WebMO Instructions

Prelab Computational Project

This exercise is designed help reinforce some of the "big picture" concepts, such as cation stability and the Hammond postulate, and to give you an introduction to a relatively new and growing field of chemistry called computational chemistry. Many of the things we would like to study about molecules are very difficult to observe in a laboratory. By returning to the mathematical basis for molecular theory (Molecular Orbital Theory), we can study properties of molecules that we could not otherwise examine.

Read through the experiment (starting on page 163 of your *Projects* book). This will familiarize you with the questions we are asking and the chemistry we will do in the laboratory. Pay particular attention to the "optional computational chemistry experiment" starting on page 169. We will be using a program called "Guassian" to actually do the calculations. Learning how to use this program is, to be honest, less than intuitive. It is, however, a very powerful tool for chemists in nearly every sub-discipline (organic, inorganic, physical, etc.). To make the interaction with the program easier, we will use a web-based application called WebMO. Web MO was developed at Hope College to facilitate undergraduate use of complex tools like Gaussian.

You can work in groups for this, or you can work alone. If you work in groups, make sure everyone constructs and submits at least one of the five structures you will examine. the groups are as follows:

| Group 1	Group 2	Group 3	Group 4
Steve Howard (W)	Brianna Va	Kyle Carlson	Bryce Gode
Chris Lund (O)	Emily Pelton (W)	Jenna Kesty	Alex Burum
Dan Freeman	Leah Swanson	Trevor Wittwer (W)	Kelly Rozenboom (W)
Jeff Rock	Alyssa Brooks	Eric Nelson	Rachel Roberg (O)
Doug Durand	Alex Burleigh (O)	Aaron Roessler (O)	Marcus Perry
Group 5	**Group 6**	**Group 7**	**Group 8**
Andy Bryan	Erin Ge (O)	Ellen Sauter (O)	Amy Waldner
Justin Hahn (W)	David Wold	Maari Hanson (W)	Doug Schroeder
Krystal Long (O)	Matija Novakovic	Micah Deitz	Matt Royer (W)
Zack Alwine	Connor Ziegler (W)	Holly Cooper	Nick Malm
Kari Maffitt	Jennifer Krantz	Luis Valle	Brent McConahey (O)
Group 9	**Group 10**	**Group 11**	**Group 12**
Tim Lamanna (O)	Ben Levy	Steph Lewis	Morgan Wells (O)
Stephanie Soiseth	Zach Walgenbach (O)	Mackenzie Consoer	Krista Cruse
Bridget Hoesley	Erik Kraska	Chris Ditlevson (O)	Nissa Hannemann (W)
Ryan Casper (W)	Brittany Murphy	Matt Hoke (W)	Chad Olson
Fue Vang	Rachel Chaska (W)	Erik Anderson	Sarah Duncan
Group 13	**Group 14**	**Group 15**	**Group 16**
Danielle Forstner	Kristen Burson	Chris Leonard (W)	Sunny Sonabend
Katie Pesch (W)	Rachel Elvebak	Lauren Hom (O)	Scott Kyser
Rachel Poppy (O)	Mike Stangler (O)	Jill Verchota	Danielle Burras (W)
Jenna Paulsen	Emily Barnard (W)	Raychal Zupancich	Sarah Erickson (O)
Arie DeGrio	David Wray		

The rest of this document will walk you through the basics of building a molecule and submitting a calculation. Once you learn the basics, building molecules gets easier, and it is not that difficult. the hard part of computational chemistry is knowing when to trust your results. For this exercise, there are only a couple of common problems that invalidate the answers we will get. These are addressed in the Trouble Shooting section at the end of the document.

WebMO Instructions

1) Open a web browser and go to the url: **http://bert.chem.gac.edu**. A graphic of hydroxybenzyl alcohol is displayed with various links.

2) Click on **Computational Tools**. The graphic should expand to the right, and more options should appear.

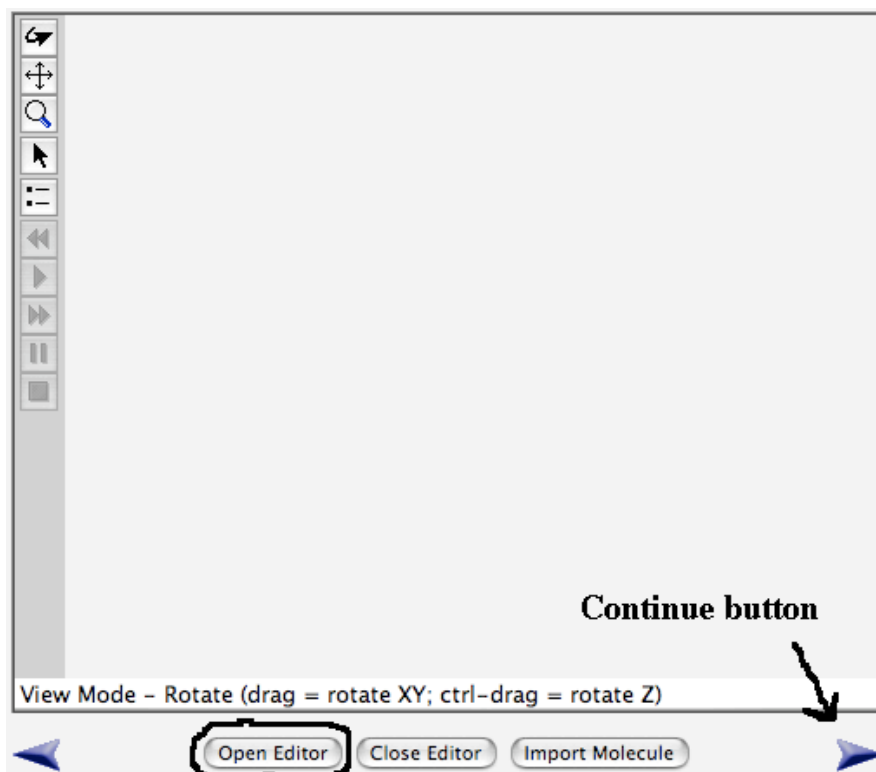3) Click on **WebMO**. A new window will appear and prompt you for a username and a password.
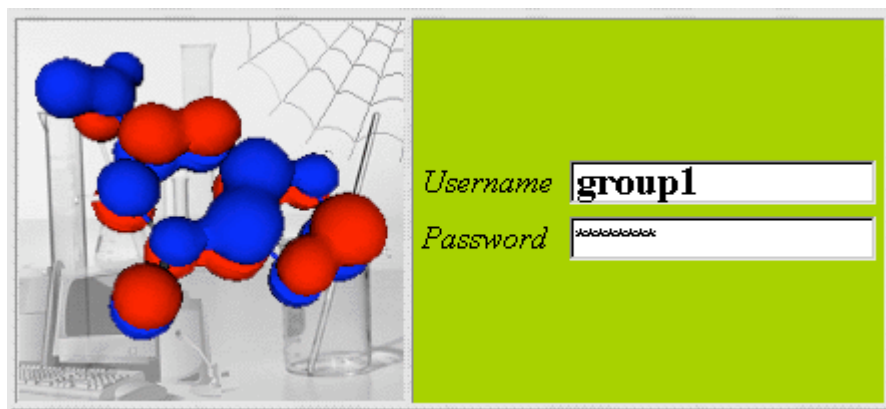
4) Enter your group number for the username and **organic** for the password (*i.e* **group1** for members of group 1, **group2** for members of group 2, etc.), then click on the **login** button. A new screen will appear with "WebMO Job Manager" at the top and "Available Jobs" in the middle. Near the top of the inset window is a line of buttons: New Job; Refresh; Download; Move To; Delete; Utilities; Logout. (Shown Below.)
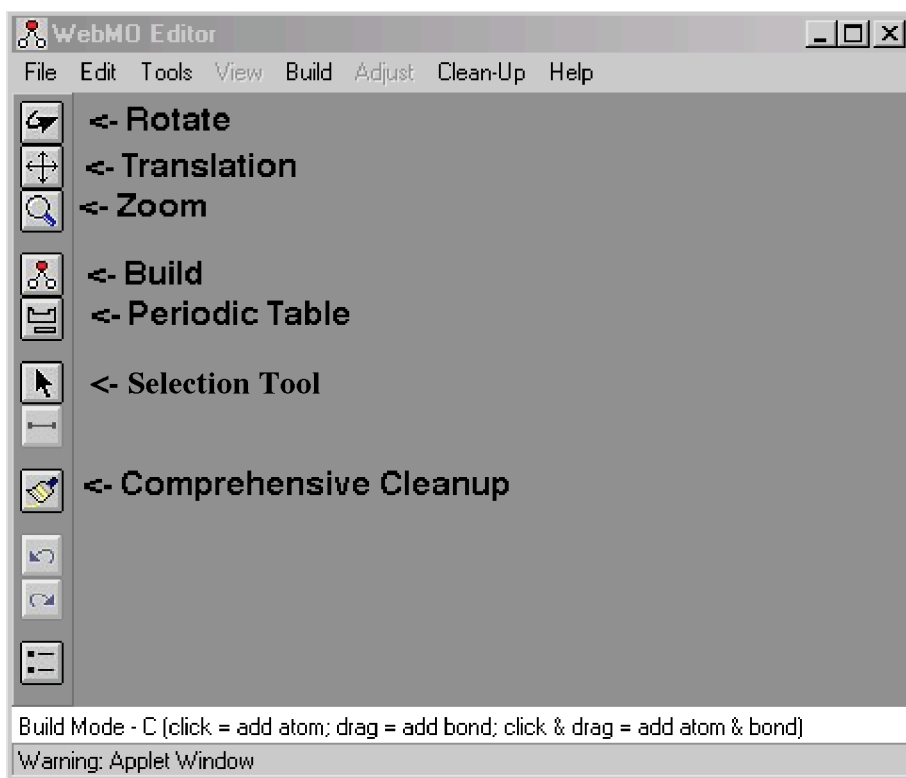
5) Click on the **New Job** button.
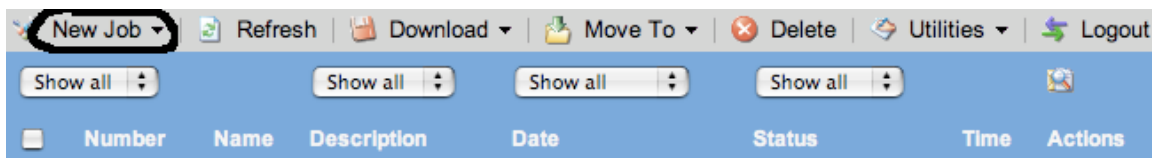
A "Build Molecule" screen appears. Three new buttons are available: Open Editor; Close Editor; Import Molecule. (See next illustration.)
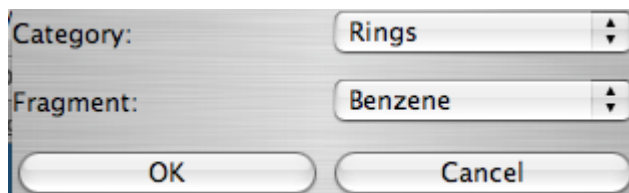
WebMO Instructions

Continue button

View Mode – Rotate (drag = rotate XY; ctrl–drag = rotate Z)

Open Editor   Close Editor   Import Molecule

6) Click on the **Open Editor** button. A new window appears.

WebMO Editor

File   Edit   Tools   View   Build   Adjust   Clean-Up   Help

<- Rotate
<- Translation
<- Zoom

<- Build
<- Periodic Table

<- Selection Tool

<- Comprehensive Cleanup

Build Mode - C (click = add atom; drag = add bond; click & drag = add atom & bond)
Warning: Applet Window

WebMO Instructions

Tool buttons appear as a column down the left of the window. As you "mouse over" the buttons, text will appear in the white bar near the bottom of the window. The text will tell you what each button does. Also notice that there are several pull down menus across the top of the window. The **Rotate** button (top button; curved arrow) will rotate a molecule. The **Translate** button (second from top; crossed arrows) will move the molecule left or right, up or down. The **Zoom** button (third from top; magnifying glass) will enlarge the drawing. The **Build** button (4th from top; three circles in a triangle) will allow you to start building a molecule. The **Periodic Table** button (5th from top; periodic table outline) allows you to select "uncommon" elements for your drawing. The **Selection Tool** (6th from the top) allows you select parts of the molecule for adjustment (deletion, rotation, etc.). The **Comprehensive Cleanup** button (8th from top; paint brush or broom) will do a "quick cleanup" to fix bond angles and hybridization. There are other buttons, but these are the main ones for this exercise.

7) Click on the **Build** button. From the "Build" pull-down menu, select the "fragment" option. A new dialogue box will appear. Select "Ring" and then "Benzene."


When these options are selected, select "OK." In the "builder" window, click anywhere and a benzene ring should appear.
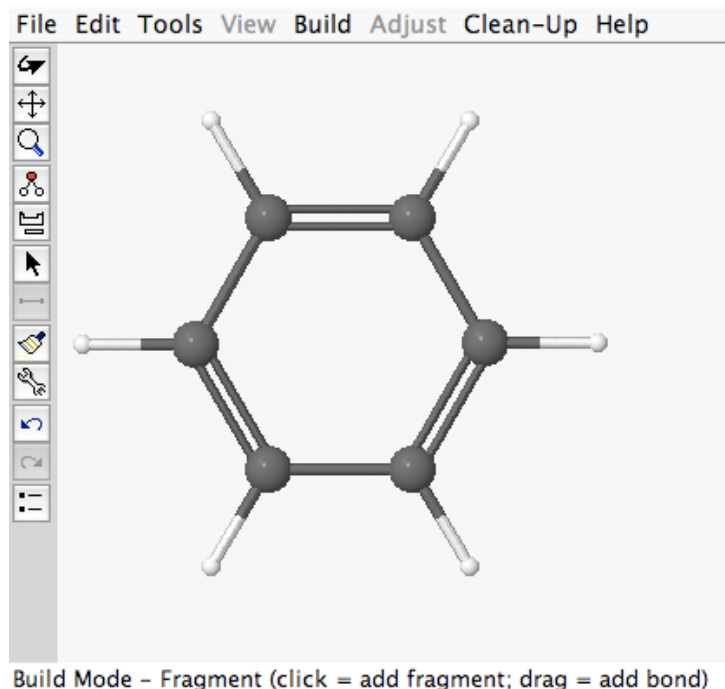
WebMO Instructions

Select the **Periodic Table** tool from the palate on the left hand side of the builder screen. A new window containing a periodic table will appear. Select "N" (nitrogen), and the window will disappear. Now, click on a hydrogen (the smaller white spheres). It should be replaced with a blue sphere. Select the **Periodic Table** tool again, and select carbon to reset the default drawing atom to carbon.
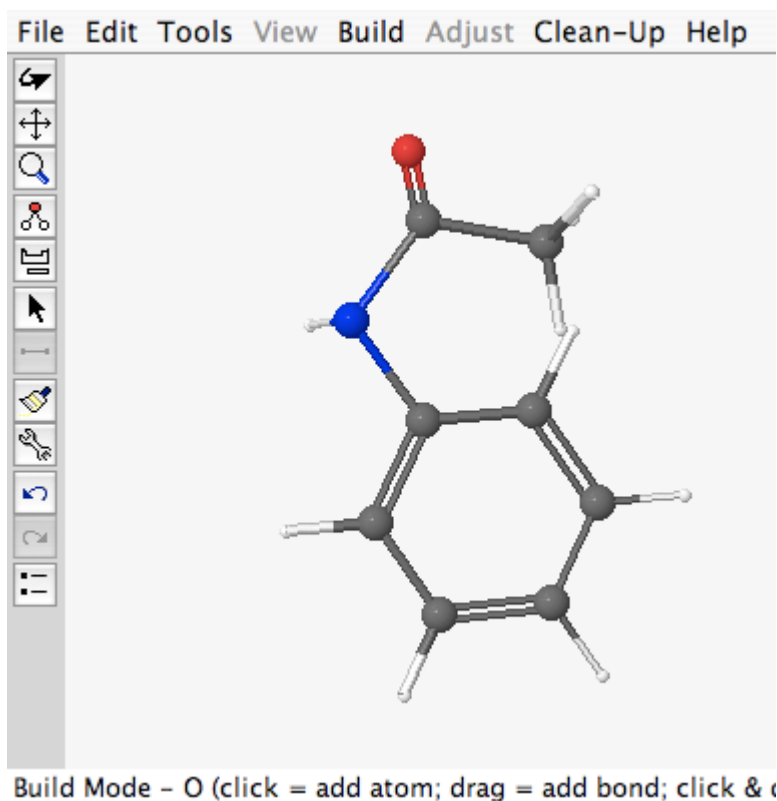
Click the **Build** button from the palate. Click and drag from the nitrogen to a blank space. This should leave a new grey sphere (a carbon atom) where you dragged, and a line connecting the nitrogen and the new carbon. This is how you build molecules: click an existing atom and drag to form a new atom and bond. Finish drawing an acetate group on the nitrogen:
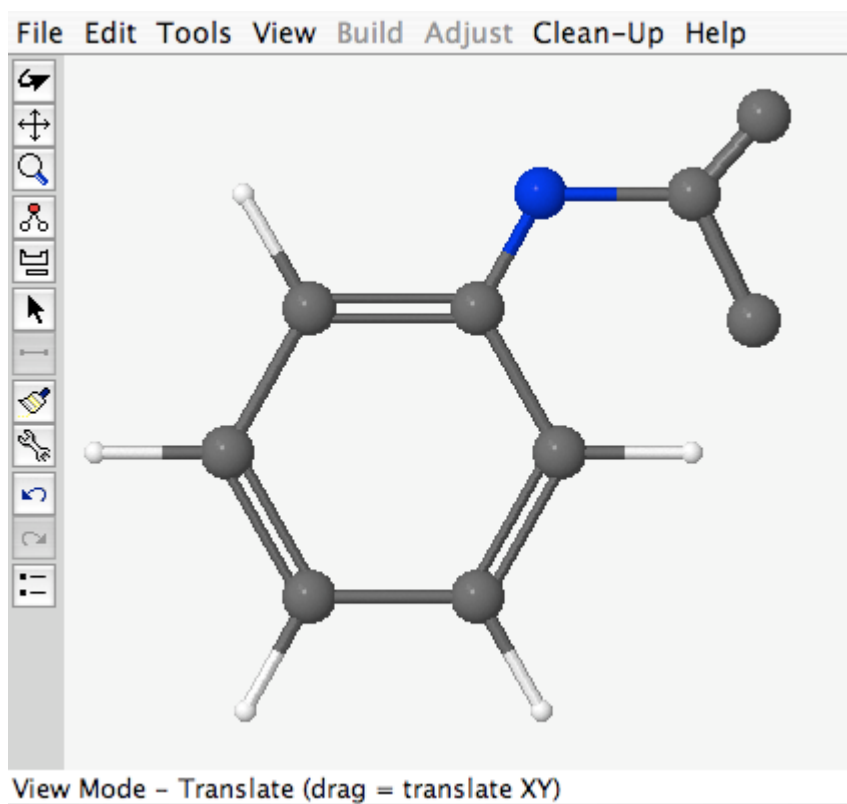
Clicking and dragging between two existing atoms will increase the bond order by one bond (*i.e.* single bond to double bond, etc.). Draw a second bond between the carbon attached to the nitrogen and one of the adjacent carbons. Then, using the **Periodic Table** tool, change the appropriate atom into an oxygen (a red sphere) to complete the acetate group.

Click the **Clean-Up** button on the palate. All the missing hydrogens should be automatically drawn in and the bond angles adjusted. Your molecule should look something like this:

WebMO Instructions

File Edit Tools View Build Adjust Clean-Up Help

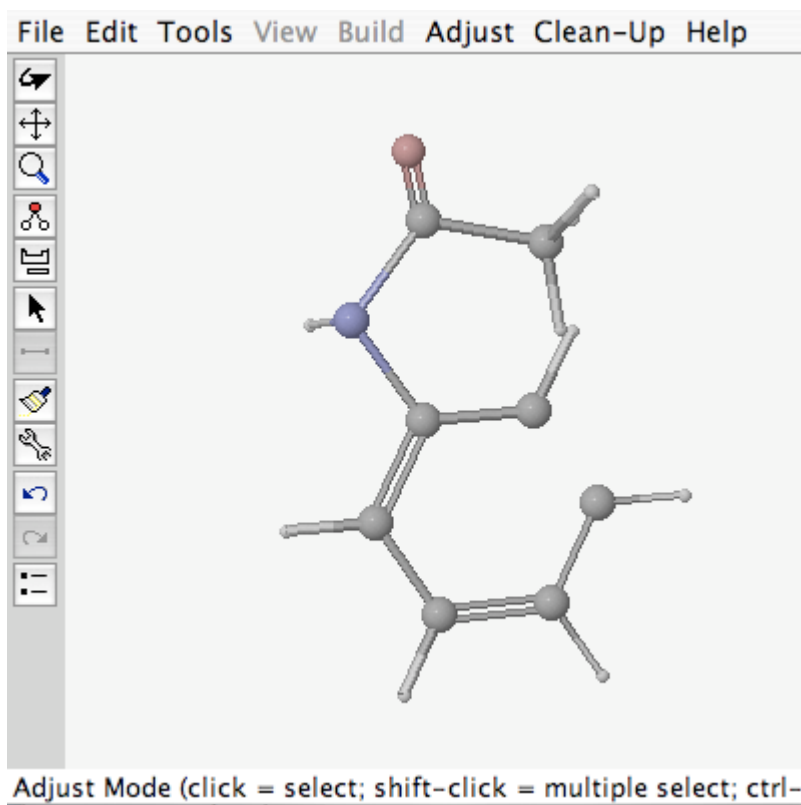Build Mode - O (click = add atom; drag = add bond; click & (

This is the structure of acetanilide. This will be the base structure for most of your calculations. Now we will add the bromine to make the intermediate carbocation. You will make three similar structures: Bromine in the ortho position, para position, and meta position:

Ortho   Para   Meta
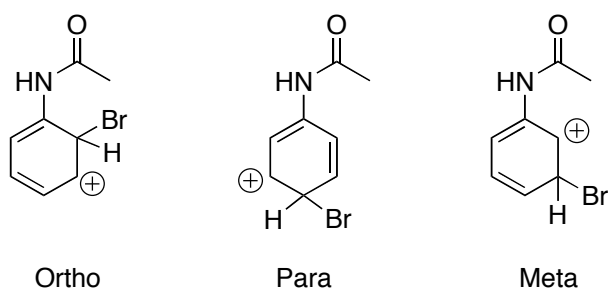
The following instructions will walk you through the construction of the ortho substituted compound. You can make the other two in a similar way.

8) Click on the **Selection Tool** button. Then click on the double bond in the aromatic ring between carbons 2 and 3. (Carbon 1 is the carbon with the nitrogen attached. This will leave the double bond the same color, but "white out" or "Fad" the rest of the structure. From the "Adjust" pull-down menu, select "Delete Selection." Your molecule should now look something like this:

6

WebMO Instructions

Select the **Build** icon from the palate, and redraw a single bond between the two carbons that used to be double bonded. Then add a new atom on carbon 2 (the ortho position) and change the atom to a bromine using the **Periodic Table** tool from your palate.

Notice: You should note that the carbon adjacent to the bromine has one valance open (it is missing a substituent). Computer programs aren't yet smart enough to understand when a hydrogen is supposed to be attached to an atom or when it isn't. Remember that when we draw structures, we often omit the hydrogens and assume they are there. The computer programs assume they are ***not*** there. This is how we tell the computer we have a carbon that is missing a substituent (like in a carbocation). We will also have to tell the computer that the charge is +1, but we will do that a little later.

You now should have a structure for the carbocation intermediate formed when the bromine adds to the ortho carbon:

WebMO Instructions


```
File  Edit  Tools  View  Build  Adjust  Clean-Up  Help
```

Build Mode – Br (click = add atom; drag = add bond; click & drag)
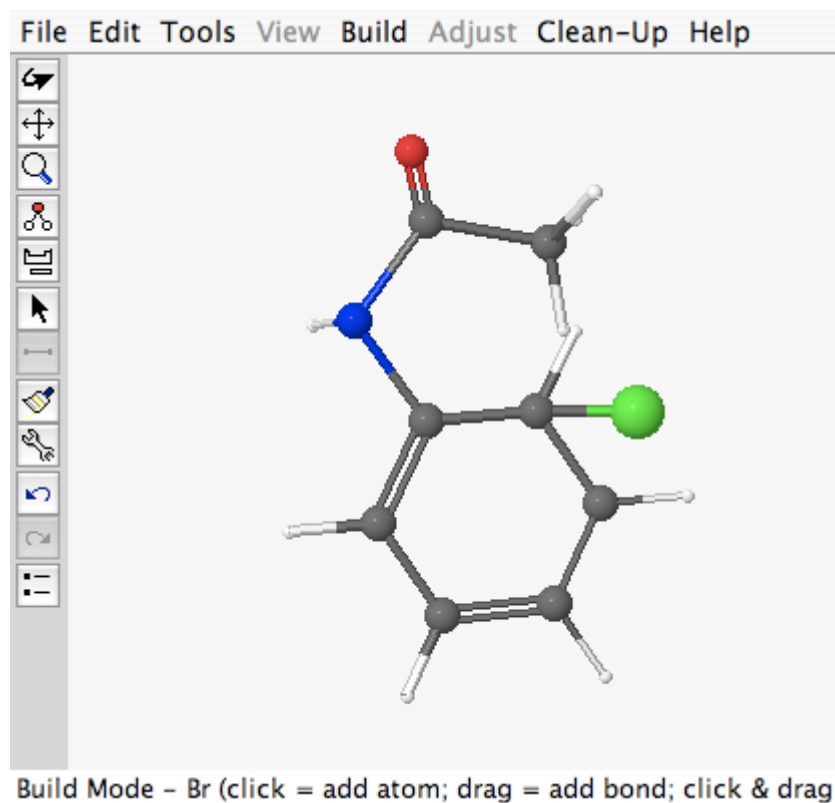
9) Under the "File" pull-down menu, select "close" to close the window. Your molecule should be transferred to the "Build Molecule" window. You now have the molecule we want to study.

10) Underneath the box containing your building tools, there are arrow buttons pointed to the right and to the left. The one pointed to the right is the **Continue Button** (see the builder window on pg 3 of this document). Click this arrow to go to the calculations set up windows. There are a lot of options in these windows that you won't understand. Trust me that the settings I give you are correct. If you want to know about what each of the options mean, feel free to ask.

11) Once you click on the arrow pointed to the right, a new window will appear:
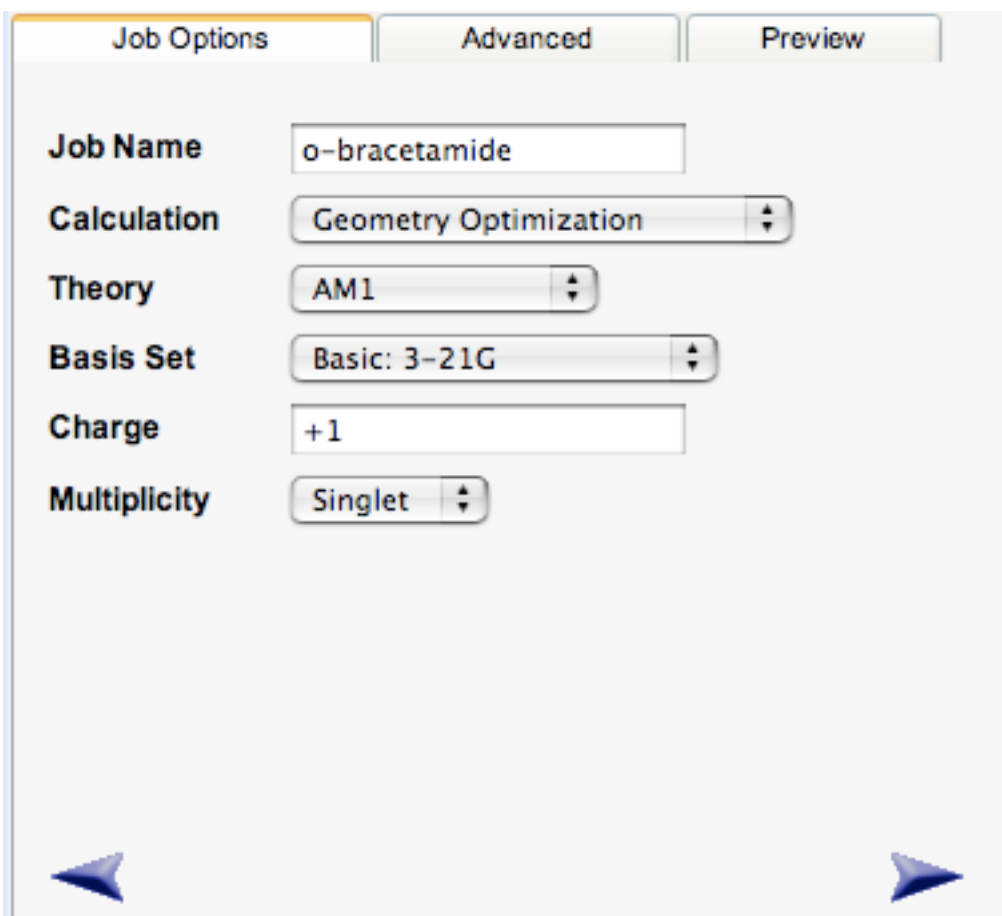
Engine	Description
⊙ **Gaussian**	Ab initio and semi-empirical calculations
Select Queue	workq

Make sure that the radio button for Gaussian is selected. (This is the actual computer program that will do the calculations.) The queue should be "workq" as shown above.

WebMO Instructions

Click the right arrow to continue.

12) A new window with a tab called "job options" will open up.
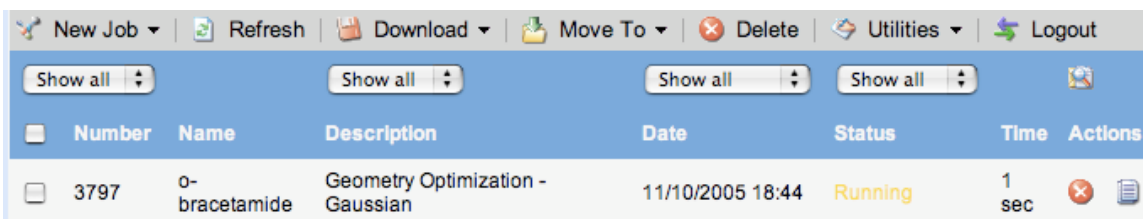
Give the job a name (one that you will remember and associate with a particular molecule), and set the rest of the settings as shown above. Then click on the right arrow to continue. This should submit the job.

13) You will be taken back to the "WebMO Job Manager" page, and your job will be listed in the "Available Jobs" box. You should notice a "status" message saying that the job is running.
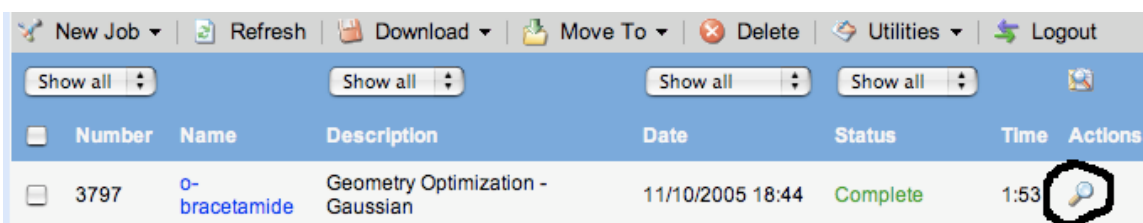
This calculation should only take a few minutes, so if you wait a few minutes and click on the **Refresh** button (Next to the **New Job** button), you can see if your job has

completed. If it is still running or is waiting to start (queued) it will tell you. Keep
refreshing periodically until your job is done.

**If your job stops with a message that it has "failed," there is something wrong.
Look at the trouble shooting section at the end of this document for common
problems that I often encounter. Don't get frustrated. It might take several false
starts to get a job successfully running!**

If your job is finished, a new "status" message will appear saying that your job is
complete. A magnifying glass icon also appears

Click the magnifying glass to obtain the energy from the results file. A new web page
will open that contains a "build" window with the new geometry of you molecule.
**Check to see that the geometry looks "right." If bonds are obviously too long, the
initial geometry may have been too far off for the calculation to work properly. Use
common sense. You will know if it is wrong just by looking at it.**
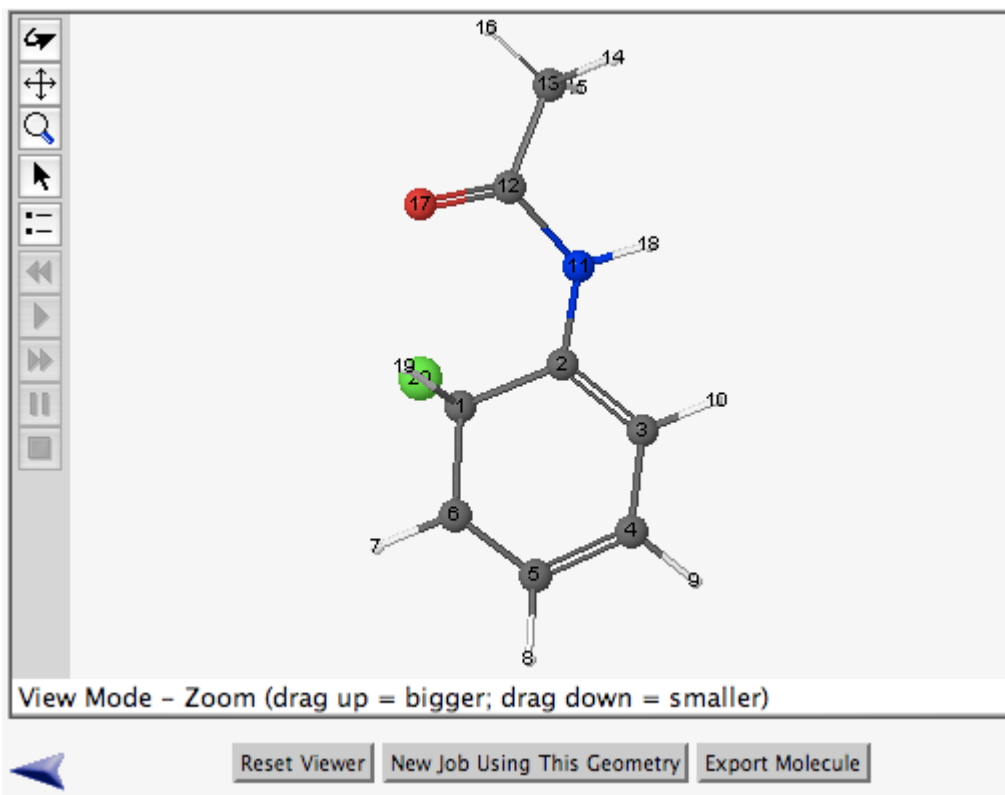
WebMO Instructions

Note: Don't click it yet, but the button **New Job Using This Geometry** can be used to build the other isomers. When you click this button, a new "builder" window will open and you can modify the structure so that it looks like one of the other molecules we need to examine. This can save some time on the other calculations as the majority of the structure is already built.

Below this builder window is list of calculated quantities. Draw the structure on a piece of paper and write down the energy (AM1 Energy) that is listed. You probably only need about 4 decimal places for the energy (*i.e.* 165.9522 for the example below). You will compare this energy to the energy of the other two molecules in this series and determine which is more stable (of lower energy). Based upon Hammond's postulate, the lowest energy transition state should correspond to the lowest energy intermediate, and this should be the predicted product for the reaction.

14) Now scroll back up and select the **New Job Using this Geometry** button. Click on the **Open Editor** button. A new window opens for you to edit the structure. Follow the same general procedure to build the para- and meta-substituted intermediate. Submit them for calculation and record the calculated energies for each. The job submission process should be the same for each structure.

15) Now that you have the acetanilide series done, consider the following series:
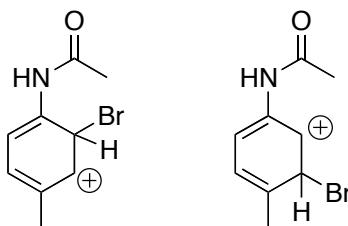
These are nearly the same, but they have a methyl group in the para position. Build these structures, submit them for calculation, and record the energies of each. Which is more stable? What should be the major product?

You should have a total of five (5) calculated energies for this excercise: o-bromo acetanilide, *p*-bromoacetanilide, *m*-bromoacetanilide, 4-methyl-2-bromoacetanilide, and 4-methyl-3-bromoacetanilide.

Trouble Shooting

There are several places where you may run into difficulties with the calculation. Here are two of the most common mistakes and what to look for.

1) If your optimized geometry just looks wrong, it will be obvious:

View Mode – Rotate (drag = rotate XY; ctrl–drag = rotate Z)
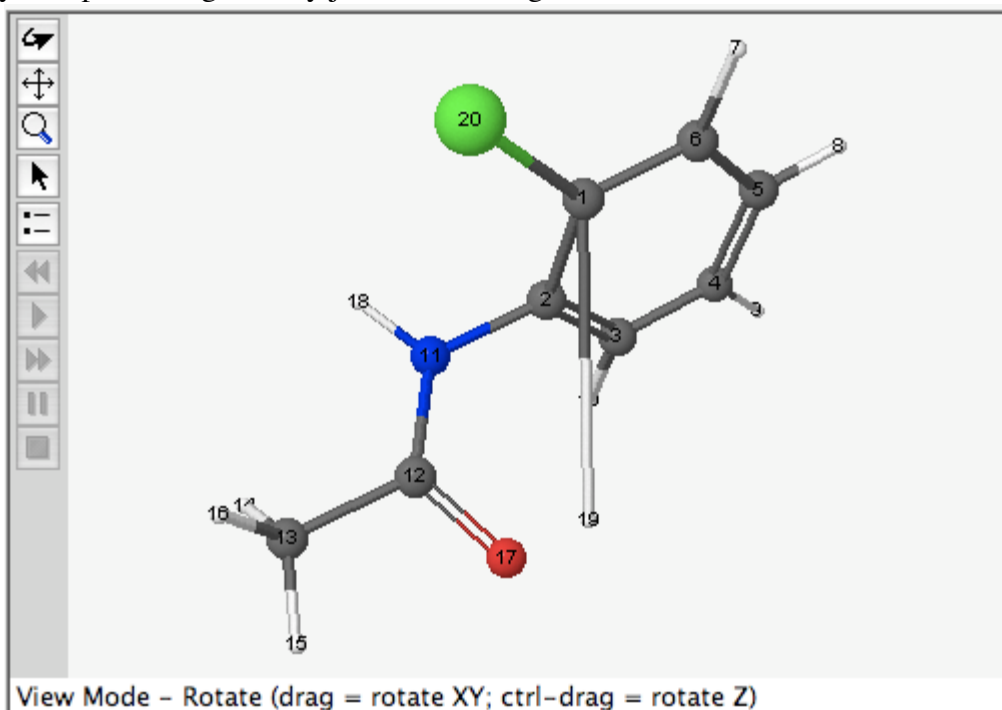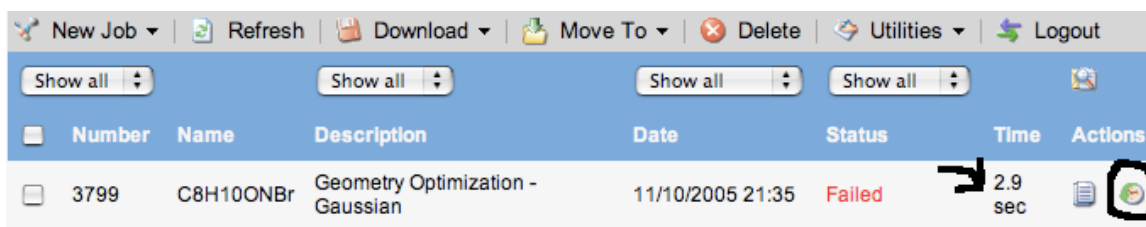
WebMO Instructions

Notice the C1-H19 bond (computer's labeling) is way too long. To fix this, click on the **New Job Using this Geometry** button. Then, click the **Open Editor** button. A new window open for you to edit the structure.

The easiest way to fix the structure is as follows:

Select the **Clean-Up** button from the palate on the left hand side of the window. This will fix the bond lengths and angles. Then select the **Rotate Tool** from the palate (top button with a curved arrow icon). Rotate the molecule in space by clicking and dragging. Notice that the clean-up function added a hydrogen where we want the carbocation. Click the **Selection Tool** icon and then select the hydrogen you want to remove. I suggest the one that is most out of the plane of the six-membered ring. From the "Adjust" pull down menu, select "Delete Selection."

Now close the window and follow the instructions listed above for submission of the job to calculation.

2) If the job never says "running" in the status column of the job manager window, it just comes back as "failed," then there is something wrong with your structure. Note the "time" listed in the figure below: 2.9 sec. The program only had enough time to know it was confused. The most common reason for this is that your structure was wrong. I often forget to delete the right hydrogen, then the electron count is wrong for the given number of atoms and the program can't handle that.

To fix this, click the icon under the "Actions" column that looks like some kind of coin (circled in the picture above). This will take you to the builder window. Click the **Open Editor** button, and see if the structure really is right. When the structure is right, close the editor and click the "continue" arrow (pointing to the right) to set up and submit the job for calculation.