1 Introduction to Computational Chemistry

Start CAChe by clicking Start / Programs / CAChe / Workspace.

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

Structure of CH_4
Click Drawing Tool (4th down, pen connecting atoms).
Select Element Type (1st dropdown) as C (only seven choices are displayed, you may
     need to go to the periodic table).
Select Hybridization (2nd dropdown) as sp^3-tetrahedron.
Select Charge (3rd dropdown) as 0 (or blank).
Select Bond Type (4th dropdown) as Single.
Click once in center of workspace (a black C atom should appear).
Click Select Tool (1st down, arrow).
Click once in workspace away from atom.
Click Beautify / Comprehensive (4 white H atoms should appear connected to C).
Click Rotate Tool (6th down, arrow in circle).
Click and drag both inside and outside the black circle around the molecule to rotate
     the molecule various ways.
Click Select Tool.
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:\CACheUser (or any suitable folder).
Save using CH4PM3.csf.
Click Experiment / New.
Choose Property of: chemical sample, Property: optimized geometry, Using: PM3
     geometry.
Click Start. (The calculations should be completed within a second or so.)
Close the Experiment Status window and the Experiment window.
Click once in the workspace away from the molecule.
Click File / Save.
Click one of the H atoms (the other atoms and bonds with "fade").
Shift and Click the C atom (both atoms and the bond will be highlighted).
Click Adjust / Atom Distance (bond length of ~1.087 Å appears) / close by clicking "ok".
Record the value of the C-H bond length _____ Å (1.091 Å literature) / close by
     clicking "ok".
Shift and Click another of the H atoms (a H-C-H combination should be highlighted).

Click Adjust / Bond Angle (bond angle of ~109.47 ° appears) / close by clicking "ok".
Record the value of the H-C-H bond angle _____° (109.4712 ° literature) / close by
        clicking "ok".
Save and Close the workspace.

Structure of NH$_3$
Click New File (1st left, paper with turned down corner).
Build NH$_3$ using the above procedure.
Click View / Show Electrons (a lone pair of electrons on N should appear–toggle on/off
        as desired).
Save the file as NH3PM3.csf.
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).
Save and Close.

Structure of H$_2$O
Click New File.
Build H$_2$O using the above procedure.
Save the file as H2OPM3.csf.
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$_3$CH$_3$
Click New File.
Click Drawing Tool.
Select Element Type as C.
Select Hybridization as sp^3-tetrahedron.
Select Charge as 0 (or blank).
Select Bond Type as Single.
Click once in center of workspace (a black C atom should appear).
Click on the C atom, drag, and release (a second C atom should appear bonded to the
        first).
Click Select Tool.
Click once in workspace away from molecule.

Click Beautify / Comprehensive (3 white H atoms should appear connected to each C with one CH_3 group staggered by 60 ° from the other looking down the bond axis).

The molecule can be rotated if desired using the Rotate Tool.

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 Adjust / Dihedral Angle (bond angle of ±60 °, ±180 °, or ±300 ° should appear) / don't close.

Click Define Geometry Label / Search (accept default values) / close by clicking "ok".

Click once in workspace away from molecule (a blue angle indicator should be present and all atoms and bonds should be returned to normal).

Save the file as C2H6PM3.csf.

Click Experiment / New.

Chose Property of: chemical sample conformations, Property: optimized map, Using: PM3 energies (one label).

Click Start

After a few seconds the calculation is finished and two windows appear–the left window shows an energy plot as a function of the dihedral angle and the right window shows the molecule. The molecule should be in the staggered form of ±60 °, ±180 °, or ±300 °. The left window shows the potential energy surface for rotation around the C-C single bond. Choose the dropdown window at the bottom of the left window and choose calc_energy.

Click (or use an arrow key) one of the tops of the energy curve (red part of the curve) and the molecule should change to the eclipsed form of 0 °, ±120 °, ±240 °, or 360 °.

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).

Save and Close all windows.

Structure of Ethene, CH_2CH_2

Click New File.

Build ethene, $CH_2=CH_2$ (use sp^2 trigonal plane C atoms with double bond) and define a dihedral angle.

Save the file as C2H4PM3.csf.

Run the same experiment using the search label between 0° and 180°.

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).

Does the maximum energy occur at 90°? _____ What happens above 127°? _____

Save and Close.

Exercise 3 Study of the Molecular Orbitals in Ethene, CH$_2$CH$_2$ (suitable for physical chemistry).

Click File / Open.
Choose C2H4PM3.csf.
Click Save As C2H4ORBPM3.csf.
Click Experiment / New.
Choose Property of: chemical sample, Property: all molecular orbitals, Using: standard procedure (MOPAC/PM3).
Click Start.
Close the Experiment Status window and the Experiment window.
Save the file.
Click Analyze / Show Surfaces.
Choose an orbital, click "ok", observe orbital (rotate structure if desired, clicking the orbital will make it "solid").
Repeat for the various orbitals.
The σ bonding between the C atoms is .MO1, the HOMO showing the π bonding between the C atoms is .MO6, and the LUMO showing the π* antibonding is .MO7.
Click Experiment / New.
Choose Property of: chemical sample, Property: electrophilic susceptibility, Using: standard procedure (MOPAC/PM3).
Click Start.
Close only the Experiment window.
Choose Property of: chemical sample, Property: nucleophilic susceptibility, Using: standard procedure (MOPAC/PM3).
Click Start.
Close only the Experiment window.
Choose Property of: chemical sample, Property: radical susceptibility, Using: standard procedure (MOPAC/PM3).
Click Start.
Close the Experiment Status window and the Experiment window.
Click Analyze / Show Surfaces.
Choosing .EFonD will show the electrophilic susceptibility, .NFonD will show the nucleophilic susceptibility, and .REonD will show the radical susceptibility. Once the surface is "solid", choose Analyze / Legend for an interpretation of colors. Various presentations (dotted, wire frame, sliced) can be obtained by choosing Analyze / Surface Attributes.
Save and close all windows.

Exit CAChe.