CHEM 3311 (Luca) First Hour Exam – Feb 13th 2018

Your Name: Answer Key

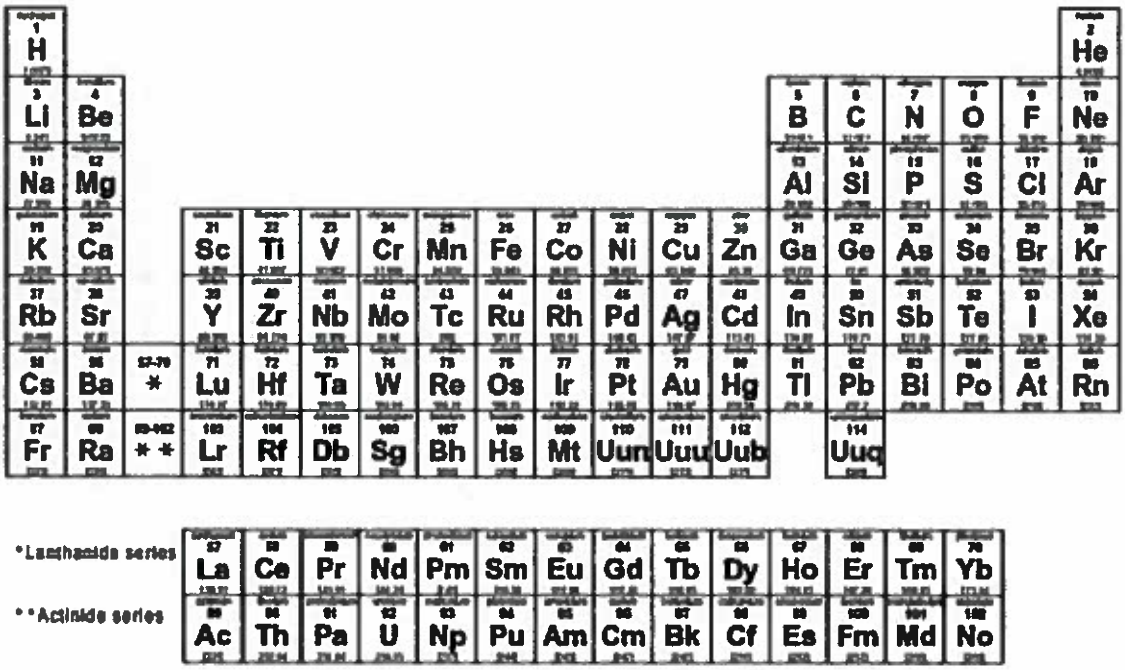
Student ID: _____

Recitation (Check one):

- o Monday 8am - Mori
- o Monday 9am - Carey
- o Monday 10am - Carey
- o Monday 11am - Carey
- o Tue 8am - Park
- o Tue 11am - Carey
- o Tue 2pm - Carey

Question	Points
1 /20	
2 /15	
3 /20	
4 /25	
5 /20	
Total /100	

This is a closed-book exam. The use of notes and cell phones will not be allowed during the exam. You may use models sets totally dismantled brought in a clear ziplock bag. Use the backs of the pages for scratch work. If your final answer is not clearly specified, you will lose points.



pKa Values

HI	-10	CH_3COOH	4.7	ArOH	10	H_2	35
HBr	-8	HN_3	4.7	RSH	10-12	NH_3	36
HCl	-6	H_2S	7.0	H_2O	15.7	$H_2C{=}CH_2$	45
H_3O^+	-1.7	NH_4^+	9.3	ROH (R=alkyl)	16-18	CH_4	60
HF	3.2	HCN	9.4	HC≡CH	26		

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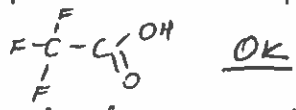
1. (20 points total)
   a. What is the least acidic compound of the compounds below? Explain your answer. (4 points)

      i. CF_3COOH ← most acidic
      ii. CH_3COOH ← least acidic
      iii. CH_2FCOOH

0 points for wrong answer
2 points for CH_3COOH without explanation
4 points for CH_3COOH with explanation either → α-polar effect halo
→ inductive halogen EWG makes proton more available / less available without

   b. Which one of the compounds has the lowest pK_a? Explain your answer. (4 points)

CF_3COOH or  OK

0 points for incorrect structure or wrong answer
2 points for correct structure with no explanation
4 points for correct structure with explanation (see a)

   c. Draw the structures for each of the conjugate bases of the acids in 1a. (6 points)

0 points for wrong structures or inappropriate bond connectivity

4 points line bond or

$CF_3COO^{\ominus}$
$CH_3COO^{\ominus}$
$CH_2FCOO^{\ominus}$

No partial credit for structure without charge.
No partial credit for $^{\ominus}CH_2COOH$ or $^{\ominus}CHFCOOH$

   d. What is the least basic of the conjugate bases from question 1c? Explain your answer (6 points)

0 points for incorrect structure or wrong answer
3 points for correct structure with no explanation
6 points for correct structure with explanation

$CF_3COO^{\ominus}$: strongest acid ⇒ weakest base

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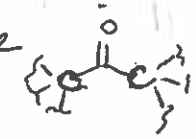
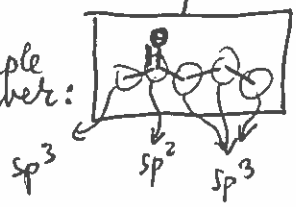
2. Give an example of molecules that meet **all** of the following requirements. For each of the examples, indicate hybridization **at all carbon** atoms (15 points total).

   a. Draw a molecule with 5 carbon atoms, one degree of unsaturation and one ketone functional group (5 points):

2 points for one π bond
2 points for → ketone
1 points for correct structure



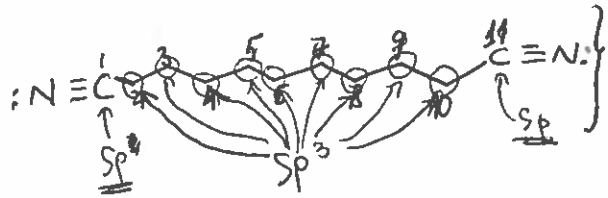
Example answer:



0 points for aldehyde 
0 points for cyclic answer
0 points for wrong # of C atoms.
1 point for correct assignment of hybridization

   b. Draw a molecule with more than 10 carbon atoms, two sp-hybridized carbon atoms and two nitriles (5 points):

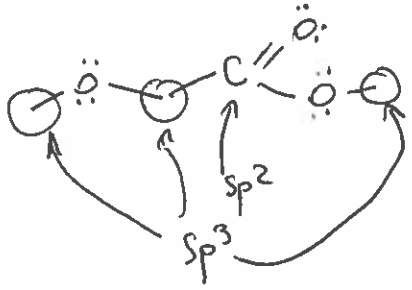
0 points for less than 10 C atoms
0 points for structures with no nitriles
0 points for structures with alkynes
0 points for structures with innapropriate bond connectivity



more than 10 C atoms ✓
two nitriles ≡ two sp hybridized C atoms

   c. Draw a molecule with an ether, a ester functional group, and one sp^2 carbon atom (5 points):

2 points for ester
2 points for ether
1 point for ester = one sp^2 C atoms



0 points if no ester and no ether

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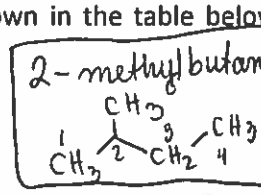
3. Draw the Newman Projection structures for 2-methylbutane, looking down the bond between carbons 2 and carbon 3 (as in the IUPAC naming). **Start with a dihedral angle between methyl groups of 0°** and draw other Newman Projections in increments of 60° **keeping the front atom stationary while rotating the one in the back clockwise** (7 points). For each of the conformations you draw, determine the interactions involved in between substituents. Indicate these interactions in the rectangles below (7 points). Consult the table and add up the energy of the interactions. Plot each energy level (for each of the conformations) and create a conformational energy diagram in the graph given (6 points). Interactions not shown in the table below are assumed to be negligible. (20 points total)

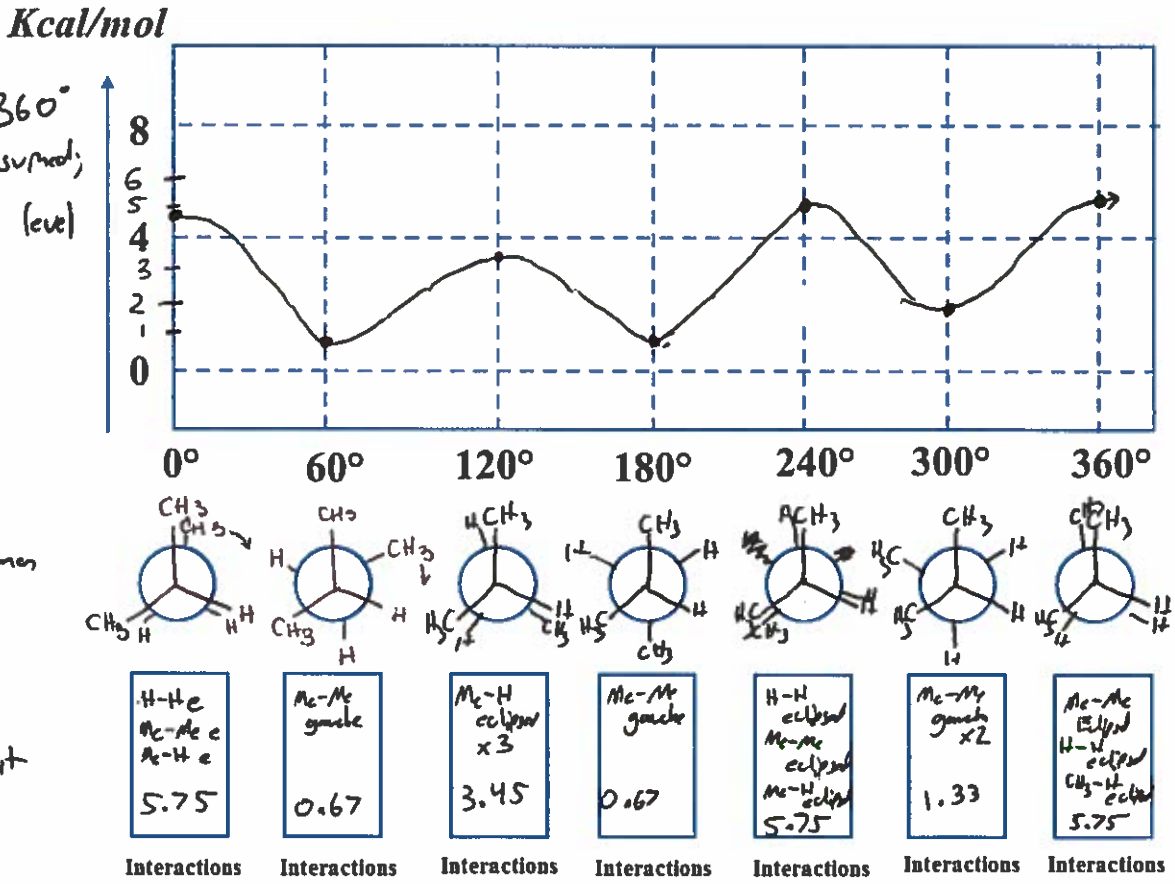
Interaction	Energy (kcal/mol)
H/H eclipsed	1
Me/H eclipsed	1.15
Me/Me Eclipsed	3.6
Me/Me gauche	0.67

2-methylbutane



0 points if wrong molecule

Getting the 360° energy is assumed; 1 pt. per energy level

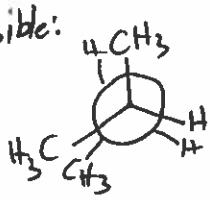


1 pt. per Newman proj. No partial credit.

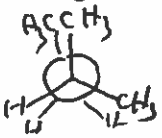
1 pt per box; no partial credit

Several starting points possible:

and ~~rotations~~ rotations of the whole molecule



eg.



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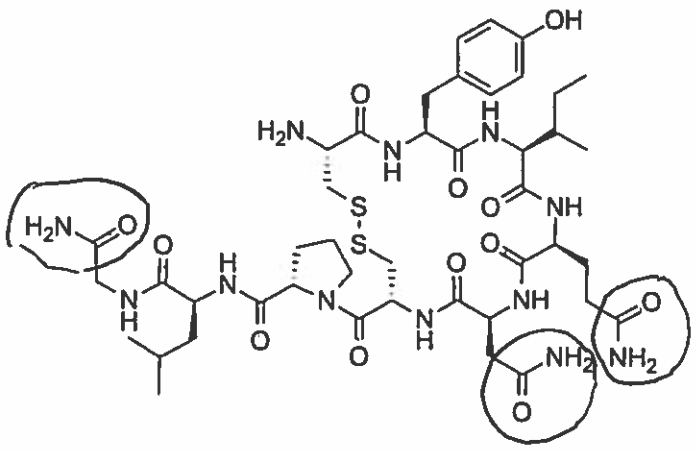
4. Oxytocin has been identified as the molecule responsible triggering feelings of love in our neural pathways. Its chemical structure is shown below. After carefully reviewing the structural features (functional groups) of this molecule, please answer the following questions: (25 points total)



a. How many degrees of unsaturation does this molecule have? (4 points)

17 is an extra two points

16 (no partial credit)

↑ not actually correct

b. How many primary amide bonds can you identify in this structure? (**place a circle around them**) (4 points)

3 (no partial credit)

c. How many π bonds does this molecule have? (4 points)

14 (no partial credit)

d. How many sp-hybridized carbon atoms does this molecule have? (4 points)

0 (no partial credit)

e. Assume you ingested oxytocin. You stomach has a pH of 1.6 and the phenol group on oxytocin has a pK_a of 10. Knowing that only deprotonated oxytocin is absorbed by your intestine, what is the ratio of deprotonated oxytocin to protonated oxytocin in your stomach? (4 points)

Correct Ratio or Fraction: 4 pts

$pH = pK_a + \log\frac{[A^-]}{[HA]}$ $\quad 10^{-8.4} = \frac{[A^-]}{[HA]} \Rightarrow \frac{[A^-]}{[HA]} = 3.98 \times 10^{-9} \Rightarrow$

Correct equation: 3 pts.

$1.6 = 10 + \log\frac{[A^-]}{[HA]}$

$-8.4 = \log\frac{[A^-]}{[HA]}$

$\Rightarrow [A^-] = [HA] \times 3.98 \times 10^{-9}$

Ratio of [HA] to $[A^-] \simeq 2.5 \times 10^8$ to 1

f. Based on your calculation at point e, how much of a 100-mg dose would be active? (5 points)

Almost all of the oxytocin exists as HA.

4 pts if said qualitatively; 5 pts. for number

$[A^-]$ is $\simeq 4 \times 10^{-7}$ mg

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5. Write out the structures of products for the following reactions. Clearly indicate charges and lone pairs on the atoms of your molecules and ions. (20 points total)

−1 if no/incorrect formal charges

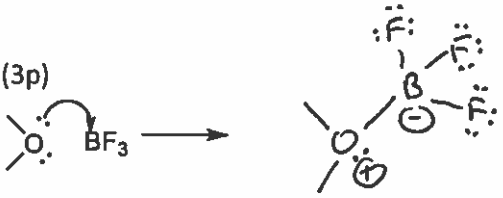
−1 if no/incorect lone pairs

a. (3p)

b. (3p)

c. (3p)

d. (3p)



e. (3p)

f. (5p)