Chem 673, Problem Set 3a
Due Tuesday, October 20, 2009

Problems from Cotton: Chapter 6: 6.2, 6.4, 6.5, 7.4

Additional problems:

(1) Perform Hückel calculations on the 4 hydrocarbons below. A web-based calculator can be found at http://www.chem.ucalgary.ca/SHMO/ – this will do the computational work if you input the graph of the molecule correctly. (If this link is dead, a less ‘friendly’ site can be used: http://neon.chem.swin.edu.au/modules/mod3/huckel.html). The SHMO calculator makes the usual Hückel assumption that all C-C bonds are equal in length (and therefore only one $\beta$ is necessary). Note: Think about $D$ before beginning work on it. Consider only $p_\pi$-$p_\pi$ overlaps — you can do almost all of the computational work for this problem with a standard Hückel MO computer program.

In all cases, construct appropriate SALCs and set up the secular determinant as if you were going to do the calculation by hand. In all cases, draw a complete $\pi$ MO diagram, including orbital irreducible representation labels. Draw figures showing the form of each $\pi$ orbital. One or more of these molecules does not have a “closed shell” configuration – calculate the unpaired spin density expected for each atom (as discussed for the naphthalene radical anion in class). Compute $\pi$ bond orders in the manner described in the text for naphthalene. For the spiro-C$_8$H$_8$ molecule shown at right, include both the usual $p_\pi$-$p_\pi$ interactions ($\beta$) and a weaker interaction between next-nearest neighbors in different rings ($\frac{1}{3}\beta$). With the orbital phases defined as indicated in the figure, that means that $H_{15} = H_{48} = -H_{45} = -H_{18} = \sqrt[3]{3}\beta$. 

![Image of molecular structures](image-url)