Practice Problem Set #2 (No credit, no due date)
See answer key at http://www.chem.umass.edu/~lahti/CHEM891.

1. Construct a set of pi-molecular orbitals for 1,3,5-hexatriene, using typical qualitative guidelines for symmetry, numbers of nodes, and p-π basis set orbitals. Be sure to show your orbitals in the proper qualitative energetic ordering, and with the appropriate numbers of electrons in each orbital. Use your set of orbitals to answer the following questions:

 (a) Which bonds are stronger in a radical anion of 1,3,5-hexatriene, relative to the neutral hydrocarbon? Which bonds get weaker? *The central bond is weakened for sure. There may be some strengthening of the 1-2 and 5-6 bonds. There may be some weakening of the 2-3 and 4-5 bonds. These arguments follow from placing one electron in the LUMO, and depend on whether you used the plausible alternative MO or not.*

 (b) Which bonds are stronger in a radical cation of 1,3,5-hexatriene, relative to the neutral hydrocarbon? Which bonds get weaker? *The central bond is weakened for sure. There may be some weakening of the 1-2 and 5-6 bonds. There may be some strengthening of the 2-3 and 4-5 bonds. These arguments follow from removing one electron in the HOMO, and depend on whether you used the plausible alternative MO or not.*
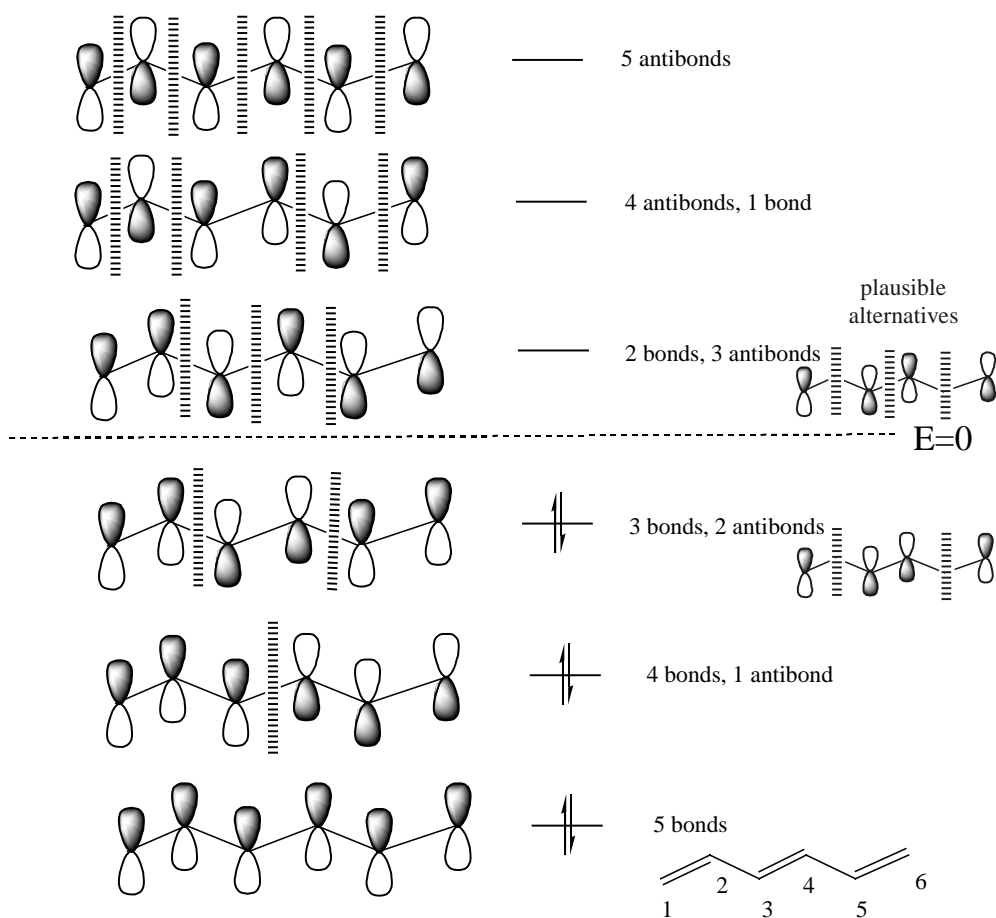
2. The AM1 coefficients of the π-SOMO (singly-occupied MO) of the phenoxyl radical are shown below (the molecule was geometry optimized before the coefficients were obtained.

(a) At what position will you find the major site of spin density on the molecule (look at the SOMO, not the picture of the molecule as drawn!)? *In the position para to the oxy-radical site*

(b) Draw the resonance structure that corresponds to placing a radical (•) at the site of major spin density. Do you find this structure surprising (if so, say why; if not, say why)? *See the structure drawn below the MO below. If we put the radical on the para position, we must destroy the aromaticity of the benzene ring.*

(c) Use resonance arguments or bond strength arguments to explain why the SOMO-derived answer is reasonable?
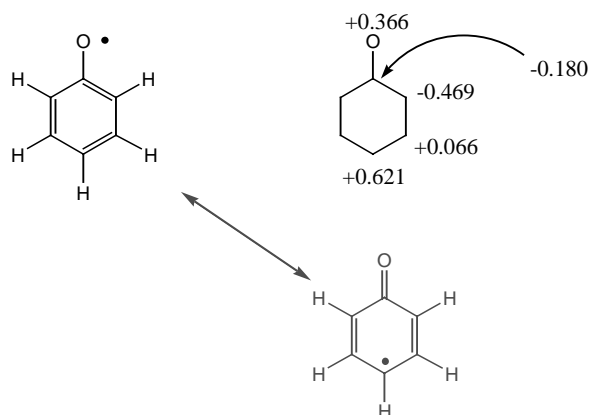
Fortunately, we can get back a lot of stabilization from the C=O formation (carbonyl formation is worth about 85 kcal/mol, as opposed to 36 kcal/mol for aromatization of one benzene ring). Thus the formation of C=O appears to overwhelm the desire to aromatize. This is confirmed by a variety of IR, computational, and ESR/EPR experiments. Please note that the value of 36 kcal/mol is the TOTAL value for loss of an aromatic ring, and includes all structural changes. Overall, the carbonyl-containing resonance structure gained 85 kcal/mol from C=O formation, and lost 36 kcal/mol of aromatic stabilization. This is not a perfect count, since we did not consider the difference between a oxy-radical and a carbon-radical, but is shows that carbonyl formation is important.

(d) Check to be sure that the sum of the squares of all the coeficients is one (normalization rule); remember symmetry! *Remember that, by symmetry, both ortho and both meta positions must have the same coefficient. If you do this and take the sum of squares of all coefficients, you will find that normalization is maintained.*

3. Draw a qualitative picture of the transition state reaction coordinate for the 1,5-hydrogen shift reaction shown below, assuming the process to be concerted. Clearly identify which bonds in your picture are most important in terms of analyzing bond lengths and orders to determine the extent of hydrogen atom transfer in the transition state.

1,5 H-shift

bond making
very important to monitor

bond breaking
very important to monitor
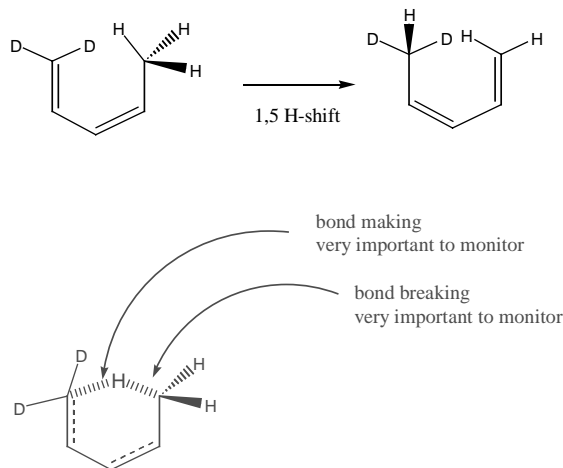
In this problem, it is important to consider the basic principle that the transition state should lie somewhere between the reactants and the products. For some reactions, this is not straightforward to figure out. For the 1,5-hydrogen shift, the transition state geometry is reasonably straightforward to deduce as shown. One can see how the hydrogen readily can be transferred from the sp^3 end of the hydrocarbon onto the sp^2 end.

4. Why does a nucleophile attack the carbon on a >C=N-R moiety, rather than the nitrogen?

(a) explain in coulombic terms, using electronegativity and charge separation arguments.

The carbon end carries a partial positive charge, based on the smaller electronegativity of carbon versus nitrogen. Thus, a nucleophile (which seeks positive charge density) will seek out the carbon end, rather than the somewhat negatively charged end. As the reaction occurs, negative charge gets pushed onto the nitrogen, which is better able to accommodate it, due to the larger electronegativity of nitrogen.

(b) explain in terms of the π-HOMO and π-LUMO, at what position you should expect that a nucleophile will want to a add electrons to the molecular structure, and that attack between coefficients of largest size will give the largest overlap and the largest probability of successful attack

The nucleophile must attack the LUMO, because you cannot place the nucleophile electrons in the already-filled HOMO of the C=N. The LUMO has its largest coefficient on the carbon (opposite to the HOMO, which is controlled by electronegativity effects). In order to have the nucleophile attack the site with the largest coefficient in the LUMO, attack must occur on the carbon end. The overall result is the same as is expected by the coulombic argument.