

## Conformational Analysis of *n*-Butane

In this exercise you will calculate the Molecular Mechanics (MM) single point energy of butane in various conformations with respect to internal rotation around the C<sub>2</sub>-C<sub>3</sub> bond and generate Excel charts of steric energy vs. dihedral angle. You will decide which factor contributes most to the total steric energy of each conformation. You should review the principles of alkane conformational analysis in an organic textbook before beginning this exercise.

### *Generating the Data in Chem3D*

1. Either open a structure drawing of *n*-butane or build a model in Chem3D. A very easy way to build a model is to click the Text Building Tool in the Tools palette and type CH3CH2CH2CH3. Save the model.

Very likely, when you first see this simple molecule it will already be close to its **global minimum energy conformation**. You already know that this lowest energy conformation has staggered C-C and C-H bonds throughout the molecule with the C1-C2 bond *anti periplanar* to the C3-C4 bond. Use a rotation tool to see if your model is in the (almost) global minimum energy conformation.

*Note:* To follow these directions, it is important that Chem3D assigns the carbon numbers 1-4 to an uninterrupted sequence of the four carbon atoms. If they are not, use the Help Index and read about "Serial Numbers, tutorial example".

Open the Output box and Measurements table windows.

2. Perform an MM2 Energy Minimization (**geometry optimization**). Accept all default values in the calculation window. There will most likely be some slight changes in the model after optimization. See "Geometry Optimization" in the "Molecular Modeling with Chem3D" document. Save the file.
3. Rotate the *n*-butane model so that you are looking down the C2-C3 bond, slightly offset from a straight line view so that you can see all the carbon atoms and the bond between C2-C3. (See illustration on the next page.) Choose **Structure | Measurements | Generate all Dihedral Angles** from the menu. [See the Figure on a following page.]

Find the C1-C2-C3-C4 dihedral angle in the Measurements window and click in the Atoms box to select all four carbon atoms in the model. (Check the box on the left if you want the dihedral angle to be displayed in the model window.)

*Note:* If the dihedral angle is not 180 degrees (or  $-180$ ), follow the instructions below for changing the dihedral angle.

In the **Actual** column, change the angle to 180.00 (or -180.00). You should see the model respond. Calculate a new **single point energy** for this slightly changed angle (*DO NOT optimize, just calculate*). See “Single Point Energy Calculation” in the “Molecular Modeling with Chem3D” document.

This is now the starting point for the conformational analysis. It might be helpful to delete any other messages in the message Output box except for the one you just generated above as the starting point.

*Note:* Any time you want to delete measurements or messages in the other windows, select the text and press Delete or Ctrl X.

The screenshot displays the Chem3D Ultra software interface for a butane molecule. The main window shows a ball-and-stick model of butane with yellow carbon atoms and white hydrogen atoms. A 'Rotation Dial' window is open, showing a circular scale with markings at 0, -90, +90, and 180. A green arrow points to the 180.0 mark. Below the dial are buttons for X, Y, Z, and other rotation options. The 'Measurement' window is open, showing a table of dihedral angles. The 'Actual' column for the C(1)-C(2)-C(3)-C(4) dihedral angle is highlighted and set to 180.0000. The 'Output' window at the bottom shows a 'Total' energy of 2.1736.

	Display	Atoms	Actual
1	<input type="checkbox"/>	C(2)-C(3)-C(4)-H(13)	60.1466
2	<input type="checkbox"/>	C(2)-C(3)-C(4)-H(14)	-60.1466
3	<input type="checkbox"/>	C(2)-C(3)-C(4)-H(12)	180.0000
4	<input type="checkbox"/>	H(11)-C(3)-C(4)-H(13)	-61.2617
5	<input type="checkbox"/>	H(11)-C(3)-C(4)-H(14)	178.4452
6	<input type="checkbox"/>	H(11)-C(3)-C(4)-H(12)	58.5918
7	<input type="checkbox"/>	H(10)-C(3)-C(4)-H(13)	-178.4452
8	<input type="checkbox"/>	H(10)-C(3)-C(4)-H(14)	61.2617
9	<input type="checkbox"/>	H(10)-C(3)-C(4)-H(12)	-58.5918
10	<input type="checkbox"/>	C(1)-C(2)-C(3)-C(4)	180.0000
11	<input type="checkbox"/>	C(1)-C(2)-C(3)-H(11)	-58.7780
12	<input type="checkbox"/>	C(1)-C(2)-C(3)-H(10)	58.7780
13	<input type="checkbox"/>	H(9)-C(2)-C(3)-C(4)	58.7780
14	<input type="checkbox"/>	H(9)-C(2)-C(3)-H(11)	180.0000

Output  
Total: 2.1736

4. You are now going to change the C1-C2-C3-C4 dihedral angle by 30-degree increments and calculate the steric energy after each rotation until it has been rotated through 360 degrees.

Change the dihedral angle in the Actual column in the Measurements window to 150. Press Enter. If it says -150, it doesn't matter.

Calculate a **single point energy**. *DO NOT minimize the energy*. See “Single Point Energy Calculation” in the “Molecular Modeling with Chem3D” document.

Now change the angle to 120 (or -120 if the Actual column showed -150 previously). Calculate a single point energy.

Repeat the above steps, changing the rotation angle each time by 30 degrees until you reach -150° (or 150°, depending on the direction of the rotation). At each rotation, calculate a single point energy. The next step would be -180°, which will be equal to 180° and you’ve now rotated through the entire 360°. Confirm the internal rotations by looking at the dihedral angle in the Measurements window.

- If you scroll in the Output Box, you’ll see the repetitive energy calculations after each rotation.
- Keep track of the actual dihedral angle in the Measurements window. Sometimes the sign of the rotation changes – it doesn’t matter as long as you don’t change the direction of the rotation. You can “undo” the last operation by pressing Ctrl-Z.
- *Periodically save the file* in case you make an error. Otherwise, you will have to start over. After finishing the entire 360-degree rotation, save the file as *butane-XXX.c3xml* where XXX are your initials.

### ***Manipulating the Data in Excel***

5. In this step, you are going to copy the energy data from Chem3D and paste it in an Excel workbook.

Press **^A** while in the Chem3D Output box (selects all), then press **^C** (copy). Select a cell in Excel and press **^V** (paste). Sometimes (!?) the descriptors and numerical data appear in two adjacent columns. Other times, all the message window output will be in one column. If so, convert the **Data | Text to columns...** in Excel (try the colon as a delimiter). Delete the **content** of the rows concerning parameter quality and “The steric energy for...”. (Don’t delete the rows themselves – they act as visual spacers.) Name the worksheet “Raw Data”.

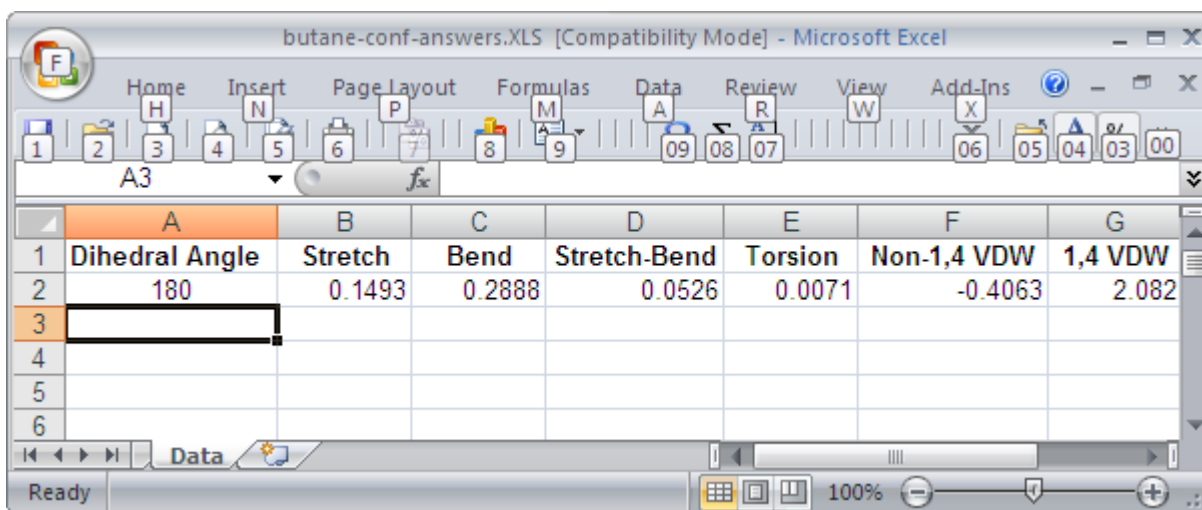
6. Activate a *new worksheet* in the Excel workbook. Name the worksheet “Data”. Beginning in a cell in column A, type in the column headings **Dihedral angle**, **stretch**, **bend**, etc. for each of the energy terms corresponding to the message output. Adjust the column widths to accommodate the headings.

In column A, beginning with 180 degrees, fill in the dihedral angles by 30-degree increments (use the auto-fill feature). Your C1-C2-C3-C4 dihedral angles as measured in Chem3D will vary

from 180 (-180) to 0 to -180 (180). In the end, you'll have covered all 360 degrees starting at 180 and ending at -180.

7. Select the column range of energy data corresponding to the 180 degree dihedral angle in the "Raw Data" worksheet (the first single point energy measurement). Copy it. In the "Data" worksheet, click in the cell in column B corresponding to the dihedral angle (B2 in the sheet shown below). From the menu choose **Home** tab | **Paste** | **Transpose**.

Continue transposing each range of single point energy data from the first worksheet into a row corresponding to the dihedral angle in the second worksheet. (I wrote a small macro to perform the above menu choices more quickly.)



8. You now have all the data you need to plot the energy changes ( $y$ ) as a function of dihedral angle ( $x$ ).

Make two charts **as separate sheets**: one chart for only the total steric energy vs. dihedral angle and the other chart for all the individual component energy terms vs. dihedral angle. For the latter, plot each energy term vs. dihedral angle as a separate series on the same chart. Be sure to include a legend on the chart.

Choose a Chart Type that draws a smooth curve between visible data points. Your dihedral angle axis should run from 180 to -180 degrees with 30 degrees as the major unit (no minor unit). The y-axis major unit should be 1 kcal/mol and the minor unit 0.5 kcal/mol. The y-axis should cross the x-axis on the far left side of the plot. The x-axis should cross the y-axis at 0. Name the chart sheets.

*Remember to include all the elements of good graphing in your chart.* The legend should appear within the chart area; chart title; axis labels and units; no gridlines.

## *Analyzing the Results*

9. Write several paragraphs in Word that explain the Purpose, Method (computational software used and “theory”; procedure (that is, how did you go about this assignment), and Results of this assignment. Use headers to separate the sections.

In your discussion, make sure it is apparent to the reader that you have read the assigned sections of an Organic Chemistry textbook on conformational analysis of alkanes. The document should read much like a lab report.

As part of your discussion of Results, incorporate the answers to these questions:

1. Which conformation(s) is/are the global minimum, the local minima, and the highest energy conformation?
2. As the conformation changes from the lowest to the highest energy, which component terms change the most? Which change the least? Explain what changes in the structure during rotation from the lowest to the highest energy is causing the largest increases in energy.
3. Explain how the steric energy associated with the 1,4-van der Waals and non-1,4 van der Waals terms changes with the dihedral angle during the rotation. Give an example of a 1,4- and non-1,4-van der Waals interaction in a conformer.

Make it clear you understand what each of these terms is, especially the 1,4- and non-1,4 van der Waals terms, and how they differ from each other. There is an example using these terms in the *cis*- and *trans*-2-butene exercise.

Copy the text from Word and paste as a Word Object in Excel in a new worksheet page named “Discussion”. *The text might not all show on the worksheet.* Copy the butane model (not the entire Chem3D window) from Chem3D and embed it in this worksheet.

Publish the Excel workbook as an HTML file (non-interactive) on your web site in a new directory named “*butane*”. Link the page to your Chem 350 projects page with a descriptive title.