Cooperative Assignment 2

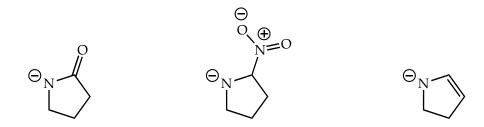
Chapter 2 & 3 - Resonance and Acid/Base

1. For the following structures, draw all of the resonances structures that contribute to the stability of the molecule or ion. With the exception of the first neutral structure, do not introduce additional charges beyond the single charge given. Head's up, "c" has 11 unique structures, 13 if you count the ring movement where the charge doesn't actually move.

a)
$$\bigoplus_{N}$$
 \bigoplus_{O} \bigoplus

2. Determine the most acidic proton on the molecule below. Explain your reasoning.

3. Three amide bases are presented below. Determine the relative basicity (strongest to weakest base) of the ions. Explain your reasoning.



4. Three amines are given below with the corresponding pK_a 's of their conjugate acids. The pK_a 's indicate that methyl amine is the strongest base (weakest conj. acid), and that cyanamide is the weakest base (strongest conj. acid). Explain the trend. Why is methyl amine more basic than cyanamide? Why does aniline fall in the middle of these two in terms of basicity? (Hint - Explain how each substituent affects the acidity of the conjugate acids.)

5. This problem is a really good one, it combines a number of very important concepts. This is the type of problem that I often put on exams, one that pulls a number of concepts together. A series of carboxylic acids are shown below with their corresponding pK_a's. Propanoic acid, given as a reference point, has a pK_a of 4.70. Your job is to explain how the different substituents bring about the observed changes in the pK_a from the reference compound. Look closely for induction, resonance, and electronegativity. How can the methoxy group (CH₃O-) cause two different effects? What is the major role of the methoxy in the first compound verse the last compound (EDG verse EWG)? In light of the previous problems in the coop, how is the double bond affecting the acidity of the acid? (by "how" I don't mean for you to answer "it's making it more acidic." It's given that it is more acidic. I want to know "how" it makes it more acidic!)

$$pK_a$$
 3.80 4.25 4.70 5.20

6. Were going to call this one the oxygen challenge. Below are four oxonium ions (molecules with a protonated carbonyl). Determine the effects of the oxygen containing substituents on the oxonium ion stability. Your answer should include whether the groups are functioning by resonance or induction, electron donating or withdrawing, and stabilizing or destabilizing.