

4 Single Point Energies and Geometry Optimizations

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

Build a model of ethenol. One of the two structures shown will appear.
Save as vinylalc.c3d.

Click View / Settings / Movie. Drag the Smoothness slider to 20° per frame. Click OK.

Click the workspace.

Select the O and C atoms. Rotate the HOCC dihedral angles by clicking on the Internal Rotation Bar at the left of the workspace and dragging.

Click Record on the Movie Controller (3rd between the workspace and the Message Window).

Double click the Internal Rotation Bar and type 360. Click Rotate.

Click Stop in the Movie Controller (2nd between the workspace and the Message Window).

Move the slider on the Movie Controller to frame 1.

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. The value of the dihedral angle can be read by holding the cursor over any of the highlighted portions of the molecule.

Click the triangle in the Message Window.

Click MOPAC / Compute Properties / PM3.

Click Run and record the angle and the value of $\Delta_r H$ _____ ° _____ kcal mol⁻¹.

Move to the next frame by dragging the slider on the Movie Controller and calculate the energy. Repeat for all 19 frames. Record values of angles and $\Delta_r H$:

____ ° _____ kcal mol⁻¹, _____ ° _____ kcal mol⁻¹, _____ ° _____ kcal mol⁻¹, _____ ° _____ kcal mol⁻¹, _____ ° _____ kcal mol⁻¹, _____ ° _____ kcal mol⁻¹, _____ ° _____ kcal mol⁻¹, _____ ° _____ kcal mol⁻¹, _____ ° _____ kcal mol⁻¹, _____ ° _____ kcal mol⁻¹, _____ ° _____ kcal mol⁻¹, _____ ° _____ kcal mol⁻¹, _____ ° _____ kcal mol⁻¹, _____ ° _____ kcal mol⁻¹, _____ ° _____ kcal mol⁻¹, _____ ° _____ kcal mol⁻¹, _____ ° _____ kcal mol⁻¹, _____ ° _____ kcal mol⁻¹, _____ ° _____ kcal mol⁻¹.

Save.

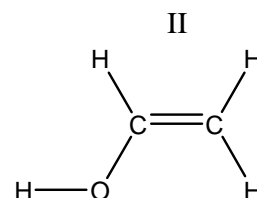
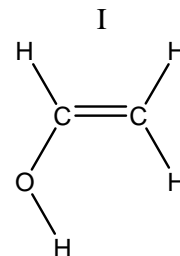
Rotation about the dihedral angle can be animated by clicking Start on the Movie Controller.

Which conformer is more stable? _____

Move the slider on the Movie Controller to the structure that corresponds to the global minimum.

Click Edit / Select All / Copy.

Close the workspace and click New Model.



Paste the global minimum and save as vinylalcpm3min.c3d.
Perform a geometry optimization using PM3 and record the value of $\Delta_r H =$
_____ kcal mol⁻¹. (More accurate molecular parameters can be obtained
using Chem3D 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 $\text{H}-\text{O}-\text{O}-\text{H}$
level.

Save as h2o2dyn.c3d.

Select the HOOH atoms to define a dihedral angle. Click Object / Set Dihedral Angle.
Click on the arrow on the Message Window.

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

Click Run.

Click Stop in the Movie Controller after a few hundred frames have been computed.

Click Start in the Movie Controller to observe the computed forms.

Observed the energy values in the Message Window 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.

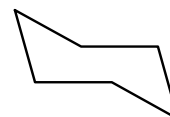
Click New Model.

Paste the global minimum and save as h2o2min.c3d.

Minimize at the PM3 level and record the value of $\Delta_r H =$ _____ 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 Chem3D 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 Tools /
Clean Up Structure. The twisted boat conformer (local minimum) should
appear.

Click the Atoms Label and Serial Number buttons (16th and 17th across top) and click
the arrow on the Message Window.

Minimize at the PM3 level and record the value of $\Delta_r H =$ _____ kcal mol⁻¹.

Save as cyclohex.c3d.

To construct the chair conformer (global minimum), 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 $\Delta_r H = \underline{\hspace{2cm}}$ 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 $\Delta_r H = \underline{\hspace{2cm}}$ 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.