Experiment 4: Molecular Modeling
(Part I: Borane-Amine Adduct)

Introduction

In this experiment, you will use Spartan molecular modeling software to determine optimized geometries and calculate chemical properties of inorganic compounds synthesized in two "wet chemistry" experiments: the Lewis acid-base adduct $BH_3NH_2C(CH_3)_3$ and the organometallic compound $[1,3,5-C_6H_3(CH_3)_3]Mo(CO)_3$. In the process, you should gain a better understanding of Lewis acid-base chemistry and HOMO-LUMO interactions; you will also predict the infrared stretching frequencies that you will later measure experimentally, in the same way that a researcher might predict the measurable properties of a new molecule to be synthesized.

Background

Since it seeks to describe the behavior of infinitesimally small particles (nuclei, electrons), much of computational chemistry is based on quantum mechanics. Properties are calculated based on solutions of the Schrödinger equation – the wavefunctions and energies of the system. You are already familiar with the wavefunctions of the hydrogen atom and their relative energies (the atomic orbitals – 1s, 2s, $2p_x$, $2p_y$, $2p_z$, 3s, etc.). These are exact solutions of $H\Psi = E\Psi$ for a 1-electron system that we use to represent the orbitals of multi-electron atoms.

For multi-electron systems, as you know, exact solutions of the Schrödinger equation are not possible; instead, we make approximations in order to arrive at wavefunctions and their energies. As you've likely learned in previous modeling exercises, the accuracy and cost of our calculations depend on the approximations we make. *Ab initio* methods make fewer, often better, approximations and tend to yield more accurate results, at higher computational cost. *Semi-empirical* methods use more simplified quantum-mechanical models and incorporate parameters to reproduce known experimental data (e.g., geometries, enthalpies, etc.). These techniques tend to be less accurate, but offer quicker results and are more easily applied to large systems. *Molecular Mechanics* models (which are *not* based on quantum mechanics) offer even faster results with greater decreases in accuracy and are often the starting point for further optimization. In this experiment, you will use molecular mechanics to obtain preliminary optimized geometries of molecules; further geometry optimization and property calculations will be done using two types of semi-empirical methods with different parameters, AM1 and PM3.

The AM1 and PM3 methods employ the same basis set of atomic valence orbitals (e.g., 2s, $2p_x$, $2p_y$ and $2p_z$ for N; 5s, the 4d set and the 5p set for Mo) and essentially the same approximations. Calculations using each method will proceed similarly: in each case, Spartan will iterate until it reaches the experimental data point(s) identified for the target molecule. The methods differ only in the specific parameters incorporated to account for empirical data. The PM3 model was designed specifically to determine the equilibrium geometries of transition-metal inorganic and organometallic compounds, and contains only parameters for empirical equilibrium geometries, while AM1 contains parameters to reproduce data of many different types.

Exercises

I. HOMO-LUMO interactions in Lewis Acid-Base Complexes

As you learned in your organic coursework, Lewis acids are species that can accept electrons; Lewis bases are those that can donate electrons. Reaction between a Lewis acid and a Lewis base can be viewed as the interaction of the base (electron donor) HOMO with the acid (electron acceptor) LUMO. In this exercise, you will build the Lewis acid BH_3 and the Lewis base $NH_2C(CH_3)_3$, calculate the appropriate MO's, and consider the effects of their interaction.

$$BH_3 \ + \ NH_2C(CH_3)_3 \ \rightarrow \ H_3B-NH_2C(CH_3)_3$$
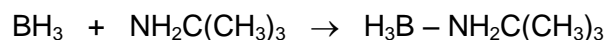
1. Log in and open Spartan (green icon in the taskbar across the top). Under **File**, choose **New** to open the builder window. Choose the **Inorganic** model kit and build BH_3. (Select B for the central atom and choose the correct connector geometry; then click Insert and click in the workspace.) Once you are satisfied with your structure, click on the **Energy-Minimization** button (capital E with an arrow) to perform the molecular mechanics (MMFF) geometry optimization. Save the file.

2. Optimize the geometry further using the semi-empirical AM1 method. Under **Setup**, select **Calculations** to open the dialog box. You will calculate an **Equilibrium Geometry** in the **Ground State**. Choose a **Semi-Empirical** method, specifically the **AM1** model; do calculations on the **Current** geometry. Be sure that the **Total Charge** reflects a neutral molecule and that the **Multiplicity** is set to **singlet** (for a molecule with no unpaired electrons). Click in the checkboxes to **Print Orbitals and Energies** and **Calculate** the **IR** spectrum. When you're finished, click **Submit**. A dialog box will appear indicating that the job has been submitted; click **OK**. Click **OK** again after the job has been completed.

3. Once calculation is complete, display the LUMO. To do this, choose **Display** and **Surfaces**. Click **Add**. Choose **LUMO** for the Surface and medium (med) resolution. Leave "none" for the property. Click OK. Click in the checkbox beside the listed LUMO surface to display it on your rendering of BH_3. Orient BH_3 so that the plane of the molecule is perpendicular to the plane of the screen and print the LUMO. Be sure to indicate regions of different sign on your printout.

4. Determine the calculated energy of the BH_3 LUMO and include this value (in eV) on your printout. To do this, choose **Display** and **Output**. The calculated molecular orbitals are listed toward the bottom of the output, numbered in order of increasing energy (energies are also specified in eV). Determine which MO is the LUMO and record its energy. [**Hint:** remember that only valence orbitals on the B and H atoms are used to calculate valence-level MOs.]

5. Repeat steps 1-4, calculating the HOMO of *tert*-butylamine, $NH_2C(CH_3)_3$ and its energy. For your printout of the molecule with its HOMO surface, display the molecule so that the three methyl (CH_3) groups form a plane above the C that is perpendicular to the plane of the screen. Be sure to save your file after completing the AM1 optimization.

6. Consider your HOMO and LUMO. How can these two MO's overlap to give a bonding (σ-type) combination? Sketch this interaction.

7. When the BH_3 LUMO and $NH_2C(CH_3)_3$ HOMO overlap, two new MO's are formed for the $H_3B:NH_2C(CH_3)_3$ adduct. Use the calculated HOMO and LUMO energies to construct an MO diagram for this interaction. Include sketches of all orbitals and label each new MO as bonding or antibonding.

8. Consider the character of the BH_3 LUMO (either bonding, anti-bonding or non-bonding). Does it make sense that this orbital accepts electron density from the Lewis base? Discuss briefly.

II. Identifying Vibrational Frequencies Diagnostic for the Borane-Amine Adduct

1. Build the borane-amine product. The easiest way to do this is to open your saved *tert*-butylamine structure and modify it (deleting and replacing the N center and adding a boron center). Make sure that you consider the new geometries that will be adopted by B and N in the product. Do the quick molecular-mechanics energy minimization, save the structure, and complete geometry optimization using the AM1 model (as you have done for the borane and the amine). Be sure to click the checkbox to calculate IR stretching frequencies.

2. Display the calculated IR spectrum and list of vibrational frequencies. (Choose **Display/Spectra** and IR; then click **Draw calculated spectrum**.) You will see a region of the IR spectrum displayed in the workspace (~500-3000 cm^{-1}). In addition, all calculated frequencies will be listed in the dialog box,

along with their relative intensities. Clicking in the checkbox beside a particular frequency will allow you to animate that motion.

3. Use the calculated IR spectrum and intensity data to choose important vibrational motions among the list of frequencies. Animate these motions, one by one, until you identify the key frequency(ies) diagnostic of product formation. **List these frequencies and the molecular motions to which they correspond.** (Although we are most concerned with the new bond(s) formed in the product, it will be helpful to predict frequencies for other functional groups, so that you can more easily identify the stretches in the your actual IR spectrum.)

   a. You may also wish to look at the calculated IR frequencies for the BH_3 and $NH_2C(CH_3)_3$ "reactant" molecules to help you identify/confirm new motions present in the adduct. If you do this, be aware that the "same" motion in a reactant and product may not occur at exactly the same frequency.

To be turned in:
- Labeled printouts of BH_3 LUMO and $NH_2C(CH_3)_3$ HOMO surfaces – include identification, signs, and MO energy
- Answers to Questions 6-8 in Section I
- Printout of borane-amine structure after geometry optimization including key IR frequencies identified (i.e., answer to Question 3 in Section II).