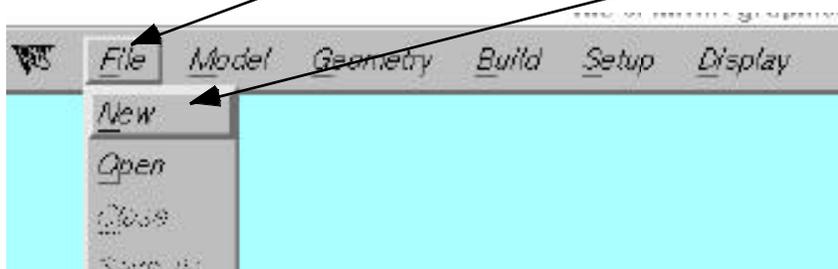


A Theoretical Investigation of the Dehydration of 2-Butanol

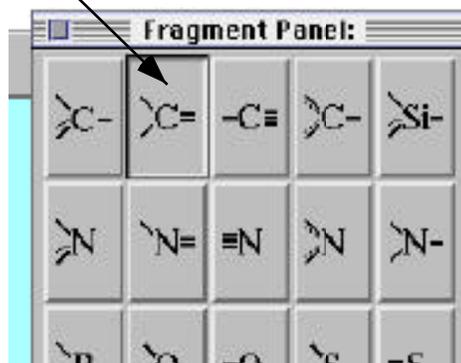
Peter Samal

2-Butanol will be dehydrated to a mixture of 1-butene, cis-2-butene, and trans-2-butene using the method described in Williamson. The product distribution will be determined by gas chromatography (gc). Steric energies will be calculated using MM2 and heats of formation will be calculated using AM1 semi-empirical MO calculations. Calculated values will be compared with experiment. The SPARTAN computer program will be used for the calculations.

Tutorial on the use of the SPARTAN computer program. This tutorial describes the use of SPARTAN on a Silicon Graphics workstation. The program MacSpartan or PC Spartan may also be used but their use is somewhat different than that of SPARTAN. Launch SPARTAN by double-clicking on the SPARTAN icon. When the main window appears, using the left mouse button, click on "File" in the menu bar, and then on "New" in the pull-down menu as shown.



In general, use the left mouse button to select items. A new "Builder" window will appear on the left with a "Fragment" window on the right. Click on the double-bonded carbon in the "Fragment" window,

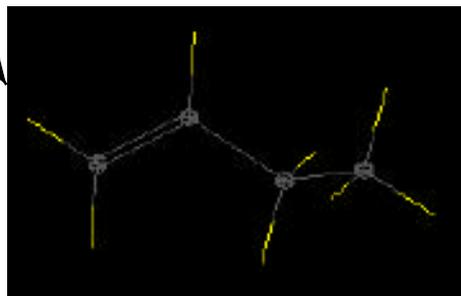


move the cursor to the "Builder" window, and click once to deposit the carbon double-bond fragment onto the "Builder" window. The fragment will have a different orientation than that shown.



Moving the mouse with the middle mouse button depressed rotates the fragment in the X/Y direction and moving the middle mouse button with the "Shift" key depressed moves the fragment in the Z direction. Other combinations of the middle and right mouse buttons with the shift and control keys do other rotations and translations of the molecule or fragment. Experiment. Rotate the carbon double bond fragment so that you can view it as shown above, then place the cursor on the outer end of the double bond and click once. This should produce the carbon-carbon double bond. Now select the tetrahedral carbon (upper left) from the fragment window, place the cursor on the end of one of the single bonds in the Builder window, and click. This will add a carbon to the molecule. Place the cursor on a single bond of the tetrahedral carbon and click again to add another carbon.

You have just built 1-butene, which should look something like this, only oriented differently.



Click on "Minimize" at the bottom of the "Fragment" window to perform a preliminary geometry optimization/energy minimization.

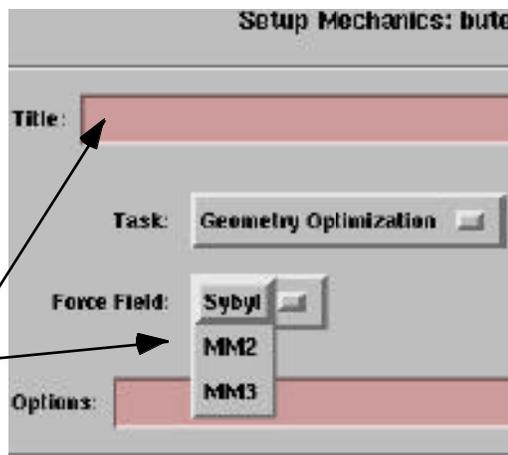
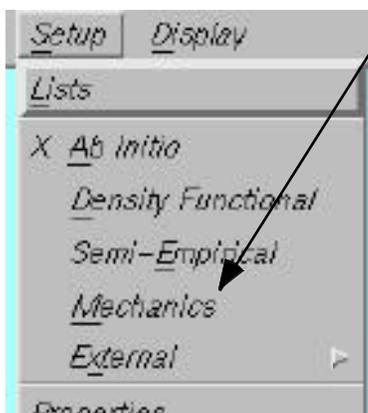
Under the File menu, choose "Save" and in the new Dialog Box that appears, type "1-butene", then click on "Save". Under "File", choose "Quit". The original SPARTAN window will appear with the molecule of 1-butene shown. (Under "Model" in the Menu Bar, you may choose different types of models with which to view the molecule and you may rotate and move them as before.) You may now set up and do calculations on this molecule.

Calculating the energy of a single conformer or molecule will be done in future experiments. This procedure is described at the end. For this experiment, where a conformer search will be performed, do the following.

Molecular Mechanics Calculations with a Conformer Search.

Once you have built 1-butene, done a preliminary minimization in the Builder and returned to the main SPARTAN window, under "Build" in the menu bar, choose "Conformer Search". A new model window will appear on the left and a "Conformer Panel" window on the right. "Systematic" should be selected under "Method". In the model window, point to one of the C-C single bonds and double click. The bond should be marked with a yellow marker. At the bottom of the Conformer Panel, change 3 under "fold-rotation" to 4. Do the same to the other C-C single bond. If necessary, rotate the model so you are able to see both bonds. Under "File", select "Save", then "Quit" to return to the main SPARTAN window. Your model of 1-butene will be present.

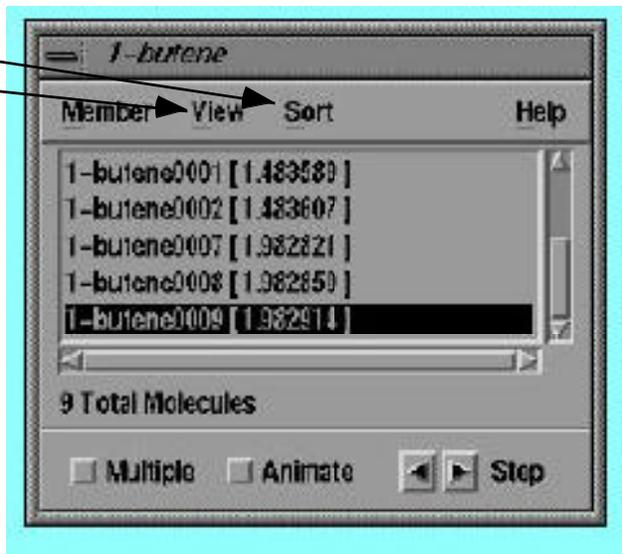
Molecular Mechanics. Run an MM2 molecular mechanics calculation on 1-butene as follows. Click on "Setup" in the Menu Bar and, in the Pull-down Menu, click on "Mechanics".



In the Dialog Box that appears, type "1-butene" in the Title area and select MM2 under "Force Field". "Task" should be set for "Geometry Optimization".



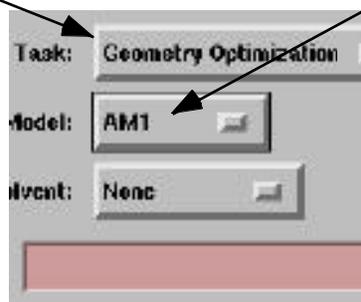
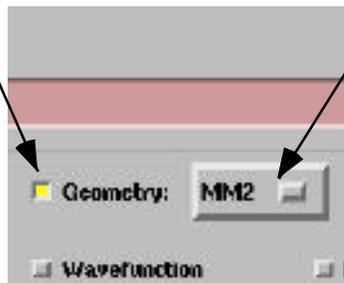
Click "Save", and under "Setup" in the Menu bar, choose "Submit". Click "Okay" when the program tells you that the job has been submitted and again when it advises you "Promoting molecule to list of molecules". A new window showing the list of the 9 conformations will appear. In that window, choose "View - Show Energy" and "Sort - By Energy".



The conformers will be sorted with the one having the lowest energy at the top of the list. To the right of the conformer name (e.g., 1-butene0007) is given the strain energy in kcal/mol. (When a Conformer Search is done using semi-empirical calculations, the heat of formation is given.) Record the strain energy of the low-energy conformation. Pointing to the name in the list produces the model of the conformation in the model window. Rotate the model to see which conformation is considered to be the low-energy conformation. Click on other conformer names to see the models of the higher-energy conformations. Note that many of the conformers will be identical. When you are finished working with the MM2 calculations for 1-butene, choose Delete from the main menu and acknowledge that this is what you want to do. Choose "New" under "File", rebuild 1-butene, and repeat the conformer search, but this time use AM1 calculations.

Conformer Search Using AM1 Calculations. With 1-butene in the main SPARTAN window, under "Build", choose "Conformer Search", and once again select both of the C-C single bonds, and Save and Quit that window as before. Under "Setup" in the menu bar, this time in the pull-down menu, click on "Semi-Empirical". In the Dialog Box that appears, for Task, select "Geometry Optimization" and for Model, select "AM1". None should be selected for Solvent.

Towards the bottom, to the right of "Start Using:", click on "Geometry" and to the right of that select "MM2".

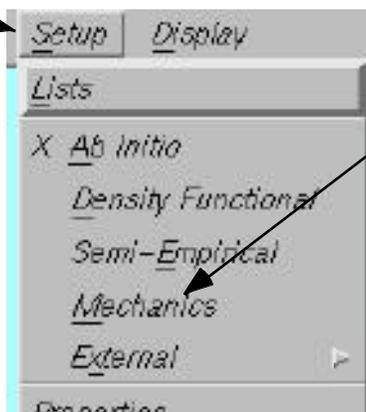


(Because the AM1 calculations are more time-consuming, starting with a geometry optimized with MM2 saves computer time.)

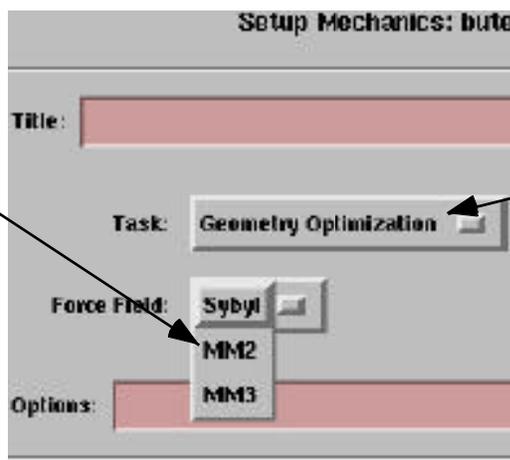
Click on "Save", and under "Setup" in the Menu Bar, click on "Submit". Click on "Okay" when the program tells you that the job has been submitted, and again when it advises you "Promoting molecule to list of molecules." A new window showing the list of the 9 conformations will appear. In that window, choose "View - Show Energy" and "Sort - By Energy" as before. The heat of formation is given to the right of each molecule in the list. Record the heat of formation of the low-energy conformation. Check the model of some of the conformations by clicking on their names and rotating the model.

Repeat the MM2 and AM1 calculations, using a conformer search, for *cis* - and *trans* - 2-butene.

Molecular Mechanics Without Conformer Search. If you are not concerned with the problem of searching for a global minimum, calculations can be done on a single conformation or molecule. The reason to not do a conformer search is to save computer time. In many cases, for rigid molecules, a conformer search would not be necessary. To run an MM2 molecular mechanics calculation on 1-butene, with 1-butene in the main SPARTAN window, click on "Setup" in the Menu Bar and, in the Pull-down Menu, click on "Mechanics".



In the Dialog Box that appears, type "1-butene" in the Title area and select MM2 under "Force Field".



"Task " should be set for "Geometry Optimization".

Click "Save", and under "Setup" choose "Submit". Click "Okay" when the program tells you that the job has been submitted and again when it is complete. Choose "Output" under "Display" in the Menu bar.



The output of the MM2 calculation will appear. Page down through the output and record the final Strain Energy for 1-butene (given after "minimization complete"). The output also shows the total strain energy partitioned into its components (stretch, bend, etc).