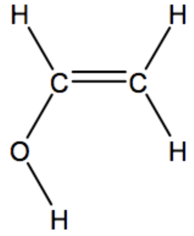
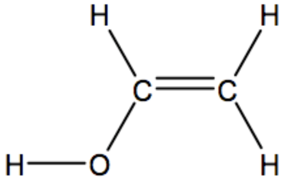
4 Single Point Energies and Geometry Optimizations

Exercise 1 Determine the Optimum Structure for Ethenol (Vinyl Alcohol).

I



II



Build a model of ethenol. One of the two structures shown will appear.

Save as vinylalc.

Select the O and C bond in your model.

Click Calculations / Dihedral Driver / Single Angle Plot.

The Dihedral Driver Chart opens. When the computation is completed, a graph is displayed showing the energy (kcal) versus the angle of rotation around the carbon-oxygen bond.

In the chart, Click on either a specific degree or energy setting and the model display rotates the dihedral to the selected conformation.

The dihedral is rotated in 5-degree increments through 360 degrees for a total of 72 conformations to produce the graph. You can view the minimized energy values for each point in the Output window or change the resolutions by right-click / Set Resolution.

Click and record the angle and the value of $\Delta_f H$ _____° __________ kcal mol^{-1}.

Move to the next frame by clicking and dragging on the chart. Repeat for all 19 frames.

Record values of angles and $\Delta_f H$:

_____° __________ kcal mol^{-1}, _____° __________ kcal mol^{-1},
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_____° __________ kcal mol^{-1}, _____° __________ kcal mol^{-1},

A plot of $\Delta_f H$ against $\angle$(HOOC) may be prepared using a spreadsheet.

Save.

Which conformer is more stable? __________

Click to the structure that corresponds to the global minimum.

Click Edit / Select All / Copy.

Close the workspace and click New.

Paste the global minimum and save as vinylalcpm3min.

Perform a geometry optimization using PM3 and record the value of $\Delta_f H$ = __________kcal mol^{-1}. (More accurate molecular parameters can be obtained using ChemBio3D as the graphical interface to Gaussian ‘03 or GAMESS.)

Save and close.

Exercise 2 Performing a Molecular Dynamics Search.

Build a molecule of hydrogen peroxide and minimize at the PM3 level.

Save as h2o2dyn.

Select the HOOH atoms to define a dihedral angle.

Click Calculations / MM2 / Molecular Dynamics. Click Job Type: Record Every Iteration and Copy Measurements to Output Box.

Click Run.

Observed the energy values in the Output Box generally become more negative as a function of the frame number.

Choose the last frame. Click Edit / Select All / Copy.

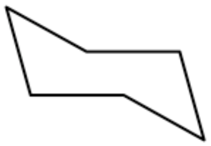
Save and close the workspace.

Click New.

Paste the global minimum and save as h2o2min.

Minimize at the PM3 level and record the value of Δ_fH = __________kcal mol^{-1}, 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°), and H-O-O-H dihedral angle __________° (literature 111.5°). (More accurate molecular parameters can be obtained using ChemBio3D as the graphical interface to Gaussian ‘03 or GAMESS.)

Exercise 3 Determine Conformers of Cyclohexane.



Build a molecule of cyclohexane. Use the Text Tool and enter CH2(CH2)5 in the text window.

Clean up the structure by clicking Edit / Select All and clicking Structure / Clean Up. The twisted boat conformer (local minimum) should appear.

Click the Atoms Label and Serial Number buttons (21st and 22nd across top) and click the arrow on the Message Window.

Minimize at the PM3 level and record the value of Δ_fH = __________kcal mol^{-1}.

Save as cyclohex.

To construct the chair conformer (global minimum), select the Move Object icon (5th across) click C(1) and drag it below the ring and click C(4) and drag it above the ring.

Minimize at the PM3 level and record the value of Δ_fH = __________kcal mol^{-1}.

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

To construct the boat conformer (one of several transition structures), click C(3) and drag it above the ring.

Click MOPAC / Optimize to Transition State / Theory: PM3 and click Run. Record the value of)$_f$H = __________kcal mol$_{-1}$. What is the energy difference between the twist-boat and the boat conformers? __________ kcal mol^{-1} (literature 1.4-1.6 kcal mol^{-1})

Close and Save.