Chem 314

Spring, 2007
Midterm Exam
Chem 314

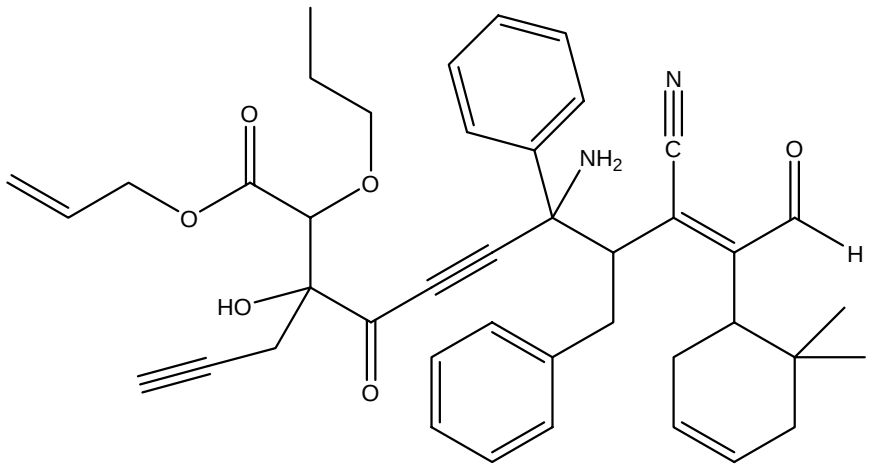
Name _____

Problem	Points	Credit
1. Nomenclature	25	
2. 2D Lewis structures	20	
3. 3D Structures, Formal Charge & Resonance	30	
4. Formulas, Functional Groups & Degrees of Unsaturation	20	
5. Specific Bond Energies or Substitution Patterns and Common Names	20	
6. Thermodynamics, Bond Energies & Reactions	32	
7. Conformations, Energy (Cylclohexanes & Chains), Newman Projections	35	
8. Physical Properties	15	
Total	197	

This is a long exam. It has been designed so that no one question will make or break you. You are not expected to completely finish the exam. 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 wherever necessary. Only write on the front side of each page. Also, consider the point values in your choice of questions. Do your best to show me what you know in the available time.

No person is free who is not master of himself. Epictetus

1. Provide an acceptable name for the following structure. (25 pts)

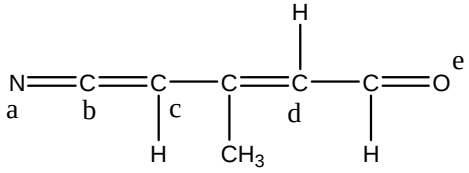


2. Draw an acceptable 2D Lewis structure for the following formula. Indicate any formal charges present, all lone pair electrons and completely draw out all atoms (e.g. do not write CH_3). (20 pts)

six carbon ring has formal charge

$(CH_3)_2CHO_2CCHCFCCCHNH_2CH(CHO)CHOHC_6H_4COCH_2CH(NO_2)CHCNCH_2CONHCH(OCH_3)CO_2^{\ominus}$

3. First, draw three other reasonable 2D resonance structures that <u>delocalize any charge that is present</u>. Include proper arrow conventions. Rank your structures from best (= 1) to poorest. Draw a three-dimensional Lewis structure for the given representation and the best resonance structure among B, C and D. Show σ bonds as lines, wedges and dashes and the p orbitals in π bonds, as well as any orbitals holding lone pairs. Draw two dots for lone pair and pi bond electrons. Indicate any formal charge present and give the hybridization, bond angles and shape of each **labeled** nonhydrogen atom (below). **<u>Assume that all non-hydrogen atoms have full octets, unless a carbocation is written</u>.** (30 pts)



A f

B

D C

3D (A) 3D (best other)

Use structure A to fill in the following table.

	Hybridization	Angles	Shape	#σ bonds	#π bonds	lone pairs
a						
b						
c						
d						
e						
f						

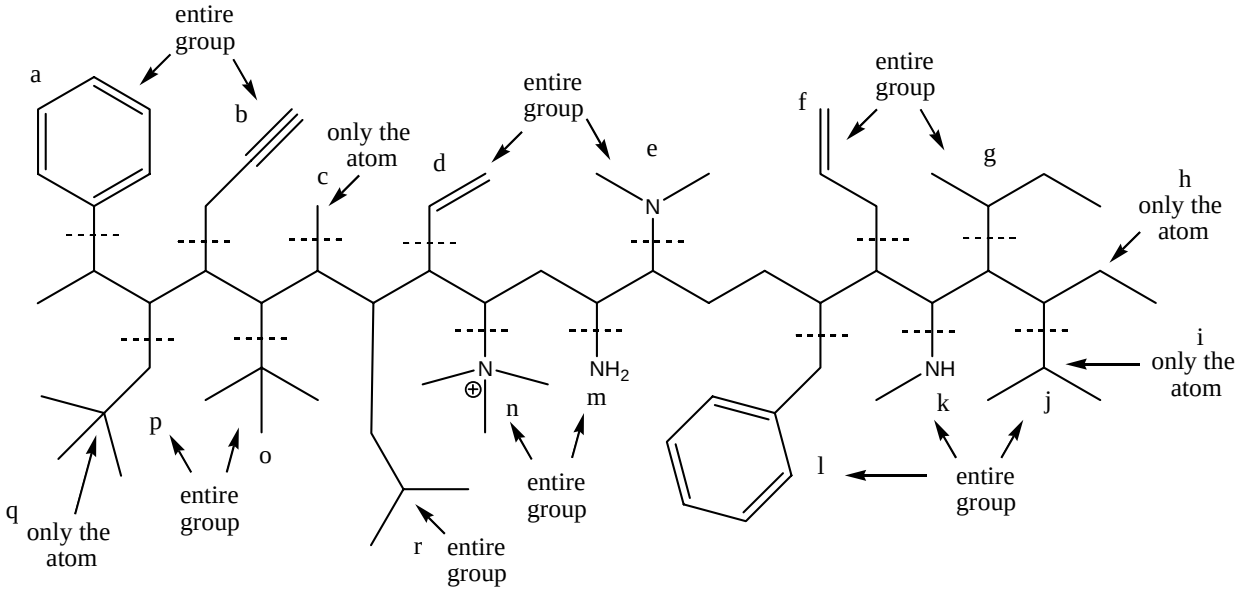
4. Use the given formula to provide an example that includes the listed functional groups. If you draw any other functional groups, identify them as well. Write the matching functional group name by its appearance in the 2D structure. Calculate the degree of unsaturation for your formula. (20 pts)

$C_{15}H_{16}ClN_3O_7$ degree of unsaturation calculation

alkyne, alkene, amine, ester,
ether, ketone, acid, amide, nitrile

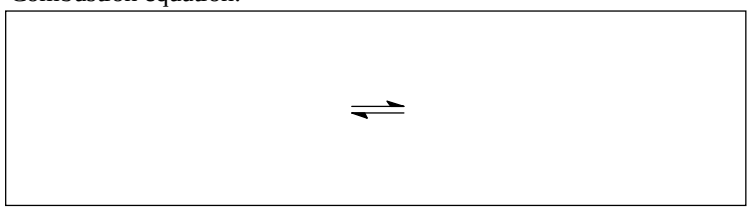
5. Match the arrows with the terms. Some arrows may be associated with more than one term. (20 pts)

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

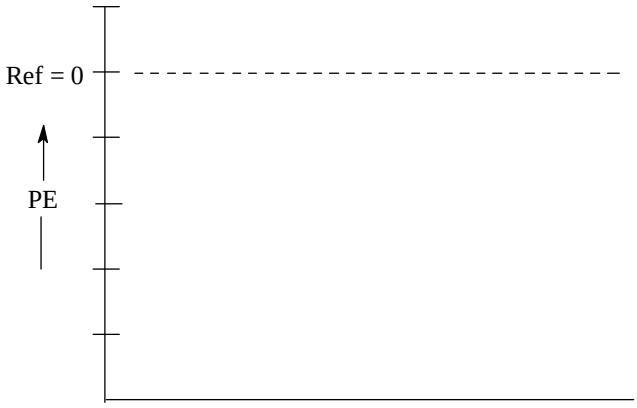


6. a The heat of combustion of **hexan-2-one** is –839.2 kcal/mole. Limited heats of formation are provided below. Write an equation for this reaction. Use this information to calculate a heat of formation for **hexan-2-one**. Draw an energy diagram that includes the zero energy reference point and the various other energy values. (15 pts)

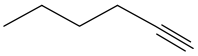
Combustion equation:



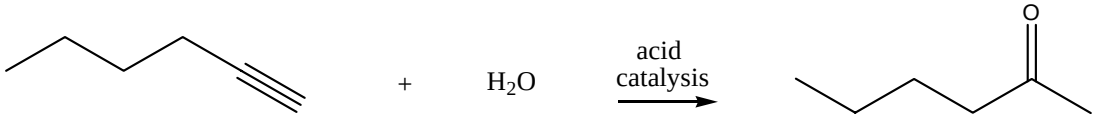
Show work.



Energy Diagram

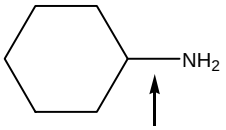
	ΔH_f^o (kcal/mole)
CO_2	-94.0
H_2O	-57.8
	+29.9

b. Calculate the heat of reaction for the equation below. Clearly show your set up and the appropriate energy values. (4 pts)

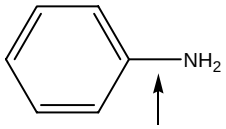


c. Calculate the same heat of reaction, as in part b, using the **average** bond energies on the last page. How does this value compare to that of part b? Hint: You may need to solve for a pi bond energy. (7 pts)

d. Find approximate bond energy values for the two carbon-nitrogen bonds pointed out in the following structures using the bond energies in the common substitution patterns table at the end of this exam. Provide a rationale for any observed differences. Draw additional structures, if appropriate to your explanation. (6 pts)



BE = _____



BE = _____

7. a. Draw both chair conformations of cis-1-bromo-2-isopropylcyclohexane and trans-1-bromo-2-isopropylcyclohexane. Draw all axial and equatorial groups at substituted positions. Indicate which conformation is more stable in each pair. Which conformation, overall, is most and least stable? Axial energy values are provided on the next page. Assume all gauche interactions are 0.8 kcal/mole. (12 pts)

cis

chair 1 ⇌ chair 2

most stable (1 or 2) = _____

most stable overall (1,2,3,4) = _____

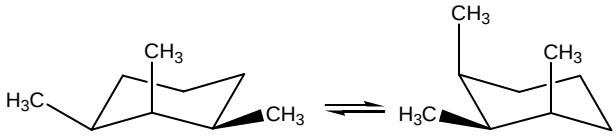
trans

chair 3 ⇌ chair 4

most stable (3 or 4) = _____

least stable overall (1,2,3,4) = _____

b. 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)



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.

ΔH ≈

K_{eq} ≈

c. Use the second most stable conformation from part a, and draw a Newman projection using bonds $C_1 \rightarrow C_2$ and $C_5 \rightarrow C_4$ for your structure (or…$C_2 \rightarrow C_1$ and $C_4 \rightarrow C_5$). Point out any gauche relationships in the branches and/or the ring. (5 pts)

d. Use a Newman projection of the C2→C3 bond of 3-methylbutan-2-ol to show the most stable and least stable conformations. Using the energy values provided, calculate the energy difference between these two conformations. Calculate a $K_{equilibrium}$ and use it to estimate the ratio between these two conformations at equilibrium. Hint: Draw a 2D structure first and "bold" the bond viewed in your Newman projection. Assume R = 2 cal/mol-K and T = 300 K. (12 pts)

Eclipsing Energy Values (kcal/mole)	
H/H	+1.0
H/CH_3	+1.3
CH_3/CH_3	+2.5
H/OH	+0.7
CH_3/OH	+1.5
any gauche	+0.8

2D structure

For part 7a

Axial Energy Values (kcal/mole)	
CH_3	+1.7
CH_2CH_3	+1.3
$CH(CH_3)_2$	+2.5
$C(CH_3)_3$	+5.0
Br	+0.5
any gauche	+0.8

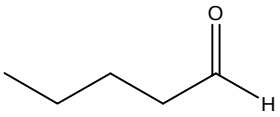
$\Delta G \approx \Delta H$

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

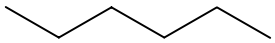
most stable
(show work)

least stable
(show work)

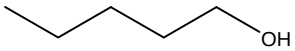
8. a. Match the given boiling points with the structures below and give a short reason for your answers. (+69°C, +103 °C, +139 °C, +230°C, 1265°C) (10 pts)



pentanal
MW = 86 g/mol

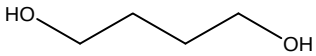


hexane
MW = 86 g/mol



pentan-1-ol
MW = 88 g/mol

KCl
lithium bromide
MW = 87 g/mol



butane-1,4-diol
MW = 9 g/mol

b. Which compound above would you expect to be the most soluble in water? Which compound would you expect to be the most soluble in octane? Briefly, explain you choices. (5 pts)

Typical Bond Energies for Common Substitution Patterns Found in Organic Chemistry (X-Y)

Y =	H-	Me-	Et- (1^o)	i-Pr- (2^o)	t-Bu- (3^o)	Ph- (phenyl)	F-	Cl-	Br-	I-	HO-	H_2N-	N≡C-
X =													
CH_3- methyl (Me-)	105	90	86	86	84	102	110	85	71	57	93	85	122
CH_3CH_2- primary (Et-)	98	86	82	81	79	98	108	80	68	53	92	82	118
$CH_3CH_2CH_2$- primary (Pr-)	98	86	82	80	79	98	107	81	68	53	92	82	117
$(CH_3)_2CH$- secondary (i-Pr-)	95	86	81	79	76	96	106	80	68	54	93	82	116
$(CH_3)_3C$- tertiary (t-Bu-)	93	84	79	76	71	93	110	80	67	52	93	82	-
C_6H_5- phenyl (Ph-)	111	102	97	96	93	115	126	96	80	65	111	102	131
$C_6H_5CH_2$- benzyl (Bn-)	88	76	72	71	70	90	-	72	58	48	81	71	-
CH_2=$CHCH_2$- allyl (al-)	86	74	70	70	67	-	-	68	54	41	78	-	-
CH_3CO- acyl (Ac-)	86	81	76	74	72	94	119	81	66	49	107	-	-
CH_3CH_2O- alkoxy	104	83	82	-	-	101	-	-	-	-	44	-	-
CH_2=CH- vinyl	110	100	96	95	90	103	-	90	78	-	-	-	130
H- hydrogen-	104	105	98	95	93	111	136	103	88	71	119	107	125

$X\!-\!Y \longrightarrow X\cdot \quad \cdot Y$ (homolytic cleavage)

Average Bond Energies (kcal/mole)

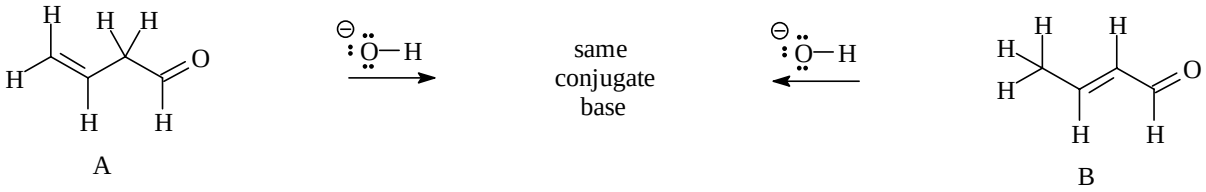
	H	C	Si	N	O	S	F	Cl	Br	I
H	104	98	76	92	109	83	135	103	87	71
C		81	72	82	92	65	116	79	66	52
Si			-	-	108	-	135	91	74	56
N				39	39	-	65	46	-	-
O					34	-	45	52	48	56
S						60	-	61	52	-
F							37	-	-	-
Cl								58	-	-
Br									46	-
I										36

Bond Energy for multiple bonds

C=C	146
C=N	147
C=O	176
C≡C	200
C≡N	213

Not used on this exam, but consider as a possible question.

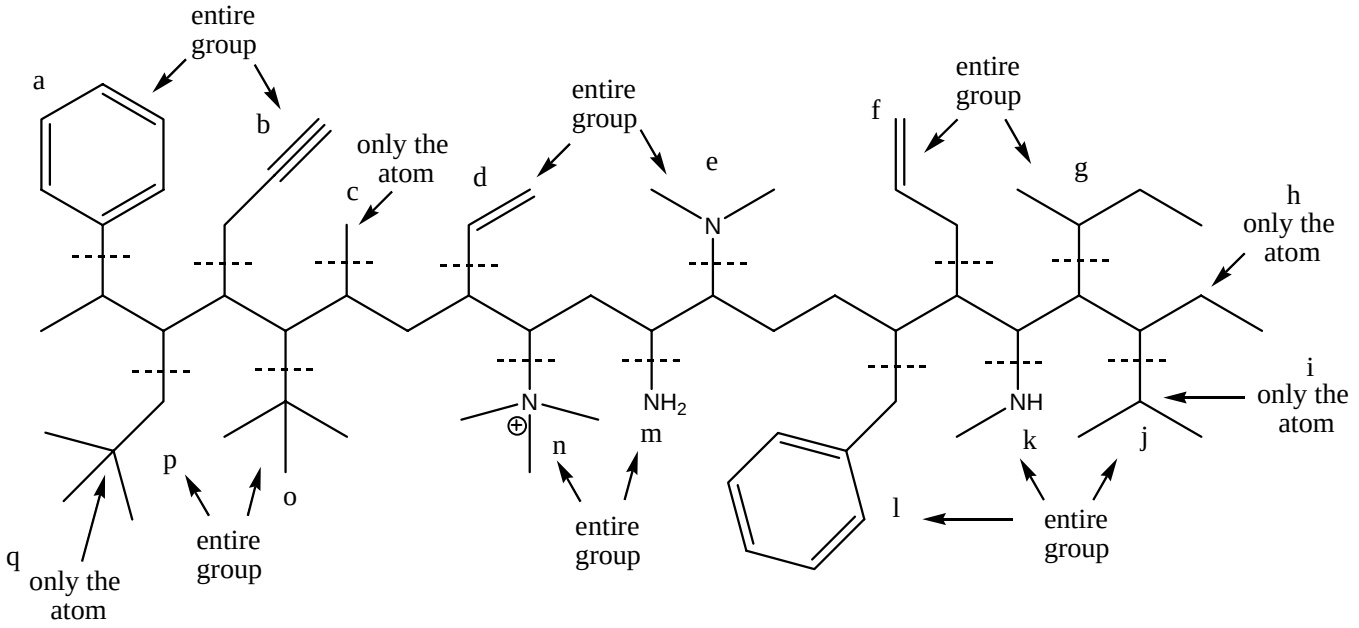
d. Acids A and B have different structures, but share a common conjugate base. Draw the curved arrows to show how the proton transfer occurs in each case and explain why the conjugate base is the same for each acid. (10 pts)



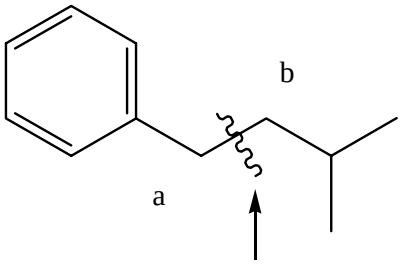
A B

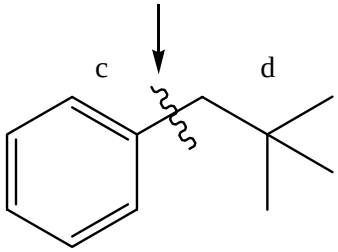
Match the arrows with the terms. Some arrows may be associated with more than one term. (20 pts)

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



9. Indicate the bond energy between the two atoms indicated. Use the specific bond energy table provided on the last page. Write the common nomenclature term of each carbon group about the bond energy requested. Draw an arrow to any part of any structure to indicate where a methyl, methylene, methine, primary, secondary, tertiary and quaternary carbon is located. A table of bond energies is provided on the last page (15 pts)





indicate bond energy between a-b _____

common name of fragment "a" _____

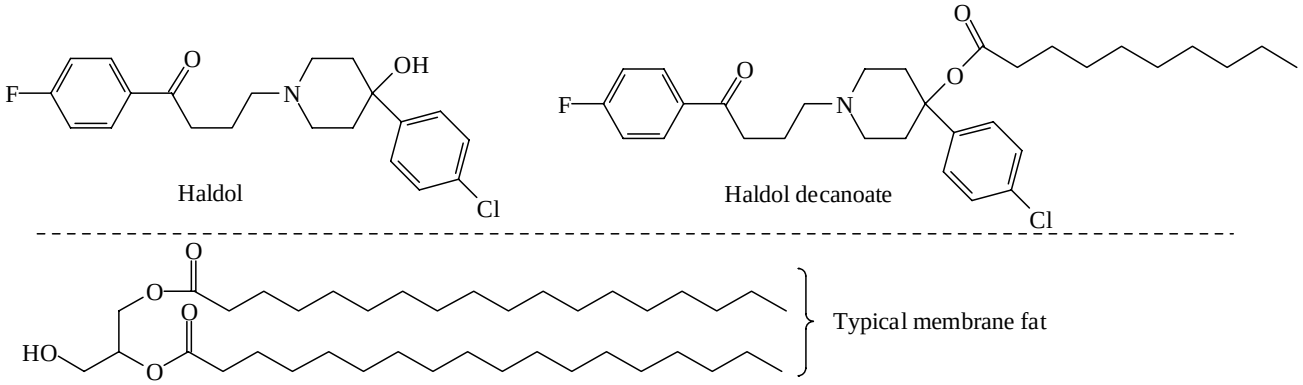
common name of fragment "b" _____

indicate bond energy between c-d _____

common name of fragment "c" _____

common name of fragment "d" _____

9. 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)



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1. high priority group plus lots of lower priority groups, alkene (E/Z), alkyne, complex branches
2. long 2D structure with lots of functional groups and a little bit of formal charge
3. just like in the example exams, need to know resonance, formal charge, arrow pushing, hybridization details, how to draw 3D shapes
4. need to know functional groups, calculate degree of unsaturation, common nomenclature, specific bond energies
5. work with heat of formation, heat of reaction, use bond energy table, sketch energy diagram
6. need to know how to put substituents on a cyclohexane ring, draw all possible chair conformations, evaluate their energy, do the same for an open chain compound (staggered / eclipsed), use ΔH to calculate an equilibrium ratio, draw Newman projections for rings and open chains
7. biological explanation using physical properties