Use of PC SPARTAN '04

(1) The Basics.

Under File in the pull-down menu select New. This brings up the "Builder" screen, where molecular models are put together and modified. Note that the default fragment at the right is an sp3 carbon. Click on the screen – methane is produced. Note that H's are automatically added to unfilled valences.

Click on one H of methane – ethane is produced.

To delete an atom: click on the delete tool [icon] in the toolbar then on the atom to delete. Try deleting one of the carbons of ethane. Note that the H's on that C are deleted as well.

Rebuild ethane.

Select Fluorine (F) from the menu at right and click on one H of ethane – fluoroethane is produced.

Hold Right mouse button down and drag mouse around – this moves the molecule around the screen.

Hold left mouse button down and move mouse around the screen – this rotates the molecule in the x,y plane.

Hold down Space key and Left mouse button and drag mouse around – this rotates the molecule in x,y,z space.

Holding down Shift key and left mouse button rotates the molecule around the Z-axis.

Holding down the Shift key and the Right mouse button changes the size of the molecule.

Clicking on the C-C bond selects that bond. Holding down the Alt key and the Left mouse button rotates about that bond. Clicking a second time on the bond deselects it.

Under Model in the pull-down menu, select the first choice, "wire". Move the molecule around to view it from different angles. View the other four types of models and move them around each time. (Depending upon what type of exercise is being done, one model may be more useful than another.) For now go to the "Ball and Spoke" model.

Click on the minimize icon [icon] in the tool bar. The bond lengths and angles for the molecule are adjusted by the program to minimize the steric energy (i.e., optimize the geometry) of the molecule. (Minimization using this button performs a quick molecular mechanics (MM) calculation to arrive at an initial estimate of the best (energetically optimum) geometry.)

To perform more sophisticated calculations do the following:

Under "Setup" choose "Calculation".

In the new window, under Calculate, change "Hartree-Fock" to "Molecular Mechanics/MMFF" and select "OK".

Under Setup, select Submit. Change Filename to fluoroethane then click on submit.

At the message "Fluoroethane has started" click on "OK". At the message "Fluoroethane has completed", click on "OK". (Calculations on larger molecules having more complex structures will take longer, as will more sophisticated calculations such as AM1, etc)

What has happened? Using the chosen method of calculation (MMFF Molecular Mechanics) the program has minimized the energy by moving bond lengths and angles to achieve what it thinks is the overall energetically optimum (lowest energy, most stable) geometry.

Under "Display" select "Output". Under "Cycle" the last cycle will give the minimized energy. Information relevant at this point would be the minimized energy, e.g., -2.40 kcal/mol and perhaps the dipole moment, 2.22 Debye.

(2) Conformational Analysis of Butane.

In this exercise, steric energy as a function of rotation about the central carbon-carbon bond (C2-C3) of butane will be examined.

-- close previously open structure windows and open a new builder (File- Close, File – New.)

- Build butane then click on the "Dihedral" tool, .

Click on the four carbon atoms to select them (be sure to not click on a H by mistake – move the model around if a carbon is obscured.)

In the window at the lower right enter 0 then enter to set the dihedral angle to 0°. Note that this produces the conformation having the methyl groups eclipsed.

Click on the "Constrain Dihedral" tool, , then select the four carbons again.

In the window at the lower right, click on the open lock icon which changes it to closed then enter 0 and "enter" to set the dihedral to 0°.

Under "Setup" in the menu bar, choose "Calculations". Change "Hartree-Fock" to "Molecular Mechanics – MMFF" and click on Subject to: "Constraints". Click on "Submit".

After the program states that the "Job has completed", under "Display" in the menu bar, select "Properties". Write down the energy in a table having two columns labelled Dihedral Angle and Energy (there will be 13 entries).

Click on the Dihedral tool, select the four carbons, and enter 30 then enter to change the dihedral angle to 30°. Click on the "Constrain Dihedral" tool, select the four carbons and change the dihedral angle to 30°. Under "Setup, choose "Calculations" and be sure that the setup is for Molecular Mechanics – MMFF and is "Subject to constraints". Submit and when the calculations are finished, under Display, Properties, find the energy and add it to your table.

Continue rotating the dihedral angle 30° each time, each time calculating the energy. (note that after 180°, the angle may go back down toward zero rather than 210° and so on. This is ok)

(3) Conformational Analysis of Monosubstituted Cyclohexanes.

In the Builder window, at the lower right, under Rings, choose cyclohexane and click on the main screen to produce cyclohexane. Make the equatorial conformer of the monosubstituted cyclohexane that has been assigned to you (assignment on separate handout). Calculate the steric energy using Molecular Mechanics (MMFF). Build the axial conformer and calculate its energy.

(4) Independent Project

Make a model of a molecule that has at least 8 carbons and two different functional groups (functional group being defined here as something other than an alkyl group). This molecule can come from your imagination or it can be a molecule from your textbook or lab text. Minimize the energy of this molecule (MMFF). Record the energy. View the molecule as different model types (wire frame, space filling, etc) and rotate it, and when you produce a view that you like, Print the model. Include this printout as part of your molecular modeling report.

Feel free to experiment with SPARTAN and to use it throughout the semester. Later experiments will require calculations using SPARTAN. Use it to help you visualize molecules that you encounter in class or lab. It can also be helpful in studying stereochemistry.

The Report. This will be graded as one lab experiment. The report should include (1) the minimized energies for fluoroethane, (2) the data and graphs for the conformational analysis of butane, (3) the data and calculations for the monosubstituted cyclohexane analysis (report $\Delta H°$, K, % ax, and % eq), and (4) the data and printout for the molecule in the Independent Exercise. The report should also include a comparison of your data to experimental values for butane, and your assigned cyclohexane, and a discussion. Experimental values can be found in your lecture and lab texts.

Calculations for the cyclohexane equilibrium. For your report calculate the enthalpy difference for the equilibrium and from that, the equilibrium constant, and from that, the percentage of axial and equatorial conformers in the equilibrium mixture. Because the entropy change in the equilibrium is small, we can assume that $\Delta G° = \Delta H°$. Also assume that the change in steric energy is equal to the change in enthalpy.
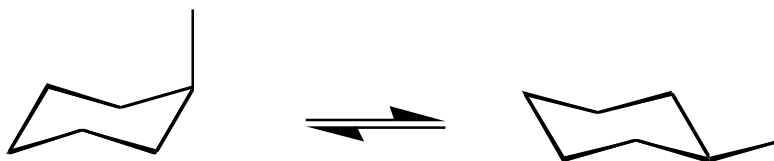
For the equilibrium shown above then, $\Delta H° = H° (eq) - H° (ax) = \Delta G°$.

Using the equation, $\Delta G° = -RT\ln K$, where R (gas constant) = 1.987 cal/deg-mol, T = absolute temperature in °Kelvin, and K = equilibrium constant, and making the assumption that $\Delta G° = \Delta H°$, calculate K. To compare your calculated value to the experimental values given in your textbook use a temperature of 298°K in the equation. Compare your calculated value with the experimental. Be sure to use the correct units (e.g., don't mix cal and kcal).

Using the relationships Nax + Neq = 1 and K = Neq/Nax, where N is mole fraction, calculate the % of ax and % of eq. (Do all calculations after you are finished using SPARTAN so you do not tie up the computer.)

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* SPARTAN '04 – http://www.wavefun.com/

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