

CH 241 EXPERIMENT #2

WEEK OF OCTOBER 1, 2001

MOLECULAR MODELING PART I

Introduction: The ability to calculate structures and 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 (in Keyes 404) 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 rudiments of molecular modeling.

The computational program known as Spartan is a popular and easy-to-learn software program that will be used throughout this lab. The PC version of Spartan is laid out somewhat differently from the Silicon Graphics (or SGI) version although the capabilities are essentially the same in both. Beside each computer you will find a tutorial that will guide you through the program. When you come to lab, work through the first two chapters of the tutorial (they are really short!) to learn some of the basic operations. The following skills are especially important:

- Building molecules and using the "Model" menu to cast them in different views (e.g. ball and stick, space filling, tube etc.)
- Manipulating molecules by rotating and moving them around.
- Changing colors of the models and layout.
- Querying and changing parameters such as bond lengths, bond angles, and dihedral angles. These operations are under the "Geometry" menu.
- Using the "Setup" menu to set up and submit calculations.
- Using the "Display" menu to examine energies, surfaces, electrostatic potentials and molecular orbitals.
- Saving and printing.

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 line drawings, suddenly come to life on the computer screen. These models can be then viewed and probed in a variety of ways to gain a better understanding of the compounds they represent. Given below are a set of exercises that will not only help you learn the program 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? What do aspirin and caffeine really look like? How awful is a triple bond in a small ring or a double bond at a bridgehead? How does the shape of pentane compare with neopentane? Check it out.

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

- Build methane and minimize. Optimize the geometry using the semi-empirical AM1 method. Note bond lengths and bond angles in this molecule.
- In an analogous manner, calculate the bond length and bond angle parameters for ethane, ethylene, and acetylene.

Part II. Conformational analysis of butane

- Build butane. Change the C1-C2-C3-C4 dihedral angle to 0° so that the two methyl groups eclipse each other. Do not minimize. Instead, calculate the single point energy of this particular conformation using the semi-empirical AM1 method. Note the energy.
- Repeat the above steps by changing the dihedral angle through 60° , 120° , 180° , 240° , and 300° . Be sure to note the single point energy for each conformation.

Part III. Molecular orbitals of hydrogen sigma bond and ethylene pi bond

- Build H_2 . Set up a semi-empirical AM1 calculation. Before submitting the calculation, request that the HOMO and LUMO surfaces be computed. Submit the calculation and, when it is finished, display the HOMO (bonding) and LUMO (antibonding) orbital surfaces. Examine these orbitals individually and together. What is the energy difference between the two orbitals?
- Repeat the above steps for ethylene.

Part IV. Shapes of molecules and functional groups

- Build and minimize 1-butanol, 2-butanol (or *sec*-butyl alcohol), 2-methyl-1-propanol (or isobutyl alcohol), and 2-methyl-2-propanol (or *tert*-butyl alcohol). Optimize the geometry of each compound by using the semi-empirical AM1 method. Before submitting the calculation, request that the electron density surface and electrostatic potential property be computed. Submit the calculation and, when it is finished, display the electron density surfaces with the electrostatic potential. Identify the positively and negatively charged regions for each molecule.
- Compare the electron density surfaces computed above with the space-filling models.
- Note the dipole moments of each molecule.
- Build and minimize organic compounds of your choice containing the following functional groups. Note the dipole moment of each compound.
 - (a) alkyl halide (b) aldehyde (c) ketone (d) amine (e) ether
 - (f) nitrile (g) thiol (h) carboxylic acid (i) ester (j) amide

Part V. Stability of alkenes

- Build models of 1-hexene, 2-methyl-2-pentene, (*E*)-3-methyl-2-pentene, (*Z*)-3-methyl-2-pentene, and 2,3-dimethyl-2-butene. Optimize the geometry of each molecule using the semi-empirical PM3 method. Note the energy of each alkene.

Pre-Lab Exercises for Experiment #2

- (1) Tabulate the bond angles and carbon-carbon bond lengths for methane, ethane, ethylene, and acetylene.
- (2) Write the structures of 1-butanol, 2-butanol (or *sec*-butyl alcohol), 2-methyl-1-propanol (or isobutyl alcohol), and 2-methyl-2-propanol (or *tert*-butyl alcohol). Record their boiling points. Show the direction of the bond dipole in two of the most polar bonds in each molecule.
- (3) Provide an example for each of the following organic compounds.
 - (a) alkyl halide (b) aldehyde (c) ketone (d) amine (e) ether
 - (f) nitrile (g) thiol (h) carboxylic acid (i) ester (j) amide
- (4) Arrange the following isomers in the order of increasing stability.
1-hexene, 2-methyl-2-pentene, (*E*)-3-methyl-2-pentene, (*Z*)-3-methyl-2-pentene, and 2,3-dimethyl-2-butene.

Laboratory Report for Experiment #3

Name_____

Section_____

Date_____

Data Section

Part I.

Record the bond angle and bond length parameters for methane, ethane, ethylene, and acetylene.

Part II.

- (a) Record the single point energies of butane as a function of the C1-C2-C3-C4 dihedral angle.
- (b) Plot a graph depicting the variation of energy as the dihedral angle is changed.

Part III.

Record the energies of the bonding and antibonding orbitals of the sigma bond in H₂. Do the same for the pi bond in ethylene. Print and attach copies of the orbitals.

Part IV.

- (a) Arrange the 4 alcohols in the order of their electron density surface.
- (b) Record the dipole moments of each alcohol.

Part V.

Note the energies of the isomers and arrange them in order of increasing stability.

Discussion Section

- (1) Compare the calculated values in part I with the experimental values recorded in your prelab.
- (2) Compare the shapes of 1-butanol, 2-butanol (or *sec*-butyl alcohol), 2-methyl-1-propanol (or isobutyl alcohol), and 2-methyl-2-propanol (or *tert*-butyl alcohol). Show how the shapes affect the trend in boiling points that you recorded for the prelab.
- (3) Compare the results for Part V with the answer that you proposed for question 4 of the prelab.