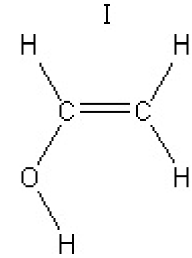
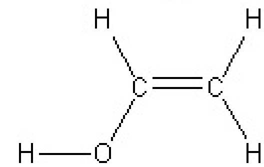
4 Single Point Energies and Geometry Optimizations

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

I



II



Build a model of ethenol. Use two Carbon Trivalent Element Fragments to construct ethene and click an Oxygen Tetravalent fragment on one of the H atoms to generate one of the two structures shown.

Click the Clean icon.

Click the Redundant Coordinate Editor icon to open the editor dialog window and click the Redundant Coordinate Editor icon to open the editor dialog window. Click the Create a New Coordinate icon. In the Coordinate table choose dihedral; click the H atom, the O atom, and the two C atoms to define the dihedral angle and the atom numbers will replace the ? entries; and click Scan Coordinate and enter 36 and 10. In the Set Value table choose Set to 180, a minimum of -180, and a maximum of 180. Click OK.

Click Calculate / Gaussian. Job: Scan and Relaxed (Redundant Coord); Method: Semi-empirical and PM3; use an appropriate title and save as vinylalc.chk and vinylalc.cjf.

The calculation will take a few minutes to complete.

From the Calculation Summary window, record the energies of conformer #1 (180 °) __________ Eh, conformer #9 (~100 °) __________ Eh, and conformer #19 (0 °) __________ Eh. Which conformer is more stable? __________

Close the results, but leave the original view window open.

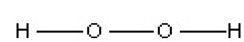
Make sure that the structure on the screen corresponds to the global minimum structure. If necessary, click the Modify Dihedral icon (1st row, 8th across) and click the same four atoms defining the dihedral angle to open the Semichem SmartSlide window. Simply move the slider to a value near the value for the global minimum structure and click OK.

Click the Redundant Coordinate icon and click the Delete Current Coordinate icon (2nd across). Click OK.

Perform a geometry optimization using B3LYP/6-31G(d). Be sure that the Job Type is set as a minimization and use appropriate file names. This calculation will take a few minutes. Record the energy of the optimized structure. __________ Eh.

Close everything except the main Control Panel.

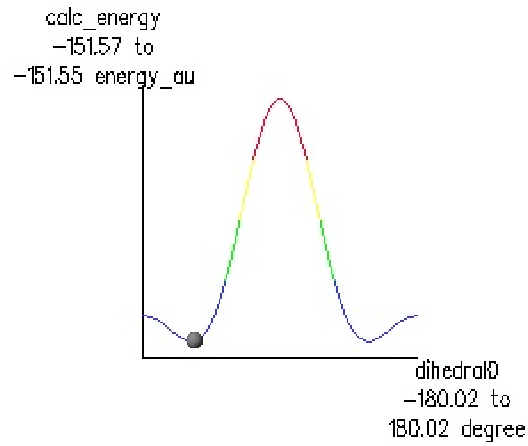
Exercise 2 Performing an Energy Optimization without Searching for the Global Minimum.



Build hydrogen peroxide using the Oxygen Tetravalent fragment twice.

Click the Clean icon. Most model builders will generate a planar molecule when "cleaning up" the structure.

Optimize at the B3LYP/6-31G(d) level. Use an appropriate title and save as H2O2FLAT.chk and H2O2FLAT.cjf. Record the energy of the optimized structure __________ Eh and the value of the dihedral angle __________ °.



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? __________

Retain the structure in the View window for the next Exercise.

Exercise 3 Optimizing a Thermally Excited Molecule.

Click the Modify Dihedral icon (1st row, 8th across) and click the four atoms in the order of H - O - O - H to open the Semichem SmartSlide dialog box. Use the slider to adjust the dihedral angle to ~90 °.

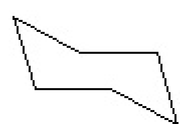
Run the B3LYP/6-31G(d) optimization. Save the files with appropriate names.

Record the energy __________ Eh, 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°), and H-O-O-H dihedral angle __________° (literature 111.5°).

Close everything except the main Control Panel.

Exercise 4 Determine a Portion of the Energy Map for Cyclohexane.

Build a molecule of C_6H_{12} in the chair form by clicking the Ring Fragment icon and choosing the chair form (5th row, 4th across).



Minimize at the PM3 level and record the energy __________ Eh.

Close everything but the main Control Panel.

Build a molecule of C_6H_{12} in the twisted boat form by clicking the Ring Fragment icon and choosing the appropriate form (5th row, 5th across).

Minimize at the PM3 level and record the energy __________ Eh.

Close everything.

Which conformer is the more stable? __________ What is the energy difference between the two stable conformers? __________ kcal mol^{-1} (literature 4.0-5.5 kcal mol^{-1})