

## 4 Single Point Energies and Geometry Optimizations

### Exercise 1 Determine the Optimum Structure for Ethenol (vinyl alcohol).

Build a model of ethenol using  $sp^2$  C atoms connected by a double bond and a  $sp^3$  O atom. Add H atoms. The model builder should generate one of the two structures shown.

Define a dihedral angle consisting of the H atom, the O atom, and the two C atoms by holding down the shift key and clicking the four atoms. Click Adjust / Dihedral Angle and select define geometry label and search. Choose the search angles so that the rotation of the dihedral angle will complete a full  $360^\circ$  using 72 steps and click ok.

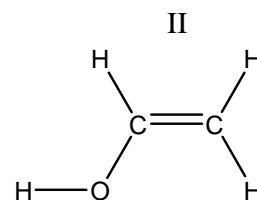
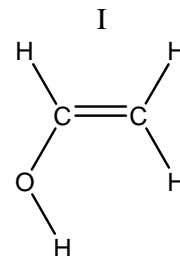
Save as vinylalc.csf. Prepare a PES as a function of the dihedral angle by selecting Experiment / New and selecting chemical sample conformations with an optimized map using PM3 energies (one label). Record the values of the energy of conformer I

\_\_\_\_\_ kcal mol<sup>-1</sup>, conformer II \_\_\_\_\_ kcal mol<sup>-1</sup>, and the barrier \_\_\_\_\_ kcal mol<sup>-1</sup>. Which conformer is more stable? \_\_\_\_\_

Make sure that the structure on the screen corresponds to the global minimum structure. If necessary, rotate the OH by reselecting the atoms making up the dihedral angle, click Adjust / Dihedral Angle, entering the desired value, and unselect define geometry label.

Save as vinyldft.csf. Perform a geometry optimization using density functional theory by selecting chemical sample with optimized geometry using B88-LYP DFT geometry (DZVP basis set). Record the energy of the optimized structure.

\_\_\_\_\_ Eh. Save the file.



### Exercise 2 Performing a Grid Search.

Build a molecule of hydrogen peroxide using  $sp^3$  O atoms connected by a single bond. Add H atoms. Most model builders will generate a planar molecule when “cleaning up” the structure.



The number of internal degrees of freedom in this molecule is  $3(4) - 6 = 6$  and these are the two O-H bond lengths, O-O bond length, two H-O-O bond angles, and H-O-O-H dihedral angle.

Define the first O-H bond label by holding down on the shift key and clicking the two atoms. Click Adjust / Atom Distance and select define geometry label and search. Choose 0.9 and 1.2 using 15 steps and click ok. Similarly define the second O-H bond label. Likewise define the O-O bond label using 1.2 and 1.7 with 25 steps.

Define the first H-O-O bond angle by holding down on the shift key and clicking the three atoms. Click Adjust / Bond Angle and select define geometry label and

search. Choose  $90^\circ$  and  $120^\circ$  using 30 steps and click ok. Similarly define the second O-O-H bond angle.

Define the H-O-O-H dihedral angle by holding down the shift key and clicking the four atoms. Click Adjust / Dihedral Angle and select define geometry label and search. Choose  $-180^\circ$  to  $180^\circ$  using 90 steps and click ok.

Save as h2o2confseq.csf. Run the conformation sequence determination by selecting experiment / new and choosing chemical sample conformations using sequence of conformations. Select MM3 multiple passes and perform the calculations. Record the O-H bond length \_\_\_\_\_ Å (literature 0.965 Å), O-O bond length \_\_\_\_\_ Å (literature 1.452 Å), H-O-O bond angle \_\_\_\_\_ ° (literature  $100.0^\circ$ ), and H-O-O-H dihedral angle \_\_\_\_\_ ° (literature  $111.5^\circ$ ). A table listing several low energy conformations can be displayed by selecting window / new conformation analysis window.

Copy the global minimum structure to the clipboard. Close and save all files. Open a new document, paste the global minimum structure from the clipboard, and save the file as h2o2confseqmin.csf. Perform a geometry optimization using B88-LYP/DZVP (see Exercise 1). Record the O-H bond length \_\_\_\_\_ Å, O-O bond length \_\_\_\_\_ Å, H-O-O bond angle \_\_\_\_\_ °, and H-O-O-H dihedral angle \_\_\_\_\_ °.

### **Exercise 3 Performing a Molecular Dynamics Search.**

Build a molecule of hydrogen peroxide (see Exercise 2).

Save as h2o2dyn.csf. Run the dynamics calculations by selecting Experiment / New and choosing chemical sample conformations using dynamics trajectory. Select MD simulation (MM3) and perform the calculations. The table listing several low energy conformations can be displayed as in Exercise 2. Copy the global minimum structure to the clipboard. Close and save all files.

Open a new document, paste the global minimum structure from the clipboard, and save the file as h2o2dynmin.csf. The geometry information can be determined by selecting two atoms, three atoms, or four atoms and selecting Adjust / Atom Distance, Bond Angle, or Dihedral Angle, respectively. Record the O-H bond length \_\_\_\_\_ Å, O-O bond length \_\_\_\_\_ Å, H-O-O bond angle \_\_\_\_\_ °, and H-O-O-H dihedral angle \_\_\_\_\_ °.

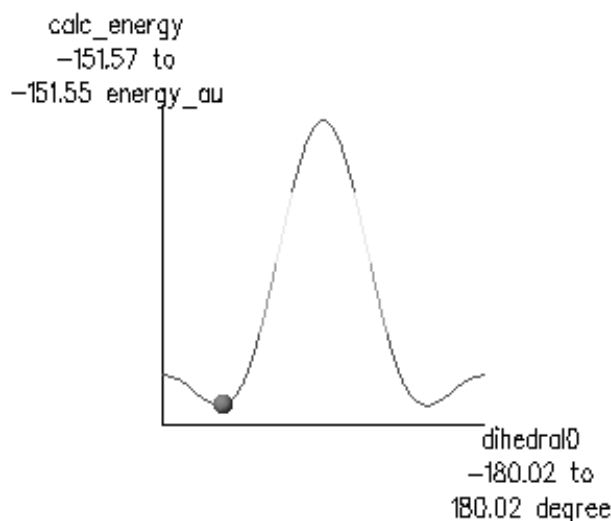
Repeat the B88-LYP/DZVP minimization (see Exercise 2) on this structure. Record the O-H bond length \_\_\_\_\_ Å, O-O bond length \_\_\_\_\_ Å, H-O-O bond angle \_\_\_\_\_ °, and H-O-O-H dihedral angle \_\_\_\_\_ °. Compare the results of the optimized structure from Exercise 2 with these results. \_\_\_\_\_

### **Exercise 4 Performing an Energy Optimization without Searching for the Global Minimum.**

Build a molecule of hydrogen peroxide (see Exercise 2). Save as h2o2flat.csf.

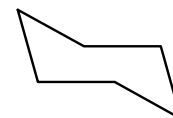
Using this structure, perform the B88-LYP/DZVP minimization (see Exercise 2) and report the H-O-O-H dihedral angle obtained.

\_\_\_\_\_ ° To what feature of the PES (with the H-O-O-H dihedral angle as the variable at 10 ° intervals from -180 ° to 180 ° using B88-LYP/DZVP) does the extremum determined correspond? \_\_\_\_\_



### Exercise 5 Determine the Energy Map for Cyclohexane.

Using the “ball and cylinder” view, build a molecule of C<sub>6</sub>H<sub>12</sub> using sp<sup>3</sup> C atoms. Add H atoms. Most model builders will generate the chair form when “cleaning up” the structure.



Define a dihedral angle consisting of the “head”, two “seat” and “foot” C atoms by holding down the shift key and clicking the four atoms in a counter-clockwise direction. Click adjust / dihedral angle and select define geometry label and search. Choose -60° and 60° using 120 steps and click ok.

Save as cyclohex.csf. Prepare a PES as a function of the dihedral angle by selecting Experiment / New and selecting chemical sample conformations with an optimized map using PM3 energies (one label). Record the values of the energy 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 (peak) \_\_\_\_\_ kcal mol<sup>-1</sup>.

Which conformer is the most stable? \_\_\_\_\_ What is the energy difference between the two stable conformers? \_\_\_\_\_ kcal mol<sup>-1</sup> (literature 4.0-5.5 kcal mol<sup>-1</sup>)

What is the potential energy barrier between the two stable conformers?

\_\_\_\_\_ kcal mol<sup>-1</sup> (literature 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> (literature 1.4-1.6 kcal mol<sup>-1</sup>)