

Molecular Modeling and Conformational Analysis with PC Spartan

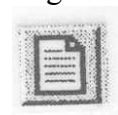
Introduction:

Molecular modeling can be done in a variety of ways, from using simple hand-held models to doing sophisticated calculations on supercomputers. Because of the rapid advances in personal computer speed made in the last several years, relatively good molecular modeling can be done on an inexpensive PC. Molecular modeling allows for the visualization and manipulation of molecules real and imagined. In this exercise you will build models of a number of simple organic molecules and investigate their conformations and relative stabilities.

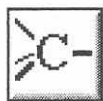
The instructions below will guide you through the process of building ethane and determining the bond angles, bond distances, dihedral angles, and relative energies of the conformations of ethane.

Procedure:

1. *Click* on the **Start** button, then *click* on **Programs** and finally *click* on **Spartan Student V3.1.2**. Spartan's window will appear with a menu bar across the top of the screen. Below the menu bar, several icons will also appear. You may either use the menu bar or the icons to build your molecules.
2. *Click* on the word **File** in the upper left corner of the screen and then *click* **New**. To do the same process, you may simply *click* the following icon:



3. A new screen will appear that contains several parts. The left side of the screen is the work area where molecules can be built and changed. The right side is the **Model Kit** which contains a variety of common pieces of molecules. We will use this panel to create molecules, minimize the energies of these molecules, and analyze their structures.
4. We will begin by creating a molecule of ethane.



Click the left mouse button once on the tetraivalent carbon or sp^3 atom (see above, it may already be selected, in which case continue), then *click* anywhere on the window in the middle of the screen to place the sp^3 carbon atom in the builder screen. If you *click* and hold down the left mouse button, you can rotate the image. If you *click* and hold down the right mouse button, you can move the image about the screen.

- To add a second sp^3 hybridized carbon to the original carbon atom, *click* the left mouse button on any of the yellow unfilled valences on the carbon atom (note: be sure that you are still selecting a tetravalent carbon atom). You should now have a working skeletal structure for ethane on your screen.
- Rotate the carbon atoms around so that all six of the unfilled valences are visible.
- Add hydrogens to each of the unfilled valences by *clicking* the left mouse button on the hydrogen button in the Model Kit (on the right hand side of the screen), then *clicking* the left mouse button on each of the six yellow unfilled valences in the work area. Congratulations! You have just built your first molecular model.
- You are now ready to put the molecule in the lowest energy conformation and make calculations faster. To do this, *click* on **Build** and then *click* on **Minimize**. Alternatively, you can *click* the following icon to minimize the molecule:



In the lower right hand corner, an output box will appear listing a preliminary energy value. (You may need to move the screen up to view this box.) Do not record this value.

- To view the molecule, *click* on **Build** and then *click* on **View**. Alternatively, you may *click* the following icon:



The image shown should be very close to the lowest energy conformation of ethane (staggered). Note that the Model Kit should no longer be on the screen.

- To calculate and display the relative energy of the staggered conformation of ethane, *click* **Setup** and then *click* on **Calculations...** A new screen will appear. The upper left option should be **Equilibrium Geometry**. The upper right box will have the default option Hartree-Fock/3-21G. *Click* on the triangle next to this box and choose **Molecular Mechanics**. (Molecular mechanics is a simpler calculation program than Hartree-Fock. If you use Hartree-Fock, your calculations might take several minutes to compute.)

Finally, *click* on the **Submit** button at the bottom of the dialog. Before the calculations can start, you will need to supply a name for the file which will be created to save your data. **Be sure to save you data on the desktop under My Documents. Ask you instructor if you do not know how to designate this location.** For you file name, type in stag_eth (or any reasonable file name you choose). Do not change the file type. *Click* on **Save**.

11. A screen will appear which will state that the calculations have started. *Click* OK.
12. When the calculations are completed, a new screen will appear which states this. *Click* OK.
13. To bring up your data, *click* on **Display** and then on **Properties**. A new window will open which has the calculated relative energy for the staggered conformation of ethane. Record the Energy of the molecule in Table I. Note: we are not concerned with the actual value of the Energy. Rather, we will be comparing the Energy of the staggered conformation to the Energy of the eclipsed conformation. This **difference of energies** is what we will be comparing to the textbook values.. You will work with the eclipsed conformation beginning with step #21.
14. You can now investigate the structure of the staggered conformation of ethane. Start by measuring the distance between one of the hydrogens and the carbon to which it is attached. Begin by moving the molecule around so that both a hydrogen and the carbon to which it is attached are visible. *Click* the left mouse button on **Geometry** (menu bar at the top of the screen) and then choose **Measure Distance**. Determine the distance between the carbon and hydrogen atoms by *clicking* the left mouse button the hydrogen atom, and then on the carbon atom. At the bottom right hand corner of the screen, an output box will appear indicating the distance. (Note again that you may need to move the screen upward to view the output box.) Record this value in Table I. Alternatively, you can simply *click* the left mouse button on the bond between any two atoms to determine the distance.
15. To determine the C-C bond distance, you can simply *click* on the bond and the distance between these two atoms will appear in the output box. Record this value in Table I.
16. To determine the distance between two hydrogens attached to different carbon atoms, *click* on the two hydrogens that are closest to each other. Note that you may need to rotate the molecule to determine which hydrogens are closest to each other. Record this value in Table I.
17. To determine the angle of a hydrogen-to-carbon-to-hydrogen (H-C-H) connection, *click* the left mouse button on **Geometry** and then choose **Measure Angle**. Select the three atoms (H-C-H) using the left mouse button and record the H-C-H angle in Table I. Be sure that you select the atoms in the correct sequence (i.e. H followed by C followed by H: **Don't** click on C followed by H followed by H).
18. Using the same procedure as in step 17, measure the C-C-H bond angle and record your result.

19. To measure the dihedral angle, *click* the left mouse button on **Geometry** and then choose **Measure Dihedral**.
20. Start by rotating the ethane molecule so that you can see all of the atoms. (None of the atoms should overlap). *Click* the left mouse button on any one of the hydrogen atoms, then the carbon to which that hydrogen is attached, then the carbon to which the first carbon is attached to, followed by the hydrogen attached to the second carbon. The dihedral angle should now be displayed in the output box. The dihedral angle is the angle between two hydrogens that you choose when the ethane molecule is viewed in such a way that the two carbon atoms overlap each other (recall the Newman projection). You can rotate the ethane molecule so that you are looking down the C-C bond to verify this. Record the dihedral angle in Table I. Note that depending on the order in which you choose your atoms, you might get a dihedral angle with a negative value. If you select the atoms in the opposite direction, you will get a positive value. You may simply record the absolute value of the dihedral angle in Table I.
21. We are now going to create the **Eclipsed Conformation of Ethane**. Start by closing the file for your staggered conformation of ethane by *clicking* the left mouse button on the following icon:



22. Following steps 2 through 7, build another molecule of ethane. **Do not do steps 8 or 9. If you do, close out your screen and start over again by building a non-minimized and non-viewed ethane.**
23. Rotate your model of ethane so that you can view the C-C bond. *Click* the left mouse button on this bond. A red arrow will appear around this bond. This indicates that you can rotate atoms about this bond. You will do this in order to build your eclipsed ethane conformation.
24. Rotate your ethane molecule so that one carbon atom is directly in front of the other carbon atom (i.e. a Newman projection). While holding down the **alt** key, *click and hold down* the left mouse button, drag the mouse to rotate about the C-C bond to make your eclipsed conformation of ethane.
25. To get the energy of the eclipsed conformation, you must set the dihedral angle to be zero degrees. *Click* the left mouse button on **Geometry** and then choose **Constrain Dihedral**. Select the four atoms (H-C-C-H*) using the left mouse button, where H and H* are the eclipsed hydrogens. In the lower right hand corner, an output box labeled “constrain (H1 C1 C2 H3) = “ will appear. On the far right of this box, you should see a “purpled-color un-locked padlock”

icon. Click on this icon. The un-locked padlock icon will change to a locked padlock, and inside the box, the value of the dihedral angle will appear. If this value is not 0 (the number zero), change the value to 0 by typing over the number and followed by the **enter** key on the keyboard. 0.00° will appear inside the box.

26. Before you calculate the relative energy of the eclipsed conformation of ethane, you can do a quick calculation by *clicking* the left mouse button on the **Minimize** icon:



followed by *clicking* the left mouse button on the **View** icon:



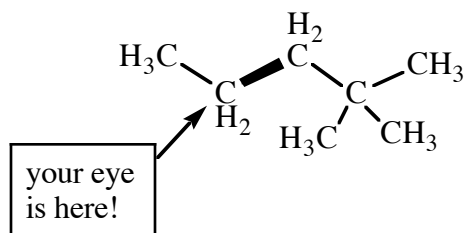
27. To calculate and display the relative energy of the eclipsed conformation of ethane, *click* **Setup** and then *click* on **Calculations...** A new screen will appear. The upper left option should be **Equilibrium Geometry**. The upper right box will have the default option Hartree-Fock/3-21G. *Click* on the triangle next to this box and choose **Molecular Mechanics**.

Finally, *click* on the **Submit** button at the bottom of the dialog. Before the calculations can start, you will need to supply a name for the file which will be created to save your data. **Be sure to save you data on the desktop under My Documents. Ask you instructor if you do not know how to designate this location.** For you file name, type in ecli_eth (or any reasonable file name you choose). Do not change the file type. *Click* on **Save**

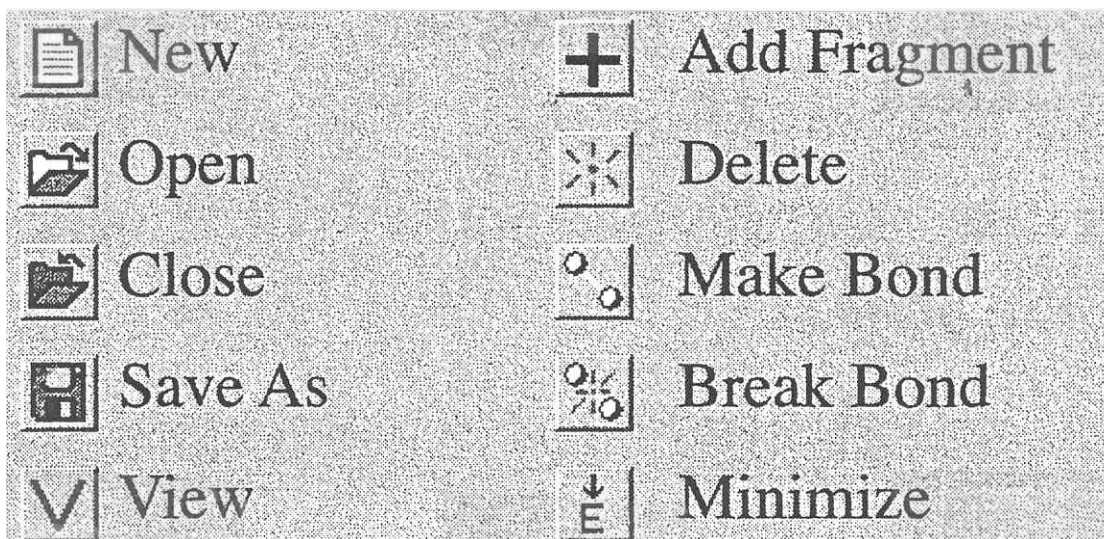
28. A screen will appear which will state that the calculations have started. *Click* OK.
29. When the calculations are completed, a new screen will appear which states this. *Click* OK.
30. To bring up you data, *click* on **Display** and then on **Properties**. A new window will open which has the calculated relative energy for the eclipsed conformation of ethane. Record the Energy of the molecule in Table I.
31. Following the procedure for the analysis of staggered ethane, determine the requested data in Table I for eclipsed ethane.
32. Following the same steps as above, build, minimize the energy, constrain the dihedral angle (if needed), and analyze the four conformations of butane obtained by rotation about the C₂-C₃ bond. Record the requested information in

Table II. **You must decide** the degrees of the angle needed when you constrain the dihedral angle.

33. Repeat the process for the four conformations around the C₄-C₃ bond in 2,2-dimethyl pentane and fill in the requested values in Table III. A picture of the molecule is shown below with the C₄-C₃ bond shown in bold and with an arrow representing your point of view. When drawing your Newman projections, keep in mind the three “things” (or substituents) attached to C₃ and C₄. One carbon has a t-butyl group and two hydrogens, while the other carbon has a methyl group and two hydrogens.



34. When making more complicated molecules (such as cyclohexane molecules), you can use some of the icons listed below to add fragments, add and break bonds (along with the other icons). Alternatively, you can choose **Cyclohexane** from the options for **Rings** (see the bottom of the Model Kit).



35. When you are finished, you should delete any files you saved on the computer. If you don't know how to, inform your instructor. Don't guess on how to do this. You don't want to delete any files which are required to run PC Spartan.

Molecular Modeling with PC Spartan

Table I Ethane	Energy kJ/mol	Distance C-H Å	Distance C-C Å	Distance H-H* Å	Bond Angle H-C-H degrees	Bond Angle H-C-C degrees	Dihedral Angle H-C-C-H* degrees
Staggered Ethane							
Eclipsed Ethane							

*Distance from H on one carbon to the **closest** H attached to the other carbon.

1. What is the difference in energy between the staggered and eclipsed conformations? Does this value come close to the energy differences from lecture (and the textbook)? Which conformation is more stable?

Table II Butane	Energy kJ/mol	Energy difference	Bond Angle H-C-H degrees	Bond Angle H-C ₂ -C ₃ degrees	Dihedral Angle C ₁ -C ₂ -C ₃ -C ₄ degrees
Staggered anti conformation					
Staggered gauche conformation					
Eclipsed conformation I					
Eclipsed conformation II					

2. How do the energy differences between the two staggered conformations compare to the energy differences from lecture (and the textbook)? Do the same comparison for the two eclipsed conformations.

Table III 2,2-dimethylpentane	Energy kJ/mol	Energy difference	Dihedral Angle C ₂ -C ₃ -C ₄ -C ₅ degrees
Staggered anti conformation			
Staggered gauche conformation			
Eclipsed conformation I			
Eclipsed conformation II			

3. How do the energy differences between the staggered conformations in **Table III** compare to the energy differences between the staggered conformations in **Table II**? Explain any differences. Do the same comparison for the eclipsed conformations.