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 (in Keyes 403) 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 GaussView is a popular and easy-to-learn software that will be used throughout this lab to build molecules, submit calculations, and analyze results. The actual calculations themselves will be performed with a different software program called Gaussian. Your lab instructor will demonstrate the use of GaussView and Gaussian.

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 then 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 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? How awful is a triple bond in a small ring or a double bond at a bridgehead?

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

- Build methane and minimize. Optimize the geometry at the default HF/3-21G level. Record the bond lengths and bond angles in this molecule.
- In an analogous manner, determine the bond length and bond angle parameters for ethane, ethylene, and acetylene and record all values in your lab notebook.

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. Determine the energy of this particular conformation using HF/3-21G.
- Repeat the above steps by changing the dihedral angle through 60°, 120°, 180°, 240°, and 300°. Record the single point energy for each conformation in your lab notebook.

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

- Build and optimize H₂ at HF/6-31G. When done, display the HOMO (bonding) and LUMO (antibonding) orbital surfaces and sketch the general shape of the two orbitals in your notebook. Examine these orbitals individually and together and record the energies of these orbitals.
- Repeat the above steps for ethylene.
Part IV     Shapes of molecules and functional groups

• Build and minimize organic compounds from your prelab containing the following functional groups. Note the value of the dipole moment of each compound.
  (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, 2-methyl-2-pentene, and 2,3-dimethyl-2-butene. Optimize the geometry of each molecule at HF/3-21G. Record the energies of the alkenes in your notebook and arrange them in order of increasing stability.

Part VI     More complicated molecules

• Build aspirin and caffeine. Optimize the geometry of each molecule at HF/3-21G. Use the result to describe how these molecules look in three-dimensions, comparing their appearance to the two-dimensional structures drawn on paper.
• With any time remaining, have fun building molecules of your choice, such as putting a double bond or a triple bond in a three-membered ring.

PRELAB PREPARATION

1. Read about computational modeling of molecules, using this resource (which has been read over by a theoretical physical chemist to ensure its accuracy):
   http://en.wikipedia.org/wiki/Computational_chemistry If you would enjoy reading about a couple of scientists that made significant contributions to the area, see the following:
   http://www.nobelprize.org/nobel_prizes/chemistry/laureates/1998/pople-bio.html and
2. Tabulate bond angles and bond lengths for methane, ethane, ethylene, and acetylene.
3. 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 while keeping it pretty 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
4. Write the structures and arrange the following isomers in the order of increasing stability:
   (E)-3-hexene, (Z)-3-hexene, 2,3-dimethyl-2-butene, 1-hexene, 2-methyl-2-pentene.
5. Write the 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 use 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?

*Do not exceed a total of two pages of text, supplemented with one page of pictures and references (please print this double-sided and send an electronic copy to your lab instructor)*

1. Title of the experiment with your name, lab section, and date.
2. Introduction to computational molecular modeling chemistry (1 paragraph)
3. Results and Discussion, including an analysis of the data for each part. Where relevant, compare the calculated values/trends with those available in your textbook or other reliable reference. Use tables to display data clearly and concisely when appropriate.
4. ChemBioDraw structures for each molecule in Parts IV, V, and VI
5. Conclusion (1 paragraph)