

Chem 314

Fall, 2014
Midterm Exam
Chem 314
Beauchamp

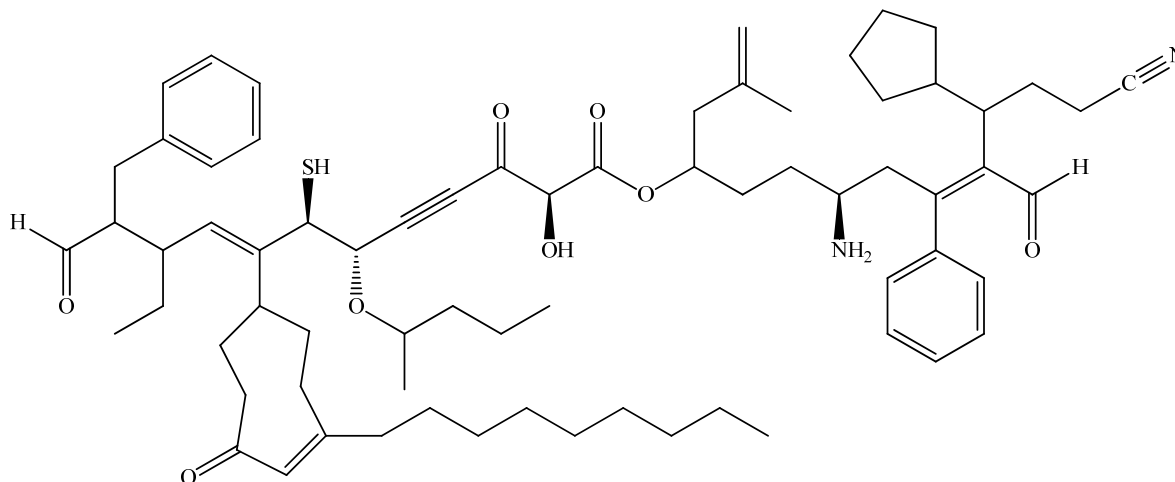
Name _____

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. Conformations, Energy (Cyclohexane chairs), Newman Projections	28	
6. Conformations, Energy (Chains), Newman Projections	30	
7. Stereochemical Analysis	30	
8. Degrees of Unsaturation & Functional Groups or Various Nomenclature Terms	25	
Total	198	

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.

"Friendship is one mind in two bodies." Mencius

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 CH₃). (20 pts)

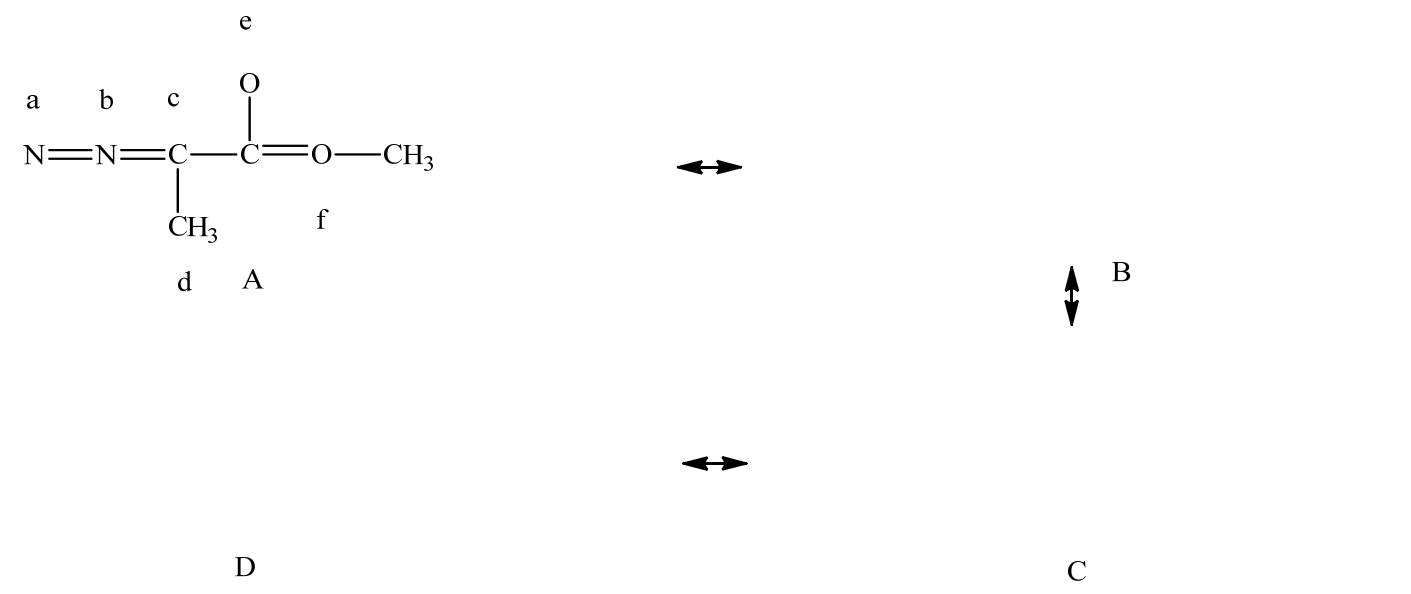
six carbon ring



has formal charge



3. First, draw three other reasonable 2D resonance structures that delocalize charge that allow you to determine the hybridization of every atom (start with the right side of the molecule). 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). **Assume that all non-hydrogen atoms have full octets, unless a carbocation is written.** (34 pts)



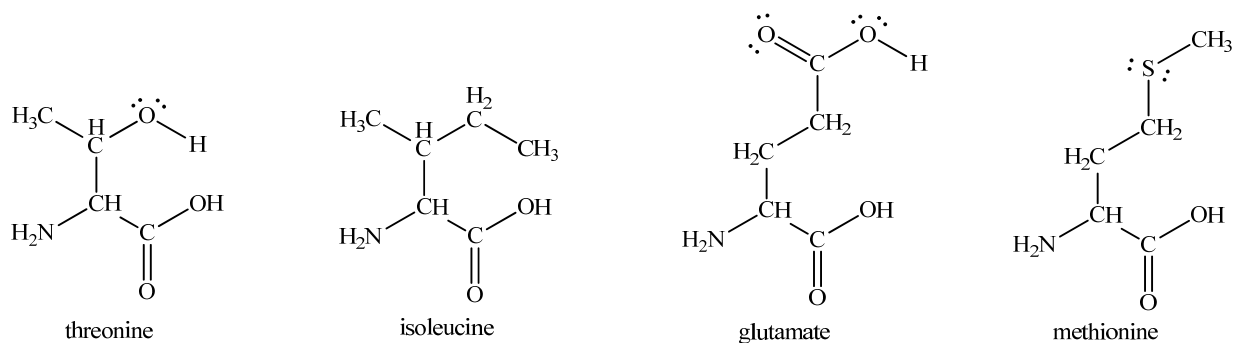
3D (A)

3D (best other)

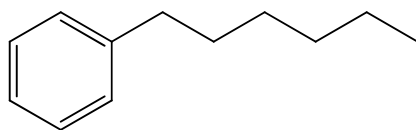
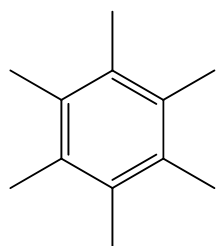
Use structure A to fill in the following table.

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

4. a. Four of the 20 common amino acids making up proteins are shown below. State whether you would expect each amino acid to be mainly hydrophobic or mainly hydrophilic. Explain your reasoning. Sulfur is similar in electronegativity to carbon. (7 pts)



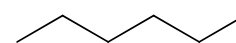
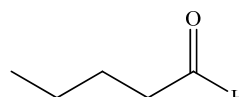
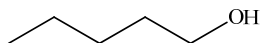
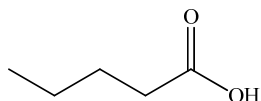
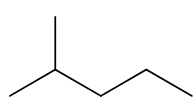
- b. Match the melting points and boiling points with the given structures and provide a very brief explanation. Your matches must be completely correct. Temperatures = -61°C , 165°C , 265°C and 321°C . (7 pts)



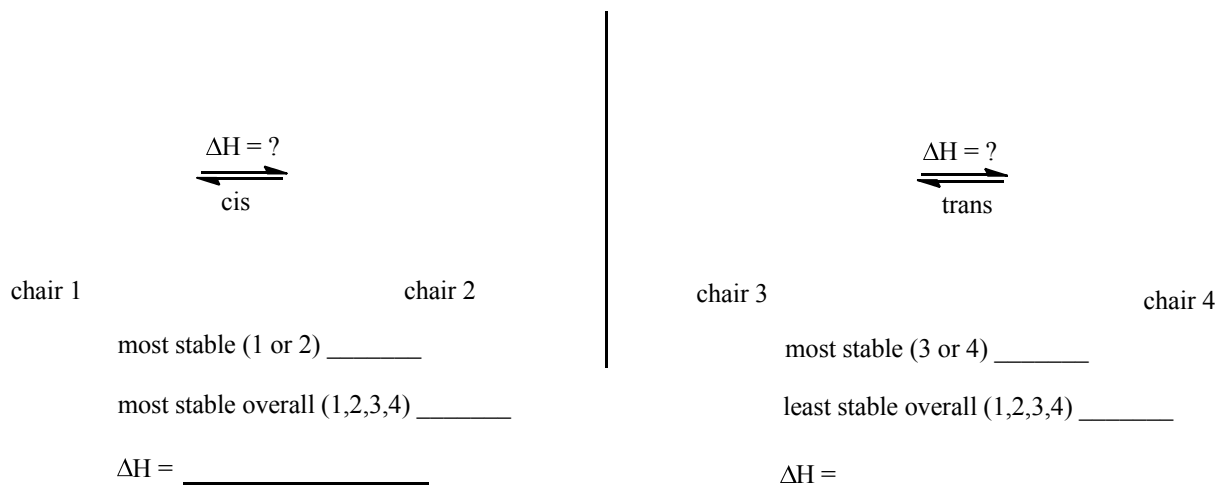
B.P.	
M.P.	

B.P.	
M.P.	

- c. Match the boiling points with the compounds and provide a very brief explanation. Temperatures = 61°C , 69°C , 102°C , 139°C , 164°C . (7 pts)



5. Draw both chair conformations of cis-1-t-butyl-2-methylcyclohexane and trans-1-t-butyl-2-methylcyclohexane (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. Find the t-butyl/methyl gauche energy in the table on the next page.** (18 pts)



Data for part 7a

Axial Energy Values (kcal/mole)	
-CH ₃	+1.7
C(CH ₃) ₃	+5.0
gauche - see table on next page	

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

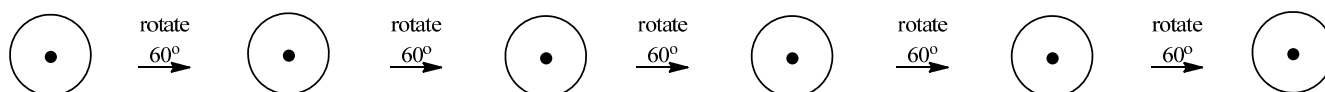
$\Delta G \approx \Delta H$ $K_{\text{eq}} = 10^{\frac{-\Delta H}{2.3RT}}$	Ratio Calculation (chair 1 \rightleftharpoons chair 2)
----------------------------------------------------------------------------	----------------------------------------------------------

- c. Use the least stable conformation from part a (1 = t-butyl), and draw a Newman projection using bonds $C_2 \rightarrow C_1$ and $C_4 \rightarrow C_5$ for your structure (or... $C_1 \rightarrow C_2$ and $C_5 \rightarrow C_4$). Point out any gauche relationships in the branches and/or the ring. (6 pts)

6. a. Use a Newman projection of the C3→C4 bond of 2,3,3-trimethyl-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. (structure provided for 2 points) (26 pts)

2D structure

most stable
conformation



$\Delta H^\circ =$

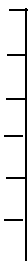
$\Delta H^\circ =$

$\Delta H^\circ =$

$\Delta H^\circ =$

$\Delta H^\circ =$

$\Delta H^\circ =$



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

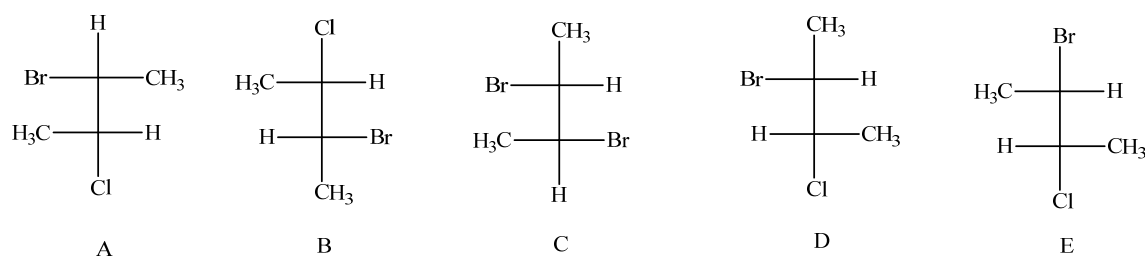
$$\Delta G \approx \Delta H \quad K_{\text{eq}} = 10^{\frac{-\Delta H}{2.3RT}}$$

least stable conformation \rightleftharpoons most stable conformation

$\Delta H = ?$

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

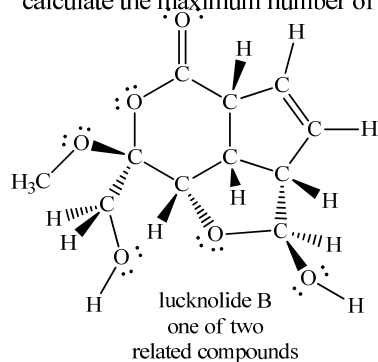
7. For the following set of Fischer projections answer each of the questions below by circling the appropriate letter(s) or letter combination(s). Hint: Redraw the Fischer projections with the longest carbon chain in the vertical direction and having similar atoms in the top and bottom portion. Classify all chiral centers in the first structure as R or S absolute configuration and write an acceptable name for that isomer. (17 pts)



- | | |
|--------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------|
| a. Which are optically active? | A B C D E |
| b. Which are meso? | A B C D E |
| c. Which is not an isomer with the others? | A B C D E |
| d. Which pairs are enantiomers? | AB AC AD AE BC BD BE CD CE DE |
| e. Which pairs are identical? | AB AC AD AE BC BD BE CD CE DE |
| f. Which pairs are diastereomers? | AB AC AD AE BC BD BE CD CE DE |
| g. Which pairs, when mixed in equal amounts will not rotate plane polarized light? | AB AC AD AE BC BD BE CD CE DE |
| h. Draw any stereoisomers of 2-bromo-3-chlorobutane as Fischer projections, which are not shown above. If there are none, indicate this. (3 pts) | |

- i. Would anything change if, in compound D, the Br was replaced with a Cl group? How about compound A? (2 pts)

- j. The structure of lucknolide B was recently determined (and the absolute configuration of all chiral centers!). It was isolated from the terrestrial bacteria, *Streptomyces* sp. ANK-289, in screenings for new medicinal lead compounds (*Org. Lett.* p.3800, 2010). Circle all chiral centers and any other stereochemical features, and calculate the maximum number of stereoisomers possible. (8 pts)



8. Use the given molecular formula to calculate the degree of unsaturation. Draw an example molecule that has the indicated functional groups. Include lone pairs of electrons. Identify functional groups by name (25 pts)

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

"The chains of habit are too weak to be felt until they are too strong to be broken." Samuel Johnson