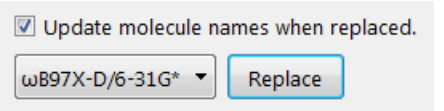
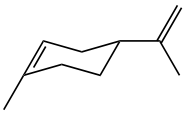
Chapter 5
Spectra and Properties of Organic Molecules from SSPD

The tutorials in this and the two chapters that follow involve the molecules that you built or sketched in the preceding two chapters. The emphasis shifts from providing input structures, to analyzing the results of quantum chemical calculations (in this and the following chapter) to actually doing calculations (in the final chapter in this section).

The Spartan Spectra and Properties Database (SSPD) provides atomic and molecular properties and NMR spectra for >300,000 molecules, calculated using the ωB97X-D/6-31G* density functional model and properties, IR and NMR spectra for the same set using the less accurate and less "costly" EDF2/6-31G* model. In addition, the ωB97X-D/6-31G* set contains more than 2,000 transition-metal organometallics and organolanthanides. Except for the *trans*-stilbene tutorial, you can use either ωB97X-D/6-31G* or EDF2/6-31G* models to explore what is calculated without having to actually run calculations. We suggest the former. Selection is made from the menu at the bottom of the dialog which results from *clicking* on the molecule name at the bottom of the screen.



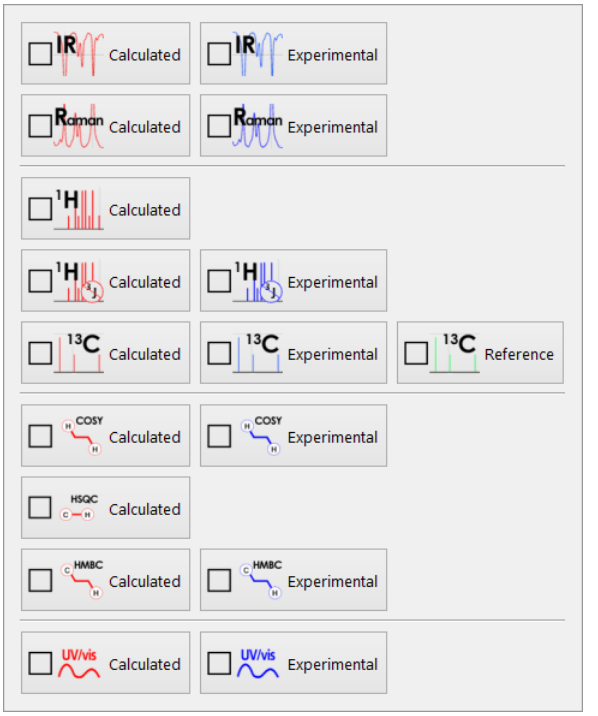
^{13}C Spectrum of Limonene



1. Build limonene ( ), minimize ( ) and exit the builder ( ).
   Alternatively, sketch limonene ( ) and exit the sketcher ( ).

2. *Click* on the name ***limonene*** at the bottom of the screen. Make sure that ωB97X-D/6-31G* is selected from the dialog that appears and *click* on **Replace**. Properties and spectra for limonene are now available.

3. Select **Spectra** from the **Display** menu, or *click* on ( ) if it appears at the top of the screen. *Click* on at the top of the spectra pane that results to show available calculated spectra (in red) and (possibly) available experimental spectra (in blue).



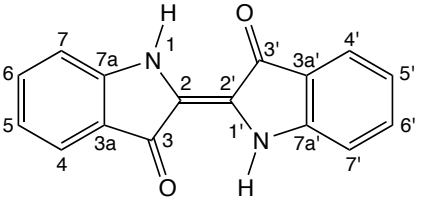
Select 13C Calculated. The calculated ^{13}C NMR spectrum appears in the spectra pane. There are ten lines corresponding to ten unique carbons in limonene. Up and down triangles demark a moveable cursor. *Click* on either (or on the dotted line connecting them) to select and with the left mouse button (or your finger), move horizontally over the spectrum. When you intersect a NMR resonance, it will be highlighted in the spectrum, the value of the chemical shift indicated, and the carbon (or carbons) in the structure responsible will be highlighted in the structure model (on the main screen).

4. Again, *click* on  at the top of the spectra pane, but this time, select  . The experimental ^{13}C spectrum of limonene will be superimposed on top of the calculated spectrum.* Visual comparison will give you an idea of the quality you can expect from NMR calculations. To get an even better idea, shift the range of the scale (initially from 150 to 0 ppm), move the cursor over the spectrum and zoom in with the center mouse wheel. You can return to the original setting by *clicking* on () in the bar at the top of the spectra pane.


Move one finger over the spectrum to select a line. Move two fingers over the spectrum to shift the range of the scale and pinch two fingers to zoom in and out.

5. Close ***limonene***.

Proton Spectrum of Indigo



1. Build indigo (), minimize () and exit the builder (). Alternatively, sketch indigo () and exit the sketcher ().
2. *Click* on the name ***indigo*** at the bottom of the screen. ωB97X-D should still be selected from the menu in the dialog that results. *Click* on **Replace**. Properties and spectra for indigo are now available. If the name does not appear, then you have made an error. In this case, re-enter either the builder by selecting **Edit Build** from the **Build** menu (), or the sketch pad by selecting **Edit Sketch** from the **Build** menu () and correct your model.

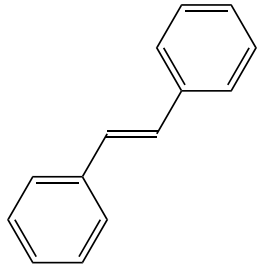
3. The calculated proton NMR spectrum of indigo can be displayed in two ways. The simpler "idealized" presentation assumes that

* The experimental spectrum comes from the NMRShiftDB. Requires on-line access.

three-bond HH coupling constants are zero. Select **Spectra** from the **Display** menu ( ) to bring up the spectra pane and *click* on in the bar at the top to show available calculated spectra (in red) and possibly available experimental spectra (in blue). Select from the palette. The spectrum that results shows only lines corresponding to the four unique hydrogens. To see a "familiar" proton spectrum, *click* again on , but this time select . The same four lines appear, but all are split (as in an experimental proton spectrum). The lines at 6.72 and 7.88 ppm are doublets due to C_7 and C_4, respectively (and split by C_6 and C_5, respectively). The lines centering at 6.89 and 7.44 are quartets (doublet of doublets), due to C_5 and C_6, respectively (and split by C_4 and C_6 and C_5 and C_7, respectively).

4. Close ***indigo***.

Infrared Spectrum of *trans*-Stilbene



You will need to use the EDF2/6-31G* collection in SSPD for this example, as IR spectra are not available for the ωB97X-D/6-31G* model.

1. Build *trans*-stilbene ( ), minimize ( ) and exit the builder ( ). Alternatively, sketch *trans*-stilbene ( ) and exit the sketcher ( ).

2. *Click* on the name ***trans-stilbene*** at the bottom of the screen, select **EDF2/6-31G*** from the menu at the left of the dialog that appears, and finally *click* on **Replace**.

3. Select **Spectra** from the **Display** menu ( ). *Click* on in the bar at the top of the spectra pane and select . The

calculated IR spectrum of *trans*-stilbene appears in the spectra pane.

4. As with NMR spectra, up and down triangles demark a moveable cursor. Select and move it horizontally over the spectrum. You will see that as you intersect a line in the spectrum, it will turn yellow and the value of the frequency will appear at the bottom. In addition, the molecular model "vibrates" to reflect the motion that the molecule undergoes. Examine the motions of one or more lines of moderate intensity in the vicinity of 1500 cm^{-1} (at 1446, 1494 and 1609 cm^{-1}). You might find it useful to expand the scale (use the scroll wheel) or to shift it (move the mouse horizontally over the spectrum while holding down the left button). You can return to the original settings by *clicking* on () in the bar at the top of the spectra pane.

Move one finger over the spectrum to select a line. Move two fingers over the spectrum to shift the range of the scale and pinch two fingers to zoom in and out.

5. *Click* on  from the bar at the top of the spectra pane and select 

. The experimental IR spectrum of *trans*-stilbene obtained from the freely-available NIST database will be superimposed onto the calculated spectrum. You will need to be online. Note that the two spectra are similar although the experimental spectrum exhibits a number of (small) lines not found in the calculated spectrum.

To see lists of the 3N-6 calculated IR frequencies as well as the (≤ 3N-6) frequencies assigned to the experimental spectrum together with intensities relative to their respective most intense frequency, *click* on  at the left of the spectra dialog. *Checking* individual lines (in the calculated IR) moves the cursor on the spectrum and animates the vibrational motion.

6. Close **trans-*stilbene***.