

Same as before — lots of practice problems on the first two pages, the last two pages have the ones you need to turn in for credit on Wed 9/23.

End-of-chapter problems from Hornback: Ch1: 30, 34, 35, 39.

Ch3: 20 - 29, 31-38, 40. I'd include one more for 24d than what the SG shows. 25a — that 3rd structure should not be called an unimportant contributor — it's nonsense. Same for b, c, d. There's a big difference between a valid but less important arrangement of electrons (e.g., 2nd structure in 25a) and a flaming rubbish (e.g., all the others). So let's rephrase this — Explain why those structures are meaningless drivel.

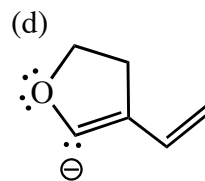
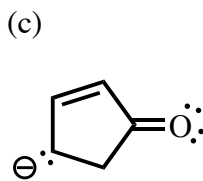
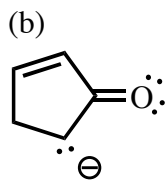
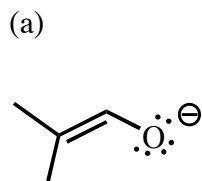
1. Draw the important resonance structures for each of the following compounds, and indicate their relative importance. Use curved arrows to show the shifts of electrons needed to get from each structure to the next one. There may be only one good structure; no more than 3 should be necessary for any compound. Show all lone pairs and formal charges. The formulas given show the overall charge and connectivity — don't change it! (*None of the compounds is cyclic.*)

- (a)  $\text{CH}_3\text{OCHNH}_2^+$                       (b)  $\text{CH}_3\text{CH}_2\text{NC}(\text{CH}_3)\text{O}^-$   
 (c)  $(\text{CH}_3)_2\text{BCHCHO}^-$                       (d)  $\text{CH}_2\text{C}(\text{CH}_3)\text{NH}_3^+$

The next two are unusual — neutral, even # of  $e^-$ s, but you can't draw one "perfect" Lewis struct  
 (e)  $\text{CH}_3\text{CH}_2\text{CNO}$                       (f)  $(\text{CH}_3)_2\text{CHNO}_2$  (both Os are attached to N)

(g)  $\text{CH}_3\text{CHNCH}_2$  (careful — no, this is not a typo — it's a free radical)

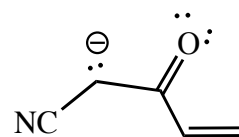
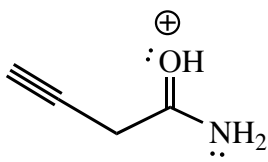
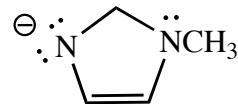
2. Identify the electrons that are part of the conjugated  $\pi$ -system, then draw the important resonance structures for each of the following compounds. Use curved arrows. For this problem, concentrate on using "common electron shift" type-1 discussed in class — (lone pair in, bond pair out). Expect 1 – 3 resonance structures (total) for each; don't include minor structures with more than one formal charge.



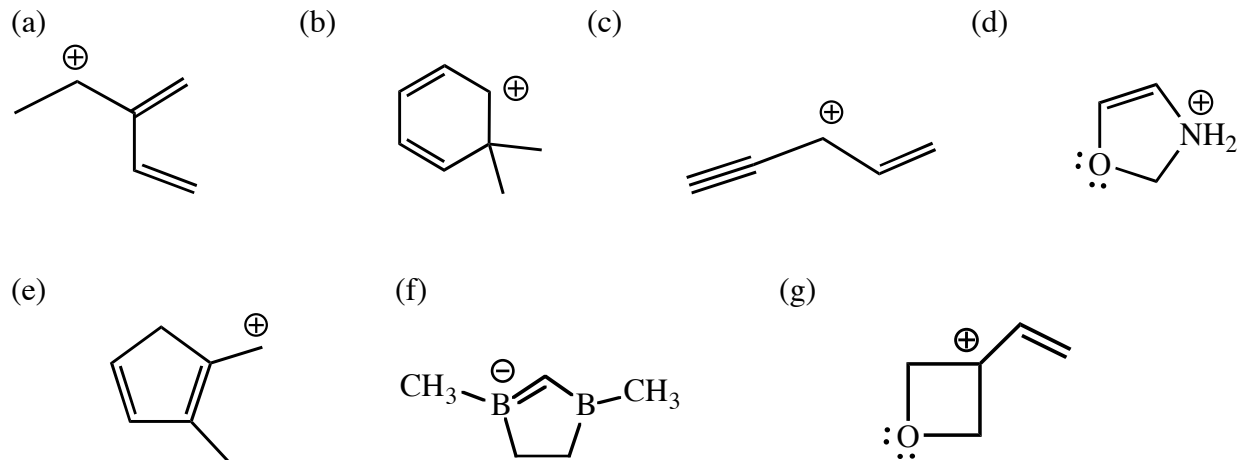
(e)

(f) yes, that's a +, not a - ... hmmm...

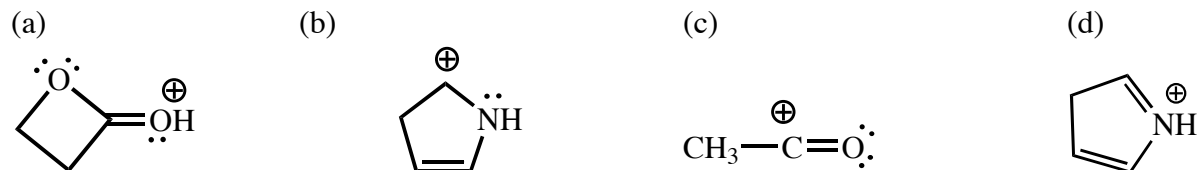
(g) what's the struct of the NC group?



3. Same instructions, but concentrate on using the second type of shift (the "windshield wiper").



4. For the following five, look for opportunities to do the "type 3 and 4" shifts — lone pair makes a bond to complete the octet on a neighboring atom, and its reverse.

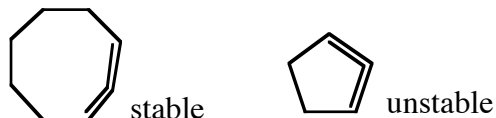


5. (a) Allene,  $\text{CH}_2=\text{C}=\text{CH}_2$ , might be planar or perpendicular. For each possibility, sketch the *p-orbitals* that make up the  $\pi$ -bonds in their correct spatial orientations, and decide which should be the correct geometry. (Do not waste time with the  $\sigma$ -orbitals — these are the same in each structure, right? Just represent the  $\sigma$ -bonds as lines and focus on the p-orbital overlaps.)



(b) Draw  $\text{CH}_2\text{CCCH}_2$ , showing its geometry clearly.

(c) 1,2-cyclooctadiene is stable at room temperature, but 1,2-cyclopentadiene is extremely unstable. Keeping in mind what you learned from part a, briefly explain why the latter molecule is so miserable energetically. Models will help. Models are fun. Make lots of models.



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**Chem 21**

Fall 2009

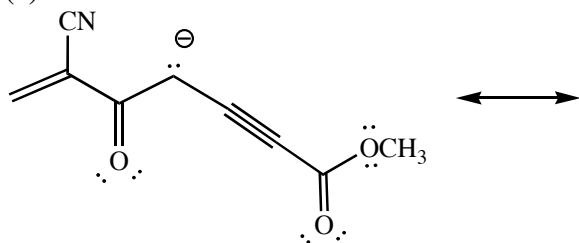
**HW set 2**

30 points; due Wed, Sept 23

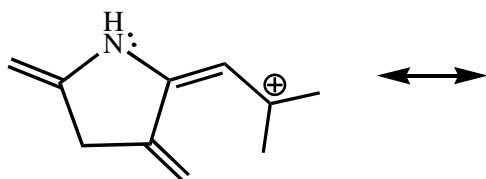
Name \_\_\_\_\_

1. Draw the other important resonance structures of each ion below *in skeletal form*. Use curved arrows to show shifts of electrons. It's up to you to decide how many are worth drawing.

(a)



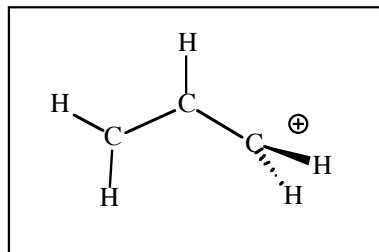
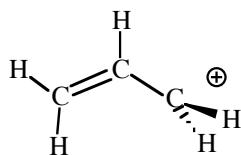
(b)



(c) In the space at right, draw the actual structure (or "resonance hybrid") of the *anion* above. (i.e., which one is an *anion*, a or b?)

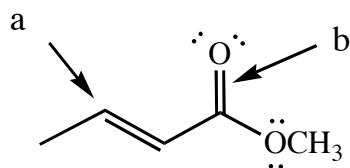
2. Draw  $\text{CH}_2=\text{C}=\text{N}-\text{CH}_3$ , showing its geometry clearly. Sketch the p and *lone pair* orbitals and indicate the  $\pi$ -overlaps. (the  $\sigma$ -bond orbitals aren't interesting, so just use "lines for  $\sigma$ -bonds.)

3. Look carefully at the cation below. (a) The structure in the box shows the cation's  $\sigma$ -framework. Add the p-orbitals to the drawing in the box, showing their positions clearly. Be sure to include empty orbitals, if any. (b) If one or more  $\pi$ -bonds are present, indicate which of your orbitals overlap to form the  $\pi$ -bond(s).



Paying careful attention to the geometry shown above, are there any other important resonance structures? If so draw it/them; if not write "none".

4. The following structures are good first-order descriptions of the molecules, but minor (ca. 5 - 10%) resonance contributors are often invoked to explain more subtle features. Use resonance structures to explain why the carbon marked "a" is found to have a slight positive charge and the carbonyl double bond (b) is found to be slightly weaker than the carbonyl of  $\text{CH}_3\text{CO}_2\text{CH}_3$ .



Use resonance structures to explain why the Cs marked "c" are each found to have a slight negative charge.

