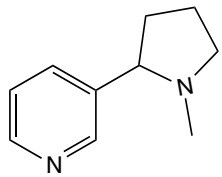
Chapter 6
Graphical Models for Organic Molecules from the Spartan Spectra and Properties Database

The tutorials in this chapter illustrate two of the most commonly-used graphical models, the electrostatic potential map for elucidating molecular charge distributions, and the local ionization potential and LUMO maps for anticipating electrophilic and nucleophilic reactivity, respectively.

Entries in the Spartan Spectra and Properties Database (SSPD) not only include the molecular structure, energy, properties and spectra, but also the wave function. This allows graphical models to be requested and displayed "on-the-fly". You will use the SSPD entries obtained from the ωB97X-D/6-31G* model for the examples in this chapter.

Electrostatic Potential Map for Nicotine



1. Build nicotine ( ), minimize ( ) and exit the builder ( ). Alternatively, sketch nicotine ( ) and exit the sketcher ( ).
2. *Click* on the name ***nicotine*** at the bottom of the screen. Make sure that **ωB97X-D/6-31G*** is selected from the menu in the dialog that results and *click* on **Replace**. Your structure will be replaced by that in SSPD making the wave function available.

3. Select **Surfaces** from the **Display** menu or *click* on () if it appears at the top of the screen. *Click* on **Add** (at the bottom of the **Surfaces** dialog that results) and select **electrostatic potential map** from the menu. This requests an electrostatic potential map (an electron density surface onto which the value of the electrostatic potential is color mapped). The line ***electrostatic potential map*** appears at the top of the dialog.

   The graphics calculation will run automatically following your request.* When it completes in a few seconds, *check* the box to the left of ***electrostatic potential map*** in the **Surfaces** dialog. The surface itself corresponds to the electron density, and provides a measure of the overall size and shape of nicotine. The colors indicate values of the electrostatic potential on this surface. By convention, colors toward red correspond to negative potential (stabilizing interaction between the molecule and a positive charge), while colors toward blue correspond to positive potential. The two nitrogen atoms show the largest negative potential (red). You will see that the nitrogen in the pyridine ring is more negative than the nitrogen in the pyrrolidine ring.

4. Quantify your observation. Select **Properties** from the **Display** menu or *click* on () if it appears at the top of the screen and *click* anywhere on the electrostatic potential map to bring up the **Surface Properties** dialog.

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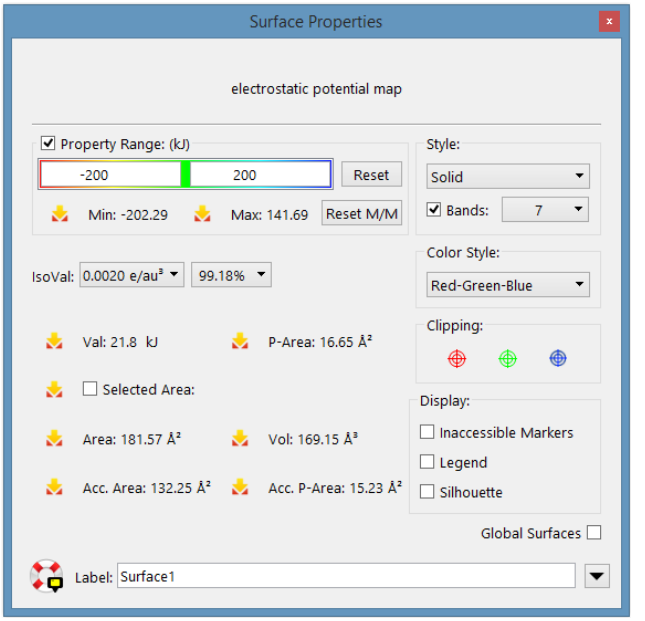
* If they don't, then you need to check the box to the left of **Auto-Gen Graphics** under **Miscellaneous** from the **Setting** tab in the **Preferences** dialog from the **Options** menu (**Chapter 25**)..

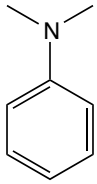


Check the box to the left of **Display Legend** towards the bottom right of the dialog to display the property range on screen. To translate the legend, *click* on the legend to select, then hold down the right mouse button and move the mouse. The legend is useful when making qualitative comparisons of property values. Turn the map such that you can clearly see the pyridine nitrogen and *click* on the area that is "most red". An arrow marks the point on the surface and the value of the potential is shown to the right of the legend. Do the same for the pyrrolidine nitrogen.

Tap on the legend to select. Move two fingers to move it around the screen. Pinch two fingers to make the legend smaller or larger.

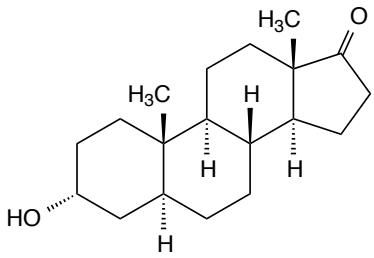
5. Nicotine is relatively small and it is easy to associate regions on the map with the underlying molecular skeleton. This becomes more difficult with increasing molecular size. Change the presentation, from the **Style** menu located inside the **Surface Properties** dialog or at the bottom right of the screen. Select **Transparent** or **Mesh**. You now can "see through" the map to the underlying molecular structure.
6. Close ***nicotine*** and any open dialogs.

Local Ionization Potential Map for N,N-Dimethylaniline



1. Build or sketch N,N-dimethylaniline and *click* on .
2. *Click* on ***N,N-dimethylaniline*** at the bottom of the screen. ωB97X-D/6-31G* should be selected from the menu in the dialog that results. *Click* on **Replace**. Your structure will be replaced by that in SSPD.
3. Select **Surfaces** from the **Display** menu ( ). *Click* on **Add** at the bottom of the **Surfaces** dialog that results and select **local ionization potential map** from the menu. This requests a map showing the energy required to remove an electron (the "ionization potential") as a function of its location on the electron density surface. Calculation will only take a few seconds. When completed, *check* the box to the left of **local ionization potential map** in the **Surfaces** dialog. The color convention is the same as for the electrostatic potential map, although the scale is completely different. Local ionization potentials are always positive. The default scale (5 to 15 eV) can be changed to highlight the differences. Select **Properties** from the **Display** menu ( ) and *click* on the local ionization potential map. Change "5" at the left below **Property Range** to "10" and close the dialog. Colors toward red correspond to small ionization potentials (greatest electrophilic reactivity) and colors toward blue correspond to large ionization potentials. Note that the red regions on the map are over the *ortho* and *para* ring positions. This is exactly what is experimentally observed.
4. Close ***N,N-dimethylaniline*** and any open dialogs.

LUMO Map for Androsterone



1. Sketch androsterone ( ) and exit the sketcher ( ).

2. *Click* on the name ***androsterone*** at the bottom right of the screen. If the (correct) name is not provided, then you have made a mistake. In this case, re-enter the builder by selecting **Edit Sketch** from the **Build** menu ( ), and make any necessary changes. **ωB97X-D/6-31G*** should still be selected from the menu in the dialog that results. *Click* on **Replace** to replace your structure by that in SSPD.

3. Select **Orbital Energies** from the **Display** menu or *click* on ( ) if it appears at the top of the screen. An orbital energy diagram will appear at the left of the screen. To examine the molecular orbital corresponding to a line in the diagram, *click* on the line. You will see that the LUMO is a π* orbital localized on the carbonyl group, although it is not at all clear whether it is more or less concentrated on the face away from the two methyl groups. This subtle distinction might be important, for it would be expected that nucleophilic addition would occur from the face on which the LUMO is more concentrated. A LUMO map provides a much clearer picture.

4. Select **Surfaces** from the **Display** menu ( ). *Click* on **Add** and select **|LUMO| map** from the menu. The graphics calculation will require only a few seconds. When completed, *check* the box to the left of ***|LUMO| map*** inside the **Surfaces** dialog. The largest (absolute) values of the LUMO are colored blue. Rotate to examine both the face with and without the two methyl groups. From the |LUMO| map you can clearly see that the LUMO is more concentrated on the face away from the methyl groups.

5. Close ***androsterone*** and any open dialogs.

In this example, the LUMO corresponds to the expected π^* orbital primarily localized on the carbonyl bond. This may not always be the case, and it may be necessary to look at higher-energy unoccupied molecular orbitals, LUMO-1, LUMO-2, etc. ***Spartan*** allows any orbital to be superimposed on the electron density surface.