**Chem 314**

Spring, 2013
Midterm Exam
Chem 314
Beauchamp

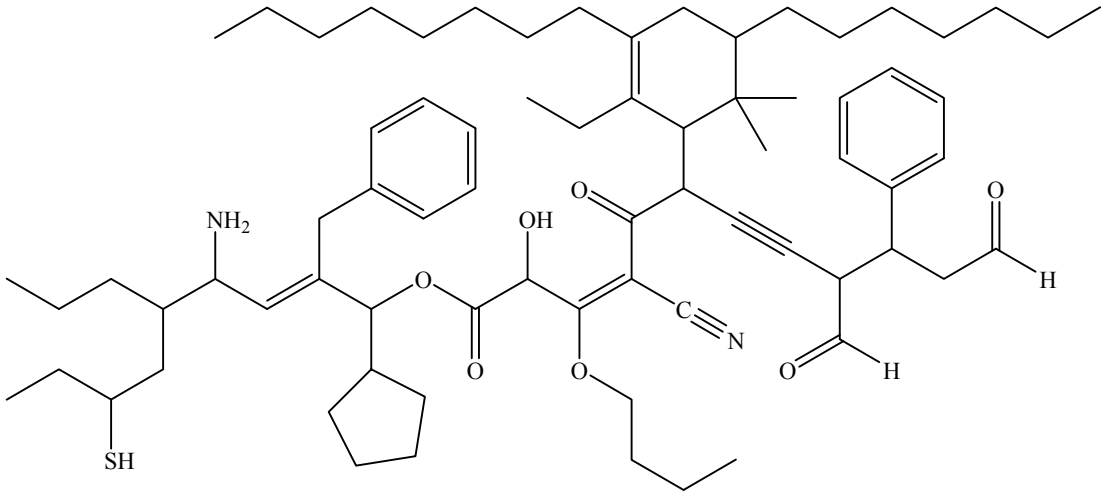
Name _____

| Problem | Points | Credit |
|---|---|---|
| 1. Nomenclature | 30 | |
| 2. 2D Lewis structures | 20 | |
| 3. 3D Structures, Formal Charge & Resonance | 34 | |
| 4. Physical Properties or Functional Groups & degree of unsaturation | 21 | |
| 5. Molecular Orbital Diagram or Special Nomenclature Terms | 15 | |
| 6. Thermodynamics, Bond Energies & Reactions | 30 | |
| 7. Conformations, Energy (Cylclohexane chairs), Newman Projections | 25 | |
| 8. Conformations, Energy (Chains), Newman Projections | 25 | |
| **Total** | 200 | |

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 in the space available. Also, consider the point values in your choice of questions. Do your best to show me what you know in the available time.

The important thing is this: To be able at any moment to sacrifice what we are for what we could become.
Charles DuBois

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

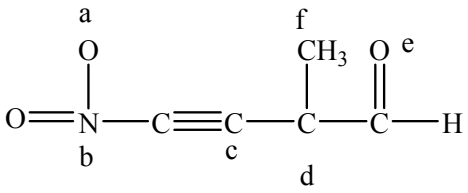



2. Draw an acceptable 2D Lewis structure for the following formula. Indicate any formal charges present, all lone pair electrons and completely draw out all atoms (e.g. do not write $CH_3$). (20 pts)

six carbon ring ↓ has formal charge ↓

$(CH_3)_3CCCCHCCH_3CHNH_2CO_2C_6H_4CONHCHCNCHOHCOCH_2OCH(COCH_3)CH(NO_2)CH(OCH_3)CH(CO_2H)CO_2CHO$

3. First, draw three other reasonable 2D resonance structures that <u>delocalize the **most** unstable 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)




A

B

D

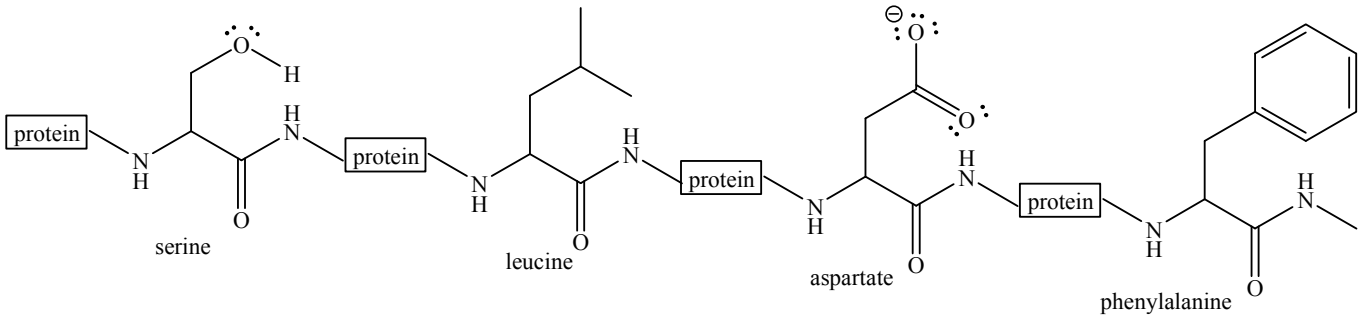
C

3D (A) 3D (best other)

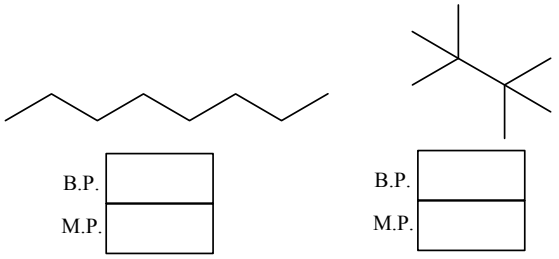
Use structure A to fill in the following table.

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

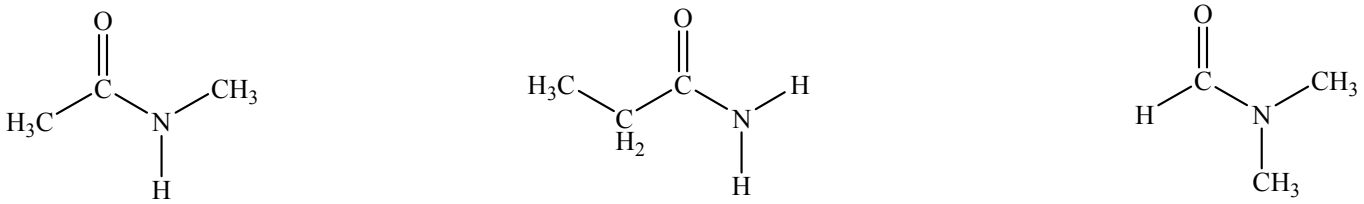
**4.** a. Hydrophobic lipid bilayers are a large component of cell membranes. They help separate the aqueous environments of blood and cytosol. There are many proteins embedded in the cell membrane, pointing outward toward the blood, inward toward the cytosol or completely spanning the membrane. Four of the 20 common amino acids making up proteins are shown below. State whether you would expect each amino acid to prefer the hydrophobic cell membrane or the aqueous cytosol/blood environment. Explain your reasoning. (7 pts)



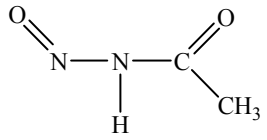

b. Match the melting points and boiling points with the given structures and provide a very brief explanation. Your matches must be completely correct. Temperatures = -57°C, 100°C, 106°C and 125°C. (7 pts)




c. Match the boiling points with the compounds and provide a very brief explanation. Temperatures = 152°C, 205°C, 213°C. (7 pts)

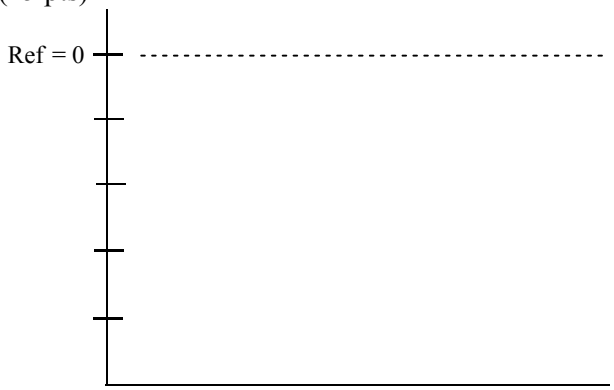


**5.** Draw a qualitative molecular orbital diagram for the following molecule. Include all sigma bonds to hydrogen together at the same energy. Include all other sigma bonds together at a different energy (assume these are stronger bonds). Include all pi bonds together at a different (and appropriate) energy. Also, place nonbonding electrons at an appropriate energy. Label your molecular 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)




6. a. The heat of combustion of **2-hydroxybutanal** is –509.7 kcal/mole. Write an equation for this reaction. Limited heats of formation are also provided below. Use this information to calculate a heat of formation for **2-hydroxybutanal**. 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)

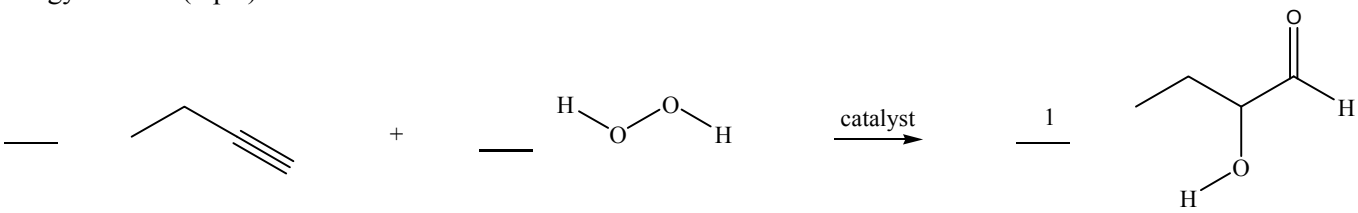
Combustion Equation




Energy Diagram

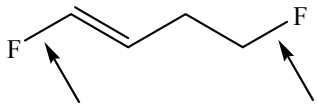
| | $\Delta H_f^o$ (kcal/mole) |
|---|---|
| $CO_2$ | -94.0 |
| $H_2O$ | -57.8 |
| $H_2O_2$ | -32.5 |
|  | +39.5 |

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 at the end of this exam. How does this value compare to that of part b? (6 pts)

d. Determine the bond energies of the C-F bonds below (use the specific substitution pattern bond energy table at the end of this exam). Provide a possible explanation for any differences. (5 pts)




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

7. Draw both chair conformations of cis-1-ethenyl-3-ethynylcyclohexane and trans-1-ethenyl-3-ethynylcyclohexane (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 of side chain substituents are 0.8 kcal/mole.** (16 pts)

ΔH = ?
⇌
cis

chair 1 chair 2

most stable (1 or 2) _____

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

ΔH = _____

ΔH = ?
⇌
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=$CH_2$ | +1.7 |
| CCH | +0.5 |
| 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. Assume R = 2 cal/(mol-K) and T = 300 K. (4 pts)

$\Delta G \approx \Delta H$

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

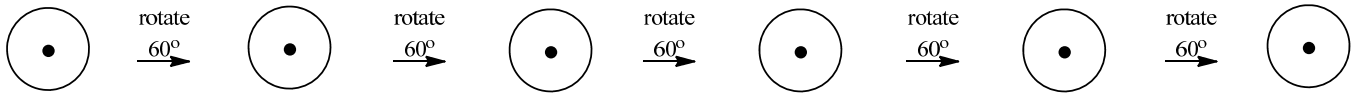
Ratio Calculation (chair 1 ⇌ chair 2)

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→C2 bond of 3-ethyl-2,4-dimethyl-2-phenylpentane 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. (structure provided for 2 points) (21 pts)

2D structure

most stable conformation




$\Delta H^o =$ $\Delta H^o =$ $\Delta H^o =$ $\Delta H^o =$ $\Delta H^o =$ $\Delta H^o =$

**Approximate Eclipsing Energy**
Values (kcal/mole)

| | H | Me | Et | i-Pr | t-Bu | Ph |
|---|---|---|---|---|---|---|
| H | 1.0 | 1.3 | 1.4 | 1.6 | 3.0 | 1.7 |
| Me | 1.3 | 2.5 | 2.7 | 3.0 | 8.5 | 3.3 |
| Et | 1.4 | 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 |

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

least stable conformation ⇌ most stable conformation

$\Delta H = ?$

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

**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 | | |