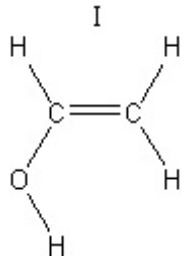
4 Single Point Energies and Geometry Optimizations

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

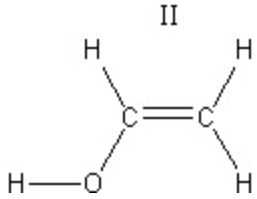
Build a model of ethenol by clicking on the build tool, clicking the add H tool to remove the H atoms, and clicking the add bond tool to change the C-C bond to a C=C bond. Click the add H tool to add the four H atoms. Click the periodic table tool, choose O and click on one of the H atoms (a red O atom should replace the white H atom). Close the periodic table and click the add H tool twice. One of the two structures of ethenol will be generated.



Minimize and Save as vinylalc.pcm.

Define a dihedral angle consisting of the two C atoms, the O atom, and the H atom by clicking the select atom tool and clicking the respective atoms.

Choose Compute / Dihedral Driver and the current angle should be visible in the dihedral driver window. Enter -180, 180, and 10 in the boxes and click OK. Save as vinylalcrot.pcm.



Record the values of the energy of conformer I _____ kcal mol^{-1}, conformer II _____ kcal mol^{-1}, and the barrier _____ kcal mol^{-1}. 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 clicking the rotate bond tool (12^{th} down, Rot-B) and clicking the arrow heads on the slide bar to the approximate dihedral angle for the global minimum energy structure. Click Exit.

Save as vinylalcmin.pcm. Perform an energy optimization and record the energy of the minimized structure _____ kcal mol^{-1}.

Save and Close.

Exercise 2 Performing a Metropolis Monte Carlo Search.

Build a molecule of hydrogen peroxide by clicking the build tool, clicking the add H tool to remove the H atoms, clicking the periodic table tool, choosing the O atom, and clicking each of the C atoms to change them to O atoms. Close the periodic table and click the add H tool. Most model builders will generate a planar molecule when "cleaning up" the structure.

Save as H2O2.pcm.

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.

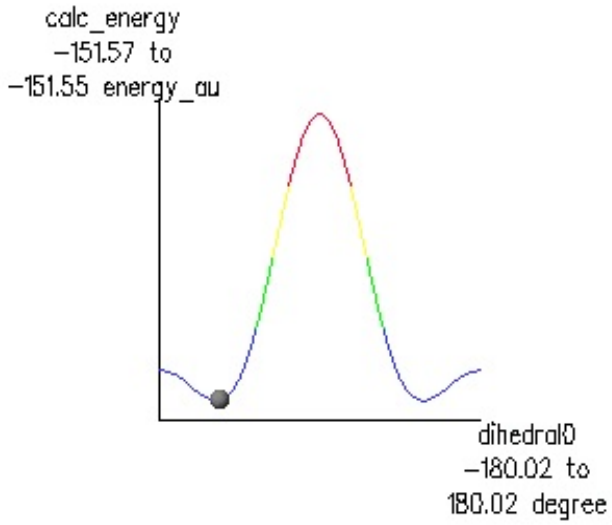
Click Compute / Metropolis MC and enter 10000 as the number of Steps and click OK.
Close the MMC Results window and click Compute / Minimize. Record the O-H bond length _____ Å (0.965 Å literature), O-O bond length _____ Å (1.452 Å literature), H-O-O bond angle _____° (100.0° literature), and H-O-O-H dihedral angle _____° (111.5° literature).
Save as H2O2MMC.pcm and Close.

Exercise 3 Performing a Vibrational Mode Search.

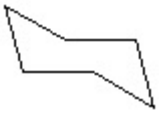
Build a molecule of hydrogen peroxide (see Exercise 2).
Click Compute / Vibrational Mode Search. Click OK. Save as H2O2vibmol.pcm. Click OK in the Smooth Run window that pops up at the end of the calculations and close the GMMX Running window.
Click File / Open and choose H2O2vibmol.pcm. Click Yes for erase, choose the last untitled structure in the list, and click OK.
Record the O-H bond length _____ Å, O-O bond length _____ Å, H-O-O bond angle _____°, and H-O-O-H dihedral angle _____°.
Save and Close.

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

Build a molecule of hydrogen peroxide (see Exercise 2). Save as h2o2flat.pcm.
Using this structure, perform a MMX minimization 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? _____
Save and Close.



Exercise 5 Determine the Energy Map for Cyclohexane.



Build a molecule of C_6H_{12} by clicking on the build tool to form CH_3CH_3, clicking on one of the H atoms to form $CH_3CH_2CH_3$, clicking on one of the end H atoms to form $CH_3CH_2CH_2CH_3$, clicking on one of the end H atoms to form $CH_3CH_2CH_2CH_2CH_3$, and clicking on one of the end H atoms to form $CH_3CH_2CH_2CH_2CH_2CH_3$. Click the add H tool to remove the H atoms and click on the draw tool. Click and drag between the end C atoms to complete the ring. Click the add H tool.

Save as cyclohex.pcm.

Minimize and Save.

Click Compute / Vibrational Mode Search. Click OK. Save as cyclohexvibmod.pcm.

Click File / Open and choose cyclohexvibmod.pcm. Choose the last structure in the list and click OK. Which structure is this? _____

Minimize and record the MMX energy _____ kcal mol^{-1}.

Continue opening the structures and identifying the shape of the molecule until a new structure is obtained. Minimize each new structure _____ and record the MMX energy _____ kcal mol^{-1}.

Click Analyze / Movie and choose the file cyclohexvibmol.pcm. By clicking Step in the Movie Player Window, each structure can be viewed on screen.

Which conformer is the most stable? _____ Calculate the energy difference between the two stable conformers _____ kcal mol^{-1} (4.0-5.5 kcal mol^{-1} literature).

Save and Close.