

AN INTRODUCTION TO PC-SPARTAN AND TO MOLECULAR MECHANICS

Use your student drive letter (U:) for saving your files. If you wish you may use an IOMEGA 100 megabyte ZIP disk (IBM format) in order to save your files in a portable fashion. You should also read the essay "Molecular Modeling and Molecular Mechanics" in Appendix One of your lecture text, or on page 166 in your laboratory text. Also bring your calculator, or learn to use the one in Windows (found under **Start - Programs - Accessories**).

STARTING PC SPARTAN PRO

Start PC-Spartan Pro

Double-Click the ChemApps folder, choose Molecular Modeling and PC Spartan Pro (not Plus)

PART ONE THE BASIC OPERATIONS

CONSTRUCTING ETHANE

1. Select **File**→**New**
Building menus will appear in a box at the right-hand side of the Spartan window and at the top. The tab labeled **Entry** should be selected; this is the entry-level building menu.
2. Click on the button which shows the tetrahedral carbon atom (upper left-hand corner in the buttons area). When you click this, the tetrahedral carbon building piece should appear in the window just above the buttons. This small window shows the "active" or "just-selected" building piece.
3. Move the mouse cursor to the center of the workspace (largest window) and press the left mouse button. This will transfer the active piece to the workspace.
4. In the workspace, point at the end (yellow area) of one of the four bonds connected to your first carbon and press the left-hand mouse button again. This makes ethane.
5. **Minimizing (shortcut)**. A shortcut method for minimizing your structure is to click on the minimize button (blue E with arrow above) in the toolbar at the top of the screen. When you do this, the molecule will adjust to the nearest local minimum (for ethane

this will be the global minimum) and give an estimate of the strain energy of the molecule in kcal/mole. (It may be necessary to redo the minimization several times in order to reach a true minimum.) The minimization uses a molecular mechanics method called **Sybyl**. A better method will be introduced shortly. The final energy will appear in a bar at the bottom-right of the screen.

MOUSE OPERATIONS

Now that you have a molecule you can manipulate it with the mouse. Basic mouse operations are summarized in the table and discussed in the paragraphs that follow. Be sure to move the mouse away from your molecule or you will alter it.

Table of Basic Mouse Operations

KEYBOARD	LEFT MOUSE BUTTON	RIGHT MOUSE BUTTON
None	select molecule, atom, bond, XY rotate	X,Y translate
Shift key	Z rotate	Scaling (zoom)
Alt key (select first w/ mouse)	Bond rotation	Bond stretching

Rotations. Move the mouse away from your molecule. Press and hold the left mouse button. While holding the mouse button, move the mouse up/down for X rotation and left/right for Y rotation. Combinations are possible when you move at an angle. For Z rotation, hold the shift key down while you move the mouse (left button pressed) up/down.

Translations. Move away from the molecule. Press and hold the right mouse button. Moving up/down or right/left will reposition the molecule on the screen.

Scaling or Zoom. Move away from the molecule. Hold the shift key down on the keyboard and move the mouse up/down while pressing the right mouse button.

WARNING: The following operations will alter your minimized molecule. They are designed for use when building a molecule prior to minimization. However, if you alter your molecule, you may minimize it again.

Rotation of a bond. Select the desired bond by clicking on it with the left mouse button (it will become dashed). Holding the alt key down on the keyboard, press the left mouse button and move the mouse up/down.

Stretching a bond. Same as for rotation, except use the right mouse button.

BUILDING AND VIEWING

Thus far we have been in the **build mode** where all the build menus are present on the right-hand side of the screen. You can't build a molecule without the menus. You can leave the build mode and go to the **view mode** by pressing the **V** button at the top of the screen. When you press this button the build menus disappear. You can reenter the build mode (to alter your molecule) by pressing the **+** button at the top of the screen. Try switching back and forth.

Mouse operations (rotation, translation, zoom) work the same way in view mode as they do in build mode, except that you cannot rotate bonds or alter their length. You must return to build mode for these operations to be active.

TYPE OF MODEL

You may change the type of model displayed using the **Model** menu at the top of the screen. Wire, ball and wire, tube, ball and spoke and space-filling are available.

MEASURING ETHANE

Once you have made a molecule, you can measure bond lengths, bond angles, and dihedral angles. The following procedures work in either view mode or build mode.

Bond lengths. Select **Geometry**→**Measure Distance** or use the blue **<?>** button on the toolbar. Click on two atoms (they don't have to be connected) or a bond (the selected atoms will change to a yellow color). The distance will be reported in the bar at the bottom right.

Bond angles. Select **Geometry**→**Measure Angle** or use the blue **<?** button on the toolbar. Click on three atoms, or two bonds, and the angle will be reported at the bottom right.

Dihedral angles. Select **Geometry**→**Dihedral** or use the blue **\ ? ** button on the toolbar. Click on four atoms, or three bonds, and the dihedral angle will be reported at the bottom right.

SAVING YOUR FILE

Select **File**→**Save As**

If the Save As error message box ("A:\ is not accessible") appears, click **CANCEL** to remove it. You should now have the **Save As** dialog box.

Find and click on the **My Computer** entry.

Find and click on the **Removable Disk (D:)** entry or on your student disk space (**U:**).

Enter a filename (such as "ethane") and click on the **Save** button.

MINIMIZATION USING MOLECULAR MECHANICS : FULL METHOD

On page one, a shortcut method was given for using molecular mechanics to minimize a molecule. That method consisted of pressing the blue **Minimize** button (**E**) in the toolbar when the screen was in build **+** mode. The method that follows accomplishes the same thing, but allows more options, and allows the choice of semiempirical and *ab initio* methods as well as molecular mechanics (Sybyl). We will learn to use semiempirical and *ab initio* methods in a later exercise. To enter one of these methods, one usually saves the molecule as described in the paragraph above (if you don't you will be prompted when minimization begins), and enters the view mode by pressing the **V** button.

Press the **V** button to enter the view mode.

Select **Setup**→**Calculation** to obtain the setup menu.

In the first line select **Equilibrium Geometry** (minimization), **Molecular Mechanics** and **MMFF**. MMFF stands for Merck Molecular Force Field, and it generally gives superior results to the Sybyl method.

Click on the **OK** button.

Now select **Setup**→**Submit**.

If you have not previously saved your molecule, a **Save As** box will appear (see above).

A dialog box will appear telling you that the calculation has started.

Click on **OK** to remove the box.

A new dialog box will appear when the calculation is completed.

Click on **OK** to remove this box.

If the calculation terminates before it is done, it may have run out of minimization cycles and you should try submitting it again.

Select **Display**→**Properties**→**Energy** to see the energy. The energy is displayed in atomic units: 1 au = 2625 kJ/mol. You must multiply to convert to kJ. Keep all sig. figs. until done.

EXAMPLE: $-0.00754516602 \times 2625 = -19.8060608025 = -19.81 \text{ kJ/mole}$

Select **Display**→**Output** to see the full output file from the program.

The final x,y,z coordinates of the molecule can be found in this file.

Use the **X** button in the upper right-hand corner of the output file (not the main window) to close the output file.

COPY/PASTE

You can copy the picture on the screen to a Word document using the Windows Clipboard. Select **Edit**→**Copy** while in Spartan. Then minimize Spartan, open Word and use **Edit**→**Paste**. For best results, scale your drawing as large as possible on the screen before copying.

CLOSING YOUR FILE

Select **File**→**Close**.

If you have made changes on the screen, you will be asked if you want to save them. The answer is usually **NO**, otherwise you will save *only* the graphics that are on the screen. If you answer **NO** you *do not* lose the results of the calculation.

You may now proceed to construct a new molecule with **File**→**New** or exit the program with **File**→**Exit**.

PART TWO THE CONFORMATIONS OF BUTANE

CONSTRUCTING *ANTI* BUTANE

1. Select **File**→**New**
2. Build ethane as directed in the instructions given above (1-4).
3. Now add two more carbon atoms in the same way to construct butane, taking care to arrange the carbon atoms in an approximate **Z** shape. Minimize the structure, using the more extended MMFF molecular mechanics method. Record the energy and convert it to kJ/mole on the report sheet.
Close the molecule.

CONSTRUCTING *GAUCHE* BUTANE

Select **File**→**New**.

Repeat steps 1-3 above as for *anti* butane, this time arranging the carbon atoms in an approximate **U** shape. Minimize the structure, using the MMFF molecular mechanics method. Record and convert the energy on the report sheet.

Close the molecule.

CONSTRUCTING *SYN* BUTANE

Select **File**→**New**.

Repeat the steps given above as for *gauche* butane, once again arranging the carbon atoms in an approximate **U** shape.

Now you will adjust the dihedral angle to a value of 0° and **constrain it** (fix it to that value). If you did not constrain this angle the minimizer would vary it to find the closest minimum of energy (local minimum) which would be the *gauche* conformation.

- i. Select **Geometry**→**Constrain Dihedral** or the magenta constrain (lock) button on the toolbar (*looks like a small padlock between backslashes*).
- ii. Select the four carbon atoms, either by clicking on them, one at a time, starting at one end of the chain and proceeding to the other end (they will turn yellow when selected); alternatively, you may select the three bonds connecting the four atoms. You will see the atoms listed in the text box at the bottom of the screen as you select them.
- iii. Click on the violet open lock (bottom right) to lock the angle. The current dihedral angle will appear in the text box. Click in the value box and type a new value (0) followed by the **Enter** key.
- iv. The constrained angle will be marked on the molecule in magenta lines.
- v. Now click on the blue **Minimize** button (**E**) in the toolbar at the top of the screen. The constraints will not be enforced on your molecule until you minimize. The minimizer will now fix the CCCC dihedral angle to 0° , but will adjust all other angles to give a minimum energy for the 0° (*syn*) conformation.
- vi. To obtain the final energy, go to **Setup**→**Calculations** and select in the first line **Equilibrium Geometry, Molecular Mechanics** and **MMFF**. Also check in the constraints box on line three. Click on **OK** and then select **Setup**→**Submit** to perform the calculation.

Record the energy on the report sheet and convert it kJ/mole.

Close the molecule. When making your conclusions, remember that *the more positive the value, the more strain; the more negative the value, the less strain*.

PART THREE CONFORMATIONS OF METHYLCYCLOHEXANE

EQUATORIAL METHYLCYCLOHEXANE

Select **File**→**New**.

Under the atom-hybrid buttons in the menus, select rings = **cyclohexane**.

The cyclohexane ring will appear in the current selection window.

Click on the screen with the left mouse button to transfer the cyclohexane ring to the work area.

Rotate the ring to your liking.

Select the tetrahedral carbon button. It will transfer to the window.

Click with the mouse on an equatorial cyclohexane bond to build equatorial methylcyclohexane.

Save and minimize your methylcyclohexane by either of the methods given above.

Record and convert the energy to kJ/mole on the report sheet.

Don't close the molecule.

AXIAL METHYLCYCLOHEXANE

Return to the builder mode (+ button) if you are not there.

Select **Build**→**Delete** or the delete atom button (large red asterisk *) in the toolbar at the top of the screen.

Click on the carbon atom at the center of the methyl group. It will be deleted.

Click on the + button when you are finished.

Select the tetrahedral carbon button. It will transfer to the active-piece window.

Click with the mouse on an *axial* cyclohexane bond to build axial methylcyclohexane.

Save (under a new name) and minimize your methylcyclohexane using the **MMFF** method selected from the **Setup**→**Calculations** menu.

Record and convert the energy to kJ/mole on the report sheet.

Close the molecule.

PART FOUR DIMETHYLCYCLOHEXANES

THE DIMETHYLCYCLOHEXANES

Make the following molecules using the methods outlined above and find their strain energies:

trans-1,2-diaxial-dimethylcyclohexane

trans-1,2-diequatorial-dimethylcyclohexane

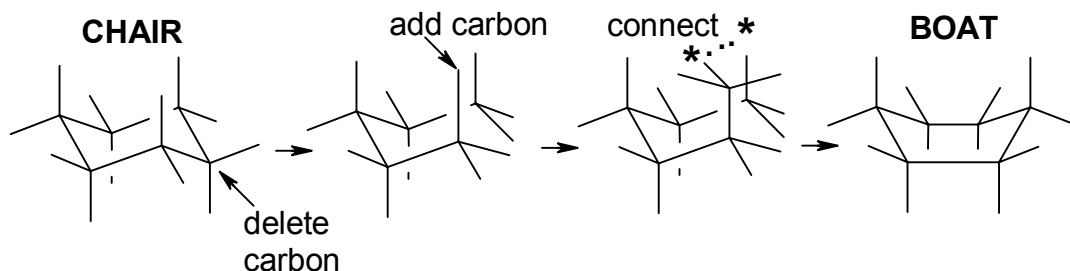
cis-1,2-axial,equatorial-dimethylcyclohexane

Which conformation of the *trans* stereoisomer has the lowest energy. Which molecule of the three has the lowest energy? Explain the differences in energy in your report.

PART FIVE *cis*-1,4-DI-*tert*-BUTYLCYCLOHEXANES

MAKING A BOAT

Transfer a chair template (rings = **cyclohexane**) from the build menus to the workspace. Orient the chair on the screen so that one of the puckered atoms puckers upward and the other one puckers downward. There will be two parallel horizontal bonds in the center of the screen.

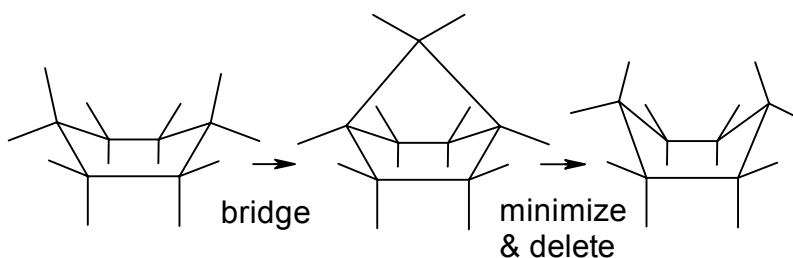


Find the **delete atom** button (red *) in the top toolbar and click on it. Now click on the puckered atom which is *down* to delete it. Click on the **+** button in the toolbar to stop deleting. Now select a tetrahedral carbon piece from the atom buttons (upper left corner) and click to transfer it to the active-piece window. Now replace the deleted atom with one that puckers upward. First select one of the bonds that points *upward* to make the first

attachment to the new carbon. Then select the **Make Bond** button (yellow, showing two atoms connected by a bond) from the toolbar. Go to the other side of the opened ring and select a bond that points *upward*. When you select it, it will become a yellow ball. Now select a downward pointing bond from the new carbon you added and click on it (select the bond that points as close and as directly as possible to the first bond you selected). When the bond is formed, select **+** to stop the bond making process. Now you have a crude boat to minimize.

NOTE: Be aware that a true boat is not at an energy minimum; in fact, it is at a local maximum linking several twist boats. It will minimize to a twist boat. If you wish to make a perfect boat, you must bridge the top of the ring with a carbon atom to make bicyclo- [2.2.1]heptane, minimize (the blue **E** button is OK), and then return to the **+** mode and delete the bridging atom.

MAKING A PERFECT BOAT



In order to obtain the approximate energy of the boat, you must use **MMFF** and choose **Single Point** (not **Equilibrium Geometry**) when you minimize or you will get a twist boat again.

cis-1,4-Di-tert-BUTYLCYCLOHEXANES

Make a crude cyclohexane boat as described above. Attach *tert*-butyl groups to the two equatorial bonds on the puckered atoms (positions 1 and 4). Save and minimize (MMFF) this molecule. Record and convert the energy on the report sheet. Close the molecule.

Now make a chair. Place one *tert*-butyl group in an axial position at one end of the chair (position 1) and place the second in an equatorial position at the other end of the ring (position 4). Save and minimize this molecule. Record and convert the energy to kJ/mole.

Close the molecule.

What do you conclude about the chair and boat conformations of this molecule? Is the chair *always* the lowest energy conformation? Explain this case.

(**OPTIONAL**) If time permits, construct the chair and boat conformations of *trans*-1,4-di-*tert*-butylcyclohexane and compare their energies.

PART SIX

***cis*- AND *trans*- DOUBLE BONDS**

***cis*- AND *trans*-2-BUTENE**

Construct *cis*- and *trans*-2-butene (separately) and compare the strain energies. To construct each molecule, first connect two trigonal planar carbons to make a double bond, then add the two tetrahedral methyl groups. You may have to rotate the first trigonal planar carbon placed on the screen to see the double-valence end of the atom. By clicking on the double-valence end, a carbon-carbon double bond will form. Construct and calculate the energies of both the *cis* and *trans* isomers and record their energies. **NOTE:** It is a good idea to use the crude minimization button (blue **E** with arrow above) before submitting your calculations (see below).* What do you conclude from your results?

* You must make sure that hydrogens on the adjacent methyl groups of each alkene stereoisomer are not pointed directly at each other (*cis* isomer) and are staggered with any adjacent vinyl (double bond) hydrogens (both isomers). The rotational positions of these two methyl groups will greatly affect the calculated energy. This is a common problem in modeling calculations, rotations around C-C bonds of groups like methyl will affect the outcome of the calculation - the user must be alert to these problems. If you come out with an energy difference between your *cis* and *trans* isomers that is less than 2 kJ / mole, you should adjust the orientation of the methyl groups. This can sometimes be done by using the (**E**) button before submission, otherwise you will have to rotate the methyl groups yourself (see the operations chart on page 2).

REMEMBER: These calculations will not exactly match experimental values. In general, however, the energies of conformations and closely-related isomers will be in the correct order. We are interested in the order here, not the exact thermodynamic values.