Chemistry 891 **CORE COURSE** **Fall 2002**

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?

(b) Which bonds are stronger in a radical cation of 1,3,5-hexatriene, relative to the neutral hydrocarbon? Which bonds get weaker?

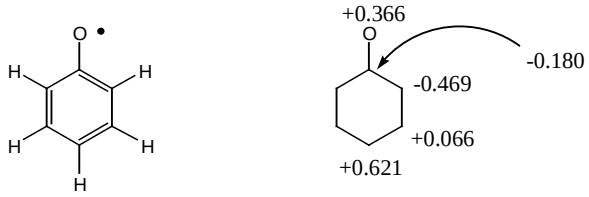
2. The AM1 coefficients of the π-SOMO (singly-occupied MO) of the phenoxyl radical are shown below (the molecule was geometry optimized before the coefficients were obtained.

(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!)?

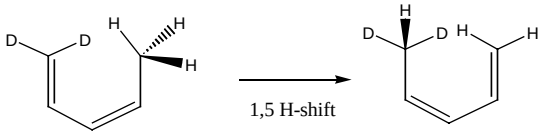
(b) Draw the resonance structure that corresponds to placing a radical (•) at the site of major spin density. Do you find this structure surprising (if so, say why; if not, say why)?

(c) Use resonance arguments or bond strength arguments to explain why the SOMO-derived answer is reasonable?

(d) Check to be sure that the sum of the squares of <u>all</u> the coeficients is one (normalization rule); remember symmetry!



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.



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

(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