Chem 201 Sample Midterm Beauchamp

Exams are designed so that no one question will make or break you. 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 where appropriate. Do your best to show me what you know in the time available.

1. Provide an acceptable name for the following molecule.



- Draw an example of each of the following. Use "R" as a carbon portion for unspecified parts of your structures.
  methyl 2. methylene 3. methine 4. primary 5. secondary 6. tertiary 7. quarternary 8. isopropyl
  isobutyl 10. sec-butyl 11. t-butyl 12. neopentyl 13. vinyl 14. allyl 15. propargyl 16. phenyl
  benzyl 18. primary amine 19. secondary amine 20. tertiary amine 21. quaternary ammonium ion
- 3. Use the given formula  $(C_8H_{14}Br_2)$  to write examples of each kind of isomerism: skeletal, positional, functional group, conformational, enantiomers, diastereomers.
- 4. Match the given boiling points with the structures below and give a short reason for your answers. (-7°C, +31 °C, +80 °C, +141°C, 1420°C)



- 5. a. Hexane (density = 0.65 g/ml) and water (density = 1.0 g/ml) do not mix. Which layer is on top? Why don't they mix?
  - b. Carbon tetrachloride (density = 1.59 g/ml) and water (density = 1.0 g/ml) do not mix. Which layer is on top?
- 6. The melting point of NaCl is very high (≈ 800°C) and the boiling point is even higher (> 1400°C). Does this imply strong, moderate or weak forces of attraction between the ions? Considering your answer, is it surprising that NaCl dissolves so easily in water? Why does this occur? Consider another chloride salt, AgCl. How does your analysis work here? What changed?
- 7. a. Which solvent do you suspect would dissolve NaCl better, DMSO or hexane? Explain your choice?b. Which solvent do you suspect would dissolve NaCl better, methanol or benzene? Explain your choice?
- 8. Different groups can be connected to the "O-H" substituent of cholesterol. What effect on water solubility do you expect for each of the following changes. Why?



9. Draw an acceptable Lewis structure (2D) for each of the following. Show <u>all</u> single, double and triple bonds with one, two or three lines. Include all lone pairs of electrons as two dots. Include formal charge, if present at the atom where present. Identify any functional groups by name (i.e. ketone, amide, etc.)

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(CH<sub>3</sub>)<sub>2</sub>CHNOCCHCHCH<sub>2</sub>COCCCO<sub>2</sub>CH<sub>2</sub>CH(CHO)CHNH<sub>3</sub>CHCH<sub>3</sub>CH<sub>2</sub>OCHCNCO<sub>2</sub>H
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10. Draw all possible chair conformations of trans-1-bromo-2-phenylcyclohexane (or 1,3 or 1,4, any of them cis or trans). Which conformation is more stable? Draw it first. Provide a reason for your answer. Draw a Newman projections of the less stable conformation using the  $C_2 \rightarrow C_1$  and  $C_4 \rightarrow C_5$  bonds to sight along. Point out any gauche interactions shown in your Newman projection. Use the axial energy of a phenyl to determine what are the relative percents of each conformation? Sketch an energy diagram that shows how the energy changes with the conformational changes.

Substituent	$\Delta G^{o}$ (A value)	:	Substituent	$\Delta G^{o}$ (A value)
-H	0.0	-	-CH <sub>2</sub> OH	1.8
-CH <sub>3</sub>	1.7	ł	-CH <sub>2</sub> Br	1.8
-CH <sub>2</sub> CH <sub>3</sub>	1.8	1	-CF <sub>3</sub>	2.4
-CH(CH <sub>3</sub> ) <sub>2</sub>	2.1		-O <sub>2</sub> CCH <sub>2</sub> CH <sub>3</sub>	1.1
-C(CH <sub>3</sub> ) <sub>3</sub>	> 5.0	į	-OH	0.9
-F	0.3	ł	-OCH <sub>3</sub>	0.6
-Cl	0.5	1	-SH	1.2
-Br	0.5		-SCH <sub>3</sub>	1.0
-I	0.5	-	-SC <sub>5</sub> H <sub>6</sub>	1.1
-CH=CH <sub>2</sub>	1.7	1	-SOCH <sub>3</sub>	1.2
-CH=C=CH <sub>2</sub>	1.5	1	-SO <sub>2</sub> CH <sub>3</sub>	2.5
-CCH	0.5	1	-SeC <sub>5</sub> H <sub>6</sub>	1.0
-CN	0.2	ł	-TeC <sub>5</sub> H <sub>6</sub>	0.9
-C <sub>5</sub> H <sub>6</sub> (pheny	(l) 2.9	ł	$-NH_2$	1.2(C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> ), 1.7(H <sub>2</sub> O)
-CH <sub>2</sub> C <sub>5</sub> H <sub>6</sub> (benzyl) $1.7$			-N(CH <sub>3</sub> ) <sub>2</sub>	1.5 (C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> ), 2.1(H <sub>2</sub> O)
-CO <sub>2</sub> H	0.6	1	$-NO_2$	1.1
-CO₂⊖	2.0	-	-HgBr	0.0
-CHO	0.7		-HgCl	-0.2
		÷	-MgBr	0.8

11. Use a Newman projection of the C3 $\rightarrow$ C4 bond of 2-methyl-4-phenylhexane to show the most stable conformation first. Rotate through all of the eclipsed and staggered conformations. Using the energy values provided in the table below, calculate the relative energies of the different conformations. Plot the changes in energy in the graph diagram provided. Hint: Draw a 2D structure first and "bold" the bond viewed in your Newman projection, then decide your line of sight.

2D structure

Approximate Eclipsing Energy Values (kcal/mole)					$-\Delta G$		
	Н	Me	Et	i-Pr	t-Bu	Ph	$\mathbf{K} = 10^{-2.5\text{K}}$ $\mathbf{R} = 2 \text{ cal/mol-1}$
Н	1.0	1.4	1.5	1.7	3.0	2.0	I = 300  K
Me	1.4	2.5	2.7	3.0	8.5	3.3	
Et	1.5	2.7	3.3	3.8	10.0	4.5	
i-Pr	1.7	3.0	3.8	7.8	13.0	8.2	
t-Bu	3.0	8.5	10.0	13.0	23.0	14.1	
Ph	2.0	3.3	4.5	8.2	14.1	8.7	

Approximate Gauche Energy Values (kcal/mole)								
	Н	Me	Et	i-Pr	t-Bu	Ph		
Н	0	0	0.1	0.2	0.5	0.3		
Me	0	0.8	0.9	1.1	2.7	1.4		
Et	0.1	0.9	1.1	1.3	3.0	1.6		
i-Pr	0.2	1.1	1.3	2.0	3.8	2.3		
t-Bu	0.5	2.7	3.0	3.8	8.2	4.1		
Ph	0.3	1.4	1.6	2.3	4.1	2.7		



12. Fill in any missing lone pairs and formal charge on the 2D structures. Assume ALL nonhydrogen atoms have full octets, unless a positive charge is shown. Draw two additional 2D resonance structures of the given structure using proper resonance curved arrows. Which structure is best (=1), second best, etc. and why? Draw a 3D structure for the given resonance structure. Show bonds in front of the page as wedges, bonds in back of the page as dashed lines and bonds in the page as simple lines. Show orbitals for pi bonds and lone pairs along with their electrons. Identify the hybridization, bond angles and descriptive shape for any of the nonhydrogen atoms.

HN	ICCHC(C	$(H_3)OCH_3$	$\left[ \text{OHCC(CH_3)CHO} \right] \ominus$					
Atom	Shape	Hybridization	Bond Angles	# $\sigma$ bonds	# $\pi$ bonds	# lone pairs		
1								
2								
3								
4								
5								

13. 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.



h. Draw any stereoisomers of 2-bromo-3-chlorobutane as Fischer projections, which are not shown above. If there are none, indicate this.

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

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.



14. Indicate all formal charges present in the following structures. Assume all electrons are shown as lines or dots. If other reasonable resonance structures are possible, draw one additional resonance structure using the proper arrow conventions.

