CH241 Experiment #2, Week of October 1, 2018

Molecular Modeling Part I

Introduction: The ability to build structures and calculate energies of compounds quickly and accurately is a useful skill that can provide valuable insights into many important aspects of chemistry. With the recent advances in computer technology and theoretical methods, it is now possible to carry out quite sophisticated calculations even on systems that are very large. At Colby, the Paul J. Schupf Scientific Computing Center (across from Olin 1) is an outstanding facility that enables us to perform many of these calculations. This week, you will use the resources at the Center to learn the basics of molecular modeling.

The computational program known as Spartan a powerful and easy-to-learn software program that will be used throughout this lab to build molecules, submit calculations, and analyze results. Once you become comfortable with the program, you can do many kinds of interesting modeling experiments. Furthermore, the structures and shapes of molecules, which may not be always obvious from our usual two-dimensional line drawings, suddenly come to life on the computer screen. These models can be viewed and probed in a variety of ways to gain a better understanding of the compounds that they represent. For instance, what do aspirin and caffeine really "look" like?

Given below are a set of exercises that will not only help you learn to use Spartan, but also let you examine molecules in the context of what has been covered in class so far. Although you are only required to complete these exercises, you are invited, indeed encouraged, to branch out on your own and explore other compounds of your choice. Feel free to let your imagination run wild and make up all kinds of molecules even if they seem really crazy. See how stable the compounds you made up are and how they look on the computer screen in three dimensions. For example, what is the most hideously twisted, horrendously unstable molecule that you can come up with?

Part I. Structures of methane, ethane, ethylene (or ethene) and acetylene (or ethyne)

- Build methane. <u>Geometry optimize</u> at the HF/6-31G* level (HF means "Hartree-Fock", and 6-31G* is the basis set). Record the bond lengths and bond angles (H–C–H) in this molecule.
- In an analogous manner, determine the bond lengths and bond angles for ethane, ethylene, and acetylene and record all values in your lab notebook. *Record both C–H and C–C bond lengths, and both H–C–H and H–C–C bond angles.*

Part II. Conformational analysis of ethane and butane

- Build ethane again, and this time <u>geometry optimize</u> using the HF/6-31G* level (save it as a separate file from Part I). Change the H-C-C-H dihedral angle to 0° and calculate and record the <u>single point energy</u> using HF/6-31G*. Close your file.
- Build ethane again, and this time <u>geometry optimize</u> using the Semi-empirical/PM3 method and record the energy. Once again change the H-C-C-H dihedral angle to 0° and calculate and record the <u>single point energy</u> using Semi-empirical/PM3. *Note: Having obtained energy data for the eclipsed and staggered conformations of ethane using two different computational methods, you will have the ability (in your report) to compare the accuracy of the methods.*

- Build butane and do a "quick" minimize. Change the C1-C2-C3-C4 dihedral angle to 0° so that the two methyl groups eclipse each other. Determine and record the single point energy of this conformation using HF/3-21G.
- Repeat the above steps by changing the C1-C2-C3-C4 dihedral angle through 60°, 120°, 180°, 240°, and 300°. Calculate and record the single point energy for each conformation. *Note: You now have energy values for the eclipsed, gauche, and staggered forms of butane, so you will have the ability to create a torsional energy profile based on your calculations.*

Part III. Molecular orbitals of the H_2 sigma-bond and the ethylene pi-bond

- Build and geometry optimize H_2 at HF/6-31G*. When done, display the HOMO (bonding) and LUMO (antibonding) orbital surfaces and sketch the general shape of the two orbitals. Visually examine these orbitals and record the energies of the two orbitals.
- Repeat the above steps for ethylene. *Ethylene has more than one bond and bond type. Which bond are you looking at when you view the HOMO and LUMO? Can you tell by visual inspection?*

Part IV. Shapes of molecules and functional groups

- Build and geometry optimize each of the organic compound types from your prelab containing the functional groups below (use HF/3-21G). Record the value and sketch the direction of the dipole moment of each compound. *Think about whether the directions and magnitudes of the dipole moments look like you would expect, especially for the alcohol (g), carboxylic acid (h), and thiol (k). Are there any surprises?*

  (a) alkyl halide (b) aldehyde (c) ketone (d) amine (e) ether (f) nitrile (g) alcohol
  (h) carboxylic acid (i) ester (j) amide (k) thiol

Part V. Stability of alkenes

- Build 1-hexene, (*E*)-3-hexene, (*Z*)-3-hexene, and 2-methyl-2-pentene, and geometry optimize each molecule using Semi-empirical/AM1. Record the energies of the alkenes and arrange them in order of increasing stability. *Does the order match what you expect? How about the magnitudes of the energy values?*

Part VI. More complicated molecules

- Build aspirin and caffeine and "quick minimize" each structure. Then exit the builder window (by pressing the "view" button on the top bar). Describe how these molecules look in three-dimensions, comparing their appearance to the two-dimensional structures drawn on paper. Try viewing them with a "space filling" model rather than a "ball and spoke" model (under the Model menu). Does this make you think about the structures differently?
- With any time remaining, have fun building molecules of your choice. What is the weirdest molecule you can build?

Pre-laboratory Preparation (Don't forget to cite sources!)

1. Tabulate bond angles and bond lengths for methane, ethane, ethylene, and acetylene. Are these measured or calculated values? Did you remember to cite your source(s)?

2. Provide a specific example for each of the following types of organic compounds by first drawing the functional group and then adding one or more hydrogen atoms or methyl groups to complete each molecule (try to keep your structures relatively simple).
   (a) alkyl halide (b) aldehyde (c) ketone (d) amine (e) ether (f) nitrile (g) alcohol
   (h) carboxylic acid (i) ester (j) amide (k) thiol

3. Draw the structures and arrange the following isomers in the order of increasing stability:
   (*E*)-3-hexene, (*Z*)-3-hexene, 1-hexene, 2-methyl-2-pentene

4. Draw the chemical structures of aspirin and caffeine.

What Should Be In Your Notebook?

1. An entry of the title, date, and page number in your table of contents.
2. An entry of the title and date on the first page of your experiment as usual.
3. A description of how to use the software sufficiently detailed to either repeat this experiment or to use as a refresher for another experiment later in the term.
4. All the items that you were asked to record for each individual part of this lab.

What Should Be In Your Laboratory Report?

Use the **Experiment 2 Report Form** to write your lab report.

Remember to:

1. Submit an electronic copy to CH241Lab@colby.edu by the date your report is due.
2. Submit a hardcopy in lab on the due date (start of lab).