ELECTROSTATIC POTENTIAL MAPS: CHARGE DISTRIBUTIONS

The charge distribution in a molecule can provide critical insight into its physical and chemical properties. For example, molecules that are charged, or highly polar, tend to be water-soluble, and polar molecules may stick together in specific geometries, such as the double helix in DNA. Chemical reactions are also associated with charged sites, and the most highly-charged molecule, or the most highly-charged site in a molecule, is often the most reactive. The sign of the charge is also important. Positively-charged sites in a molecule invite attack by bases and nucleophiles, while negatively-charged sites are usually targeted by acids and electrophiles.

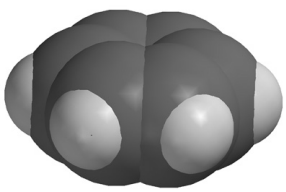
One way to describe a molecule's charge distribution is to give a numerical atomic charge for each atom. A particularly simple and familiar recipe yields so-called formal charges directly from Lewis structures. Unfortunately, formal charges are arbitrary. In fact, all methods for assigning charge are arbitrary and necessarily bias the calculated charges in one way or another. This includes methods based on quantum mechanics. The reason may be traced back to the notion that atomic boundaries are themselves ill-defined and it is impossible to decide which electrons are associated with which nuclei.

An attractive alternative for describing molecular charge distributions makes use of a quantity termed the electrostatic potential. This is the energy of interaction of a point positive charge with the nuclei and electrons of a molecule. The value of the electrostatic potential depends on the location of the point positive charge. If the point charge is placed in a region of excess positive charge (an electron-poor region), the point charge-molecule interaction is repulsive and the electrostatic potential will be positive. Conversely, if the point charge is placed in a region of excess negative charge (an electron-rich region), the interaction is attractive and the electrostatic potential will be negative. Thus, by moving the point charge around the molecule, the molecular charge distribution can be surveyed.

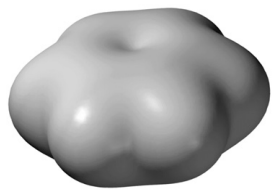
Electrostatic potentials can be depicted in various ways. For example, it is possible to make an electrostatic potential surface by finding all

of the points in space where the electrostatic potential matches some particular value. This is precisely what was previously done for both molecular orbitals and electron densities. A much more useful way to show molecular charge distribution is to construct a so-called electrostatic potential map. This is done first by constructing an electron density surface corresponding to a space-filling model (see the topic ***Electron Densities: Sizes and Shapes of Molecules***). The electrostatic potential is then mapped onto this surface using different colors to represent the different values of the electrostatic potential. Mapping requires an arbitrary choice for a color scale. ***Spartan*** uses the rainbow. Red, the low energy end of the spectrum, depicts regions of most negative (least positive) electrostatic potential, and blue depicts the regions of most positive (least negative) electrostatic potential. Intermediate colors represent intermediate values of the electrostatic potential, so that potential increases in the order: red < orange < yellow < green < blue.

The connection between a molecule's electron density surface, its electrostatic potential surface, and an electrostatic potential map is illustrated below for benzene. The electron density surface defines molecular shape and size, and performs the same function as a conventional space-filling model by indicating how close two benzenes can get in a liquid or in a crystal.



space-filling model
for benzene

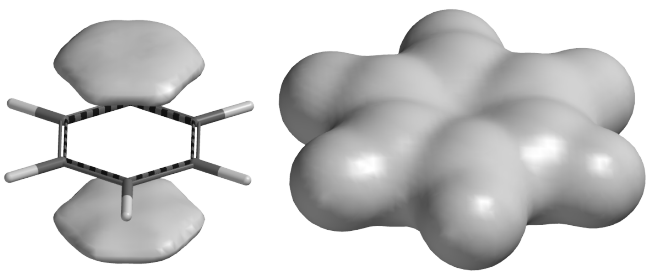


electron density surface
for benzene

Open ***benzene electron density*** in the ***topics*** directory. Two different images, a space-filling model and an electron density surface, appear side by side. You can switch between the two models (in order to manipulate them) by *clicking* on each in turn. Notice how similar they are. To get an even clearer impression, switch to a mesh surface. *Click* on the graphic and select **Mesh** from the menu which appears at the bottom right of the screen. Switch to a space-filling model (**Space Filling** from the **Model**

menu). The two are now superimposed. Close ***benzene electron density*** when you are finished.

The electrostatic potential corresponding to points where the potential is negative shows two different surfaces, one above the face of the ring and the other below. Since the molecule's π electrons lie closest to these surfaces, we conclude that these electrons are responsible for the attraction of a point positive charge (or an electrophile) to the molecule. An electrostatic potential surface corresponding to points where the potential is positive has a completely different shape. It is disk-shaped and wrapped fairly tightly around the nuclei. The shape and location of this surface indicates that a point positive charge is repelled by this region, or that a point negative charge (a nucleophile) would be attracted here.

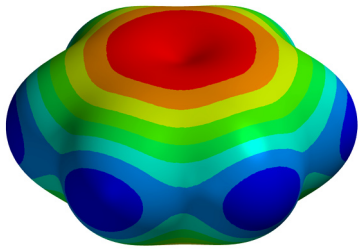


negative (left) and positive (right) electrostatic potential surfaces for benzene

Open ***benzene electrostatic potential*** in the ***topics*** directory. Two different images appear side by side. The one on the left depicts a surface of constant negative potential, while the one on the right depicts a surface of equal positive potential. You can switch between the two models (in order to manipulate them) by *clicking* on each in turn. Close ***benzene electrostatic potential*** when you are finished.

Next, combine the electron density and electrostatic potential surfaces to produce an electrostatic potential map. This simultaneously conveys both the molecule's size and shape as well as its charge distribution in a compact and easily interpretable manner. The size and shape of the map are, of course, identical to that of the electron density surface, and indicates what parts of the molecule are easily accessible to other molecules (the outside world). The colors reveal the overall charge

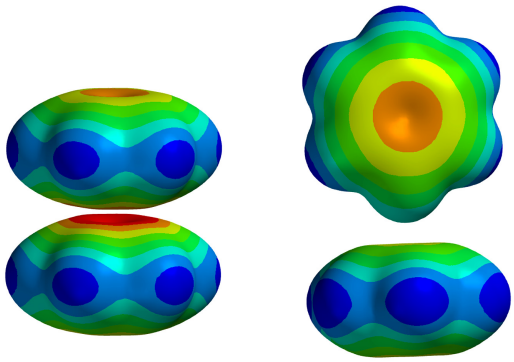
distribution. The faces of the ring, the π system, are red (electron rich), while the plane of the molecule and especially the hydrogens are blue (electron poor).



electrostatic potential map for benzene

Open ***benzene electrostatic potential map*** in the ***topics*** directory. Manipulate the image to convince yourself that the red regions are on the π faces and the blue regions are around the edges. Close ***benzene electrostatic potential map*** when you are finished.

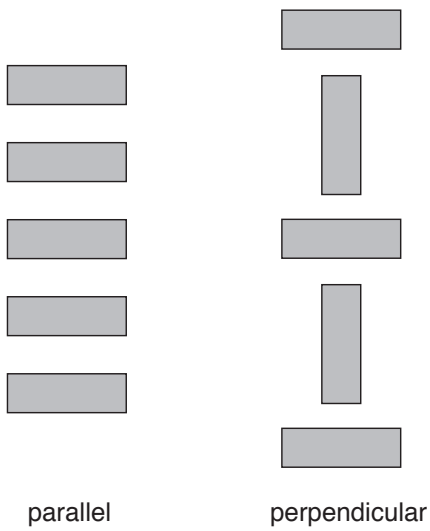
Electrostatic potential maps have made their way into mainstream general and (especially) organic chemistry textbooks as a means of displaying charge distributions in molecules. In addition, they have found application as a natural step beyond steric models for interpreting and predicting the way in which molecules fit together. A good example of this follows from the electrostatic potential map for benzene, which recall is negative on the π faces and positive around the periphery. The benzene dimer would, therefore, be expected to exhibit a perpendicular geometry, to best accommodate Coulombic interactions, instead of a parallel arrangement.



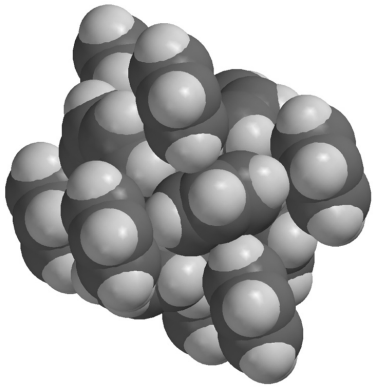
electrostatic potential maps for parallel (left) and perpendicular (right) benzene dimers

Open ***benzene dimer electrostatic potential map*** in the ***topics*** directory. Note that the parallel arrangement forces the negative region of one benzene onto the negative region of the other, while the perpendicular structure associates the negative region of one benzene with a positive region of the other. Close ***benzene dimer electrostatic potential map*** when you are finished.

Of greater interest is the structure of benzene in solid state. Intuition suggests a parallel stack. After all, benzene is flat and flat things (plates, pancakes, hamburgers) make stacks. However, Coulombs law clearly favors a perpendicular arrangement.



The experimental X-ray crystal structure indeed shows a perpendicular arrangement, albeit in three dimensions. There are two lessons here. Intermolecular interactions go beyond steric interactions and sometimes our simple one and two-dimensional views of the world will lead us astray.



X-ray crystal structure of benzene

Open ***benzene crystal*** in the ***topics*** directory. Manipulate in order to see the packing of benzene molecules. Close ***benzene crystal*** when you are finished.

Electrostatic potential maps may also be used to describe in great detail the workings of chemical reactions. For example, a map may be used to show the transfer of negative charge during the S_n2 reaction of cyanide with methyl iodide.

Open ***Sn2 cyanide+methyl iodide*** in the ***topics*** directory. One frame of a sequence of electrostatic potential maps for the S_n2 reaction will appear. Animate by *clicking* on ▶ at the bottom left of the screen (stop the animation by *clicking* on ⏸). Note that the negative charge (red color) flows smoothly from cyanide to iodide during the reaction. Note also, that cyanide (as the reactant) is more red than iodide (as the product). Iodide is better able to carry negative charge, that is, it is the better leaving group. Switch to mesh or transparent map to see the making and breaking of bonds. Close ***Sn2 cyanide+methyl iodide*** when you are finished.