Chemistry 304B, Spring 99. More-or-less relevant supplementary problems for Exam 1

[I have included some of these in order to solidify the concepts of resonance and bonding, and they are not necessarily relevant to acid/base and molecular association concepts]

1. *Hemoglobin is the key molecule in biological oxygen transport, and the key part of hemoglobin is an Fe^{+3} ion as part of its structure. A simple model suggests that the iron ion acts as a Lewis acid, bonding reversibly to oxygen. Think about the bonding of oxygen to the iron ion.*

A. Draw the oxygen molecule using Lewis structures and show all bonds, non-bonding electrons and formal charges. Then draw next to it a picture of oxygen bound to a Lewis acid; please use $\mathbf{BF_3}$ as your Lewis acid instead of Fe^{+3} (the picture will be simpler). Show all non-bonding electrons and formal charges.

Sodium cyanide (NaCN) and carbon monoxide are toxic because they compete with the oxygen in binding to the iron ion.

B. There are two reasonable resonance structures for cyanide anion, one with two bonds and one with three. Draw both resonance structures, showing all bonds, non-bonding electrons, and formal charges. Indicate the hybridization at C and at N. State which structure you feel is the more stable, and explain the basis for your choice briefly.

C. There are two reasonable resonance structures for CO, one with two bonds and one with three. Draw both resonance structures of CO, showing all bonds, non-bonding electrons, and formal charges. Indicate the hybridization at C and at O. State which structure you feel is the more stable (more important in the hybrid), and explain the basis for your choice briefly.

D. Draw a structure for cyanide anion bound to BF_3. Note that there are two "ends" to cyanide anion. Explain why you chose one particular end over the other to bind the Lewis acid. Show all bonds, non-bonding electrons, and formal charges. Indicate the hybridization at the boron atom.

E. Draw a representation of carbon monoxide bound to BF_3. Note that there are two "ends" to carbon monoxide. Explain why you chose one particular end over the other to bind the Lewis acid. Show all bonds, non-bonding electrons, and formal charges.

F. Which do you predict will bind more strongly to BF_3: oxygen, cyanide anion, or carbon monoxide? Explain your reasoning briefly.

2. Consider the isomers with the molecular formula $C_3H_6O_2$

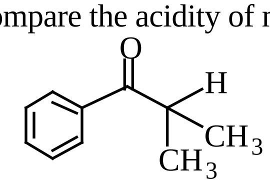
a. write the isomer which is much more soluble in 0.1 M NaOH compared to pure water. Explain your choice briefly.

b. write the isomer which is least soluble in water.

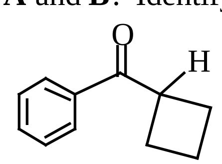
3. using any combination of 5 carbon atoms, any number of hydrogens, and two nitrogen atoms, construct the uncharged molecule with:

a. the highest solubility in cyclohexane
b. the least basic nitrogen atom
c. the most electron deficient carbon atom
d. the most acidic proton

4. Compare the acidity of molecules **A** and **B**. Identify the most acidic proton on each.



A



B

5. Phenol is a moderately acidic molecule, and was used in water solution by Pasteur as the first antiseptic. Assuming the acidity is the feature responsible for the antibiotic activity, would it have been more or less effective to use solution of phenol in DMSO instead of water? Explain by showing off your expertise regarding solvent effects on acid-base reactions.

6. Normally, when causing an acidic molecule to form its conjugate base by proton abstraction with base, it is possible to neutralize the solution and re-generate the original acid. We also imply this reversibility in the equilibrium expression:

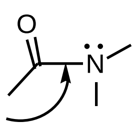
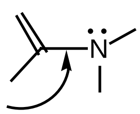
$$\text{H-A} \rightleftharpoons \text{H}^+ + \text{A}^-$$

Strangely, when the weak acid **C** was treated with base and then neutralized with acid, **C** was re-generated but two new molecules were also found, **D** and **E**. Propose structures for **D** and **E** and explain how they formed.

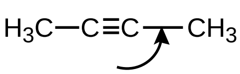
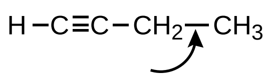
C

7. Consider the following pairs of molecules. Note the bond indicated by the arrow in each structure.

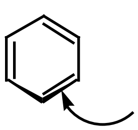
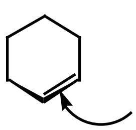
For each pair, circle the one in which the indicated bond is ***longer*** *and give* ***one*** *important reason for the difference (hybridization, delocalization, steric effects, inductive effects. Explain briefly. If you choose delocalization, draw the relevant structure(s).*

A.  vs 

1 **2**

B.  

1 **2**

C.  vs 

1 **2**

D. *In a related analysis, draw the structure of a molecule with six carbons, any number of hydrogens, no other atoms , and no formal charge which has the SHORTEST carbon-carbon SINGLE BOND distance. Explain your choice briefly. Indicate clearly which bond you think is the shortest.*