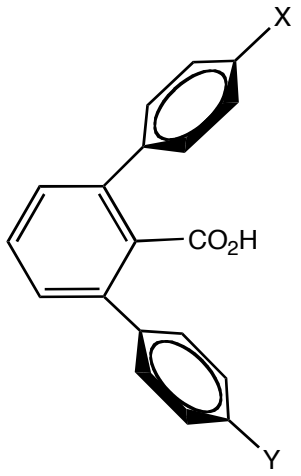
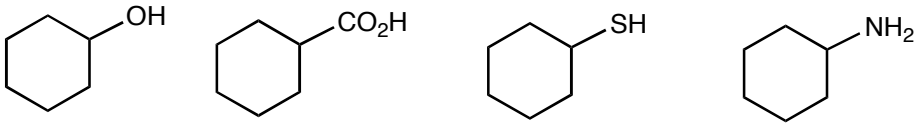
Additional Problems for Solutions and Non-covalent Interactions

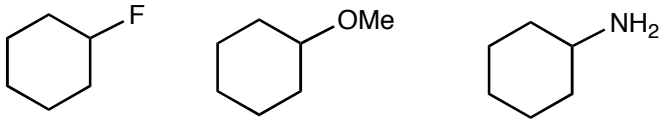
1. For the following molecule, explain why the pKa of this substituted benzoic acid X=Y=H) is 6.39, vs. 4.2 for benzoic acid itself. How would the pKa of this compound change if X and Y were electron donating groups? Electron withdrawing groups?.



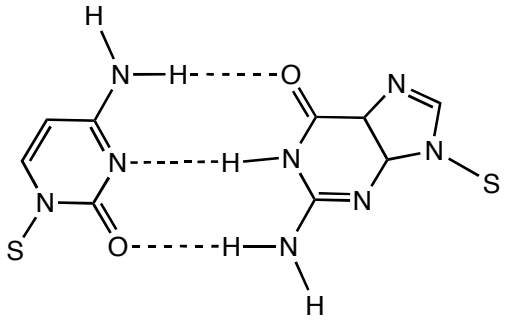
2. Arrange the following compounds in order of increasing hydrogen bond donating ability toward methylamine. Rationalize your answer:



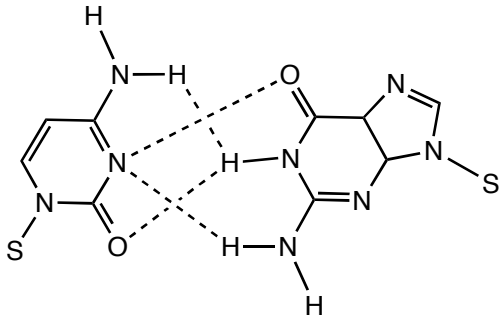
3. Arrange the following compounds in order of increasing hydrogen bond accepting ability from methanol. Rationalize your answer



4. In a G•••C base pair of DNA, there are three hydrogen bonds formed between the bases. Since the hydrogen bonds are in close proximity, there is an opportunity for secondary interactions. Consider all possible arrangements of three hydrogen bonds (three donors on one molecule, three acceptors on another, and various ways of having two plus one). Determine whether the secondary interactions are stabilizing or destabilizing for each situation. Where does the G•••C pair fall?



Primary interactions



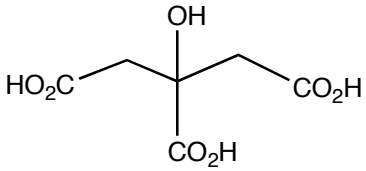
Secondary Interactions

See *JACS*, **1990**, *112*, 2008.

5. In the following compounds, the keto form dominates over the enol form in solution. Suggest a reason for this.(*Hint: Think of dipolar resonance forms for each tautomer)*

See *JACS* **1992**, *114*, 1645.

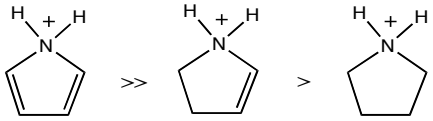
6. The three pKa's of citric acid are 3.1, 4.7, and 5.4. Explain why the first pKa is lower than normal for carboxylic acids, and why the third pKa is higher than normal.

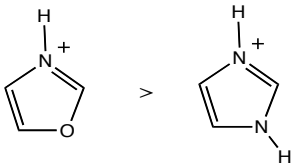


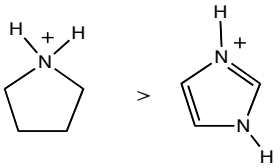
citric acid

7. The pKa's of alcohols are typically in the range 16-17. However, the pKa's of vicinal diols are commonly 14-16, and those for geminal diols are in the range of 13-14. Explain this trend.

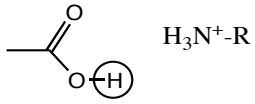
8. Explain the following trend in acidities:

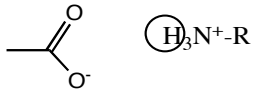
A. 

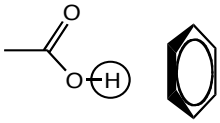
B. 

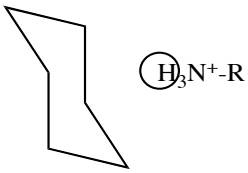
C. 

9. Predict whether you would expect the pKa values of the circled protons to shift up or down from their normal aqueous solution values in proximity to the species shown. Explain.

A. 

B. 

C. 

D. 

10. Which nitrogen atom in 4-aminopyridine is more basic? Why is 4-aminopyridine so much more basic than pyridine?

pKa(BH^+) = 9.11 pKa(BH^+) = 5.23