

7 Infrared, Thermochemistry, UV-Vis, and NMR

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:

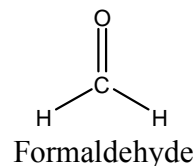
Job Name: CH2O AM1 Geom Opt

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, 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.

Repeat the process 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 or GAMESS as the computational engine. Type in/Choose the following:

Job Name: CH2O DFT Geom Opt

Calculation: Geometry Optimization

Theory: DFT

DFT Functional: B3LYP

Basis Set: 6-31G(d)

Charge: 0

Multiplicity: Singlet

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

Job Name: CH2O DFT IR

Calculation: Vibrational Frequencies

Theory: DFT

DFT Functional: B3LYP

Basis Set: 6-31G(d)

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.

As before, click on the filmstrip next to one of the frequencies and observe the corresponding vibrational motion. In the table on the below, record the frequencies.

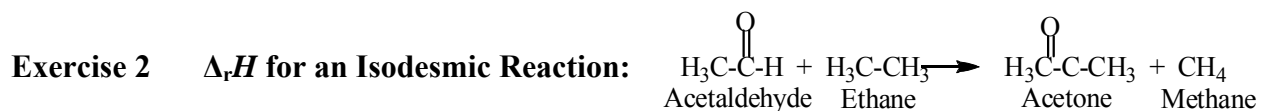
Which method seems to give the best results? _____

In the “View Job” window, click on Raw Output and investigate the contents of the file.

Due to the approximations implicit in these calculations, calculated vibrational frequencies are often higher than the experimental values. For better comparison with experimental results, the calculated frequencies are often multiplied by a scaling factor (fudge factor!). The scaling factors are listed below. Perform the corrections and list the new results in the appropriate columns. Do the scaled values give a better comparison with the experimental values?

Use the scaling factors (AM1 = 0.9532; PM3 = 0.9761; B3LYP/6-31G(d) = 0.9614)

Motion	AM1	Scaled AM1	PM3	Scaled PM3	B3LYP/6-31G(d)	Experimental values (cm ⁻¹)
						2843
						2782
						1746
						1500
						1249
						1167



An isodesmic reaction is one in which the total number of each type of chemical bond is the same in both reactants and products. Because of this equality in bond type, results of calculations using such a reaction should benefit from cancellation of errors.

Build each of the molecules shown above, and perform a geometry optimization using: (1) Mopac/AM1, (2) Mopac/PM3, (3) Gaussian with HF/6-31G(d) and (4) Gaussian with DFT B3LYP/6-31G(d).

For AM1 and PM3 methods, you will see the Heat of Formation ($\Delta_f H$) value listed in the Calculated Quantities window. To find the $\Delta_r H$ value, take the sum of the product $\Delta_f H$ values, and subtract the sum of the reactant $\Delta_f H$ values:

$$\Delta_r H = \sum \Delta_f H(\text{prod}) - \sum \Delta_f H(\text{react})$$

The HF and DFT results are given in units of hartrees and must be converted. For the HF/6-31G(d) you will see the RHF Energy listed in the Calculated Quantities window. For the B3LYP/6-31G(d) values, you will see the R-B3LYP energy listed in the Calculated Quantities window. To find $\Delta_r H$ and convert the energy units from hartrees to kcal mol^{-1} , use:

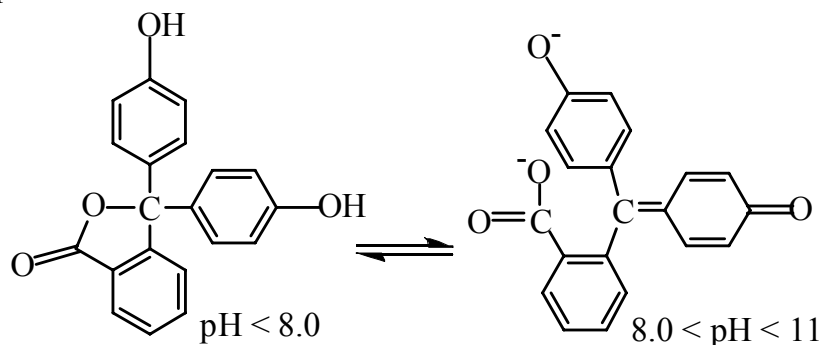
$$\Delta_r H = \left[\sum H(\text{prod}) - \sum H(\text{react}) \right] (627.51 \text{ kcal mol}^{-1} / h)$$

Place your results in the table below and compare with the experimental value.

AM1	PM3	HF/6-31G(d)	B3LYP/6-31G(d)	Experimental (kcal mol^{-1})
				-9.9 ± 0.3

Exercise 3 Electronic Transitions of Phenolphthalein at Various pH

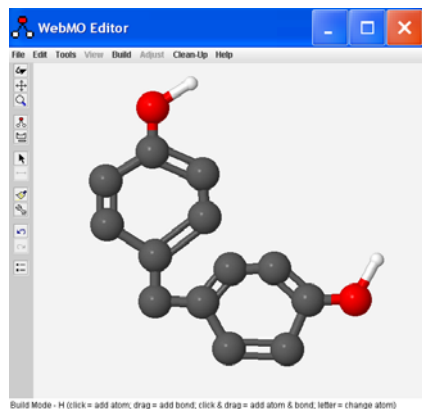
Phenolphthalein is a widely used acid-base indicator. Two forms of the molecule, shown below, will be constructed and the UV-Vis spectrum of each will be calculated. Each optimized structure will be investigated to determine the correlation between structure and absorbance of light. We will be using 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.



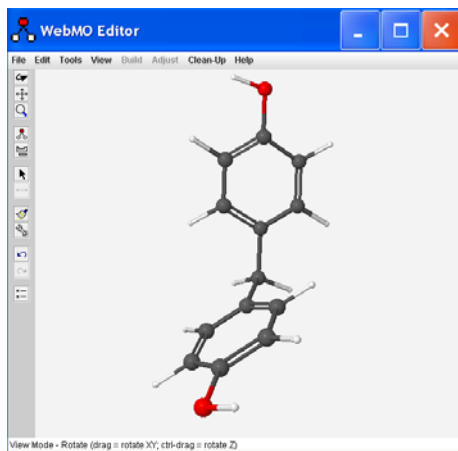
It can be challenging to draw chemical structures in three dimensions using tools that only work in two dimensions. In order to avoid overlapping atoms and other troubles, we will use a stepwise approach in constructing phenolphthalein. This approach may serve you well for building other molecules.

Building the low-pH form of Phenolphthalein

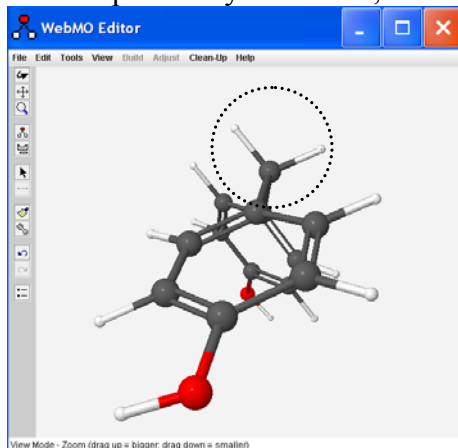
In the WebMO Editor window, build the following fragment of phenolphthalein:



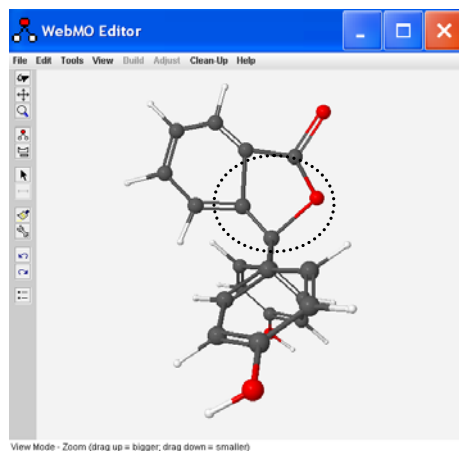
Be sure you have alternating double bonds in both rings, and include the H atoms (white) on the two oxygen atoms (red). Zooming out (magnifying glass icon) may help. Choose “Clean-Up > Add Hydrogens” followed by “Clean-Up > Geometry”. You should now have:



Use the rotate tool (1st down, left tool bar) to turn this structure so that the “CH₂” group that connects the two rings is in the plane of your screen, as shown below:



Choose “Tools > Adjust” in the WebMO Editor window. Click on one of the hydrogens circled above so that it is highlighted (rest of the molecule “grays out”), then hit “delete on your keyboard. Repeat this process for the other hydrogen atom. Build the remaining ring system (lower left of low pH structure, previous page). Choose “Clean-Up > Add Hydrogens”. You should now have the structure shown here:



Click on “Close Editor” and click on the blue “continue” arrow. Select Mopac as the computational engine. Click again on the blue arrow and select/type in the following:

Job name: C20H14O4lowpH
 Calculation: Geometry Optimization
 Theory: PM3
 Charge: 0
 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.

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: C20H14O4lowpHSpec
 Calculation: UV-Vis Spectrum
 Theory: HF
 Basis Set: other
 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 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 peak and record the wavelength at maximum absorbance (λ_{max} – displayed in the upper right of the “Spectrum Viewer” window) value here: _____ nm.

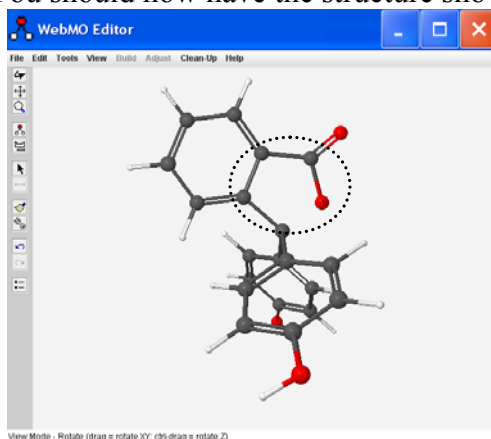
Building the mid-pH form of Phenolphthalein

Go to “Job Manager” and open the “C20H14O4lowpH” file from above. Click on “New Job Using This Geometry” followed by “Open Editor”.

Use the Rotate tool to position the molecule as shown at the bottom of the previous page.

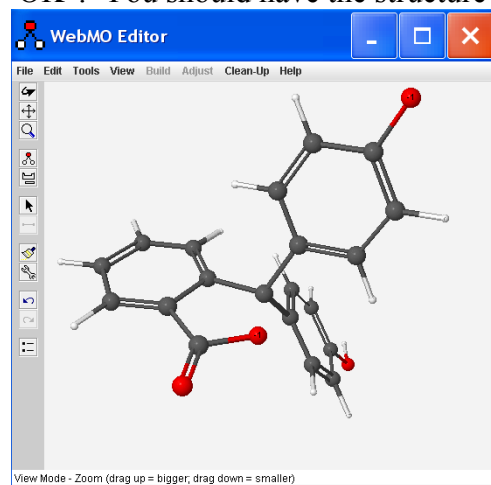
In the WebMO Editor window, choose “Tools > Adjust”. Click on the C-O bond to the central carbon atom. Hit “delete” on your keyboard to remove the bond.

Click on the O atom to highlight it. Choose “Adjust > Charge” and type in “-1”. Click “Apply” followed by “OK”. You should now have the structure shown below:



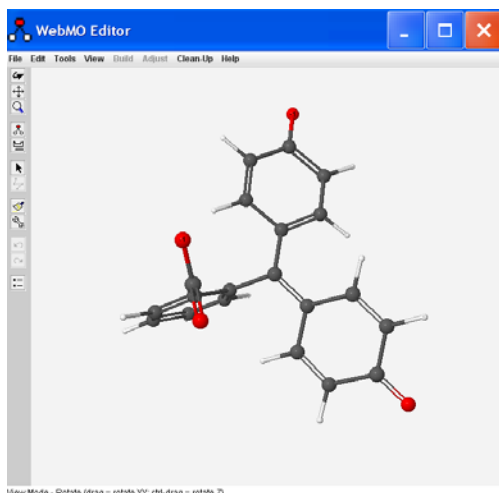
The O atom is still too close to the central carbon. We will adjust the C-C-C-O dihedral angle to move it further away. Choose “Tools > Adjust”. Click on the O atom, then hold down the shift key and click on the attached C atom, the next C atom in the ring, and the final C atom (See circled atoms above). 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 Editor 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 the ring as shown on the next page:



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

Job name: C20H14O4(-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 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: C20H14O4(-2)midpHSpec
 Calculation: UV-Vis Spectrum
 Theory: HF
 Basis Set: other
 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 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 here: _____ nm.

Has the λ_{\max} shifted relative to the low pH structure? _____ Which direction did λ_{\max} shift?

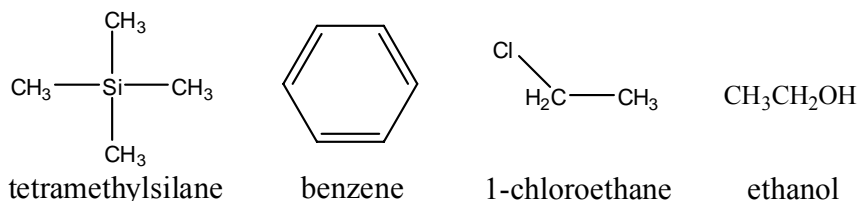
Which of these two structures is expected to absorb visible light? _____

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

Focus on the phenolic rings 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?

Exercise 4 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).



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: DFT

Basis Set: 6-31G(d)

Charge: 0

Multiplicity: Singlet

To calculate the ^1H - or ^{13}C -NMR chemical shift for a given atom, take the H or C shift and subtract the H or C value of TMS (some atoms are equivalent, but may have slightly different values). Fill in the values below 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			