

Modeling Rotation Around C–C and C=C bonds

Objective

To use WebMO to investigate the distribution of electrons in a molecule and to study the energy of a molecule as the ends of the molecule are rotated around a C to C bond.

Background

According to a theory of bonding, the overlapping of atomic orbitals allows electrons from one atom to be shared with another. This mutual attraction of two nuclei for a pair of electrons lowers the energy of the system because the electrons experience greater attraction as compared to being attracted to only one nucleus. Rotation around a bond can affect the alignment of orbitals and make the overlap less effective, and this can raise the energy of the electrons and, thus, the molecule.

Procedure

In the first part of the activity, you will build the polar molecule CH_2Cl_2 and generate an electrostatic potential map. This will allow you to observe how WebMO shows where a molecule is the most negatively and positively charged since we know that the negative charge for the polar CH_2Cl_2 molecule is centered between the two Cl atoms.

In the second part of the activity, you will build molecules of butane and butene, visualize their electrostatic potential maps, and measure the energies of the molecules as you rotate the ends of the molecule about the C_2 to C_3 bonds.

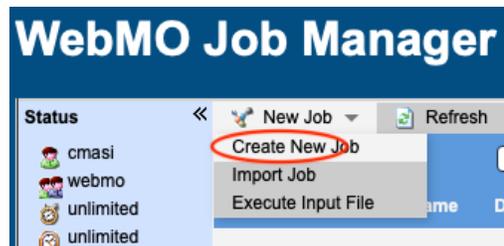
Modeling Electrostatic Potential

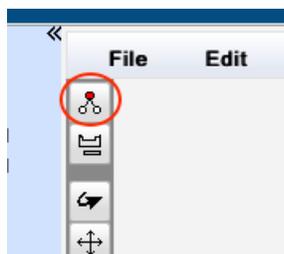
Summary: Build a model of CH_2Cl_2 and generate an electrostatic potential map.

Log into WebMO using the username “student” and the password supplied by the instructor.

There are several ways to build a molecule in WebMO, but WebMO has some tools to make molecule building easier.

Select "Create New Job" from the "New Job" menu.





After selecting "Create New Job" the "Build tool should be activated.

If the build tool is not the active tool, click the button for it.

Hint: allowing the mouse pointer to hover over the buttons will reveal the names of the buttons.

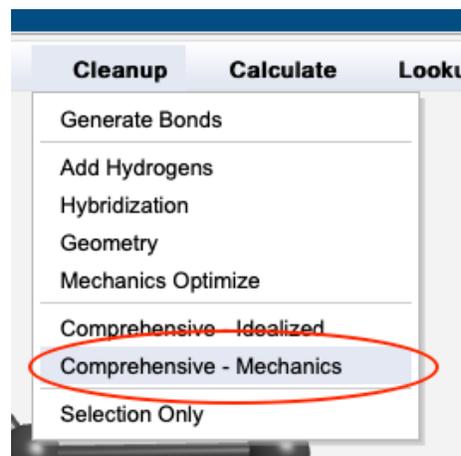
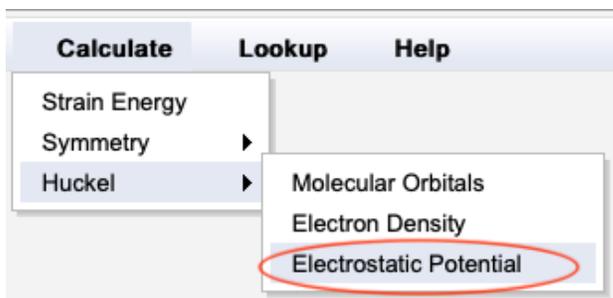
The build tool should be ready to drop a C atom into the window. Place the mouse pointer in the middle of the open window and click. If a gray C atom doesn't appear, make certain the "Build" tool is selected. If a differently colored atom appears, undo the operation and use the "Periodic Table" tool, which is directly under the "Build" tool, to select carbon.

Add a C to Cl bond by selecting a Cl atom from the "Periodic Table" tool, clicking and holding on the C atom, while still holding the mouse button dragging the pointer off of the C atom, and finally, releasing the mouse button.

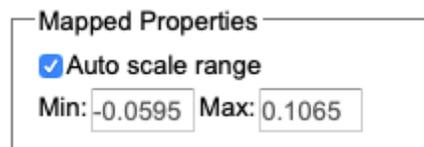
Add a second Cl atom by repeating the previous process.

Instead of adding hydrogens to the model, choose "Comprehensive - Mechanics" from the "Cleanup" menu. WebMO will add the appropriate number of H atoms to the C atom, and it will clean up the shape (it attempts to find the lowest energy).

Generate a map of the electrostatic potential of CH_2Cl_2 by choosing "Electrostatic Potential" from the "Huckel" submenu of the "Calculate" menu.



Click the "Auto scale range" checkbox to deactivate the auto scale function, change the minimum and maximum values in the "Mapped Properties" box to -0.05 and 0.05, and make a note about the distribution of colors across the surface of the model.



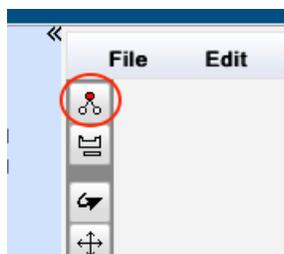
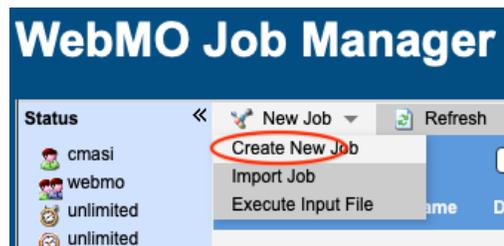
Modeling Rotation around Bonds

Summary: build models of butane and 2-butene, visualize the electrostatic potential maps, rotate the C₂ to C₃ bonds through 360° in steps of 15°, estimate and record the energies of the rotamers, and graphs the results.

Building butane

Select "Create New Job" from the "New Job" menu.

There is more than one way to build a butane (CH₃CH₂CH₂.CH₃) molecule, but the quickest way is to allow WebMO to do some of the work. After selecting "Create New Job" the "Build" tool should be activated.



If the build tool is not the active tool, click the button for it.

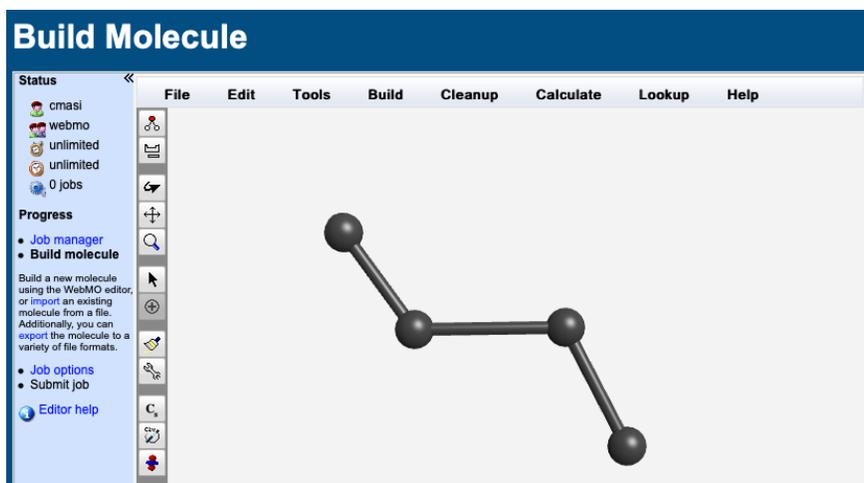
Hint: allowing the mouse pointer to hover over the buttons will reveal the names of the buttons.

The build tool should be ready to drop a C atom into the window. If it is not, use the "Periodic Table" tool, which is directly under the "Build" tool, to select carbon.

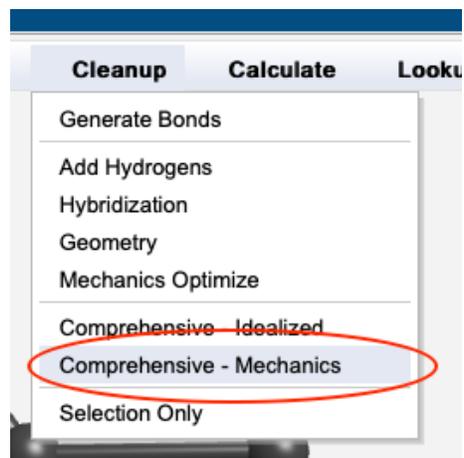
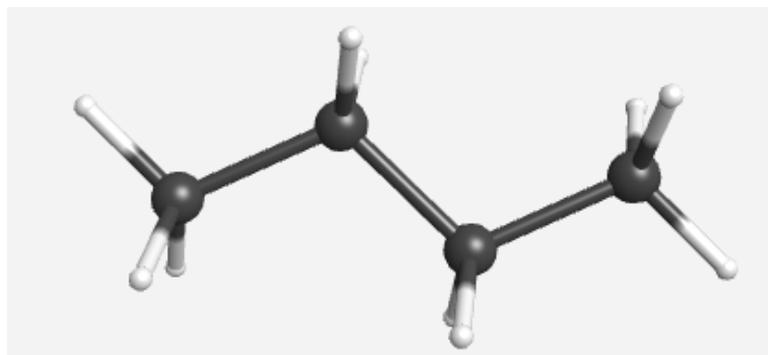
Build - C (click = add atom; drag = add bond; click & drag = add atom & bond;

Click on the open window to add a C atom.

Click and hold on the C atom, drag the mouse pointer to a new location and release to add a bond to a second carbon atom. Continue to click and hold and drag and release until there are four carbon atoms in a row.



From the "Cleanup" menu, choose "Comprehensive - Mechanics". WebMO will add the appropriate number of H atoms to each of the C atoms and it will clean up the shape (it attempts to find the lowest energy geometry).



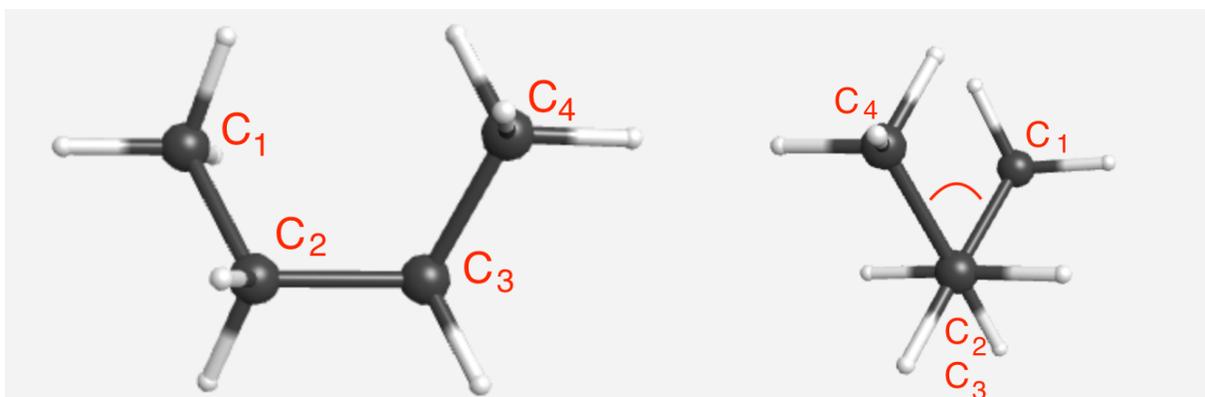
Visualizing the Electrostatic Potential Map

Choose "Electrostatic Potential" from the "Huckel" submenu of the "Calculate" menu.

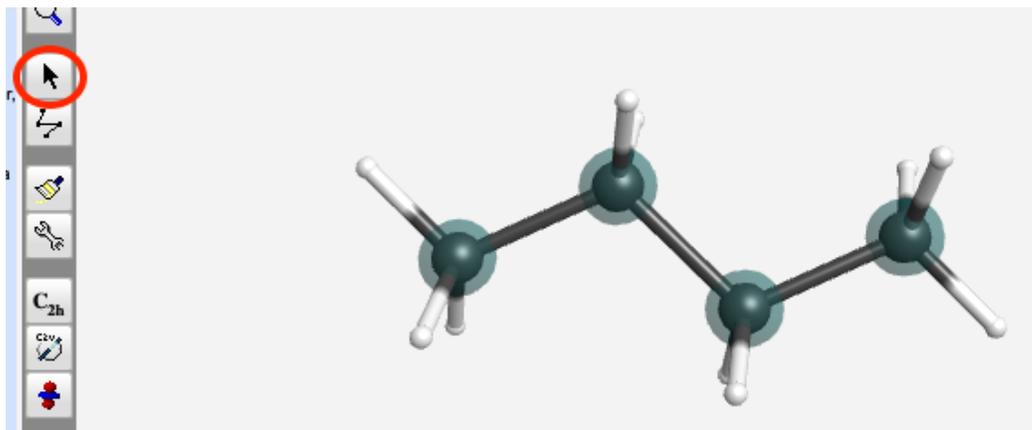
Click the "Auto scale range" checkbox to deactivate the auto scale function, change the minimum and maximum values in the "Mapped Properties" box to -0.05 and 0.05, and make a note about the distribution of colors across the surface of the model.

Creating rotamers and estimating their energies

Rotamers can be generated by varying the $C_1-C_2-C_3-C_4$ dihedral angle. The dihedral angle is the angle formed by the C_1 to C_2 bond and the C_3 to C_4 bond when the structure is viewed along the C_2 to C_3 bond.

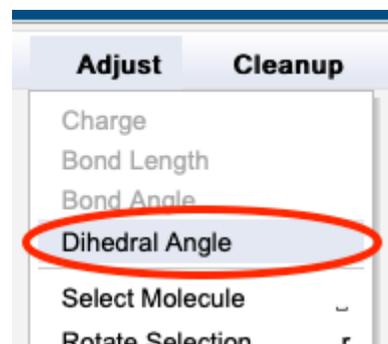


Choose the "Adjust" tool and starting on the left and proceeding in order click on the four C atoms. When the atoms are selected they will be highlighted in blue.

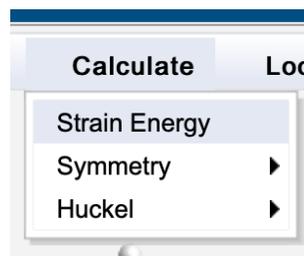
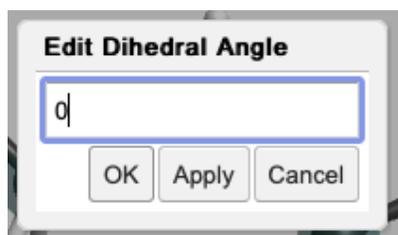


Choose "Dihedral Angle" from the Adjust" menu.

Enter "0" for the dihedral angle in the dialog box that appeared and click "OK" or press the "Return" key on your keyboard.



Choose "Strain Energy" from the "Calculate" menu, and record the total energy, which will appear in the dialog box. After recording the total energy close the dialog box by clicking "OK".



Repeat the process of varying the dihedral angle, calculating the total strain energy, and recording the result for a complete 360° rotation around the C₂-C₃ bond in steps of 15°. To help keep track, create a table in Excel that lists the dihedral angles for which the energies will be estimated and enter the energies as they are determined. It is traditional for dihedral angles to be expressed as numbers from -180° to +180°. When dihedral angles of greater than 180° are entered into WebMO, WebMO will convert them to the appropriate negative angle.

HINT: If you have not clicked anywhere in the build window, the four C atoms should still be selected and you can go right to "Adjust Dihedral Angle" after calculating the strain energy.

Build 2-butene

Build 2-butene by starting from butane:

- Use the "Adjust" tool to select a hydrogen atom on C₂ and a hydrogen atom on C₃.
- Delete the H atoms by pressing delete.
- Switch back to the "Build" tool and draw a second bond from C₂ to C₃ by clicking and holding on C₂ and dragging and releasing once the mouse pointer reaches C₃.
- Select "Comprehensive - Mechanics" from the "Cleanup" menu.

or

Build 2-butene from scratch:

- Choose "New" from the "File" menu.
- Drop a C atom into the build window.
- Click and hold on the C atom and drag and release to build a bond that ends in a second C atom. Continue to click and hold and drag and release until there is a string of four C atoms.
- Click and hold on C₂, drag the mouse pointer to C₃, and release the mouse button.
- Select "Comprehensive - Mechanics" from the "Cleanup" menu.

Visualizing the Electrostatic Potential Map

Choose "Electrostatic Potential" from the "Huckel" submenu of the "Calculate" menu.

Click the "Auto scale range" checkbox to deactivate the auto scale function, change the minimum and maximum values in the "Mapped Properties" box to -0.05 and 0.05, and make a note about the distribution of colors across the surface of the model.

Estimating energies for the rotation around the C₂ to C₃ bond in 2-butene

Repeat the process of varying the dihedral angle and recording the energies of the rotamers as described in the butane section above.

Experimental Report

1. Create data tables and graphs of the data for each of the models.

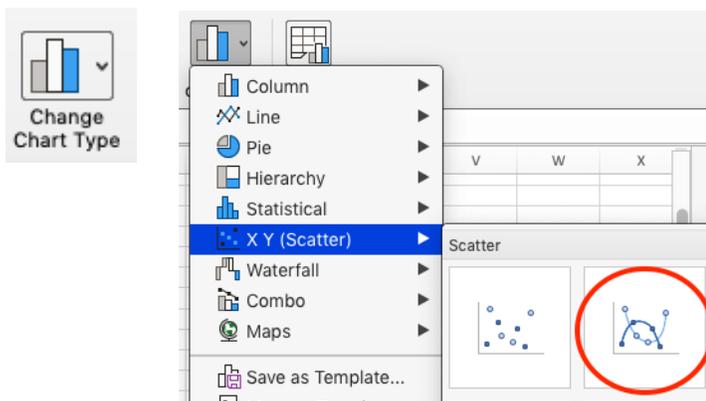
You may use any graphing program that you wish to use so long as you include the expected information: a data table with appropriate headings that describe the data and list the units used, an x,y scatter graph with lines connecting the data points (smoothed lines are preferred), a title on the graph, appropriate axes that include values and a title that describes the values and lists the units used, and a caption describing the graph. A blank example is included on the last page of this handout.

The following instructions are for MS Excel v16.41. The screen shots are from a Mac. The Windows controls are similar.

Generate a graph in Excel by selecting the data (x values in one column and y values in the adjacent column) and choosing "Chart >", "X Y (Scatter)" from the "Insert" menu. Once the chart is generated it will need to be edited.

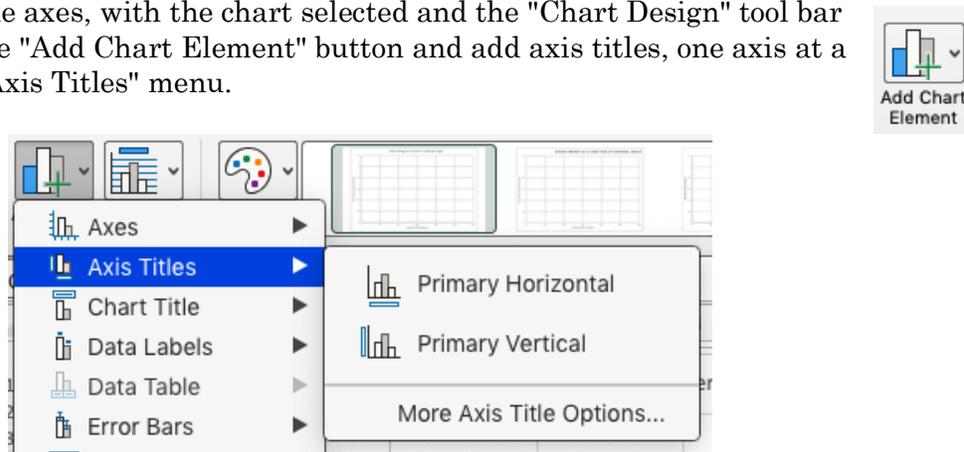
Select the chart and click "Chart Design" in the tool bar selection area.

Click the "Change Chart Type" button and choose the "Scatter with Smooth Line and Points" option.



To adjust the X axis, double click on the axis (if the Format pane on the right is already visible, only a single click is necessary) and then click on the "Axis Options" button. Set the minimum for the axis to 0 and the maximum to 360. Choose a "major unit" that makes sense so the end of the axis is labeled 360°.

To add titles to the axes, with the chart selected and the "Chart Design" tool bar active, click on the "Add Chart Element" button and add axis titles, one axis at a time, using the "Axis Titles" menu.



2. a. Go to

<https://www.westfield.ma.edu/PersonalPages/cmasi/organic/newman/newman-plain.html> to compare the two rotamers of butane presented there. Starting from the default view (if you have moved the model click the "reset" button), click on the "Rotate on y -90" button for each of the models and describe why one is labeled "Eclipsed Butane" and the other is labeled "Staggered Butane". Javascript must be allowed by your browser for the aforementioned page to work.

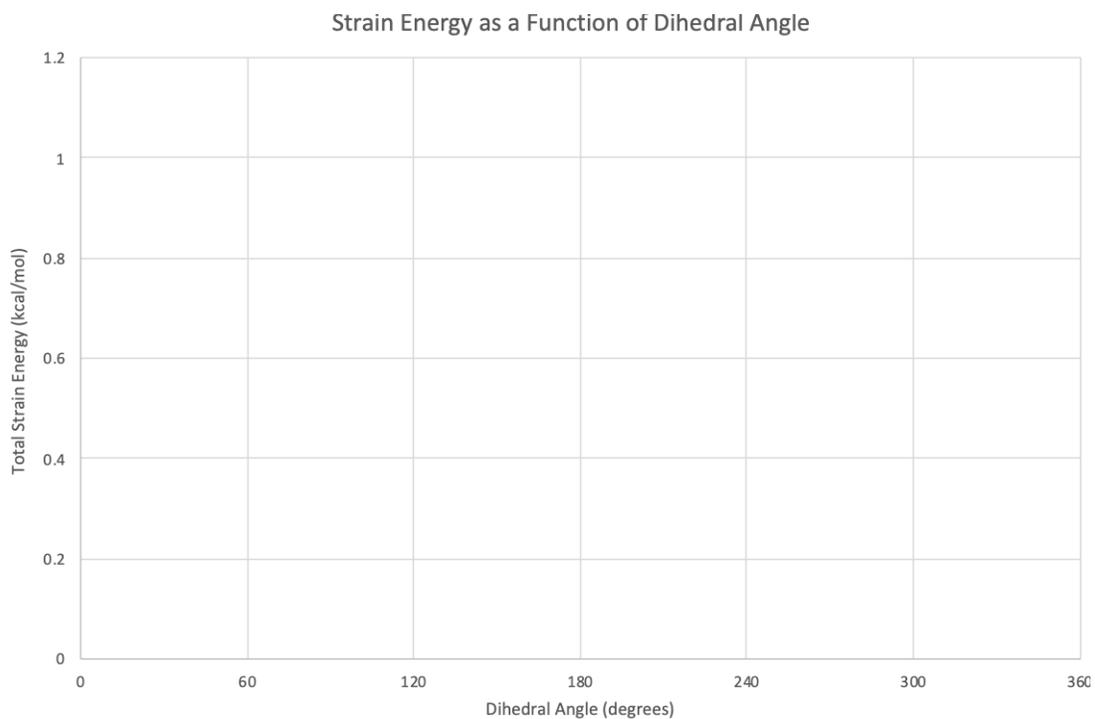
b. Based on the data you collected, which is the higher energy rotamer, the rotamer with the staggered or eclipsed geometry?

c. Using on the data you collected find the other staggered and eclipsed geometries and list the dihedral angles at which they occur and the calculated energies for the rotamers.



- d. Provide an explanation for why the energies of the eclipsed conformations are not the same.
- e. Provide an explanation for why the energies of the staggered conformations are not the same.
3. Using the data that you collected determine the barrier to rotation around the C₂ to C₃ bonds in butane and 2-butene (the barrier to rotation is the difference between the lowest and highest energy rotamers).
4. a. Go to <https://www.westfield.ma.edu/PersonalPages/cmasi/organic/2-butene/2-butene-plain.html> to compare the two rotamers 2-butene presented there. Based on the data you collected determine which is the higher energy rotamer the staggered or the eclipsed geometry.
- b. Using valence bond theory explain why the observation from part 3.a. and explain why the barrier to rotation about the C₂ to C₃ bonds in 2-butene and butane are different.

Dihedral Angle (degrees)	Strain Energy (kcal/mol)
0	
15	
30	
45	
60	
70	
71	
72	
73	
75	
90	
105	
120	
135	
150	
165	
180	
195	
210	
225	
240	
255	
270	
285	
300	
315	
330	
345	
360	



A graph of the energy of a butane molecule as the C₂ to C₃ bond bond rotates through 360°.