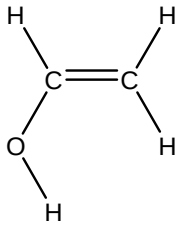
4 Single Point Energies and Geometry Optimizations

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

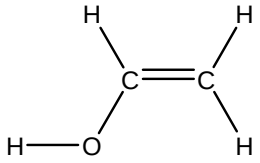
Build a model of ethenol. One of the two structures shown will appear.

I



Save as vinylalc.HIN.
Perform a PM3 optimization.
Save.
Click Select Tool.
Define a dihedral angle consisting of the H atom, the O atom, and the two C atoms. The value of the dihedral angle appears in the Status Line.
Click Compute / Potential. Enter -180, 180, 10 and click OK. After a few seconds an energy plot will appear.

II



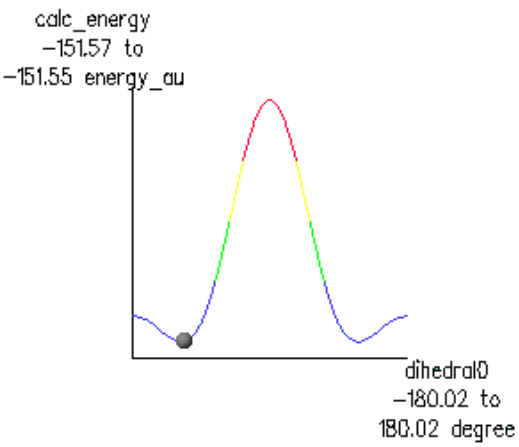
Which conformer is more stable? _____
With the dihedral angle still selected, click Build / Constrain Bond Torsion and enter the value of the angle corresponding to the global minimum. Click OK. Right click in the workspace to unselect the dihedral angle and double click the Select Tool. The structure of the global minimum appears.
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 *ab initio* calculations.)
Save and close.

Exercise 2 Performing a Molecular Dynamics Search.

Build a molecule of hydrogen peroxide and minimize at the PM3 level. Note that the dihedral angle is 180°.

Save as h2o2dyn.HIN.
Click Setup / Molecular Mechanics / MM+ and click OK (twice, if needed).
Click Compute / Molecular Dynamics. Set Heat Time to 0.1, Run Time to 0.5, Cool Time to 0.1, Step Size to 0.0005, Start Temp to 0, Simulation Temp to 1000, Final Temp to 0, Temperature Step to 30, Data Collection Period to 1 and unselect Constant Temperature.
Click Proceed. The "annealing" will take a few moments. Note that the final structure has a dihedral angle of 90° (near the global minimum).
Save.
Minimize at the B3-LYP/6-31G* level. (Note that this calculation must be run several times using the default optimization parameters and may not converge even after several hours.) 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

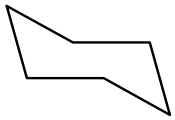
_____° (literature 100.0°), and H-O-O-H dihedral angle _____° (literature 111.5°).



Save.

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) do the two structures studied in this exercise correspond?

Exercise 3 Determine Conformers of Cyclohexane.



Build a molecule of cyclohexane. Start the hexagon at the top of the workspace and place the C atoms clockwise so that the numbering will agree with the following directions. Click Display / Labels: Number and click OK.

Double click the Select Tool to form the chair conformer (global minimum).

Rotate the model until C1 is at the head and left side of the workspace; C2, C3 are at the rear; C4 is at the foot at the right; and C5, C6 are at the front.

Save as c6h12chair.HIN.

Minimize at the PM3 level and record the value of $\Delta_f H$ = _____kcal mol^{-1}.

Save.

To construct the boat conformer (one of several transition structures), click Select and be sure Multiple Selection is checked. Double click the Selection Tool. Click on C2, C3 and C5, C6 to define a place for a reflection process. Click Select / Name Selection: Plane and click OK. Select C4, H11, H12, H13, H14, H15, H16 in addition to C3, C5, C2, C6. Click Edit / Reflect. The boat conformer appears. Unselect all atoms by right clicking in the workspace.

Save as c6h12boat.HIN.

Minimize at the PM3 level and record the value of $\Delta_f H$ = _____kcal mol^{-1}.

To construct the twisted boat conformer (local minimum), click Display and unselect Show Hydrogens. Define a dihedral angle between C1, C2, C3, C4. Click Build / Constrain Bond Torsion: Other and type in 30. Click OK. Right click in the workspace and double click the Selection Tool. A twisted boat conformer appears. Click Display / Show Hydrogens.

Save as c6h12twist.HIN.

Minimize at the PM3 level and record the value of $\Delta_f H$ = _____kcal mol^{-1}.

Close and Save.

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})

What is the energy difference between the twist-boat and the boat conformers?

_____ kcal mol^{-1} (literature 1.4-1.6 kcal mol^{-1})