

## Learning from Molecular Models I - Non-Cyclic Alkanes

Textbook Reference - Klein Chapter 4.6-4.8, Mohrig Chapter 8

### Overview

Molecular models can be very helpful for the 3-D visualization of organic molecules. The models can be manipulated (for example, bonds can be rotated) in order to mimic the types of dynamic processes the actual molecules undergo.

Computer molecular modeling programs are not as helpful with the visualization of molecules because the display is two dimensional. However, these programs can use computational methods such molecular orbital theory or molecular mechanics to predict quantitative information including bond angles, torsion angles, total energy, and distances between atoms.

In this lab you will use molecular models in conjunction with Avogadro molecular modeling software to discover and learn about some of the most important concepts that allow us to predict the most stable conformation(s) of an organic molecule.

### Pre-lab Assignment

Download Avogadro from the Avogadro website (<http://avogadro.cc/>) and install the program on your laptop.

### Some Important Definitions

**Conformation** - A particular molecular structure that is arrived at through single bond rotation. Different conformations of a molecule are easily interconverted by single bond rotation(s).

**Conformer** - A conformation of a molecule that corresponds to a potential energy minimum for the molecule. Only conformers will have lifetimes appreciably longer than a molecular vibration (about  $10^{-14}$  s). All other conformations can be considered as transition states for bond rotation.

**Strain** - Any interaction in a structure that causes it to have a higher potential energy is called strain. The difference in potential energy between any particular conformation and the lowest energy conformer of the same molecule is a measure of the amount of strain that conformation possesses.

**Molecular mechanics** - A computational method that allows the relative energies of different conformations of a molecule to be approximated. (Note the terms "relative" here. The energy of a structure calculated using molecular mechanics **only has meaning when compared to similarly calculated energies for other conformations of the same molecule.**) Molecular mechanics is based on the same basic principles that chemists use

qualitatively to judge conformation stability.

**Geometry Optimization** – Also referred to as “Energy Minimization”, is the process of finding the lowest energy conformations (the conformers) of a molecule. By design, the algorithms used for geometry optimization, avoid changing the molecule in a way that even temporarily increases the energy. For this reason, they are not guaranteed to find the overall lowest energy conformation of a particular structure (the “global minimum”). Read more about global versus local minima in the lab manual reading assignment.

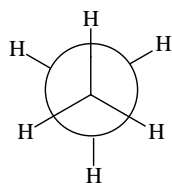
## PROCEDURES

Make all models both with your model kit and on your computer in Avogadro. See <https://avogadro.cc/docs/getting-started/drawing-molecules/> for an introduction on how to build molecules in Avogadro. (Complete “cookbook” instructions on how to use Avogadro throughout this experiment would be very difficult to put in writing and counterproductive. You need to get a feel for how to use this program both for this lab and for future experiments.)

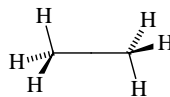
When using the kit make sure to use tetrahedral carbon atoms (the black balls with 4 holes!)

### Conformations of Ethane

**Staggered Ethane.** Construct a model of ethane,  $\text{CH}_3\text{-CH}_3$ . Look straight down the C-C bond and rotate it until the C-H bonds in front exactly bisect the H-C-H angles of the back carbon. You now have a model of the staggered conformation of ethane. This structure can be represented on paper in a number of ways, including wedge-dash formulas and Newman projections (see next page).



Newman projection



Wedge/Dash formula

The Newman projection sights straight down the bond with the bonds off the front carbon represented by the three lines that meet in the middle of the circle. The bond off of the back carbon are represented by the lines that end at the edge of the circle. Practice drawing Newman projection and wedge/dash structures of staggered ethane in the space below.

The angles between groups around the outside of a Newman projection describe stages of rotation of the bond being depicted and are termed “dihedral” or “torsion” angles.

What are the torsion angles between Hs in staggered ethane? \_\_\_\_\_

*In Avogadro, use the Build tool to connect two carbons two each other. The program automatically adds the hydrogens and the resulting ethane model is already in the staggered conformation. The model can be rotated around in space using the left, right, up, down arrows on the keyboard and it can be resized using the middle scroll wheel of a computer mouse (or use left click and drag while depressing the Shift key). The left, right, up, down arrows will move the molecule from side to side or top to bottom if the control key is first held down. You can also use the Manipulate tool to rotate the molecule around in space (left click and drag) and move it from side to side (right click and drag).*

*Use the Auto Optimization tool to optimize the structure. Select the force field as MMFF94 and click start. When the optimization is complete record the minimized energy (these values are in kJ/mol). Click stop or the program will immediately try to optimize when you make further changes to the molecule later.*

**Eclipsed Ethane.** Rotate the C-C bond  $1/6^{\text{th}}$  of a turn ( $60^\circ$ ) so that all of the C-H bonds are lined up. You now have a model of the eclipsed conformation of ethane.

*In Avogadro you can rotate the C-C bond of your ethane model using the Bond Centric Manipulation tool. Click on the bond, then use the left, right, up, down keys to rotate the model so that you are looking straight down the C-C bond (i.e., Newman projection view) and then click and drag on one of the Hs to rotate the bond.*

Draw Newman projection and wedge/dash depictions of eclipsed ethane in the space below.

What are the torsion angles between Hs in eclipsed ethane? \_\_\_\_\_

*Before you optimize eclipsed ethane you need to tell the program to not rotate the C-C bond. (What happens if you forget this step?) This is done through the Extensions menu. First click on the Display Settings button and select the box for “labels”. The result is that every atom in your structure is now numbered. Then go to Extensions, Molecular Mechanics, Constraints. In the box that opens, set Type = Torsion Angle and Constraint Value = 0.00 (eclipsed). Then fill in the atom indices with the labels of four atoms (H-C-C-H) sequentially (i.e. from left to right). Remember to click the Add button. Close the box and use Extensions, Optimize Geometry followed by Extensions, Molecular Mechanics, Calculate Energy to get the total energy for the molecule.*

## Eclipsed vs Staggered Ethane.

Which conformation is strained and how much strain does it possess? \_\_\_\_\_

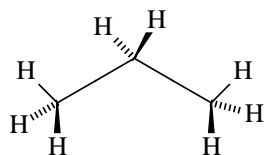
Think about the underlying assumption behind VSEPR theory and try to come up with an explanation for where this strain comes from. Explain below.

Use the space below to sketch a graph of relative potential energy versus the torsion angle). Start with the eclipsed conformation (torsion angle =  $0^\circ$ ) and go through one full rotation ( $360^\circ$ ). Indicate on the graph where each conformation would be found.

Which conformation of ethane can properly be referred to as a conformer? \_\_\_\_\_

## Conformations of Propane

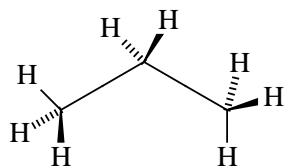
**Staggered Propane.** Remove a hydrogen from the ethane model and add a  $\text{CH}_3$  group in its place. You now have a model of propane. Rotate each of the C-C bonds so that both of these bonds are staggered. A wedge/dash formula of the model should look like the figure below.



Staggered propane

In the space to the right of the above wedge/dash formula draw a Newman projection that represents this conformation of propane. Represent the extra methyl group simply by " $\text{CH}_3$ ". (Note - the Newman projection should look the same regardless of which C-C bond you sight down.)

**Eclipsed Propane.** Rotate one of the C-C bonds in this model so that it is now eclipsed. It should look like the figure below.



Eclipsed propane

In the space to the right of the above wedge/dash formula draw a Newman projection that shows the conformation around the eclipsed bond.

*In Avogadro, add a carbon to your ethane model and you have propane. Using procedures analogous to those described above for ethane obtain minimized energies for both the fully staggered conformation and the eclipsed conformation. Make sure all geometry optimizations are carried out with the same force field, MMFF94.*

Staggered energy \_\_\_\_\_ Eclipsed Energy \_\_\_\_\_

**Eclipsed vs Staggered Propane.** Sketch a graph of energy versus torsion angle for one of the C-C bonds in propane. (Assume the other C-C bond stays staggered.)

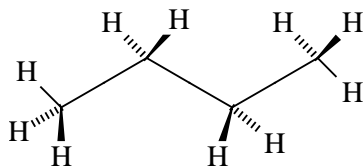
Which propane conformation is strained and by how much? \_\_\_\_\_

What is a reasonable explanation for this strain? \_\_\_\_\_

Which conformation of propane is a conformer? \_\_\_\_\_

### Conformations of Butane

Make a model of butane. Rotate each of the C-C bonds so that they are all staggered and the two end CH<sub>3</sub> groups are opposite each other. A wedge/dash formula of the model should look like the figure below. This model represents the “**anti**” conformation of butane. We will also refer to it as conformation **A**.



At left below, draw a Newman projection that shows the conformation of the bond between the center two carbons (use "CH<sub>3</sub>" to represent each of the end carbons).

Energy                    **A**                    **B**                    **C**                    **D**  
\_\_\_\_\_

Now rotate the center C-C bond 60°. This is conformation **B**. Draw a Newman projection of this conformation in the appropriate location above and record the energy.

Rotate the center bond another 60° to give conformation **C**. This model represents the **gauche conformation** of butane. As before, draw a Newman projection and record the energy.

Rotate the center bond another 60°. This is conformation **D**. Once again, draw a Newman projection and record the energy.

Rotate the center bond another 60°. Is this a new conformation of butane or is it the same as one of those already examined?

Rotate the center bond another 60°. Is this a new conformation of butane or is it the same as one of those already examined?

Rotate the center bond another 60° and what do you have? \_\_\_\_\_

*In Avogadro, add a carbon to your propane model to get butane. Using procedures analogous to those described above for ethane obtain minimized energies all four conformations (A-D). Record the energies in the provided spaces under the Newman projections you drew above.*

*Also record the minimized torsion angles between the methyls in the gauche and anti conformations and label those in the above Newman projections. To find these, use "View", "Properties", "Torsion Properties" and find the CCCC torsion angle in the table that pops up. Alternatively, you can use the Measure tool and select the 4 carbons in order that define the torsion angle and the angle (labeled as "dihedral angle") will be displayed as a message at the bottom of the window.*

Sketch a graph of energy versus torsion angle for the central C-C bond in butane.

Which butane conformations are strained and by how much? \_\_\_\_\_

Which conformation(s) of butane is(are) conformer(s)? \_\_\_\_\_

The instructor will discuss the generally accepted explanation for the relative energies of the butane conformations.

### **Conformations of some other Compounds**

Now make models of and then draw a Newman projection of the gauche and anti conformers around the C3-C4 bond of each of the following compounds. Use the concepts learned from ethane, propane, and butane to predict approximate relative energies of each conformer.

*Also calculate minimized energies for all of these using Avogadro and record these energies alongside the Newman projections.*

pentane

2 -methylpentane

2,2-dimethylpentane

Make a model of 2,3-dimethylbutane. Look at the C2-C3 bond. There are two conformers of nearly equal stability for this molecule. Draw a Newman projection of each. Which one do you think is lower in energy and by how much should it be lower? Draw Newman projections below that explain why?

*Test your answer above using the MMFF94 force field in Avogadro. If the calculations are at odds with the answer you gave above suggest an explanation. (Looking at the torsion angles between methyl groups could provide some insight here.)*

**More Questions - Answer these in the form of a lab report with Results Tables and Results and Discussion sections.**

1. Compare the difference in energy between the eclipsed and staggered conformations of ethane to that of propane. Explain.
2. Make a table that shows the individual strain interactions calculated in this lab alongside those given in Table 4.6 on p 164 of Klein. (Show all calculations in the attachments.) How do the molecular mechanics results compare to the values given in Klein? Propose explanations for any significant differences.
3. Make a table or chart that compares the difference in energy (i.e., the strain) between the *gauche* and the *anti* forms of butane (C2-C3), pentane (C3-C4), 2-methylpentane (C3-C4), and 2,2-dimethylpentane (C3-C4). Describe the trend seen and attempt to elucidate the factors that explain it through careful observation of molecular models of these compounds.

(Hint: all of these molecules are of the form, Me-CH<sub>2</sub>-CH<sub>2</sub>-R with butane having R = Me, pentane having R = Et, 2-methylpentane having R = i-Pr, and 2,2-dimethylpentane having R = t-Bu).

Methyl = "Me" = CH<sub>3</sub>

Ethyl = "Et" = CH<sub>3</sub>CH<sub>2</sub>

Isopropyl = "i-Pr" = (CH<sub>3</sub>)<sub>2</sub>CH-

*tert*-butyl = "t-Bu" = (CH<sub>3</sub>)<sub>3</sub>C-

4. Discuss and explain the relative stabilities of the 2,3-dimethylbutane conformers.