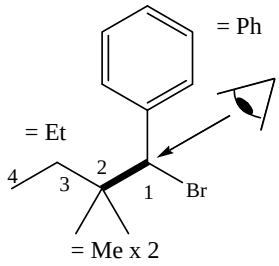
$\Delta H \approx 2(1.7) = 3.4$ kcal/mole

The energy table is not shown here.

$\Delta(\Delta H)$ = 3.4 - 2.5 = 0.9 kcal/mole

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

4. Use a Newman projection of the $C_1 \rightarrow C_2$ bond of 1-bromo-1-phenyl-2,2-dimethylbutane 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. (25 pts)



$C_2 \rightarrow C_3$

3-ethyl-2-phenylhexane

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

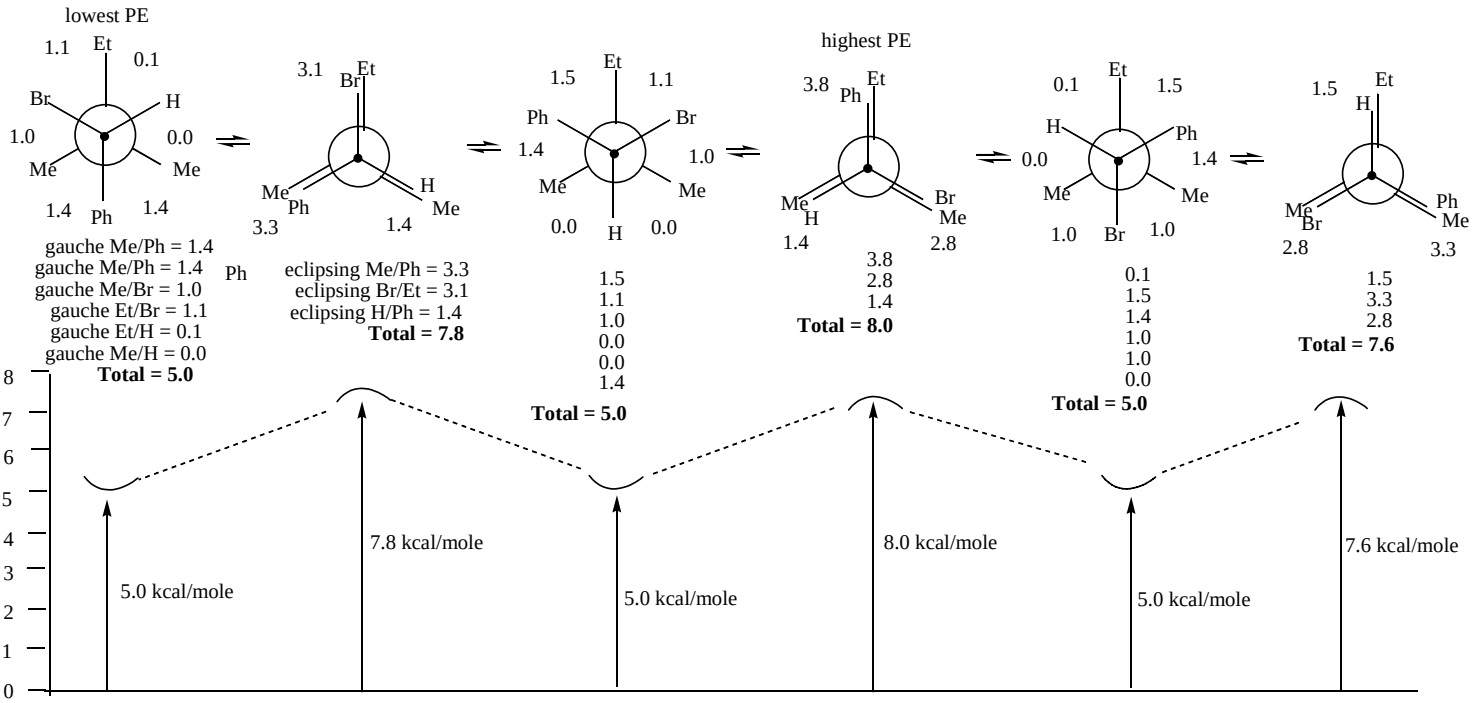
$\Delta G \approx \Delta H$

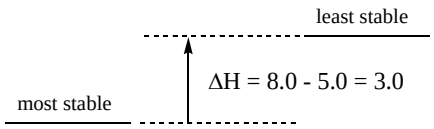
$K_{eq} = 10^{\frac{-\Delta H}{2.3RT}}$

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	1.1
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	1.1	1.6	3.3	1.9	1.1

Newman projections:



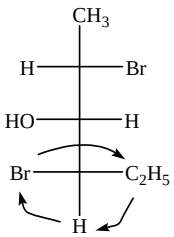


$\Delta(\Delta H) = 8.0 - 5.0 = 3.0$ kcal/mole

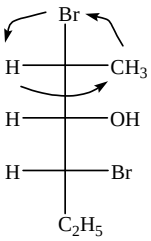
$K_{eq} = 10^{\frac{-3000}{1380}}$

$K_{eq} = 10^{-2.17} = 0.0067 = 1 / 150 = (\text{least}) / (\text{most})$

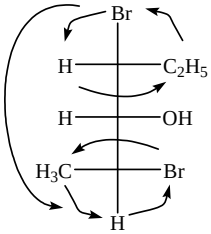
5. Use the following set of Fischer projections to answer each of the questions below by circling the appropriate letter(s) or letter combination(s). Hint: Redraw the Fischer projections with the longest carbon chain in the vertical direction and having similar atoms in the top and bottom portion. Classify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



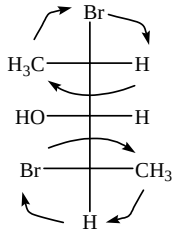
(3 pts) A



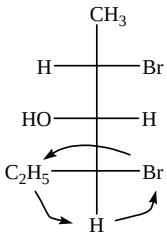
B



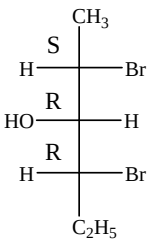
C

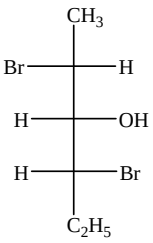


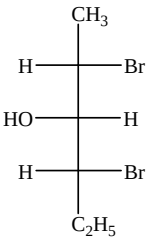
D

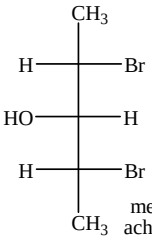


E

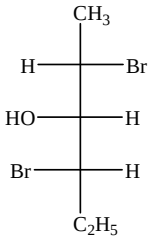








meso achiral



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

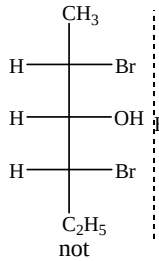
e. Which pairs are identical? AB (AC) AD AE BC BD BE CD CE DE

f. Which pairs are diastereomers? (AB) AC AD (AE) (BC) BD BE CD (CE) DE

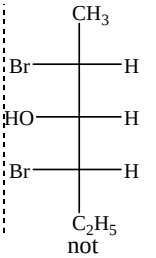
g. Which pairs, when mixed in equal amounts will not rotate plane polarized light? AB AC AD AE BC BD (BE) CD CE DE

(17 pts)

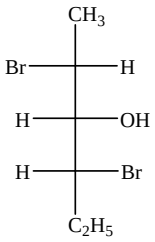
h. Draw any stereoisomers of 2,4-dibromohexan-3-ol as Fischer projections, which are not shown above. If there are none, indicate this. (5 pts)



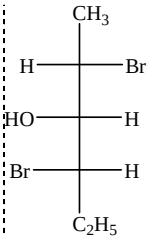
not shown



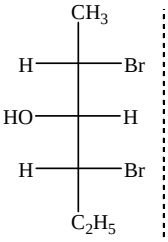
not shown



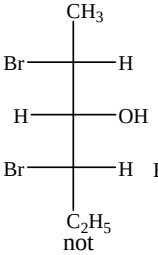
B



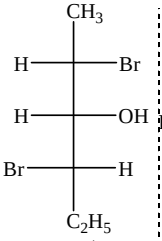
E



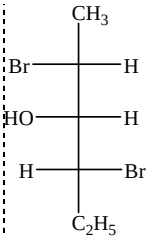
A = C



not shown



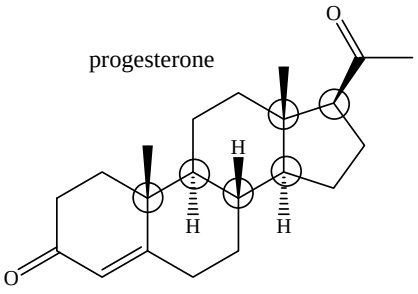
not shown



not shown

i. Progesterone is a crucial steroid in metabolism and various corticosteroids and sex hormones are made from it. It prepares the uterus for implantation and inhibits lactation while a women is pregnant. However, men need it too. Circle all of the chiral centers. How many stereoisomers are possible? Show work. (5 pts)

progesterone



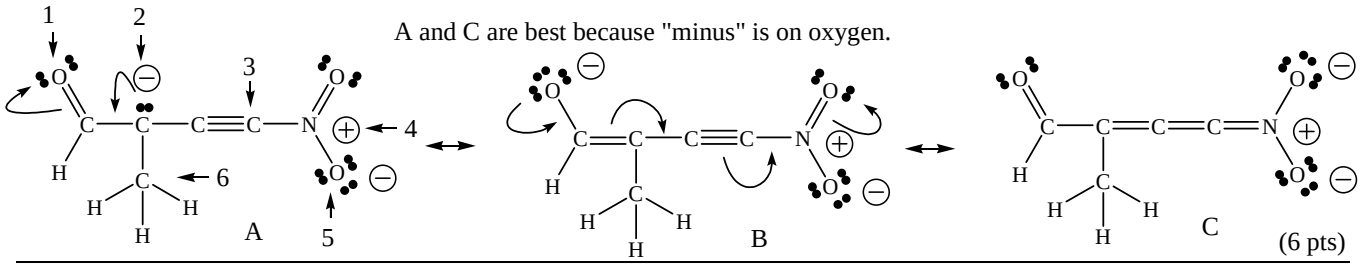
chiral centers are sp^3 atoms with 4 different groups attached

chiral centers = 6

possible stereoisomers = $2^6 = 64$

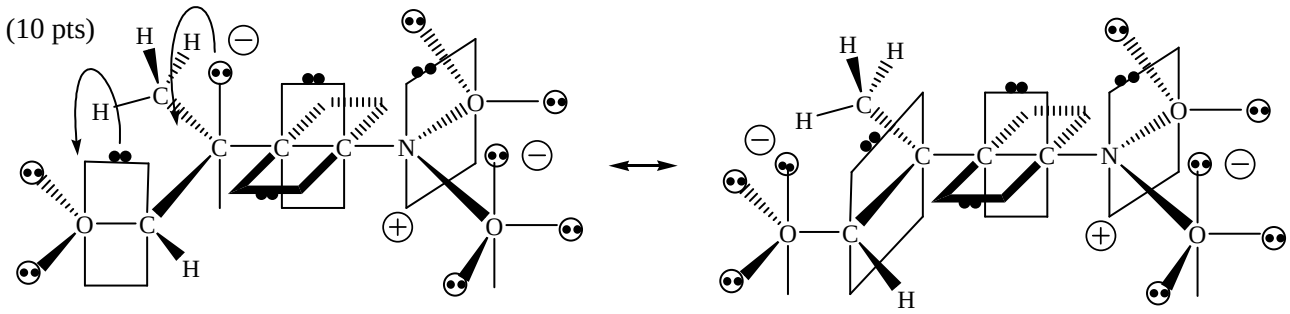
6. Draw two additional "**better**" 2D resonance structures of the given structure. Assume all nonhydrogen atoms have full octets unless + is written next to carbon. Add in any necessary lone pairs and use proper curved arrows to show electron movement. Which structure(s) is(are) best and why? Draw a 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. (30 pts)

A and C are best because "minus" is on oxygen.



(6 pts)

(10 pts)



This is the required structure.

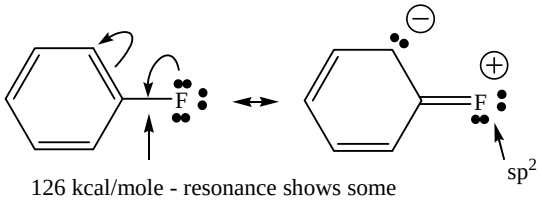
Not required, but drawn to show the similar shapes of all the atoms in different resonance structures.

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

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

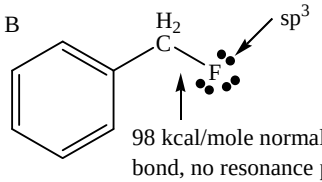
Explain the different C-F bond energies. Use structures in your explanation. Include any necessary lone pairs, formal charge, curved arrows, etc. What is the hybridization of the fluorine atom in A and B? (4 pts)

A



126 kcal/mole - resonance shows some double bond character between C and F

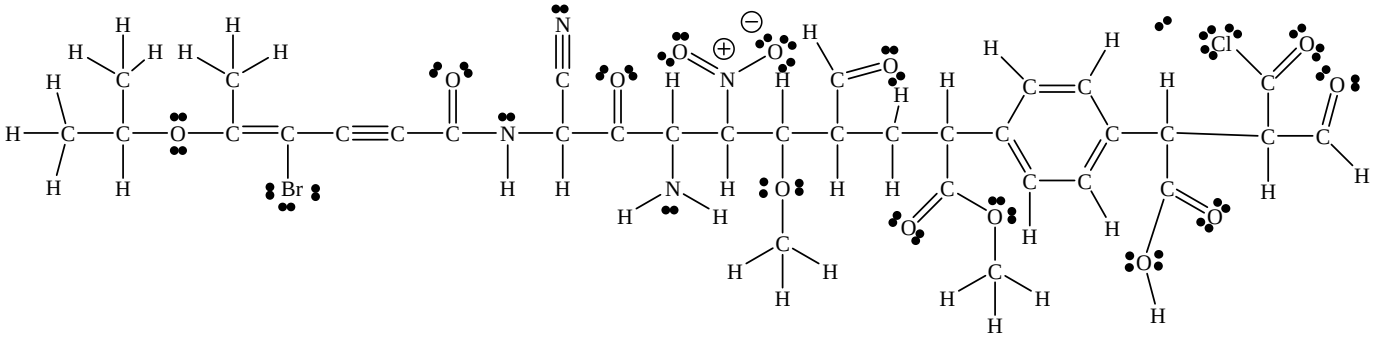
B



98 kcal/mole normal single sp^3 C-F bond, no resonance possible into an sp^3 carbon atom.

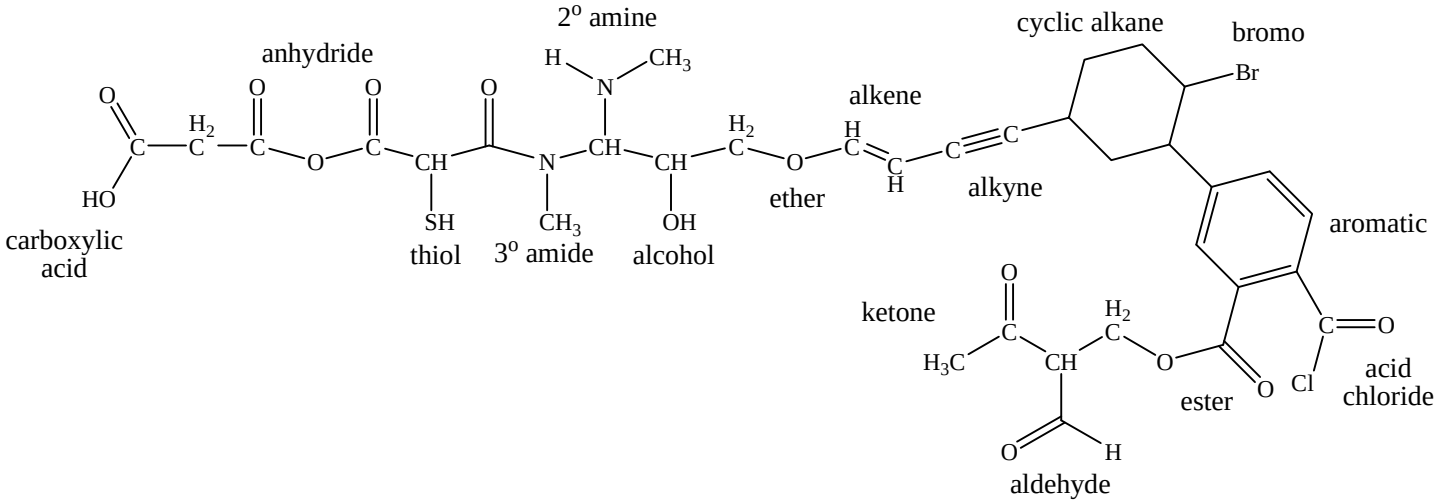
7. Draw an acceptable Lewis structure (2D) for the following structure. Show <u>all</u> single, double and triple bonds with one, two or three lines. Include all lone pairs of electrons as two dots. Include formal charge, if present at the atom where present. (20 pts)

$\left[(CH_3)_2CHOC(CH3)CBrCCCONHCH(CN)COCHNH_2CHNO_2CH(OCH_3)CH(CHO)CH_2CH(CO_2CH_3)C_6H_4CH(CO_2H)CH(COCl)CHO\right]^{\oplus\ominus}$



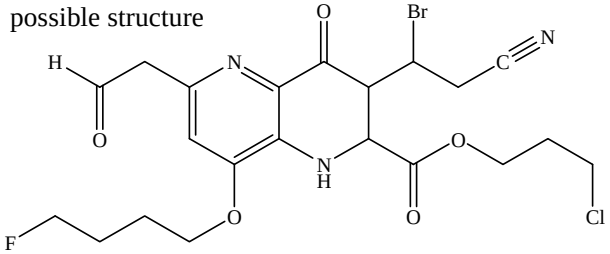
8. Draw an example molecule that has the indicated functional groups. Name each functional group. (25 pts)

functional groups: carboxylic acid, anhydride, thiol, 3° amide, 2° amine, alcohol, ether, alkene, alkyne, cyclic alkane, bromo, aromatic, acid chloride, ester, aldehyde, ketone



Use the given molecular formula to calculate the degree of unsaturation. Show work. $C_{25}H_{27}BrClNO_7S_2$, (5 pts)

possible structure



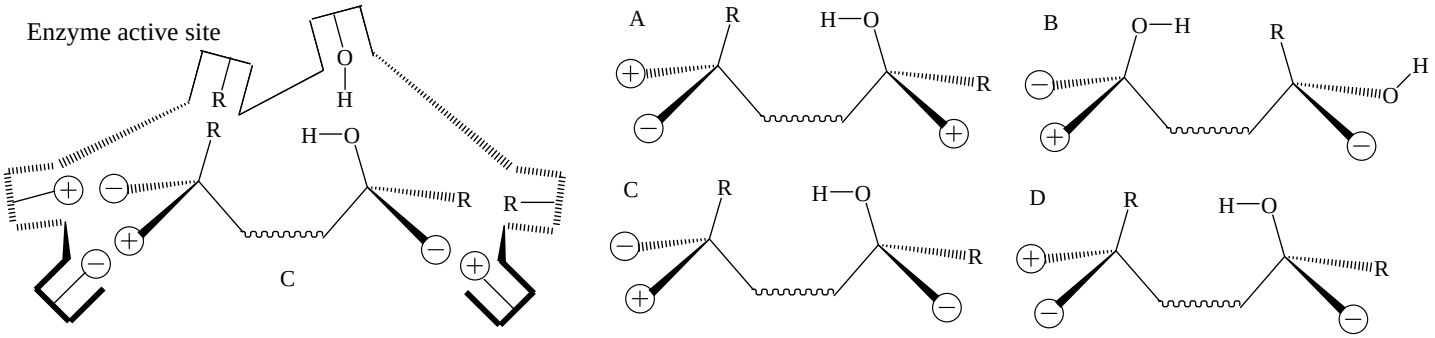
$C_{21}H_{24}BrClFN_3O_5$

$2(21) + 2 + 3 = 47$

$- 27$

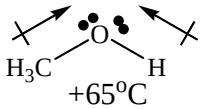
$= 20/2 = 10^{o}$ unsaturation

9. a. The active site of an important liver enzyme has just been discovered. Several key regions are shown in the enzyme active site, just below. As an employee of Bronco Pharmaceutical, you are trying to design an inhibitor molecule that will strongly bind to the key regions of the active site so that the normal substrate cannot get in and react. Four possible inhibitors are shown below. Pick the molecule you think will block the enzyme cavity the best and draw it in the active site. Dashes represent "behind" the page, heavy lines indicate in "front" of the page and simple lines are "in" the page. R represents a nonpolar group. Give a very brief explanation for why choice will work best. (10 pts)

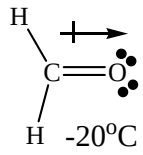


C fits best in the active site. Hydrophobic regions (R - R) are close together, opposite charges are close together and attract very strongly and the adjacent 'OH' groups can hydrogen bond with each other moderately strongly.

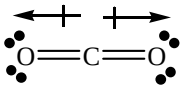
b. Methanol, methanal and carbon dioxide become gases at -78°C, -20°C and +65°C. Match each temperature with the correct compound and provide an explanation for you answer. (10 pts)



+65°C



-20°C

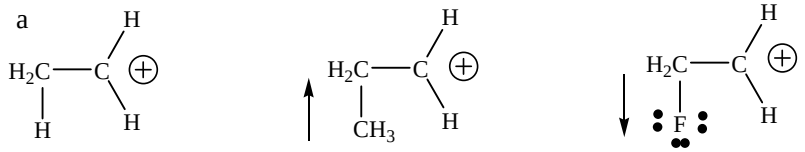


-78°C

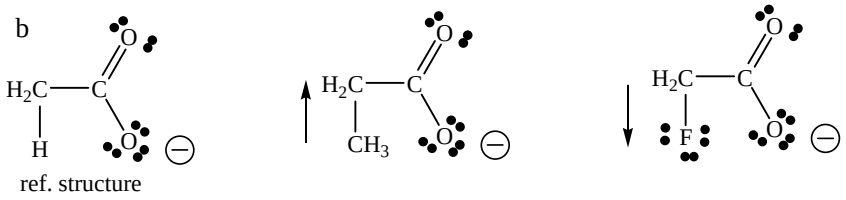
Bond dipoles are shown. All C and H bonded to oxygen are polar bonds. All 3 molecules have polar bonds with oxygen, but CO_2 bonds cancel, so the molecule is nonpolar and has the lowest temperature to vaporize. CO_2 goes straight from solid to gas (sublimation) at -78°C. Both methanol and methanal have polar bonds, but methanol has a polar O-H bond which can form very strong "hydrogen" bonds, giving it the highest boiling point (+65°C). Methanal is polar but does not have any hydrogen bonds and boils at -20°C.

10. Logic arguments of organic and biochemistry

a. The first molecule in each row is a reference point. Explain if the indicated substitution will be stabilizing, destabilizing or have no effect relative to the reference structure. Provide an explanation for your answer. (10 pts)



"R" groups (methyl, here) are inductively electron donating. This proves stabilizing to electron poor carbocations as in the second structure. Fluorine is extremely inductively electron withdrawing which is destabilizing for an electron poor carbocation in the third structure.



The inductive effects are similar to part a, "R" groups (methyl, here) are inductively electron donating and fluorine is extremely inductively electron withdrawing. However, the carboxylate has excess negative charge. Electron doantion proves destabilizing to the electron rich carboyxlate while electron withdrawal by the fluorine proves stabilizing for the negative charge.

b. Which atom has the higher first ionization potential and why? (O or P) (20 pts)

O is farther to the right (higher Z_{eff}) and higher in a column (closer to the nucleus). Both of those predict a stronger attraction for electrons, so ionization potentials are O > P. IP_1 (O) = 315 kcal/mole and IP_1 (P) = 242 kcal/mole

c. Which neutral atom has the larger atomic radius and why? (S or P)

Sulfur and phosphorous are in the same row. S has a Z_{eff} of +6 and P has a Z_{eff} of +5, so S will hold on to its electrons tighter than P. This should contract the electron cloud making the radius of sulfur (r_S = 88 pm) smaller than phosphorous (r_P = 98 pm).

d. Which anion has the larger radius and why? (F^{-1} or O^{-2})

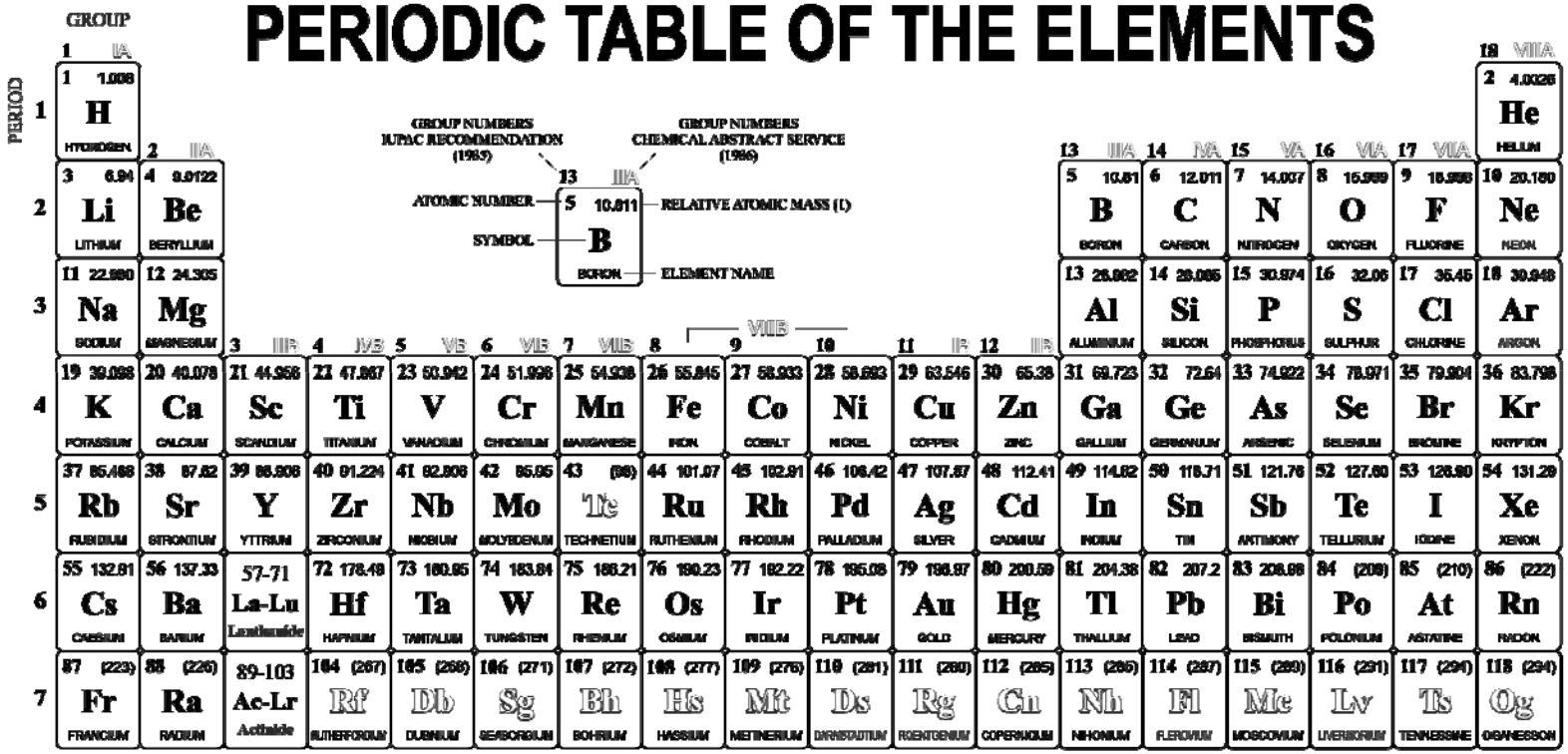
Both F^{-1} and O^{-2} are in the same row and have a full n=2 shell (full octets). Oxygen has Z_{eff} of +6 and F has a Z_{eff} of +7, so F will hold on to its electrons tighter than O so fluoride is smaller than oxide. The radius of oxide (r_{O-2} = 126 pm) is larger than fluoride (r_{F-} = 119 pm)

e. Which cation has the larger radius and why? (Be^{+2} or B^{+3})

Both Be^{+2} and B^{+3} have lost all of their n=2 valence electrons and have a full n=1 shell (core electrons = $1s^2$). Be has Z_{eff} of +2 and B has a Z_{eff} of +3, so B will hold on to its electrons tighter than Be. The radius of B^{+3} (r_{B+3} = 41 pm) should be smaller than Be^{+2} (r_{Be+2} = 59 pm).

Change is the end result of all learning. Leo Buscaglia

PERIODIC TABLE OF THE ELEMENTS



LANTHANIDE

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

ACTINIDE

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

www.periodni.com

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