Computational Chemistry Lab Module: Conformational Analysis of Alkanes

Introduction

In this experiment, we will use CAChe software package to model the conformations of butane, 2-methylbutane, and substituted cyclohexanes.

Conformational isomers (or in short conformations or conformers) are a result of rotation around a single bond (such as in butane and 2-methylbutane) or that of “ring flip” (cyclohexanes). In this experiment, we will use CAChe to build the models of these compounds and calculate the energy of many conformations of each compound. Theoretical discussion of conformational analysis can be found in Wade’s Chapter 3, sections “Conformations of Butane” and “Cyclohexane Conformation”. Introduction to theoretical molecular modeling using computer software can be found in the lab manual (page 63) and Chapter 29 of Pavia’s book.

The following step-by-step procedure is provided for you to follow in the lab:

(Please DO NOT write on this handout as it will be used by other sections)
Experimental Procedure
Part 1:

1. click “Start”, “Programs”, “CAChe”, then “Workspace”, release the mouse button
2. The CAChe program should run and the window will look like the following:
Note that at the bottom of the desktop there are two programs running “CAChe” and “CalcMgr”. Never close “CalcMgr” while CAChe is running.

3. We will now build a molecule with the built-in editor. To do this, click on the icon:

Notice the default properties (atom, hybridization, charge, and bond order) in the following picture:

![Atom Properties](image)

Now click on the screen in the empty window to place a carbon (sp$^3$) there. Click on the middle of the first carbon atom and drag to a new location the mouse button pressed down. A carbon-carbon bond has just been made. Continue to make new bonds until butane molecule is built. Note the last atom placed on the screen is highlighted, which means it is selected. Further operations (such as change to a different element, etc.) will only affect the selected atoms or bonds. For our purpose, we want to select the entire molecule for further operation. To do that click on the selection tool:

![Selection Tool](image)

and then click on an empty space anywhere in the window. This selects the entire molecule (highlighted).

The screen now looks similar to the following:

![Molecule](image)

4. Beautify the molecule (add hydrogens, clean up the bond angles, etc.) by clicking on the
The bottom tool (magnifying glass) allows for enlargement or shrink of the molecule. The hand allows for movement, and the curved arrow allows for rotation of the molecule as the whole. Try them out!

5. Rotate the molecule so that you are viewing it from its side (with zig-zag carbon chain going from left to right on a horizontal plane). We will now learn how to measure the property of the molecule (bond angle, length, and dihedral angle). To measure bond length, pick the selection tool (straight arrow) and click on the middle of an atom. This highlighted it. Now hold the shift key down while selecting a second atom. The two atoms are now highlighted. To find out the bond length, click “Adjust” on the menu and then “Atom Distance”. To leave the distance unchanged, click cancel to return to the editing window. To measure bond angle, select three connected atoms in sequence and “Adjust” “Bond Angle”.

Dihedral angle is a term used to describe the angle between two planes (like holding two pieces of paper at an angle). In a molecule, we need four connected atoms (in sequential order) to define a dihedral angle. Go ahead and select four carbons in sequence (from left to right in this case, of course you can do it from right to left but not from the middle!). The first plane is defined by the selected carbon 1, 2 and 3. The second plane is defined by carbon 4, 3, and 2. In this case the angle between the two planes is 180°. You can also find the value by clicking on “Adjust” “Dihedral Angle”.

Try these operations before continue.

6. We will now select the dihedral angle defined by one H on the carbon #2, carbon #2 itself, carbon #3, and one H on the carbon #3. So go ahead and select those four atoms. Now rotation the molecule so that you are viewing down the carbon#2-carbon#3 bond. The screen looks like:
7. Note that changing this defined dihedral angle would actually be equivalent to spinning around the C2-C3 bond. Convince to your lab partner that this is indeed the case.

We are now ready to ask the program to change the dihedral angle incrementally (which yields many conformations) and calculate the energy of each conformation and plot it as a graph. (this is called conformational analysis). To do that, click on “Adjust” “Dihedral Angle”. Check on “Define Geometry” then “Search” and type in “using 36 steps”. Click on OK to return to the editing window. Note a geometry search label (blue lines) has been placed on the four atoms selected. You can see the animated change in dihedral angle by clicking “Adjust” “Animate Geometry Label”.

8. Save the molecule by clicking “File” “Save “ and give it a name such as butane-yourinitial.

9. Click on “Experiment”, “New”, select “Chemical Sample Conformations” in the “Property of” field, “Optimized map” in the “Property” field, and click start button. The program starts to calculate the optimized energy (lowest) of each conformation by varying the dihedral angle. At the end of the calculation, two small windows are presented: the energy diagram on the left and the molecular structure on the right. Change “dihedralAngle1” in the first window to energy. Now click on the small arrows (see picture below) in the right window to step through each conformation:

![Image of energy diagram]

Note as you step through each conformation, the left window is updated to reflect the energy associated with that conformation as well as its position on the energy diagram. You can still rotate the molecule in the right window to view it from a different angle. Record the following before closing windows:

1) Which conformation has the lowest energy? Write down the energy and draw the structure of the conformation in your lab notebook. (you will learn the correct way of drawing Newman projection of conformations in the lecture)
2) Repeat these measurement for each valley and peak point in the energy diagram. You will need these values and structures for the lab report. Make a table to display these values, with Newman projection structure of each conformation, the dihedral angle H-C2-C3-H of each conformation, the calculated relative energy of each conformation, and the relative energy level given in Chapter 3 of Wade for each butane conformation.

10. Close all the windows and answer “yes” to any questions. Now let the other partner build a molecule of 2-methylbutane (methyl group off the second carbon) and repeat the above procedure. Again you need to draw all structures and write down energy values for each point of valley and peak.
Part 2:
In this part of the lab, we will build molecules of cyclohexane and substituted cyclohexane and calculate their relative energies.

1. Build a molecule of cyclohexane. Beautify it with comprehensive mode. Rotate the molecule and answer these questions:

   1) how many different kinds of C-H bonds are there in this molecule?
   2) Rotate the molecule so that you are looking from the top of the carbon framework. If we now treat the “hexagon” (not really a hexagon) as the steering wheel, what is the angle we have to turn before we see the same geometry again?

The next exercise involves building two molecules and calculate their energies. Each partner takes turn doing this and record information in each notebook.

2. Build two versions of 1-methylcyclohexane as separate files (not in the same window!). (the first version with CH3 pointing straight up or down—axial position, and second version pointing side way—equatorial position). Save them as different names.

3. Calculate their energies by doing the following: choose “Experiment”, “New”, and choose “MM geometry (MM2)” in “Using:” field. Let the calculation finish and record the energy associated with each structure. What is the difference in energy value? Which one is more stable (i.e. methyl on the axial or equatorial)?

4. Return this handout to your instructor and show the results to your instructor before leaving. Type up the lab report with:

   1) date of this experiment
   2) Title of this experiment
   3) Name
   4) Section
   5) Purpose of the experiment
   6) answers to all the questions in this handout.

This handout will be emailed to you or placed on the web for you to download.