1 Introduction to Computational Chemistry

Start Chem3D by clicking Start / Programs / ChemOffice / Chem3D

Exercise 1 Study of H-X-H Bond Angles (suitable for general chemistry).

Structure of CH_4
Click the Text Tool (8th down).
Click in the workspace, type CH4, and hit the Enter key (CH_4 appears).
Click Trackball (Rotate) Tool (2nd down).
Click and drag both inside and outside the white circle around the molecule to rotate the molecule various ways.
Click Select Tool (1st down).
This structure contains idealized bond lengths and angles. A more accurate structure can be found by carrying out an energy minimization using molecular mechanics, semi-empirical methods, or *ab initio* calculations. To reduce the time required for the calculations and to obtain reasonable results, the semi-empirical method PM3 will be used. This method is available in most molecular modeling programs.
Click File / Save.
Navigate to c:\chem3d lab (or any suitable folder).
Save using CH4PM3.c3d.
Click MOPAC / Minimize Energy.
Choose Job Type: Minimize Energy, Theory: PM3, Properties: Heat of Formation and Gradient Norm.
Click Run.
The calculations should be completed within a second or so.
Click File / Save.
Hold the cursor midway over a C-H bond.
Record the value of the C-H bond length _____Å (1.091 Å literature).
Click on one of the H atoms and Shift and Click the C atom and one of the other H atoms (a H-C-H combination should be highlighted).
Record the value of the H-C-H bond angle _____° (109.4712 ° literature).
Close and Save the workspace.

Structure of NH_3
Click New Model (1st left, paper with turned down corner).
Build NH_3 using the above procedure.
Save the file as NH3PM3.c3d.
Perform the PM3 geometry optimization as above.
Record the value of the N-H bond length _____Å (~0.999 Å, 1.012 Å literature).
Record the value of the H-N-H bond angle _____° (~108.2 °, 106.67 ° literature).
Close and Save.

Structure of H_2O
Click New Model.
Build H_2O using the above procedure.
Save the file as H2OPM3.c3d.
Perform the PM3 geometry optimization as above.
Record the value of the O-H bond length _____Å (~0.951 Å, 0.959 Å literature).
Record the value of the H-O-H bond angle _____° (~107.7 °, 103.9 ° literature).
Save and Close.

What conclusion(s) can you make concerning the H-X-H bond angle and the number of unshared (lone) pairs of electrons around the central atom X?

Exercise 2 Study of Rotation Barrier Energy about Carbon-Carbon Bonds (suitable for organic chemistry).

Structure of Ethane, CH_3CH_3
Click New Model.
Click Single Bond Tool (4th down on left).
Click and drag in center of workspace (CH_3CH_3 appears).
Save as C2H6PM3.c3d.
Perform a PM3 optimization.
Save.
Click Select Tool.
Click one of the H atoms. Shift and click the attached C atom, the other C atom, and one of the H atoms attached to the second C atom to define a "dihedral" angle.
Click Object / Set Dihedral Angle (Measurement Table appears).
Edit the highlighted text by typing 0 and hit the Enter key (dihedral angle changes to 0°).
Click MOPAC / Compute Properties / Theory: PM3.
Click Run (the calculation will finish in a few seconds).
Click the arrow on the Message Window at the bottom to open it. Scroll up to the entry for $\Delta_f H$ and record the value for ∠(HCCH) = 0° _____kcal mol^{-1}.
Change the dihedral angle in the Measurement Table to 20°, calculate the $\Delta_f H$, and record the value for ∠(HCCH) = 20° _____kcal mol^{-1}.
Repeat the calculations for the remaining angles: 40° _____kcal mol^{-1}, 60° _____kcal mol^{-1}, 80° _____kcal mol^{-1}, 100° _____kcal mol^{-1}, 120° _____kcal mol^{-1}, 140° _____kcal mol^{-1}, 160° _____kcal mol^{-1}, 180° _____kcal mol^{-1}, 200° _____kcal mol^{-1}, 220° _____kcal mol^{-1}, 240° _____kcal mol^{-1}, 260° _____kcal mol^{-1}, 280° _____kcal mol^{-1}, 300° _____kcal mol^{-1}, 320° _____kcal mol^{-1}, 340° _____kcal mol^{-1}, 360° _____kcal mol^{-1}. (Note that the dihedral angles greater than 180° are automatically recalculated as negative values because dihedral angles usually are expressed as -180° to 180°.)

A plot of $\Delta_f H$ against ∠(HCCH) may be prepared using a spreadsheet.
Record the greatest and least values of the energy and calculate the barrier energy for rotation of the CH_3 groups around a C-C bond _____kcal mol^{-1} - _____kcal mol^{-1} = _____kcal mol^{-1} (2.9 kcal mol^{-1} literature).
Close the worksheet.

Structure of Ethene, CH_2CH_2
Click New Model.
Use the Double Bond Tool (5th down on left) to build ethene, $CH_2=CH_2$.
Save the file as C2H4PM3.c3d.
Optimize at the PM3 level and save.
Define a HCCH dihedral angle using H atoms *cis* to each other and open the Measurement Table.
Run the same calculations for $\Delta_f H$ using dihedral angles between 0° and 180°:
0° _____kcal mol^{-1}, 20° _____kcal mol^{-1}, 40° _____kcal mol^{-1}, 60° _____kcal mol^{-1}, 80° _____kcal mol^{-1}, 100° _____kcal mol^{-1}, 120° _____kcal mol^{-1}, 140° _____kcal mol^{-1}, 160° _____kcal mol^{-1}, 180° _____kcal mol^{-1}.
Does the maximum energy occur at 90°? ____ Run the calculation _____kcal mol^{-1}.
Record the greatest and least values of the energy and calculate the barrier energy for rotation of the CH_2 groups around a C=C bond _____kcal mol^{-1} - _____kcal mol^{-1} = _____kcal mol^{-1} (68 kcal mol^{-1} literature).

Close.

Exercise 3 Study of the Molecular Orbitals in Ethene, CH_2CH_2 (suitable for physical chemistry).

Click File / Open.
Choose C2H4PM3.c3d.
Click Save As C2H4surfacesPM3.c3d.
Click MOPAC / Compute Properties.
Choose Properties: Electrostatic Potential, Molecular Surfaces / Theory: PM3.
Click Run.
Save the file.
Click View / Molecular Orbitals.
Choose HOMO-5 (N=1) / Show Surface to observe the σ bonding between the C atoms (rotate structure if desired). Various presentations (wire mesh, dots, translucent) can be chosen.
Repeat for the various orbitals. The π bonding between the C atoms is HOMO (N=6) and the LUMO showing the π* antibonding is LUMO (N=7).
Click Hide Surfaces and close the Molecular Orbital Surface window.
Click View / Molecular Electrostatic Potential.

Click Show Surface (the calculations may take a few moments). The most postive MEP is red (site of electrophilic susceptibility) and the most negative MEP is blue (site of nucleophilic susceptibility).

Close and save all windows.

Exit Chem3D.