University of Windsor
Chemistry and Biochemistry
Chemistry 59-651, Fall Term 2004

Assignment 1

Due: Monday, November 8

Question #1

(i) Prove that the set of sp^3 hybrid orbitals that I provided in the class notes are, in fact, orthogonal and normal.

(ii) Provide a different complete set of ortho-normal hybrid orbitals that are suitable to use for the sigma bonding in a tetrahedral molecule. Be sure to include drawings or diagrams that clearly indicate the hybrid orbital described by each LCAO.

(iii) Assuming a square-based pyramidal (C_{4v}) structure, use character tables and symmetry arguments to determine the hybrid orbitals on Sb used in $SbMe_5$. If $SbMe_5$ is recrystallized in the presence of a different solvent, the pentamethylantimony adopts a trigonal bipyramidal geometry; explain how the hybridization of Sb changes and the significance of the experimental observation.

Question #2
(i) Use symmetry arguments and your chemical knowledge to construct a molecular orbital (MO) diagram for the molecule $[R_3P{=}N]^{-1}$ (a phoshinimide anion used in Dr. Stephan's lab). Use your MO diagram and drawings to explain why it is not reasonable to draw the molecule with a phosphorus-nitrogen double bond.

(ii) Amine-*N*-oxides of the type R_3N-O are analogous to phosphine oxides but the nitrogen-oxygen bond is always drawn as a single bond. Construct an MO diagram to demonstrate why this is the case (use only a 2s orbital on each R ligand).

Question #3
(i) Use symmetry arguments to construct an MO diagram for the π-bonding in a putative planar cyclo-octatetraene. Show all of your work and make reasonable drawings of each of the molecular orbitals.

(ii) Explain how an MO diagram and orbitals would change between the isoelectronic planar molecules benzene and borazine ($B_3N_3H_6$).

Question #4

Determine the point groups for the following interhalogen compounds (the central atom is on the left-hand side of the formula in each case): ClF, ClF_2^+, ICl_2^-, ClF_3, ClF_4^+, ClF_4^-, ClF_5, ClF_6^+. Remember that lone pairs of electrons will always occupy equatorial positions.

Question #5

(i) Phosphonium cations (PR_4^+) are isovalent with species such as methane or ammonium cations and they almost always have a tetrahedral geometry about the central atom. Driess et al. (*Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 3677) recently prepared the first example of a planar (D_{4h}) phosphonium cation. Perform a symmetry analysis to identify the hybridization on P and to construct an MO diagram to describe the σ-bonding for the planar molecule PH_4^+.

(ii) Provide a short but detailed explanation as to why your result from (i) is different than the conclusion obtained by Driess.