Chem 314

Winter, 2009
Midterm Exam
Chem 314

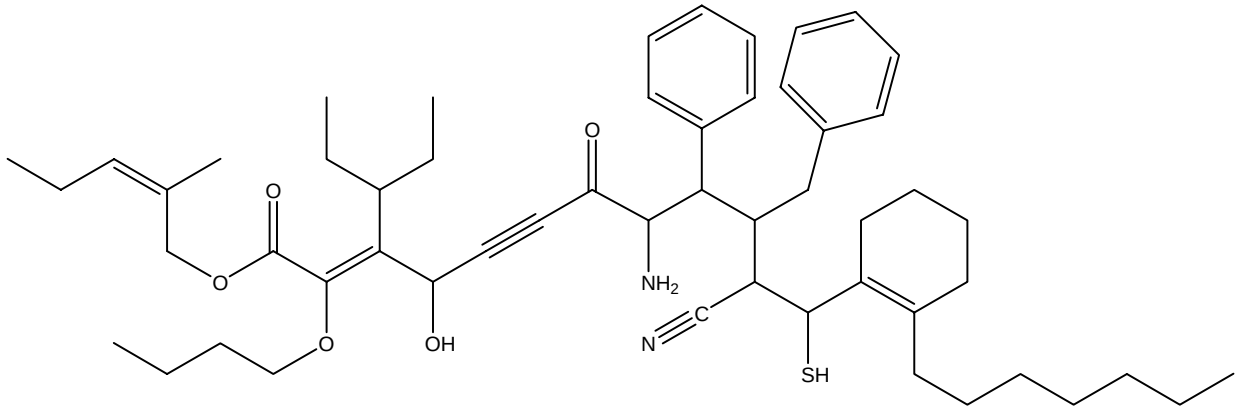
Name _____

Problem	Points	Credit
1. Nomenclature	25	
2. 2D Lewis structures	20	
3. 3D Structures, Formal Charge & Resonance	30	
4. Specific Bond Energies or Substitution Patterns and Common Names	20	
5. Molecular Orbital Diagram	15	
6. Thermodynamics, Bond Energies & Reactions	31	
7. Conformations, Energy (Cylclohexanes & Chains), Newman Projections	36	
Total	177	

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.

Quote

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

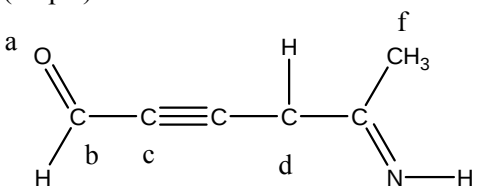


2. Draw an acceptable 2D Lewis structure for the following formula. Indicate any formal charges present, all lone pair electrons and completely draw out all atoms (e.g. do not write CH_3). (20 pts)

has formal charge six carbon ring

$(CH_3)_3CCCCHCHCONHCH_2CH(NO_2)C_6H_4CHCNCH_2CHOHCH(OCH_3)CH(COCl)CO_2CHBrCH(CHO)CHNH_2CO_2H$

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>.** (30 pts)



A

B

C

D

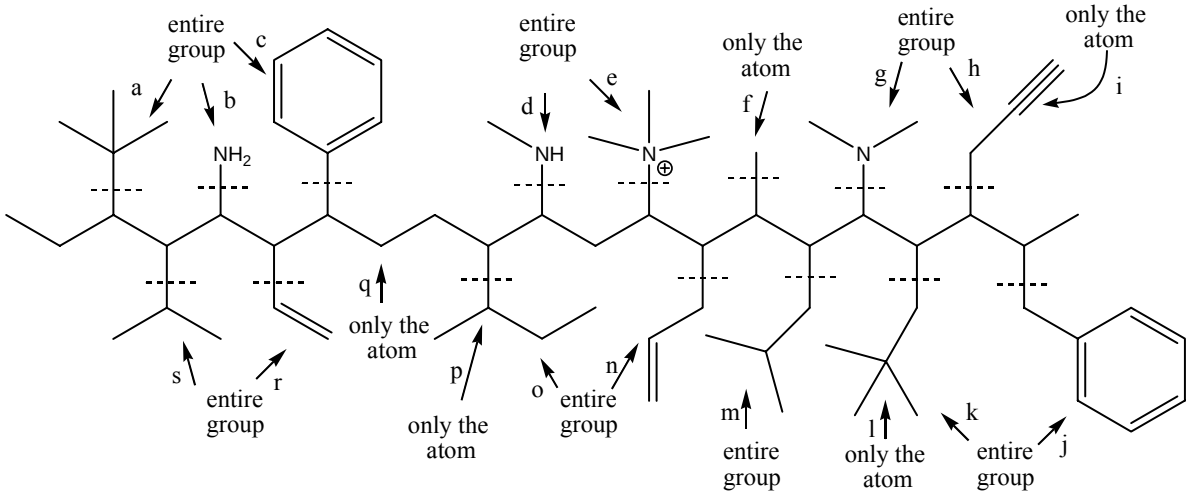
3D (A) 3D (best other)

Use structure A to fill in the following table.

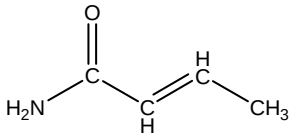
	Hybridization	Angles	Shape	#σ bonds	#π bonds	lone pairs
a						
b						
c						
d						
e						
f						

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

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

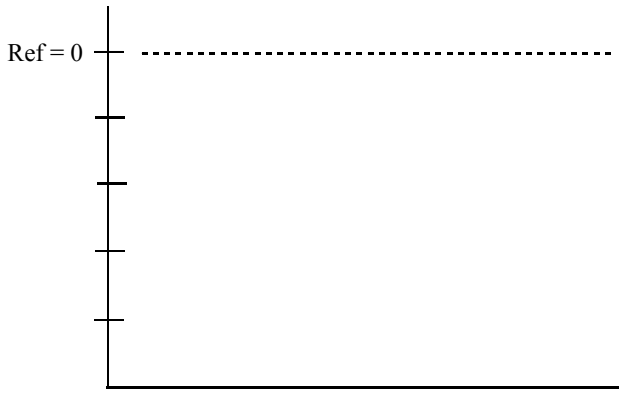


5. Draw a qualitative molecular orbital diagram for the following molecule. Include all sigma bonds to hydrogen together at the same energy. Include all other sigma bonds together at a different energy (assume these are stronger bonds). Include all pi bonds together at a different (and appropriate) energy.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



6. a The heat of combustion of **pent-1-yne** is –735.5 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 **pent-1-yne**. 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. (14 pts)

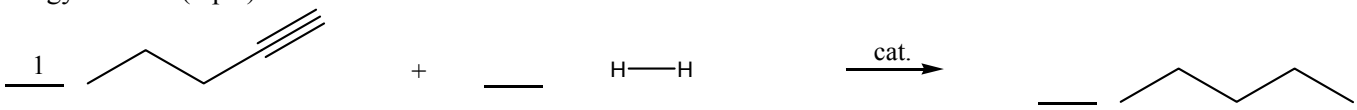
Combustion Equation



Energy Diagram

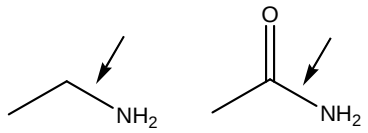
	ΔH_f^o (kcal/mole)
CO_2	-94.0
H_2O	-57.8
	-34.9

b. Balance the following equation and calculate the heat of reaction. 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 pi bond energies. (7 pts)

d. Determine the bond energies of the C-N bonds below (use the typical substitution pattern bond energy table on the last page). Provide a possible explanation for any differences. (6 pts)



B.E. = _____ B.E. = _____

7. a. Draw both chair conformations of cis-1-methyl-3-isopropylcyclohexane and trans-1-methyl-3-isoproylcyclohexane. Draw all axial and equatorial groups at substituted positions (includes hydrogen atoms). 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.** (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) = _____

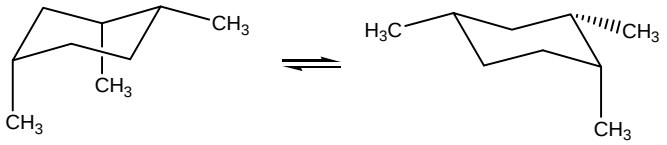
least stable overall (1,2,3,4) = _____

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. Use the second most stable conformation from part a, 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. (4 pts)

c. Calculate an approximate ΔH difference between the two conformations. Use energy values provided in the box. Show your work. (4 pts)

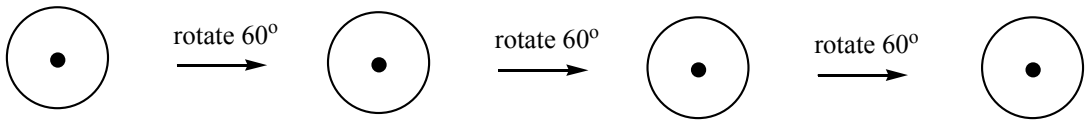


ΔH ≈

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.

d. Use a Newman projection of the C4→C3 bond of 2-methylpentane to **show the most stable conformation first**. Rotate through eclipsed and staggered conformations until you draw the least stable conformation. Using the energy values provided below, calculate the relative energies of the different conformations. Calculate a $K_{equilibrium}$ between the most stable and least stable conformation. 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. (16 pts)

2D structure



least stable
ΔH^o =

ΔH^o =

ΔH^o =

most stable
ΔH^o =

Eclipsing Energy Values (kcal/mole)	
H/H	+1.0
H/CH_3	+1.3
H/$CH(CH_3)_2$	+2.0
CH_3/$CH(CH_3)_2$	+3.0
any gauche	+0.8

$\Delta G \approx \Delta H$

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

You always have time for the things you put first. Okaa-san

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-	HO-	H_2N-	N≡C–
CH_3- methyl	105	90	86	86	84	102	110	85	71	57	93	85	122
CH_3CH_2- primary	98	86	82	81	79	98	108	81	68	53	92	82	118
$(CH_3)_2CH$- secondary	95	86	81	79	76	96	106	81	68	54	93	82	116
$(CH_3)_3C$- tertiary	93	84	79	76	71	93	110	81	67	52	93	82	(113)
CH_2=$CHCH_2$- allyl	86	74	70	70	67	(87)	(96)	68	54	41	78	(67)	(104)
$C_6H_5CH_2$- benzyl	88	76	72	71	70	90	(98)	72	58	48	81	71	(107)
CH_2=CH- vinyl	110	100	96	95	90	103	(124)	90	78	(63)	not stable	not stable	130
C_6H_5- phenyl	111	102	97	96	93	115	126	96	80	65	111	102	131
CH_3CO- acyl	86	81	76	74	72	94	119	81	66	49	107	98	not common
CH_3CH_2O- alkoxy	104	(96)	(92)	(91)	(90)	101	low	low	low	low	44	low	low
H- hydrogen	104	105	98	95	93	111	136	103	88	71	119	107	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	83	135	103	87	71	X
C		83	76	82	92	65	110	81	68	52	X
Si			53	85	108	70	135	91	74	56	X
N				40	48	X	65	46	X	X	X
O					35-47	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	256
C=S	137	N≡N	225
N=N	100		
N=O	145		
P=O	130		
O=O	118		
S=O	125		
S=S	102		

$C_{17}H_{18}BrN_3O_{11}$

anhydride,
aldehyde,
alcohol,
ether,
alkyne,
amine,
ester,
acid,
amide,
nitrile

degree of unsaturation calculation

$2(17)+2+3=39$

$=-19$

$20\div2=10$ degrees of unsaturation