

Intermediate Molecular Modeling



<http://www.webmo.net/>



Spectroscopy

Exercise 1: Method Dependence and Scaling for the Infrared Spectrum of Formaldehyde

Build a molecule of formaldehyde. Use Clean-Up > Comprehensive – Mechanics.

Choose Mopac as the computational engine. Type in/Choose the following:

Job Name: CH2O AM1 GO (The “GO” stands for **G**eometry **O**ptimization)

Calculation: Geometry Optimization

Theory: AM1

Charge: 0

Multiplicity: Singlet

Click on the blue “continue” arrow. You should now see your job listed. When the calculation is finished, open the file by clicking on the name, then click on New Job Using This Geometry, and Type in/Choose the following:

Job Name: CH2O AM1 IR

Calculation: Vibrational Frequencies

Theory: AM1

Charge: 0

Multiplicity: Singlet

Click on the blue “continue” arrow. You should now see your job listed. When the calculation is finished, open the file and scroll down to the Vibrational Modes window.

How many transitions are shown (count the number of frequencies)? _____ Is this the number expected? _____

Click on the filmstrip next to one of the frequencies and observe the corresponding vibrational motion. Try to identify the type of motion for each transition. (The molecule can be rotated if needed). In the table on the next page, record the frequencies and type of motion for each. To help identify the type of motion, see the link available at:

http://en.wikipedia.org/wiki/Infrared_spectroscopy

Repeat the processes described above, but use “PM3” in place of “AM1”. Observe the vibrational motions, and record the frequency data in the appropriate column on the next page.

Start a New Job, and build a molecule of formaldehyde. Clean up the structure by selecting Clean-Up > Comprehensive – Mechanics.

Choose Gaussian as the computational engine. Type in/Choose the following:

Job Name: CH2O DFT GO

Calculation: Geometry Optimization

Theory: B3LYP

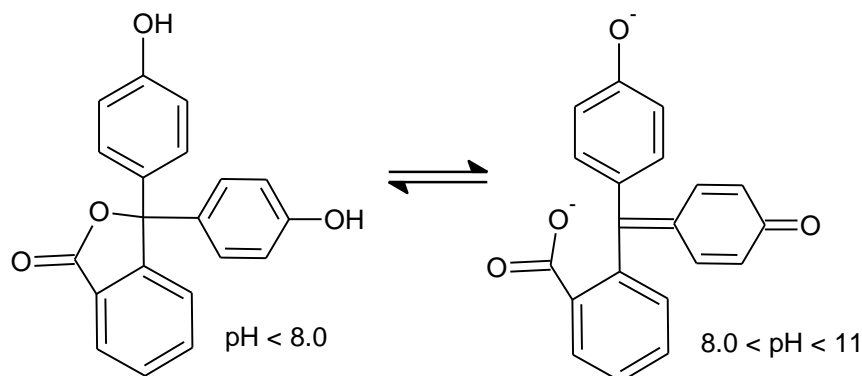
Basis Set: Routine: 6-31G(d)

Charge: 0

Multiplicity: Singlet

Exercise 2: Electronic Transitions of Phenolphthalein at Various Values of pH

Phenolphthalein is a widely used acid-base indicator. Two forms of the molecule, shown below, will be constructed and the UV-Vis spectrum of each will be calculated. Each optimized structure will be investigated to determine the correlation between structure and absorbance of light. We will be using the PM3 method for geometry optimizations and ZINDO for UV-Vis calculations, so the results will not be *quantitative*. We should see the correct *qualitative* changes in the spectra of the two forms.



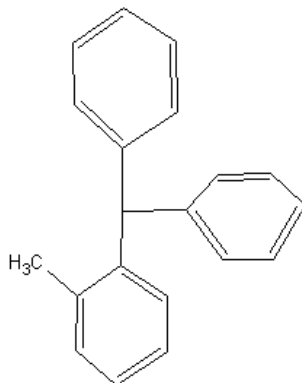
It can be challenging to draw chemical structures in three dimensions using tools that only work in two dimensions. ChemSketch is generally easier to use in building complex structures than is WebMO. We can import the ChemSketch built-and-saved structure into WebMO, fix it up a little bit, then do our calculations.

★THE INSTRUCTORS WILL PROVIDE THE CHEMSKETCH STRUCTURES FOR YOU. The instructions below are for later reference. Continue at the ★ symbol on the next page.

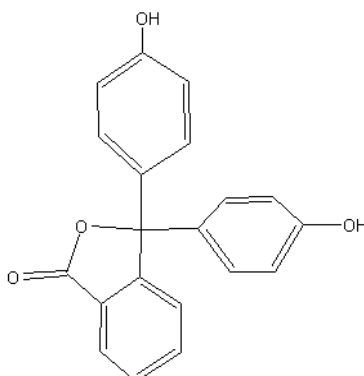
Building the low-pH form of Phenolphthalein in ChemSketch

Open **ChemSketch**. Make sure the **Structure mode** is chosen (button, upper left). Under the ACD/Labs pull down at the top, click **3D Viewer**. Click **ChemSketch** on the lower left.

Choose **carbon** on the left-hand toolbar, and draw the carbon backbone of the low pH form of phenolphthalein. To make double bonds, simply click and drag twice between the two carbon atoms. You should end up with something like the structure shown below:



When you have the above structure, it's time to add the oxygen atoms. Choose **oxygen** on the left-hand toolbar and place the O atoms in the correct locations, including the double bond. You should now have the structure shown below:



We need to adjust bond lengths and angles. Choose **Tools > Clean Structure**.

Now we need to go from 2D to 3D. Choose **Tools > 3D Structure Optimization**.

Click on **Copy to 3D** (lower left button).

Use the tools in the 3D Viewer to rotate, view ball-and-stick, etc. Notice how the three rings are arranged sort of like a propeller.

Choose **File > Save as**, use the Save as type: pull down menu and choose **MDL Molfiles (*.mol)**, and name the file **indicatorLowpH.mol**. Save to the Desktop (or another location you'll remember).

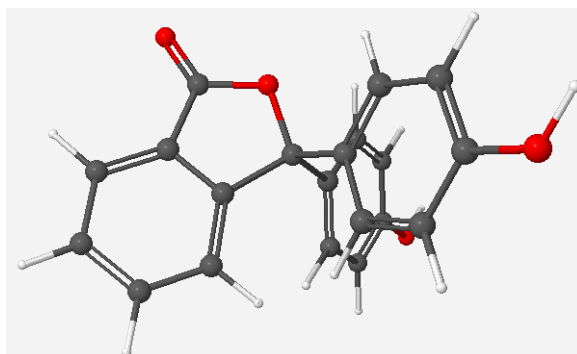
★ START HERE

Open a browser and log in to the WebMO server:

Choose **New Job > Create New Job**, then click the **Import Molecule** button.

In the Import Molecule window, choose **MOL Format** from the Format pull down menu, click in the **Generate Bonds** box so it is checked, then **Browse** to the location of your file, click open, followed by **Import Molecule**. You should now see your molecule in the Build Molecule window of WebMO.

Unfortunately, the correct structure is not always imported. We need to fix several things. Click the Periodic Table icon (5th down on right), choose the C atom, and make alternating double bonds in all three rings by clicking and dragging once between the appropriate carbon atoms:



TRIPLE check the structure to make sure it is correct (compare with the structure on Page 1)!

Click the blue “continue” arrow on the right, and choose **Mopac** as the computational engine.

Click again on the blue arrow and select/type in the following:

Job name: C20H14O4 lowpH
Calculation: Geometry Optimization
Theory: PM3
Charge: 0
Multiplicity: Singlet

Submit the job by clicking on the blue continue arrow.

When the job is done, click on the filename and use the rotate tool to investigate the structure. Check the relative orientation of the planes of the three rings.

Click on **New Job Using This Geometry**. Click the blue “continue” arrow and select **Gaussian** as the computational engine. Click the arrow again and select/type in:

Job name: C20H14O4 lowpH UV-Vis
Calculation: UV-Vis Spectrum
Theory: Hartree-Fock
Basis Set: Other (null)
Charge: 0
Multiplicity: Singlet

Click on the **Advanced tab**. Type in **ZINDO** in the **Additional Keywords** window.

Click on the **Preview tab**, then click **Generate**. Edit the first line to read:

#N CIS=(NStates=10)/ZINDO

(i.e. remove “null” and the space after the slash).

Submit the job by clicking on **Submit job** on the lower left side. Click **OK** in the pop up window.

When the job is complete, click on the filename and scroll down to view the “Excited States” table. Near the bottom of the table, click on the magnifying glass to view the calculated spectrum.

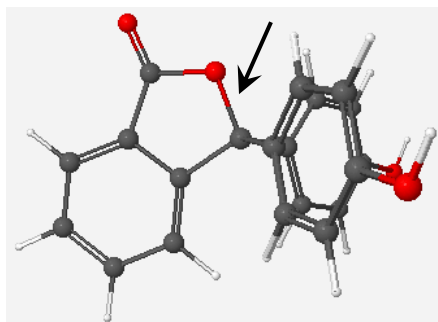
In the View Job window, use your mouse and place the cursor on the top of the peak and record the wavelength at maximum absorbance value below (the x -coordinate represents λ and is displayed just above the spectrum):

_____ nm.

Building the mid-pH form of Phenolphthalein

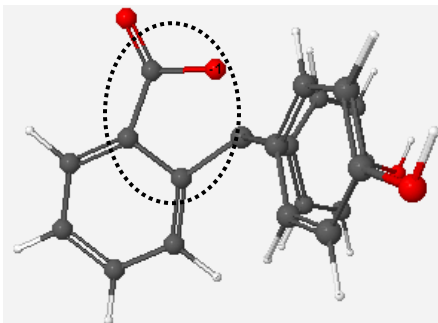
Go to **Job Manager** and open the **C20H14O4 lowpH** geometry optimization file from before. Click on **New Job Using This Geometry**.

Use the Rotate tool to position the molecule as shown on the next page:



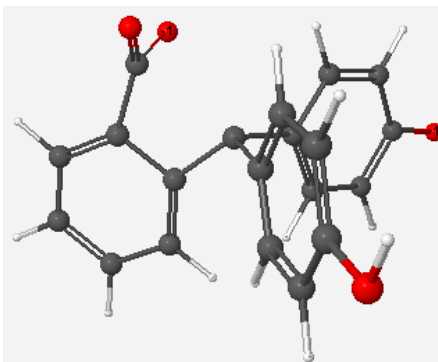
In the WebMO Build Molecule window, choose **Tools > Adjust**. Click on the C-O bond to the central carbon atom (See arrow above). Hit **Delete** on your keyboard to remove the bond.

Click on the O atom to highlight it. Choose **Adjust > Charge** and type in **-1** in the pop-up window. Click **Apply** followed by **OK**. You should now have the structure shown below with a negative charge on the O atom:



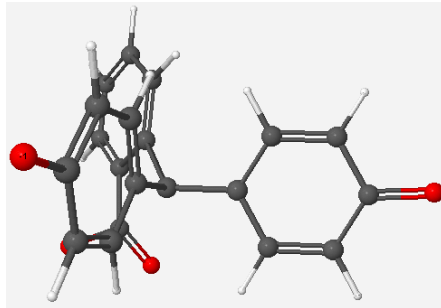
The O atom is still within bonding distance of the central carbon. We will adjust the C-C-C-O dihedral angle (circled above) to move it further away. Choose **Tools > Adjust**. Click on the O atom, then hold down the shift key and click on the attached C atom, the next C atom in the ring, and the final C atom (See circled atoms above). Choose **Adjust > Dihedral Angle**, and type in **90** in the **Adjust Dihedral Angle** window. Click **Apply** followed by **OK**.

Use the Rotate tool to turn the molecule so that one of the rings with an O-H is clearly visible. In the WebMO Build Molecule window, choose **Tools > Adjust**. **Click on the hydrogen atom** of the O-H group to highlight it. Hit **Delete** on your keyboard to remove the atom. **Click on the O atom** to highlight it. Choose **Adjust > Charge** and type in **-1**. Click **Apply** followed by **OK**. You should have the structure shown below:



Use the Rotate tool to turn the molecule so that the other ring with the O-H is flat on the screen. **Follow the above steps** to remove the hydrogen atom. **Click on and delete the double bonds**

in the ring. Choose the “Periodic Table” icon and click on “C” in the Periodic Table. Redraw the bonds on this ring as shown below:



Click the blue “continue” arrow. Select **Mopac** as the computational engine, click the blue “continue arrow”, and select/type in the following:

Job name: C20H12O4(-2) midpH
Calculation: Geometry Optimization
Theory: PM3
Charge: -2
Multiplicity: Singlet

Submit the job by clicking on the blue continue arrow.

When the job is complete, click on the filename and use the rotate tool to investigate the structure. Look carefully at the orientation of the planes of the three rings relative to one another. Pay close attention to the two rings that have single oxygen atoms attached.

Click on **New Job Using This Geometry**. Click the blue “continue” arrow and select **Gaussian** as the computational engine. Click the arrow again and select/type in:

Job name: C20H12O4(-2) midpH UV-Vis
Calculation: UV-Vis Spectrum
Theory: Hartree-Fock
Basis Set: other
Charge: -2
Multiplicity: Singlet

Click on the **Advanced tab**. Type in **ZINDO** in the **Additional Keywords** window.

Click on the **Preview tab**, then click **Generate**. Edit the first line to read:

#N CIS=(NStates=10)/ZINDO

(i.e. remove “null” and the space after the slash).

Submit the job by clicking on **Submit job** on the left side. Click **OK** in the pop up window.

When the job is complete, click on the filename and scroll down to view the “Excited States” table. Near the bottom of the table, click on the magnifying glass to view the calculated spectrum.

In the Spectrum Viewer window, use your mouse and place the cursor on the top of the most intense peak and record the wavelength at maximum absorbance (λ_{max} – displayed in the upper right of the “Spectrum Viewer” window) value on the next page:

_____ nm

Has the λ_{max} shifted relative to the low pH structure? _____

Which direction did λ_{\max} shift?

Which of these two structures is expected to absorb visible light? _____

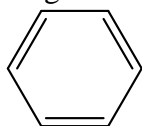
Does the shift in absorption wavelength you calculated make sense? _____

Focus on the phenolic rings (the two rings with a single O attached) of each structure. For the structure with an expected absorbance in the visible region, what is the difference in the position of two of the rings?

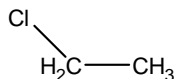
What is happening to the structure to cause the change in λ_{\max} ?

Exercise 3 – NMR Chemical Shift Calculations

Build the following molecules, clean up each structure by selecting Clean-Up > Comprehensive – Mechanics, and perform a geometry optimization using Gaussian > B3LYP/6-31G(d).



benzene



1-chloroethane



ethanol

Once the geometry optimization is complete, open one of the files and choose “New Job Using This Geometry”. Click the blue “continue” arrow, choose Gaussian and Type in/Choose the following:

Job Name: (Use an appropriate name of your choice)

Calculation: NMR

Theory: B3LYP

Basis Set: Routine: 6-31G(d)

Charge: 0

Multiplicity: Singlet

Once the job is complete, open it and scroll down to see the relative ¹H- and ¹³C-NMR chemical shifts. Some atoms are equivalent, but may have slightly different values due to the static structure at which the calculation was performed. Fill in the values on the next page and compare with the experimental values.

| Benzene | Calc. | Exp. | CH₃CH₂OH | Calc. | Exp. |
|---------------------------------------|--------------|-------------|---------------------------------------|--------------|-------------|
| H's | | 7.16 | Methyl H's | | 1.16 |
| C's | | 128.4 | Methylene H's | | 3.59 |
| | | | Hydroxyl H | | 4.00 |
| CH₃CH₂Cl | | | Methyl C | | 17.6 |
| Methyl H's | | 1.48 | Other C | | 57.0 |
| Methylene H's | | 3.57 | | | |
| Methyl C | | 18.7 | | | |
| Other C | | 39.9 | | | |

Recall that the calculated numbers are gas phase values compared to the solution phase experimental values. More accurate values could be obtained using a larger basis set (with added computational expense!).

Exercise 4 – Use of Parallel Processing for the Geometry Optimization of Benzene

Look at the Job Manager and find the time for the geometry optimization job performed in Exercise 3 above for benzene. Note this times in the table below under “One Processor time”:

Geometry Optimization Times [B3LYP/6-31G(d)]

| Molecule | 1 Processor Time | 2 Processor Time | 4 Processor Time |
|----------|------------------|------------------|------------------|
| Benzene | | | |

Build benzene again, using Comprehensive – Mechanics to clean the structure up. Then perform a geometry optimization as indicated below:

Choose Gaussian as the computational engine. Type in/Choose the following:

Job Name: (choose an appropriate name, indicating “2 processors” or “4 processors”)

Calculation: Geometry Optimization

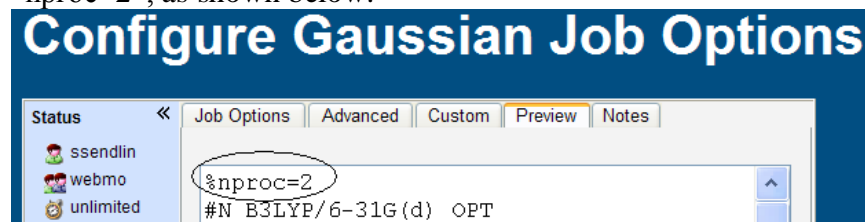
Theory: B3LYP

Basis Set: Routine: 6-31G(d)

Charge: 0

Multiplicity: Singlet

Click on the **Preview** tab in the Configure Gaussian Job Options window, then click the **Generate** button. Place the cursor to the LEFT of the # symbol at the start of the file and hit Enter on the keyboard to create a blank line at the top of the file. Then type in the keyword “nproc=2”, as shown below:



This directs the program to use two processors for the geometry optimization.

Click the Submit job link to the lower left, then click OK in the pop-up window. You should now see your job listed. Once the job is complete, note the time required and enter the value in the table on the previous page.

Repeat the above process for benzene, but this time use “nproc=4” to employ four processors.

Since the cluster we are using is a shared resource, the job completion times may depend on other factors than just the number of processors we assign. However, you should see a *decrease* in the time required to complete a geometry optimization as the number of processors used increases. This is the so-called “speed up curve”. You might think that a *further* increase in the number of processors would always lead to *decreasing* calculation times. This is often NOT the case however. As a given job is split into pieces for each processor to handle, a limit is reached where the time it takes to put all the data back together again outweighs the advantage of splitting things up in the first place. Sometimes data may have to be periodically shared among the processors in order for each to complete its part of the overall task. This will also tend to negate the parallel advantage.