Chem 314

Sample Midterm Exam
Chem 314
Beauchamp

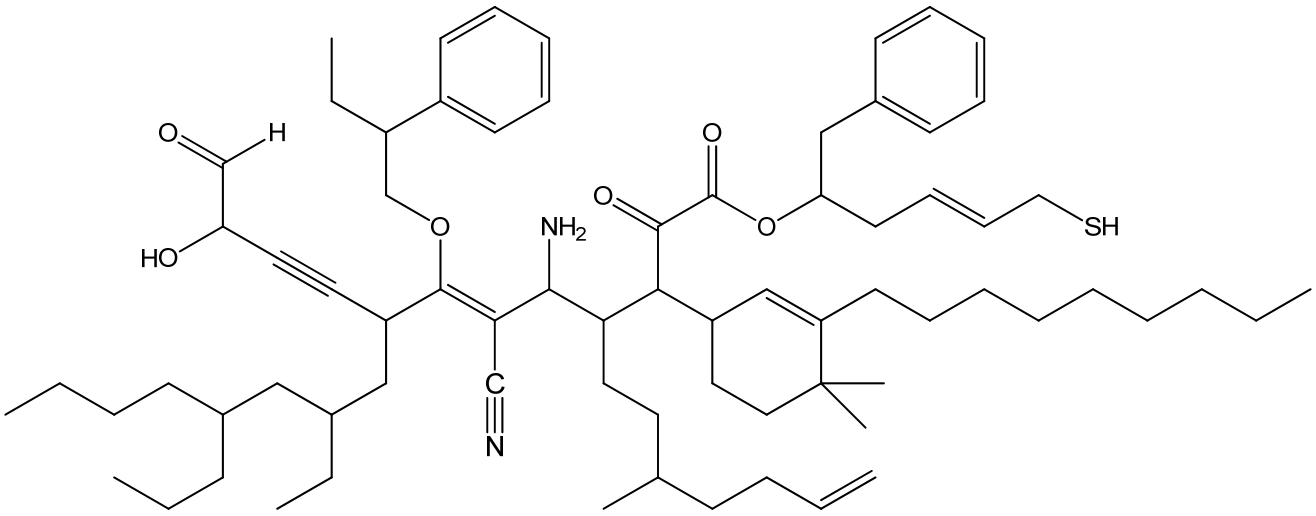
Name _____

Problem	Points	Credit
1. Nomenclature	30	
2. 2D Lewis structures	20	
3. 3D Structures, Formal Charge & Resonance	30	
4. Physical Properties and/or Substitution Patterns & Common Substituent Names	29	
5. Molecular Orbital Diagram and/or Degrees Unsat. & Functional Groups	15	
6. Thermodynamics, Bond Energies & Reactions	32	
7. Conformations, Energy (Cylclohexane chairs), Newman Projections	45	
8. Conformations, Energy (Chains), Newman Projections		
Total	201	

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. Also, consider the point values in your choice of questions. Only write on the front side of each page. Do your best to show me what you know in the available time.

The price of anything is the amount of life you exchange for it. Henry David Thoreau

1. Provide an acceptable name for the following structure. (30 pts)

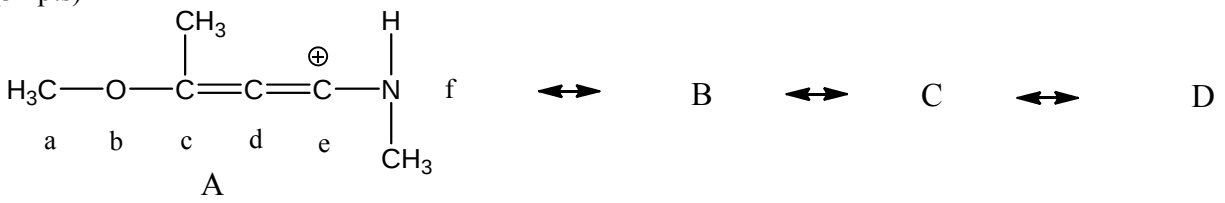


2. Draw an acceptable 2D Lewis structure for the following formula. Indicate any formal charges present, all lone pair electrons and completely draw out all atoms (e.g. do not write CH_3). (20 pts)

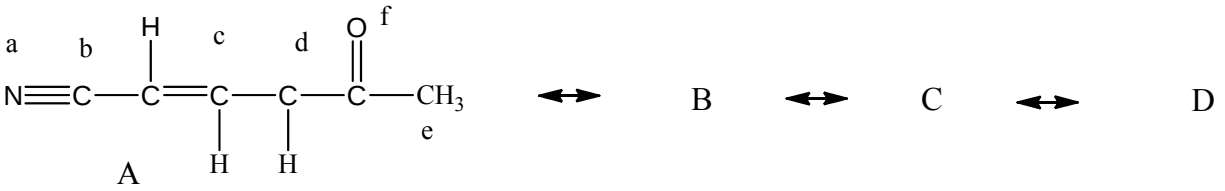
six carbon ring ↓ has formal charge ↓

$(CH_3)_2CHCOC(CH_3)CHCCCO_2CH(CN)C_6H_4CH(NO_2)CHNH_2CH(OCH_3)CONHCH(CHO)CHCHCO_2COCH_2CO_2H$

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>.** (34 pts)



or



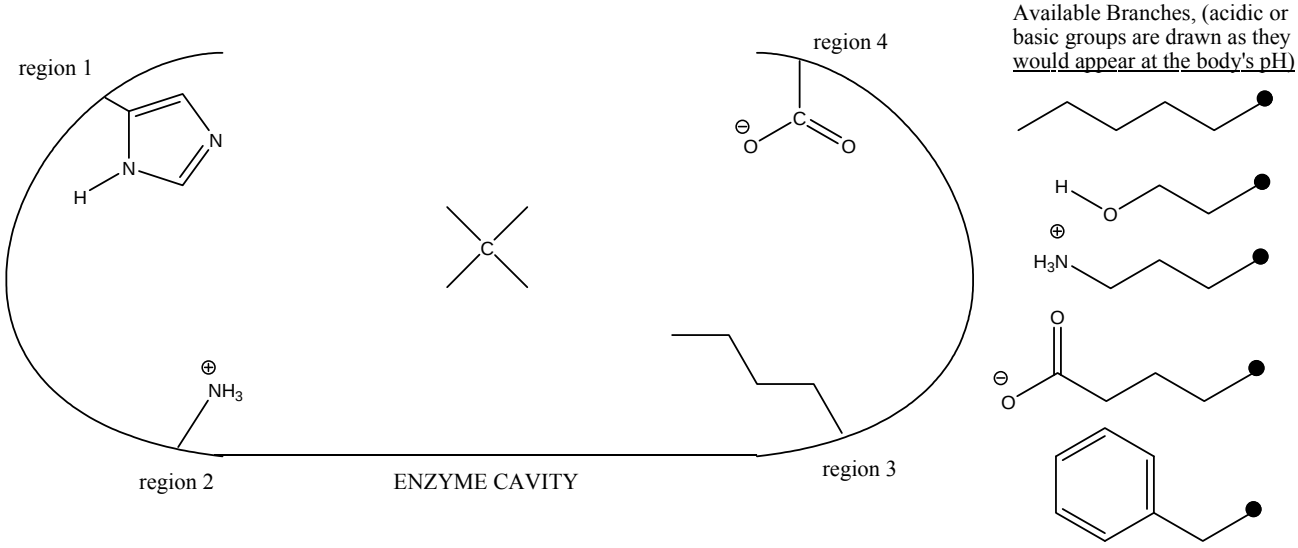
3D (A) 3D (best other)

Use structure A to fill in the following table.

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

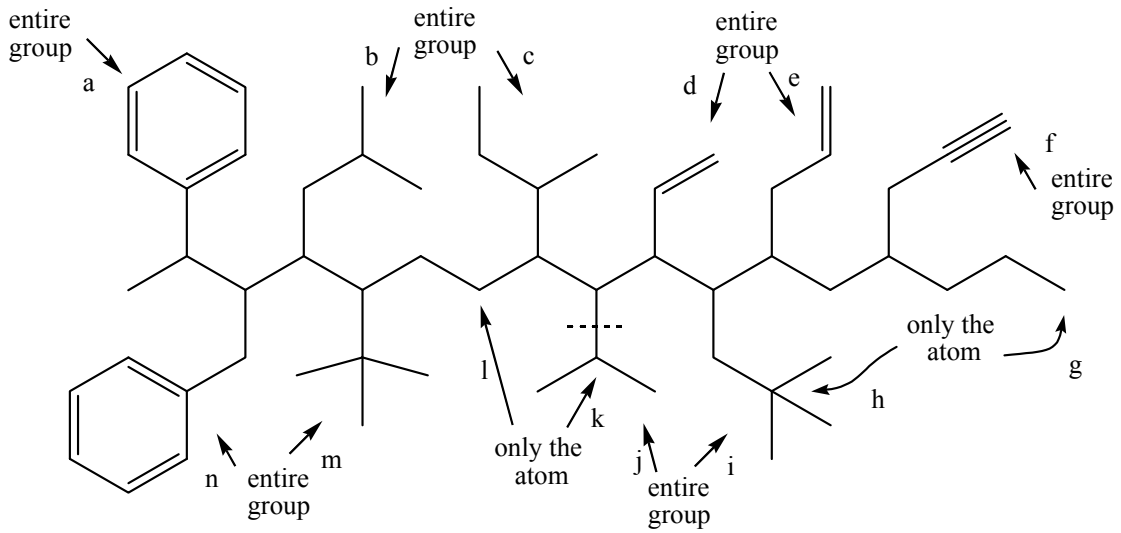
4. a. The active site of an important liver enzyme has just been discovered. Four key regions are shown in the enzyme cavity, just below. As an employee of Bronco Pharmaceutical, you are trying to design an inhibitor

molecule that will strongly bind to the key regions of the active site so that the normal substrate cannot get in and react. You have a variety of branches that you can attach to a central sp^3 carbon atom. Pick appropriate branches and show how your molecule will sit in the enzyme cavity. Give a very brief explanation for why each branch has its special affinity. (12 pts)

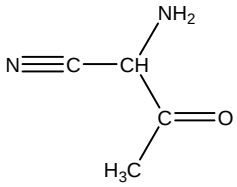


b. Match the arrows with the terms. Some arrows may be associated with more than one term. (17 pts)

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 _____



c. Draw a qualitative molecular orbital diagram for the following molecule. Include all sigma bonds to hydrogen together at the same energy. Include all other sigma bonds together at a different energy (assume these are stronger bonds). Include all pi bonds together at a different (and appropriate) energy. Also, place nonbonding electrons at an appropriate energy. Label your molecular orbitals with σ, σ*, π, π* and n, along with identifying subscripts that show what bonded atoms they represent. Identify the HOMO and LUMO orbitals (15 pts)

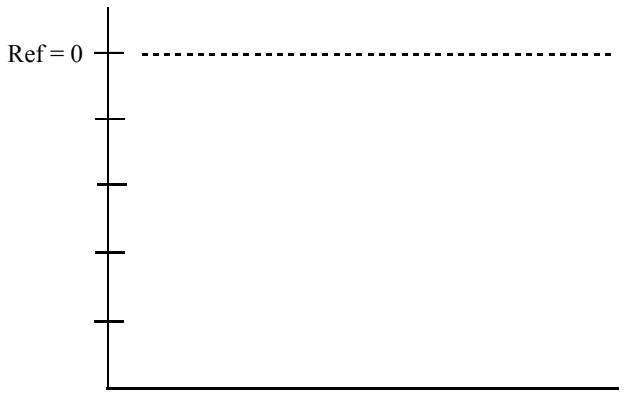


d. Use the given molecular formula to calculate the degree of unsaturation. Draw an example molecule that has the indicated functional groups.

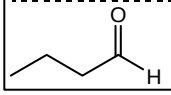
$C_{25}H_{27}BrClNO_7S_2$, functional groups: carboxylic acid, anhydride, thiol, sulfide, amide, alkyne, ring, bromo, aromatic, acid chloride

6. a The heat of combustion of **hexan-2,3-diol** is –846.8 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-2,3-diol**. Draw an energy diagram that includes the zero energy reference point, the various other energy values and the compounds associated with them. Show your work. (15 pts)

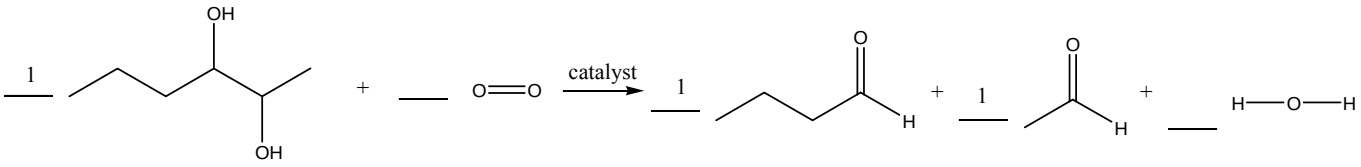
Combustion Equation



Energy Diagram

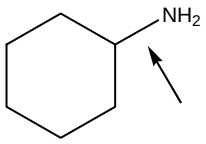
	ΔH_f^o (kcal/mole)
CO_2	-94.0
H_2O	-57.8
H_2O_2	-32.5
	-39.7
	-49.0

b. Balance the following equation and calculate the heat of reaction. Clearly show your set up and the appropriate energy values. (5 pts)

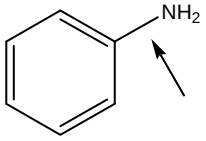


c. Calculate the same heat of reaction, as in part b, using the **average** bond energies on the last page. How does this value compare to that of part b? (7 pts)

d. Determine the bond energies of the C-N bonds below (use the specific substitution pattern bond energy table on the last page). Provide a possible explanation for any differences. (5 pts)



B.E. = _____



B.E. = _____

7. a. Draw both chair conformations of cis-1-t-butyl-4-phenylcyclohexane and trans-1-t-butyl-4-phenylcyclohexane (structure provided for 2 pts). **Clearly draw all axial and equatorial groups at substituted positions, including hydrogen atoms.** Calculate a ΔH between the two conformations of each isomer. Indicate which conformation is more stable in each pair. Which conformation, overall, is most and least stable? **Axial energy values are provided just below. Assume all carbon-carbon gauche interactions are 0.8 kcal/mole.** (16 pts)

$\Delta H = ?$ ⇌ cis

chair 1 chair 2

most stable (1 or 2) _____

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

ΔH = _____

$\Delta H = ?$ ⇌ trans

chair 3 chair 4

most stable (3 or 4) _____

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

ΔH = _____

Data for part 7a

Axial Energy Values (kcal/mole)	
CH_3	+1.7
CH_2CH_3	+1.8
$CH(CH_3)_2$	+2.1
$C(CH_3)_3$	+5.0
C_6H_5 (phenyl)	+2.5
any gauche	+0.8

b. Calculate a $K_{equilibrium}$ between the two cis conformations. Use it to estimate the ratio between these two conformations at equilibrium (chair 1 & chair 2). Assume R = 2 cal/(mol-K) and T = 300 K. (4 pts)

$\Delta G \approx \Delta H$

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

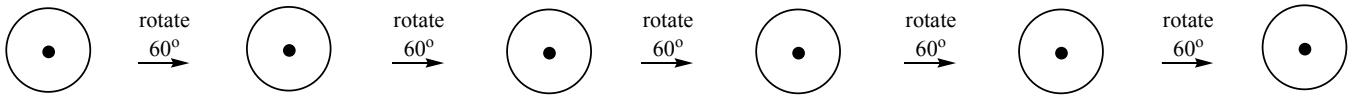
Ratio Calculation (chair 1 ⇌ chair 2)

c. Use the least stable conformation from part a (1 = t-butyl), and draw a Newman projection using bonds $C_1 \rightarrow C_6$ and $C_3 \rightarrow C_4$ for your structure (or…$C_6 \rightarrow C_1$ and $C_4 \rightarrow C_3$). Point out any gauche relationships in the branches and/or the ring. (5 pts)

8. a. Use a Newman projection of the C3→C4 bond of 2,3-dimethyl-4-phenylhexane to show the conformations and relative energies**. Show the most stable conformation first**. Rotate through all of the eclipsed and staggered conformations. Use the energy values provided below to calculate the relative energies of the different conformations. Hint: Draw a 2D structure first, "bold" the bond viewed in your Newman projection and sight down the correct direction. (21 pts)

2D structure

most stable conformation



ΔH^o = ΔH^o = ΔH^o = ΔH^o = ΔH^o = ΔH^o =

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

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

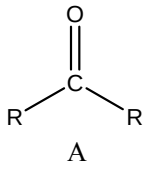
$\Delta G \approx \Delta H$ $\quad K_{eq} = 10^{\frac{-\Delta H}{2.3RT}}$

least stable conformation ⇌ most stable conformation

b. Calculate a $K_{equilibrium}$ between the most stable and least stable conformations. Assume R = 2 cal/(mol-K) and T = 300 K. (4 pts)

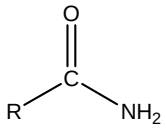
Extra considered questions.

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

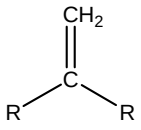


A

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)

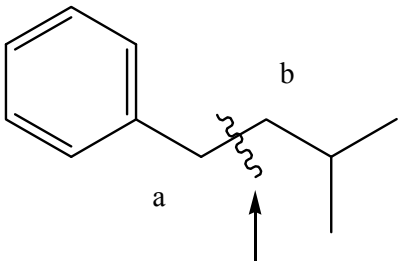


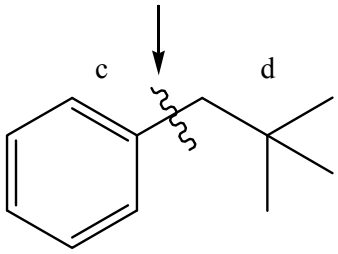
B



C

10. 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 (10 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" _____

Typical Substitution Pattern Bond Energy Table (X-Y = bond) (* values in parentheses are estimated)

X — Y =	H-	Me-	Et-	i-Pr	t-Bu	Ph	F-	Cl-	Br-	I-	RO-	H_2N-	N≡C—
CH_3- methyl	103	88	85	84	81	101	110	85	71	57	(96)	87	116
CH_3CH_2- primary	98	85	82	81	78	99	110	82	70	54	(92)	87	114
$(CH_3)_2CH$- secondary	95	84	81	79	74	97	109	81	69	54	(91)	86	112
$(CH_3)_3C$- tertiary	93	81	78	74	68	94	(108)	80	66	51	(90)	85	(111)
CH_2=$CHCH_2$- allyl	88	75	72	71	67	(87)	(96)	70	56	42	82	75	(104)
$C_6H_5CH_2$- benzyl	85	73	71	70	67	83	94	68	55	40	79	72	(100)
CH_2=CH- vinyl	110	98	95	93	89	108	(124)	92	79	(63)	not stable	not stable	128
C_6H_5- phenyl	111	101	97	95	92	110	124	95	80	64	111	104	128
CH_3CO- acyl	87	81	78	76	72	93	119	82	68	51	107	95	not common
CH_3CH_2O- alkoxy	104	(96)	(92)	(91)	(90)	101	low	low	low	low	40	low	low
H- hydrogen	119	103	98	95	93	111	135	103	88	71	111	93	125

Average Bond Energies (kcal/mole) (1 kcal = 4.184 joules)

	H	C	Si	N	O	S	F	Cl	Br	I	P
H	104	99	76	93	111	81	135	103	88	71	77
C		83	76	82	92	65	110	81	68	52	70
Si			53	85	108	70	135	91	74	56	76
N				40	48	X	65	46	X	X	X
O					40	X	45	52	48	48	80
S						60	68	61	52	X	X
F							37	X	X	65	117
Cl								58	X	50	78
Br									46	42	63
I										36	44
P											48

Multiple Bond Energies

C=C	146	C≡C	200
C=N	147	C≡N	213
C=O	179	C≡O	258
C=S	137	N≡N	226
N=N	109	P≡P	117
N=O	143		
P=O	130		
O=O	118		
S=O	128		
S=S	102		
P=P	84		