Molecular Modeling and Computational Chemistry – Substituted Cyclohexanes and Butanes

Reading: Based on Experiment 19C in Pavia (5th edition), Essay *Molecular Modeling and Molecular Mechanics* (p. 106-164). Klein (3rd edition), Chapter 4, especially Sections 4.7 and 4.12, and Tables 4.6 and 4.8.

Overview

Physical molecular models (Maruzen, Molymod, Princeton, etc.) are useful not only to see the overall structure of a molecule, but also to visualize the interaction of neighboring groups which lead to steric strain. Alternatively, using a computer and a molecular mechanics program, the geometry and energy of molecules can be estimated – the degree of accuracy depends roughly on the computational power of the computer, which determines the length (in terms of time) of the calculation. Importantly, the energies of different conformations of the same molecules can be calculated and compared to known literature values.

In this experiment you will use Spartan Student (v7) to calculate the energies of various conformations of methylcyclohexane, 2-methylbutane, and 2,3-dimethylbutane. Each calculation will minimize the geometry of the select conformation using the so-called *Hartree-Fock* method and the *6-21G** basis set. You will also use traditional model sets to compare and visually inspect each conformation in addition to comparing the results with predictions from simple conformational analysis (from Chapter 4 in Klein).

Prelab

Include the usual entries, **Name**, **Title**, and **Purpose**. Also, in your notebook, draw each of the conformations mentioned in the projects below. Draw all cyclohexanes in the standard chair notation (no boats) and the butane conformations using Newman projections. All of the diagrams should be clearly labelled as indicated below. Leave ample space next to each figure or Newman projection to record the obtained values for each calculated energy.

> *List of diagrams needed:*
> methylcyclohexane chairs, one with axial an methyl group and the other with an equitorial methyl
> 2-methylbutane, both unique staggered conformations, one has a single gauche interaction, the other has two gauche interactions
> 2,3-dimethylbutane, both unique staggered conformations - on

Procedure

Project 1 – methylcyclohexane
Using the model kit, build methylcyclohexane and "flip" the model between both chair conformations where the ethyl group is *axial*, then *equitorial*. Assess which chair conformation is more stable by considering steric and/or torsional interactions – these conformations should match what is shown in your notebook.

Build the *axial* and *equitorial* conformations on Spartan Student (v7). Minimize the energy of each using the Equilibrium Geometry, Hartree-Fock, 6.21G* settings (see below for instructions). Record the output energy for both chairs next to each chair diagram in your notebook. (The energy is in units of *hartrees* and is always a negative value. You will convert to kJ/mol later)

Project 2 – 2-methylbutane
Build a model of 2-methylbutane and rotate the central bond to observe the two unique staggered conformations. Note which ones are different in energy and note the source of the differences by tallying the strain present in each.

Build the two unique staggered conformations in Spartan. Minimize the energy of each using the Equilibrium Geometry, Hartree-Fock, 6.21G* settings. Record the output energy next to the appropriate Newman projection in your notebook.

Project 3 – 2,3-dimethylbutane
Build a model of 2,3-dimethylbutane and rotate the central C2-C3 bond to "observe" the two unique staggered conformations – one with the "gauche" hydrogens and the other with the "anti" hydrogens – label them as such. Note the view down the C2-C3 bond of the model and compare to the Newman projections in your notebook.

Build both of these conformation in Spartan. Minimize the energy of each using the Equilibrium Geometry, Hartree-Fock, 6.21G* settings.

Building Structures

Using Spartan Student (v7), for **Project 1** start by selecting **Build New** under the **File** menu.
Click the **Rings** button and select **Cyclohexane**, then double-click the left mouse button in the main window to produce a cyclohexane (see screen shot below).

Use the mouse keys (or trackpad) to move and rotate – hold the left mouse button and drag to rotate in 3D; hold the right mouse button and drag to move across the screen. Scroll the mouse button to move closer or farther. Select an sp^3 carbon (upper left blue button) and add a carbon by clicking on an axial or equitorial hydrogen of the cyclohexane ring. Add more carbons as necessary the same way. Use the delete button (left button below) if you make a mistake. Click the **Minimize** button (right button below with E) after adding each carbon.
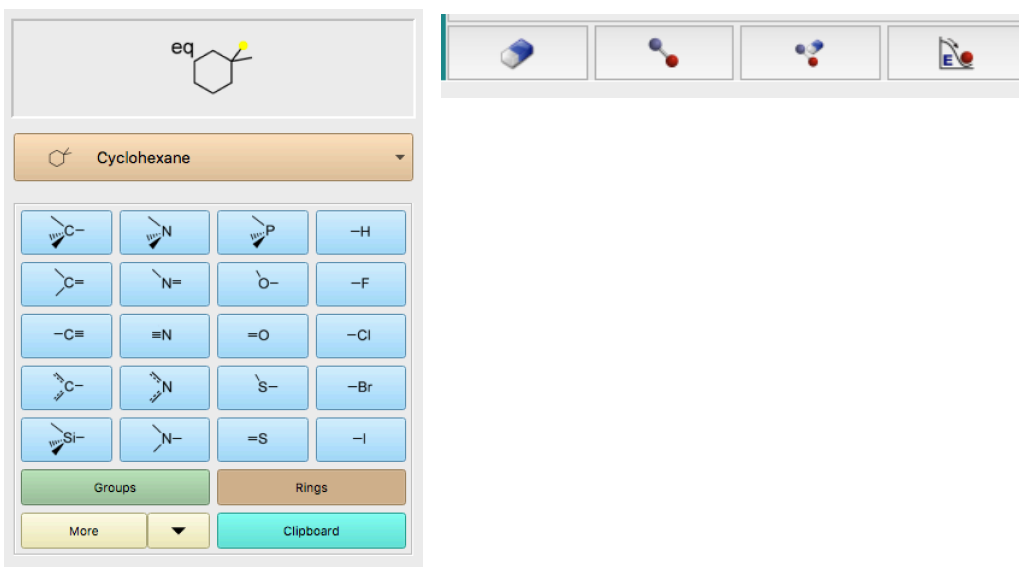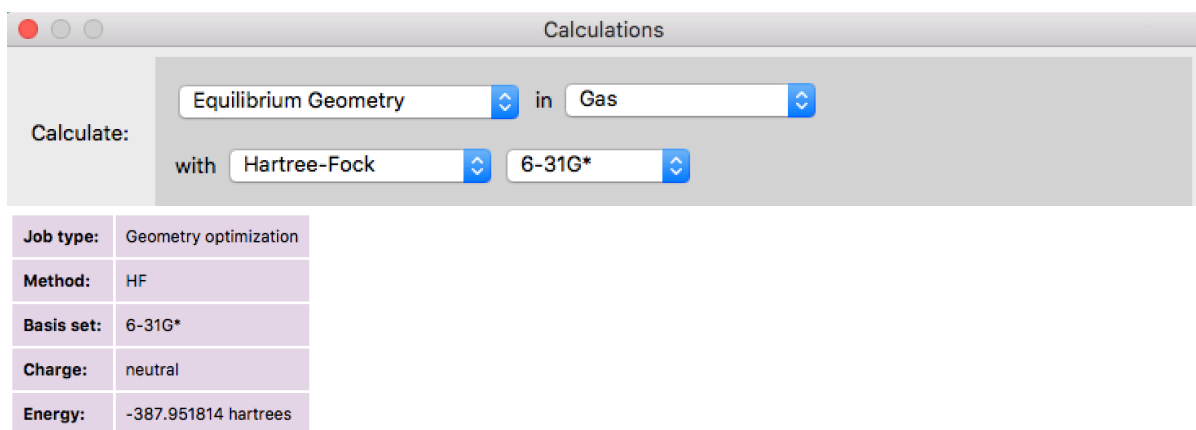
Save the file with a descriptive file name (e.g., axial methylcyclohexane). Each conformation will need a separate file name. Once you have made the first cyclohexane derivative you can delete and add carbons to produce the next structure and save with a different file name by using the Edit Build menu item.

For **Projects 2** and **3**, select **New Build** under the **File** menu, and select the sp^3 carbon button. Double-click in the main window to show the first carbon, then add carbons in sequence by clicking on hydrogens. Note that if you select the appropriate hydrogens you can easily generate the desired staggered conformations. Once you have generated the first structure and have minimized the energy, save the file with a unique name, then you can save again under a new file – select **Edit Build** under the **Build** menu and adapt the structure by deleting a carbon and adding another to generate the other staggered conformation.

Performing Calculations

While the conformation file of interest is open, do the following:

   a. Under the **Setup** menu, choose **Calculations**
   b. In the calculate dialog box, select Equilibrium Geometry, Hartree-Fock, and 6-21G* as shown below.
   c. Click the **Submit** button (if you haven't saved the file, it will prompt you for a file)
   d. Once the calculation is complete, the program will alert you, then under the **Display** menu, select **Output**.
   e. Record the calculated Energy in your notebook, and always add the negative sign. (see the example output file below)

Job type:	Geometry optimization
Method:	HF
Basis set:	6-31G*
Charge:	neutral
Energy:	-387.951814 hartrees

To Complete the Experiment (partial report)

For **Project 1**, calculate the difference in energy between the two chair conformations of methylcyclohexane in units of *hartrees*. Note that since the value of the calculated energy for each conformation is negative in sign, the larger the negative value, the more stable it is - calculate the absolute value of the difference. Convert the energy units to kJ/mol (1 hartree = 2625.5 kJ/mol). Calculate the expected equilibrium between the two chairs at room temperature (25 C) using the standard formula, ΔG = -RTlnK_{eq}. Compare the result to the known (literature) value for the 1,3-diaxial interaction of a methyl substituent, which can be found in Table 4.8 in Klein.

Similarly, for **Project 2**, calculate the energy difference between the two staggered conformations and convert to units of kJ/mol. Also, using the data in Table 4.6, predict which of the staggered conformations of 2-methylbutane is the most stable (note that the only interactions in the staggered conformations are gauche

interactions) and calculate the difference in energy between them. How does this compare to the result calculated using Spartan?

For **Project 3**, as above calculate the difference in energy between the two staggered conformations of 2,3-dimethylbutane in *hartrees*, then convert the answer to kJ/mol. Using the data in Table 4.6, predict which of the staggered conformations of 2,3-dimethylbutane is the most stable (note that the only interactions in the staggered conformations are gauche interactions) and calculate the difference in energy between them. Which of the two staggered conformations is predicted to be the most stable according to the results from Spartan?

Calculate the expected equilibrium between the two unique staggered conformations (note that there are two identical staggered conformations) at room temperature (25 C) using the standard formula, ΔG = -RTlnK_{eq}.

The experimentally determined equilibrium ratio of the two staggered conformations is actually 1:2 anti/gauche. How does this compare to your results above?

Final Summary of Tasks:
1. Using Spartan results, calculate the difference in energy between the two chairs of methylcyclohexane (report results in kJ/mol)
2. Compare to the value in Table 4.8
4. Calculate K_{eq} for the equilibrium between the two chairs
3. Using Spartan results, calculate the difference in energy between the two staggered forms of 2-methylbutane
5. Compare to the difference in energy calculated from the data in Table 4.6
8. Calculate the difference in energy between the two staggered conformations of 2,3-dimetylbutane.
9. Compare to the difference in energy calculated from the data in Table 4.6
10. Determine the equilibrium distribution of the staggered conformations using data from Table 4.6
11. Compare/reconcile the result with the experimental ratio data for these conformations

Summarize the results from all three projects as your final **Conclusion**. Include the required cover page and attach all copies of the notebook pages at the end to complete this experiment.

How to obtain Spartan Student (v7):

Visit the following website and download the student version. Click at this link.
(or copy this address into your browser - https://store.wavefun.com/product_p/spstudent.htm)
Use discount code "LANEY25" to get the $25 discounted price.