Name
Section
Rec TA

Side 1 of 3

Ch 1a, Problem Set Eight
Due Friday, November 17, 2006
at 4:00 PM in the Ch1a Box

Problems 2 and 3 are designated (☞) as "no collaboration" problems.

1. (30 Points) Molecular size is governed by factors including bond lengths and atomic radii. For each pair below, identify which molecule is larger. Explain each decision on the basis of bond lengths, atomic radii, or both.

   a. O_2 or O_2^+
   b. HCl or HF
   c. NH_3 or PH_3
   d. H_2CCH_2 or HCCH
   e. $SiBr_4$ or CCl_4
   f. NO or O_2

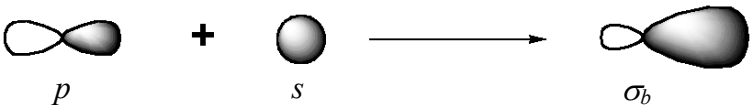
☞ 2. (40 Points) In large molecules it is often hard to determine the structure due to free rotation around single bonds. However the double and triple bonding arrangements in some compounds allow one to say a great deal about the structure.

   a. Draw the molecules H_2CCCCH_2 and $H_2CCCCCH_2$. For each carbon, indicate the hybridization and the approximate bond angles. Draw the molecules graphically showing the basic π molecular orbitals. For example:

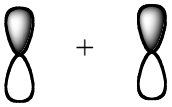
   b. One of these molecules has coplanar H_2C groups. Which one and why?

   c. In the molecule that does not have coplanar H_2C groups, what is the angle between the planes of the two H_2C groups?

☞ 3. (30 Points) The following diagrams illustrate pairs of atomic orbitals approaching each other to form a molecular orbital (shading indicates the relative sign of the wavefunction). Sketch the molecular orbital formed by the atomic orbitals; for antibonding interactions, draw a line for the antibonding node. Also, indicate the type of molecular orbital (σ_b, σ^*, π_b, π^*, *nb*) that results. Example:



a.



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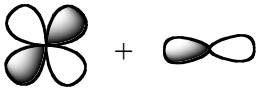
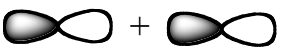
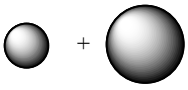
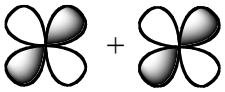


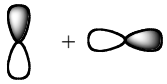
c.

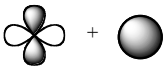


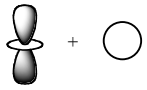
d.



e. 

f. 

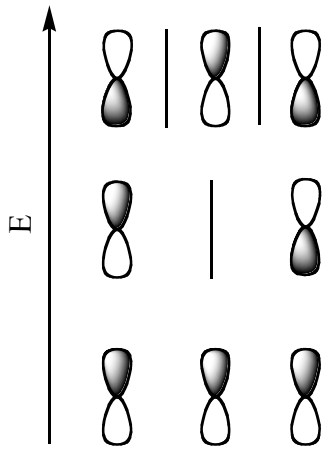
g. 

h. 

4. (40 Points) The formula for the conjugated alkene octatetraene is $H_2C(CH)_6CH_2$.

   a. Draw the structure of octatetraene, and indicate the hybridization of each carbon atom. Try to keep the molecule as straight as possible, and make the structure geometrically accurate.

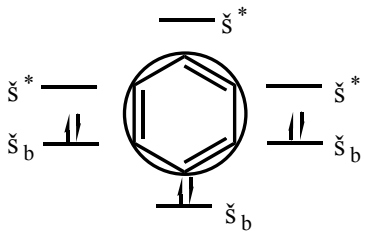
   b. The basis atomic orbitals for the π molecular orbitals for H_2CCHCH_2 (allyl radical) are given below. Draw all eight π molecular orbitals for octatetraene in this same fashion. Indicate the phase of the orbitals and show the nodes.



5. (60 Points) Cycloheptatriene, C_7H_7, is a cyclic radical sometimes found in metal chemistry.

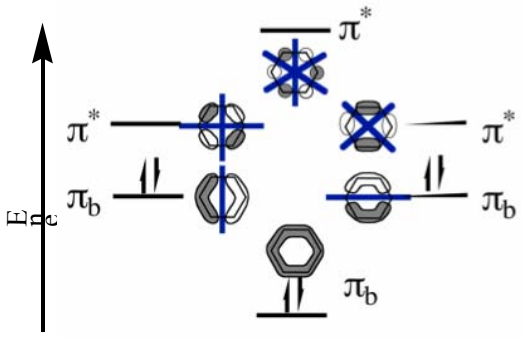
a. Draw seven Lewis dot structures for the cycloheptatriene radical. What is the hybridization for the seven carbons?

b. There is a graphic device for cyclic π-bonded π MO systems that can be used to order the π molecular orbitals in energy. It involves inscribing the molecule **point-down** in a circle. Each vertex then corresponds to a π orbital. For example, benzene gives the following:



Draw a similar diagram for cycloheptatriene. Label the MOs either π_b or π^* and fill in the π electrons. *(hint: there are three π bonding orbitals)*

c. We can use the π MO diagram from b. (called a Frost circle) to draw the shape of the π orbitals for our cyclic systems. As with atomic orbitals, as you add nodes to the π MOs, the energy goes up. For our benzene example, we go from zero to three angular nodes in our MOs and they go up in energy.



Construct such a diagram for cycloheptatriene, showing the nodes and the sign changes for the MOs.

d. Use your diagram to predict the bond order (of π's only) for cycloheptatriene, the cycloheptatrienyl cation, and the cycloheptatrienide anion. For example, benzene has a π bond order of 3.