1 Introduction to Computational Chemistry (Spartan)

Start Spartan by clicking Start / Programs / Spartan Then click File / New

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

Structure of CH_4
Using the 'Entry" level builder, click on the sp^3-hybridized C atom (first row, first column).
Click in the workspace. The CH_4 skeleton appears.
Click on the "View" icon (5^{th} across top).
Rotate by left clicking and dragging.
Rotate in the plane of the screen by Shift left clicking and dragging.
Translate by right clicking and dragging.
Zoom by Shift right clicking and dragging vertically.
Choose Setup / Calculations. Choose Equilibrium Geometry at Ground State with Semi-Empirical PM3.
Click Submit. Save as ch4pm3.spartan in an appropriate folder.
Click "OK" to started message and "OK" to completed message.
Click on the Distance icon (11^{th} across the top) and on a C-H bond. Record the C-H bond length (lower right corner of screen): _____ Å (1.091Å lit.).
Click on the Angle icon (12^{th} across top) and click on the H, C, H atoms (the order is important). Record the H-C-H bond angle: _____ º (109.4712º lit.).
Save and Close the file.

Structure of NH_3
Click New File (1^{st} icon at left at the top; paper with turned down corner).
Click on the sp^3-hybridized N atom (first row, second column).
Click in the workspace. The NH_3 skeleton appears.
Click on the "View" icon.
Choose Setup / Calculations. Choose Equilibrium Geometry at Ground State with Semi-Empirical PM3.
Click Submit. Save as nh3pm3.spartan in an appropriate folder.
Click "OK" to started message and "OK" to completed message.
Click on the Distance icon (11^{th} across the top) and on a N-H bond. Record the N-H bond length: _____ Å (1.012Å lit.).
Click on the Angle icon (12^{th} across top) and click on the H, N, H atoms (the order is important). Record the H-N-H bond angle _____ º (106.67º lit.).
Save and Close the file.

Structure of H_2O
Click New File (1^{st} icon at left at the top; paper with turned down corner).
Click on the sp^3-hybridized O atom (second row, third column).
Click in the workspace. The H_2O skeleton appears.
Click on the "View" icon.
Choose Setup / Calculations. Choose Equilibrium Geometry at Ground State with Semi-Empirical PM3.

Click Submit. Save as h2opm3.spartan in an appropriate folder.
Click "OK" to started message and "OK" to completed message.
Click on the Distance icon (11th across the top) and on an O-H bond. Record the O-H bond length: _____ Å (0.959Å lit.).
Click on the Angle icon (12th across top) and click on the H, O, H atoms (the order is important). Record the H-O-H bond angle _____ º (103.9º lit.).
Save and Close the file.

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 the Rotation Barrier Energy about Carbon-Carbon Bonds (suitable for organic chemistry)

Method A: *Structure of Ethane, CH_3CH_3*
Click New File.
Using the "Entry" level, click on the sp^3-hybridized C atom (first row, first column).
Click in the workspace (the methane skeleton appears).
Click again on the end of one of the yellow "valences" (the staggered ethane skeleton appears).
Click on the "view" icon.
Choose Setup / Calculations. Choose Equilibrium Geometry at Ground State with Semi-Empirical PM3.
Click Submit. Save as stagethanepm3.spartan in an appropriate folder.
Click "OK" to started message and "OK" to completed message.
Click Display / Output. Scroll down and find the Heat of Formation towards the bottom. Record the value here _____ kcal mol^{-1}.
Close the output window.
Save and Close the file.
Click New File
Draw Ethane as instructed above, but DO NOT click the "view" icon. You should have a red "rotation arrow" on the C-C bond.
Rotate (left click and drag) until you are looking down the C-C bond (Newman projection).
Hold down the "Alt" key, place the cursor *well away* from the molecule, left click and drag until the completely eclipsed form of the molecule is produced.
Rotate so the molecule is viewed side-on ($\perp$ to the C-C bond).
Click Constrain Dihedral (18th across the top). Click on the atoms H-C-C-H so that the two H's are the ones which eclipse one another. With these four atoms highlighted, click on the "lock" icon in the lower right corner. (The numeric display should read 0.00º. If it does not, adjust it now and hit "enter" on the keyboard).
Choose Setup / Calculations. Choose Equilibrium Geometry at Ground State with Semi-Empirical PM3, Subject to Constraints.
Click Submit. Save as eclipethanepm3.spartan in an appropriate folder.
Click "OK" to started message and "OK" to completed message.
Click Display / Output. Scroll down and find the Heat of Formation towards the bottom. Record the value here _____ kcal mol^{-1}.

Close the output window.
Save and Close the file.
To calculate the barrier to rotation about the C-C bond, subtract the staggered value from the eclipsed value, and enter the result here _____ kcal mol^{-1} (2.9 kcal mol^{-1} lit.).

Method B: *Structure of Ethane, CH_3CH_3*

Click New File.
Build a molecule of ethane as instructed above., and click on the "View" icon.
Choose Geometry / Constrain Dihedral.
Click on H, C, C, H atoms so that the two H's are *anti* (180º apart).
Click on the pink "unlocked" icon in the lower right of the screen to lock it. (The numeric display in the lower right corner should read -180.00º).
Choose Display / Properties. If needed, move the "Selected" style box from in front of the molecule.
Zoom in on the molecule (Shift-Right click and drag vertically) and click on the pink constraint marker that appears on the midpoint of the C-C bond.
Click the "Dynamic" box in the Constraint Properties window.
Edit the second "value" box to 0.00º (YOU MUST HIT RETURN TO MAKE THIS CHANGE).
The top line should read Value: -180.00º to 0.00º.
Change "Steps" to 37 (YOU MUST HIT RETURN TO MAKE THIS CHANGE).
Close the Constraint Properties box.
Choose Setup / Calculations. Choose Energy profile at Ground State with Semi-Empirical PM3.
Click Submit. Save as C2H6PM3.spartan in an appropriate folder.
Click "OK" to started message and "OK" to completed message. (The calculation takes several seconds).
Save and Close the file.
Choose File / Open / C2H6PM3.Profile1
Choose Display / Spreadsheet.
Click on the Molecule001 cell to highlight it.
Click on the gray box in Column 2, Row 1 (top box) to highlight it.
Click Add / rel. E (relative energy). Click "OK".
To add the angles to the spreadsheet, choose Geometry / Measure Dihedral.
Click on the pink constraint marker on the C-C bond.
Click on the yellow "P" box in the lower right of the screen.
Choose Display / Plots. Choose X Axis / Dihedral(Con1) and Y Axes / rel. E (kcal/mol). Click "OK".
To find the two angles where the energy is a minimum and a maximum, use the "advance" and "reverse" buttons on the bottom left. The corresponding angle and energy will be highlighted in the spreadsheet. Record the maximum energy: _____ kcal mol^{-1} and minimum energy: _____ kcal mol^{-1}.
To calculate the barrier to rotation about the C-C bond, subtract the maximum value from the minimum value, and enter the result here _____ kcal mol^{-1} (2.9 kcal mol^{-1} lit.).
Pressing the "Play" button (▸) at the bottom of the screen will animate the bond rotation.
Save and Close the file.

Structure of Ethene, C_2H_4

Click New File.

Using the "Entry" level, build a molecule of ethene.

Click on the "View" icon.

Choose Geometry / Constrain Dihedral.

Click on H, C, C, H atoms so that the two H's are *trans* (180º apart).

Click on the pink "unlocked" icon in the lower right of the screen to lock it.

Choose Display / Properties. If needed, move the "Selected" style box from in front of the molecule.

Zoom in on the molecule (Shift-Right click and drag vertically) and click on the pink constraint marker that appears on the midpoint of the C=C bond.

Click the "Dynamic" box in the Constraint Properties window.

Edit the second "value" box to 0.00º (YOU MUST HIT RETURN TO MAKE THIS CHANGE).

The top line should read Value: 180.00º to 0.00º.

Change "Steps" to 37 (YOU MUST HIT RETURN TO MAKE THIS CHANGE).

Close the Constraint Properties box.

Choose Setup / Calculations. Choose Energy profile at Ground State with Semi-Empirical PM3.

Click Submit. Save as C2H4PM3.spartan in an appropriate folder.

Click "OK" to started message and "OK" to completed message. (The calculation takes some time).

Save and Close the file.

Choose File / Open / C2H4PM3.Profile1

Choose Display / Spreadsheet.

Click on the Molecule001 cell to highlight it.

Click on the gray box in Column 2, Row 1 (top box) to highlight it.

Click Add / rel. E (relative energy). Click "OK".

To add the angles to the spreadsheet, choose Geometry / Measure Dihedral.

Click on the pink constraint marker on the C=C bond.

Click on the yellow "P" box in the lower right of the screen.

Choose Display / Plots. Choose X Axis / Dihedral(Con1) and Y Axes / rel. E (kcal/mol). Click "OK".

To find the two angles where the energy is a minimum and a maximum, use the "advance" and "reverse" buttons on the bottom left. The corresponding angle and energy will be highlighted in the spreadsheet. Record the maximum energy: _____ kcal mol^{-1} and minimum energy: _____ kcal mol^{-1}.

To calculate the barrier to rotation about the C=C bond, subtract the maximum value from the minimum value, and enter the result here _____ kcal mol^{-1} (68 kcal mol^{-1} lit.).

Pressing the "Play" button (▸) at the bottom of the screen will animate the bond rotation.

Save and Close the file.

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

Click New File

Click on the sp^2-hybridized carbon atom (second row, first column).

Click in the workspace.
Click again on the small sphere at the tip of the double bond.
Click on the "View" icon.
Choose Setup / Calculations. Choose Equilibrium Geometry at Ground State with Semi-Empirical PM3, Print Orbitals and Energies.
Click Submit. Save as ethenepm3.spartan in an appropriate folder.
Click "OK" to started message and "OK" to completed message.
Choose Setup / Surfaces and Click Add.
In the Add Surface Dialog box, choose Surface HOMO, Resolution Medium, then Click "OK".-
Click Add again, choose Surface LUMO, Resolution Medium, then click "OK".
(If desired, other MO's could be chosen by choosing HOMO-1, HOMO-2, LUMO+1, etc.).
Close the Surfaces window.
Click Setup / Submit.
Click "OK" to started message and "OK" to completed message.
Choose Display / Surfaces and check the yellow box next to HOMO.
If it is in front of the molecule, move (by dragging) the "Surfaces" window.
Rotate the molecule to observe the π-orbital.
In the "Surfaces" window, uncheck the yellow box next to HOMO, and check the yellow box next to LUMO.
If needed, move the "Surfaces" window away from in front of the molecule.
Rotate the molecule to observe the π^*-orbital.
Choose Setup / Surfaces and Click Add.
In the Add Surface Dialog box, choose Surface Density, Property None, Resolution Medium, then Click "OK".
Click Add, choose Surface Density, Property Potential, Resolution Medium, then click "OK".
Click Add again, choose Surface Density (bond), Property None, Resolution Medium, then click "OK".
Click Add again, choose Surface Density (bond), Property Potential, Resolution Medium, then click "OK".
Close the Surfaces window.
Click Setup / Submit.
Click "OK" to started message and "OK" to completed message.
Click Display / Surfaces. The Surfaces window displays four densities, two of them with the property "potential". The different numbers in the "Isovalue" column represent the electron density in units of electrons/au^3. Click in the yellow box to view the electron density at an isovalue of 0.002. The volume roughly correlates to the common "space filling" view of molecules, and is an indication of molecular size (click on Model / Space Filling for comparison). Uncheck the first yellow box, and click the second one to view the electrostatic potential mapped onto the electron density. Red indicates (-) and blue indicates (+) charge. The other isovalue of electron density (0.08) shows a smaller surface (greater electron density), and better indicates the location of the bonding electrons.
Save, Close, and exit the program.