CHEM 6485: Molecular Mechanics Lab

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1 Introduction

This short lab will give you some hands-on experience with Spartan and molecular mechanics methods. We will use the "MMFF" force field built into Spartan. Your goal is to plot the torsional angle potential energy curve for two molecules, butane ($CH_3CH_2CH_2CH_3$) and 2-butanone ($CH_3CH_2COCH_3$). We are interested in the central C–C torsion in each molecule. In a nutshell, the procedure is as follows: start up Spartan, draw one of the molecules, optimize the geometry (writing down the results), and step the torsional angle from 0 to 180° in 20° increments, recording the energy for each point. Repeat the process for the other molecule. Plot your results to obtain a torsional potential curve for each molecule, and analyze the results as requested.

2 Using Spartan

2.1 Drawing Molecules

Drawing in Spartan is quite easy and somewhat similar to that in ChemDraw. Feel free to experiment with this part, it is easy to start over or to delete wrong atoms or groups. We will begin by drawing trans-butane. Under the `File` menu, select `New`. This will bring up the drawing pallete on the right-hand side of the screen. By default, the `Groups` option should be set to `Alkene`, which is perfect for our present purposes. Also, the default group should be sp^3 carbon. If not, select the tetrahedral carbon icon.

Left-click anywhere on the blue/green background field filling most of the screen. A tetrahedral carbon should appear. Off of one of its yellow free bonds, click another tetrahedral carbon. Continue this process until you have four carbons in a trans arrangement (dihedral 180°). When you are finished, go to the `Build` menu and select `View`. This will remove the drawing pallete and automatically add hydrogens to free bonds.

2.2 Geometry Optimization

Next, we need to optimize the geometry of the molecule. Go to the menu called `Setup`, and select `Calculations`. A dialog box with many options will appear. The first two boxes should say `Equilibrium Geometry` at the `Ground` state. If not, change them so that they do. Now make the next two boxes say `Molecular Mechanics` and `MMFF`. This will tell the program to do a molecular mechanics calculation with the MMFF force field, and not an ab initio or some other kind of computation. Since butane is a neutral molecule with a closed-shell, singlet ground state, `Total Charge` should be `Neutral`, and `Multiplicity` should be `Singlet`.

Once all of the options are set correctly, select `Submit` in the lower right hand of the dialog box. If you missed this and hit `OK` instead, then you can select `Submit` from the `Setup` menu. Hit the `Submit` button to make the calculation start running. At this point, a `Save As` file selector will appear. It is a good idea to make a new folder (if it doesn't exist) called `CHEM8843` to keep your files in, so they don't clutter the desktop. In that folder, make a name for your calculation, like butane, and hit `Save`. The program will then tell you that the calculation has started. Sometimes these calculations run for a while, so the program does it "in the background" while letting you continue to rotate or view your molecule. When the calculation is done, the program will inform you. If you ever get confused about whether a calculation is running or not, go to `Options` in the upper right hand corner, and select `Monitor`, which will show all running calculations.

Once your optimization is complete, you will have the MMFF best guess for the equilibrium geometry of your molecule. At this stage, you should confirm that the dihedral angle is at 180°. Do this by selecting the dihedral angle measurement tool from the toolbar near the top of the screen. It looks like a question mark with two diagonal lines coming out of it — the third icon with a question mark on it (the other two are measure distance and measure bond angle). Now click the four carbon atoms in a row, starting at one end and going to the other end of the molecule. In the lower right corner, the torsion angle is displayed. Type 180 in the box if it isn't 180, and hit enter.

At this stage, please use the measure distance tool (a question mark with two horizontal lines coming out of it) to measure the length of the three C–C bonds, and record this information for later use in your writeup.

2.3 Torsional Potential

Now you are ready to build an energy profile as the torsion is changed from 0° to 180°. Select `Constrain Dihedral` from the `Geometry` menu (this is the same as the little icon with a lock with two diagonal lines coming out of it). Click on the four carbon atoms, in turn, to define the dihedral angle to constrain. Now click on the open lock icon in the lower right corner of the screen.

The bottom right corner of the screen should now say "Constraint(C1,C2,C3,C4)=180" and the lock icon should now show a closed lock to indicate that the constraint is applied. There is now a pink zigzag icon around the middle C–C bond; this is a graphical representation of the constraint you have applied.

To allow a series of possible torsions, and not just 180°, select `Display` and then `Properties`. This will bring up a dialog box with currently irrelevant information. Click on the zigzag constraint icon around the middle C–C bond. The property dialog box should now be titled "constraint properties." Check `Dynamic` to allow the constraint to change to other values. Now the program lets you type in starting and ending values and how many steps to take. *This dialog box is very annoying; you MUST hit enter after changing any of the values!* Tell the program to go from 180° to 0° in 10 steps. (I had some trouble trying to go the other way, from 0° to 180°). Close the Constraint Properties window by hitting the close-window X icon in the upper right corner. Now the program knows you want to do a series of calculations for different values of the CCCC torsion angle.

To do the different calculations, go to `Setup` and select `Calculations`. Next to `Calculate`, select `Energy Profile`. Make sure the other options are still set to molecular mechanics with the MMFF force field. Now hit the `Submit` button. The program will tell you that the job has started. Wait for a minute or two, and then the job should complete. At this stage, you want to quit looking at the single geometry and look at your series of 10 geometries/energies. Select `File`, `Close` to close out your starting geometry (save it first if you wish, in case something goes wrong). Now go to `File`, `Open`, and look for your filename, but now with a `Profile1` in it (because you just did an energy profile calculation). Click on that file to load all ten geometries and their energies. When you do, one of the series of geometries will be displayed. The other geometries are also present but are not immediately displayed. You can look through all the geometries by using the forward and backward buttons on the bottom left part of the screen. The program sometimes picks strange geometries for this example as you go across the range of values. If you get something odd-looking, stop here and re-do the last part.

We can make the cycling through different geometries look a little nicer if we align three of the carbon atoms to be in the same place on the screen in all of the geometries. We can do this using the `Align` tool, which is near the right side of the top toolbar, represented graphically by three vertical red wavy lines. Click on this icon, and then click on three of the carbon atoms in turn, starting from the left. Now click on the word `Align` in the bottom right corner. Now cycle through the geometries again, and you will observe that they are all lined up except for one methyl group which rotates. This is easier to view!

Now we can use a very nifty feature of Spartan, it's built-in spreadsheet and graphing capabilities. Bring up a spreadsheet by selecting `Display` and spreadsheet. You may need to drag the edges of the box to make it bigger. Click on `Molecule 001` and then click on the cell to the right of it. Click `Add` at the bottom of this window to add a column here. Select `rel. E` (relative

energy), in kcal/mol. This will give you the relative energies of all the different conformations you looked at. They should range from 0-5.2 kcal/mol. Now click on the box two to the right of `Molecule001` to add another column. Go to the top toolbar and select the `Measure Dihedral` icon (the question mark with two diagonal lines coming out of it). Click the four carbon atoms in turn to select the CCCC torsion. Now click the yellow "P" button in the lower right corner. This will transfer all the torsion angles into the spreadsheet. They should go from 180 to 0 in 20° increments. Note that 180° is the same as -180°. However, having -180° would mess up our nice spreadsheet and graph (later). If you have -180°, replace it with 180° in the spreadsheet. You must hit return to make it take. Very small roundoffs should not be a problem.

Make a record of the torsional angles and relative energies for use in your writeup. Two digits after the decimal is sufficient.

At this stage, you could graph the data yourself using Excel or other software. However, let's try using Spartan's built-in graphing capabilities. Select `Display`, `Plots`. Set the X axis to be the dihedral angle, and the Y axis to be the relative energy. A very nice graph should appear which plots your data and has squares at each data point. It also keeps a display of the molecule on the screen. Clicking on the forward/backward buttons on the lower left should allow you to cycle through the geometries, as before, but it will also advance a ball which indicates which datapoint on the graph you are on. This makes it very easy to understand the graph!

3 2-butanone

To compare different torsional potentials, **now repeat the above procedure for a new molecule, 2-butanone**, $CH_3CH_2COCH_3$. Consider again the CCCC torsion.

4 Data Analysis

- Report your equilibrium bond lengths for bonds not involving hydrogen.
- For each molecule, report your force field energies for each value (every 20°) of the central C–C torsional angle considered; two digits after the decimal should be sufficient.
- Plot the force field energies as a function of torsional angle for each molecule.
- Draw Newman projections for the 0, 60, 120, and 180 conformers of each molecule.
- Compare the torsional curves for each molecule. Using chemical intuition and ideas about torsional potentials, steric effects, and van der Waals interactions, explain the qualitative features of the potential energy curve for each molecule.