

## 4 Single Point Energies and Geometry Optimizations (Spartan)

### Exercise 1 Determine the optimum structure for ethanol (vinyl alcohol)

Click New File.

Build a molecule of vinyl alcohol using appropriate hybridizations. You should end up with either **I** or **II** shown here.

Choose Geometry / Constrain Dihedral.

Click on the C, C, O, H atoms with the terminal C being first.

Click on the pink “unlocked” icon in the lower right of the screen to lock it.

Click on the pink “constraint” marker that appears on the C-O bond.

Choose Display / Properties. If needed, move the “Selected” style box from in front of the molecule.

Click the “Dynamic” box in the Constraint Properties window.

Edit the top line so that it reads Value: 180.00° to 0.00°, and change “Steps” to 37 (YOU MUST HIT RETURN IN EACH BOX TO MAKE THESE CHANGES).

Close the Constraint Properties box.

Choose Setup / Calculations. Select Energy Profile at Ground State with Semi-Empirical PM3.

Click Submit. Save as vinylalc.spartan in an appropriate folder.

Click “OK” to started message and “OK” to completed message.

Save and Close the file.

Choose File / Open / vinylalc.Profile1

Choose Display / Spreadsheet.

Click on the Molecule001 cell to highlight it.

Click on the gray box in Column 2, Row 1 (top box) to highlight it.

Click Add / rel. E (relative energy). Click “OK”.

To add the angles to the spreadsheet, choose Geometry / Measure Dihedral.

Click on the constraint marker on the C-O bond.

Click on the yellow “P” box in the lower right of the screen.

Choose Display / Plots. Choose X Axis / Dihedral(Con1) and Y Axis / E (kcal/mol). Click “OK”.

Use the “forward” and “reverse” buttons on the lower left to find energies of conformer **I** \_\_\_\_\_ kcal mol<sup>-1</sup>, conformer **II** \_\_\_\_\_ kcal mol<sup>-1</sup>, and the barrier \_\_\_\_\_ kcal mol<sup>-1</sup>. (The corresponding values will be highlighted in the spreadsheet). Which conformer is more stable? \_\_\_\_\_

Pressing the “Play” button (▶) at the bottom of the screen will animate the bond rotation.

Save and Close the file. Click New File.

Build the global minimum structure for vinyl alcohol. If you need to adjust the C=C-O-H dihedral angle, click on the C-O bond so that the red “rotation” marker appears, hold down the “Alt” key, and left click/drag until the lowest energy structure is obtained.

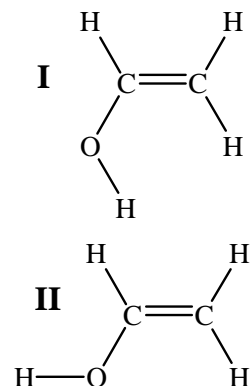
Choose Setup / Calculations. Choose Equilibrium Geometry at Ground State with Density Functional B3LYP 6-31G\*, Print Orbitals and Energies.

Click Submit. Save as vinylalc2.spartan in an appropriate folder.

Click “OK” to started message and “OK” to completed message.

Choose Display / Properties, and record the energy of the optimized structure \_\_\_\_\_ au.

Save and Close the file.



## Exercise 2 Performing a Partial Grid Search for Water

Build a molecule of water, click the ‘View’ icon (5<sup>th</sup> across the top) and move the molecule to the upper right corner of the work area.

Choose the “Constrain Distance” icon (16<sup>th</sup> across the top).

Click on one H atom, then click on the O atom. Both atoms should be highlighted.

Click on the “lock” icon located in the lower right corner.

Choose Display / Properties, then click on the pink constraint marker located on the H-O bond.

In the “Constraint Properties” box, click on “Dynamic”, then edit the top line to read “0.80Å – 1.10Å, Steps = 30”. YOU MUST HIT RETURN AFTER CHANGING THE CONTENT OF EACH BOX FOR THE CHANGES TO TAKE EFFECT.

Close the “Constraint Properties” box. .

Choose the “Constrain Angle” icon (17<sup>th</sup> across top).

Click on one H atom, then the O atom, then the other H atom. All three should be highlighted.

Click on the “Lock” icon in the lower right corner.

Choose Display / Properties. Click on the “View” icon. Click on the pink “Constraint” marker.

In the “Constraint Properties” box, click on “Dynamic”, then edit the top line to read “90.00° – 120.00°, Steps = 30”. YOU MUST HIT RETURN AFTER CHANGING THE CONTENT OF EACH BOX FOR THE CHANGES TO TAKE EFFECT.

Close the “Constraint Properties” box. .

Choose Setup / Calculations. Select Energy Profile at Ground State with Semi-Empirical PM3.

Click Submit. Save as H2OPM3.spartan in an appropriate folder.

Click “OK” to started message and “OK” to completed message.

Save and Close the file.

Choose File / Open / H2OPM3.Profile1. Move the molecule to the upper right of the screen.

Choose Display / Spreadsheet.

Click on the Molecule001 cell to highlight it.

Click on the gray box in Column 2, Row 1 (top box) to highlight it.

Click Add / rel. E (relative energy). Click “OK”.

To add the bond length to the spreadsheet, choose Geometry / Measure Distance.

Click on the constraint marker on the H-O bond.

Click on the yellow “P” box in the lower right of the screen.

To add the bond angle to the spreadsheet, choose Geometry / Measure Angle.

Click on the angle constraint marker, then click on the “P” box in the lower right.

Choose Display / Plots. Choose the “XYZ Plot” tab. Use pull down menus to plot H-O Length on the X-Axis, H-O-H Angle on the Y-Axis, and rel. E (kcal mol<sup>-1</sup>) on the Z-Axis.

Click “OK”.

Clicking on one of the graph axes causes the graph to change color. It may now be rotated (left click), moved (right click), or zoomed in on (Shift right-click). (NOTE: Sometimes the file must be saved, closed, and opened again in order for the graph to be selected in this manner).

The “forward” and “reverse” buttons on the lower left may be used to step through the plotted points. The corresponding values in the spreadsheet will be highlighted and the molecule display will be updated accordingly.

Locate the lowest energy (most negative) conformation. Record the H-O bond length, the H-O-H bond angle, and compare with the literature values. H-O bond length \_\_\_\_\_ Å (Lit. value 0.958 Å). H-O-H bond angle \_\_\_\_\_ ° (Lit. value 104.51°).

### Exercise 3 Determining the Energy Map for Cyclohexane

With the Entry builder, use the  $sp^3$ -hybridized carbon and build cyclohexane. (Close the ring by choosing Build / Make Bond, then clicking on the two required carbon valences).

Click the “View” icon (5<sup>th</sup> across the top), then the “Minimize” icon (10<sup>th</sup> across the top).

Choose Geometry / Constrain Dihedral, then click on four carbons in a row, beginning with the “head”, two “seat”, and ending with the “foot” carbon of the chair conformation.

Click on the “lock” icon in the lower right corner.

Click on the pink “constraint” marker on the C-C bond (It may help to zoom in: Shift, Right-click–Drag vertically).

Choose Display / Properties and click on the “Dynamic” box.

Edit the top line in the “Constraint Properties” box to read “-60.00° to 60.00°, Steps 120”. (AFTER CHANGING THE VALUE IN EACH BOX, HIT ‘ENTER’ FOR THE CHANGE TO TAKE EFFECT).

Close the “Constraint Properties” box.

Choose Setup / Calculations. Select Energy Profile at Ground State with Semi-Empirical PM3.

Click Submit. Save as cyclohexane.spartan in an appropriate folder.

Click “OK” to started message and “OK” to completed message.

Save and Close the file.

Choose File / Open / cyclohexane.Profile1

Choose Display / Spreadsheet.

Click on the Molecule001 cell to highlight it.

Click on the gray box in Column 2, Row 1 (top box) to highlight it.

Click Add / rel. E (relative energy). Click “OK”.

To add the angles to the spreadsheet, choose Geometry / Measure Dihedral.

Click on the constraint marker on the C-C bond.

Click on the yellow “P” box in the lower right of the screen.

Choose Display / Plots. Choose X Axis/Dihedral(Con1) and Y Axis/E (kcal/mol). Click “OK”.

Use the “forward” and “reverse” buttons on the lower left to record the energies of the chair conformer (global minimum) \_\_\_\_\_ kcal mol<sup>-1</sup>, the half-chair conformer (peak) \_\_\_\_\_ kcal mol<sup>-1</sup>, the twist-boat conformer (local minimum) \_\_\_\_\_ kcal mol<sup>-1</sup>, and the boat conformer (2<sup>nd</sup> smaller peak) \_\_\_\_\_ kcal mol<sup>-1</sup>. (The corresponding values will be highlighted in the spreadsheet). Which conformer is more stable? \_\_\_\_\_

Pressing the “Play” button (▶) at the bottom of the screen will animate the bond rotation.

Save and Close the file.

Which conformer of cyclohexane is the most stable? \_\_\_\_\_ What is the energy difference between the two most stable conformers? \_\_\_\_\_ kcal mol<sup>-1</sup> (lit. value 4.0–5.5 kcal mol<sup>-1</sup>). What is the potential energy barrier between the two most stable conformers? \_\_\_\_\_ kcal mol<sup>-1</sup> (lit. value 10.0–11.0 kcal mol<sup>-1</sup>). What is the potential barrier between the twist-boat and the boat conformers? \_\_\_\_\_ kcal mol<sup>-1</sup> (lit. value 1.4–1.6 kcal mol<sup>-1</sup>).