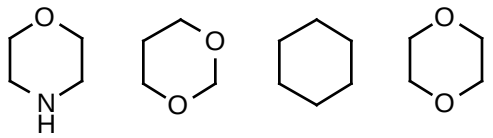
Chemistry 304B, Spring, 1999 **Problem Set 1**

1. Following is a collection of four molecules (**1-4**) and also a list of four boiling points, with no relationship implied between the two lists except that each bp is correct for one of the molecules listed.

*Match the bp with the structure, and **explain** the basis for your assignment.*

It will be clearest if you start with the lowest bp structure and compare with the second lowest, and so on until you finish with the highest bp. If there is ambiguity, explain briefly your thinking.



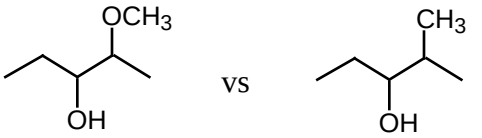
1 **2** **3** **4**

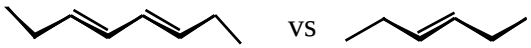
bp: 81^0, 100^0, 106^0, 129^0C

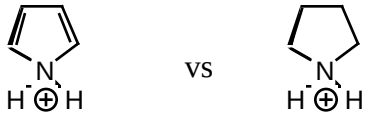
bp ____ ____ ____ ____

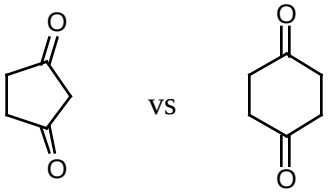
Explain lowest vs second lowest bp
Explain second lowest vs second highest bp
Explain second highest vs highest bp

2. *Draw the conjugate base for each molecule in each pair; show carefully which proton has been lost. Circle the <u>most acidic molecule</u> in each pair and explain the <u>single</u> most important reason for your choice in terms of differential resonance, inductive (electronegativity), or hybridization effects.*

A. 

B. 

C. 

D. 

3. The relative degree of self-association provided by the various mechanisms is not easy to quantify, and typically it is not possible to predict relative boiling points for molecules with quite different structures. Van der Waals forces for an atom are related to polarizability and can become large for large squishy atoms or large numbers of atoms. Dipole interactions usually focus on one strong dipole in a molecule; several bond dipoles in a molecule seldom reinforce strongly, and often cancel each other in the molecular dipole.

You should be able to compare the bp (and solubility) of similar structures for which one parameter is varied (eg, similar molecular size and type of atom, different dipole effects, or different H-bonding opportunities). You should be able to consider a set of bp (or solubility) data and explain what the differences are revealing about the relative importance of the various molecular association mechanisms.

A. Consider the following data:

	bp (^{0}C)
1-fluorohexane	90
1-chlorohexane	133
1-bromohexane	155
1-iodohexane	180
hexanal	131

Compare pairs of compounds from the list (ie, 1-fluorohexane vs 1-chlorohexane) and analyze what forces are at work and dominant in order for the relative bp to make sense.

B. Draw the structure of the molecule with the highest bp and molecular formula C_4H_7N. Explain your reasoning by comparing your choice with the structure with the second highest bp. It is unlikely there is a single correct answer. I am interested in your logic as related to your structures.

C. Draw the structure of the molecule with molecular formula $C_5H_8O_2$ and the highest molecular dipole. Explain your choice.

D. Draw the structure of the $C_5H_8O_2$ isomer with the lowest bp. Explain your choice.

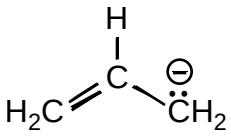
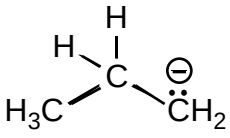
4**.** *Which molecule in each of the following pairs is more* ***basic****?*

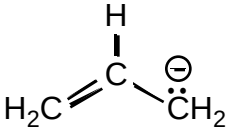
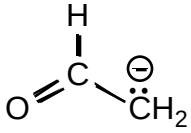
Circle the best answer and explain the basis of your choice in terms of differential resonance, inductive (electronegativity), or hybridization effects.

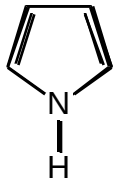
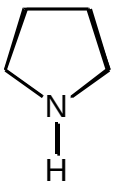
Give the ***single*** *most important reason for the difference.*

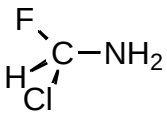
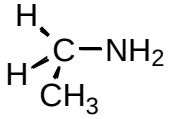
Draw the conjugate acid of the more basic molecule in each pair.

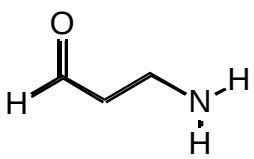
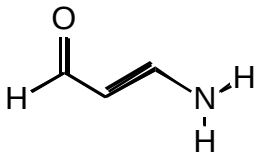
A. H_3C-F vs H_3C-OH

B.  vs 

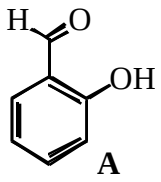
C.  vs 

D .  vs 

E.  vs 

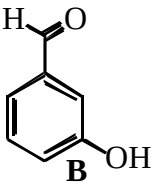
F.  vs 

5. Consider the following three molecules and the corresponding mp data.



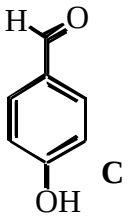
A

mp 2 ^{0}C



B

108 ^{0}C



C

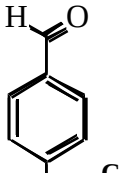
116 ^{0}C

*A. Draw below the self-association of molecule **B** (using three molecules of **B**)*

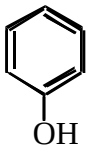
*B. Explain carefully, in words and pictures, why the mp of **A** is much lower than either **B** or **C**.*
*Give the **single** most important reason for the difference.*

*C. Compounds **A-C** are all slightly soluble in water but all dissolve readily in aqueous 1M NaOH solution. Use compound **B** as your example, and explain why it is more soluble in the NaOH solution compared to water.*

D. In a different analysis, compare molecule **C** with phenol in terms of **acidity**.
Which has the lower pKa and why?
*In your answer draw carefully the conjugate base of **C** and compare it with the conjugate base of phenol.*



C



phenol