Acidity and Electrostatic Potential
Chemistry 200 – Fall 2004 – Assignment #8
Due: October 13, 2004, high noon

Go through each of the problems below using Spartan, and then present the answers using Microsoft Word. If structures are required, follow the directions in each problem, and copy and paste the structure into Word. [Directions for doing this are at the end of this assignment.] Data should be presented in a format that is easily comprehensible to the reader. Be sure to answer all of the questions in each problem. You must submit a hard-copy of this problem set to Dr. Caran, AND a digital copy (as a single Word format document) in the digital drop-box on Blackboard. Your digital copy must be named using your JMU email username in the following way: username_C200_8.doc.

Acidities and Electrostatic Potentials

For each of the problems below, we will be calculating and visualizing the electrostatic surface potentials using a 3-21G(\*) Hartree-Fock calculation. An electrostatic surface potential map is a calculated map of the approximate van der waals shape of a molecule, and the relative electron density at different points on the surface. Areas of negative potential (high electron density) appear red, while those of positive potential (low electron density) are blue. The general procedure for this is outlined below:

- Build the molecule of interest using Spartan.
- Perform an energy minimization (hit the button with an “E” and an arrow pointing down).
- Click: Setup \rightarrow Calculations. Calculate the Equilibrium Geometry with a Hartree-Fock, 3-21G(\*) basis set. Start from initial geometry. You can leave all of the other settings alone for this calculation. Click OK. This will tell Spartan what type of calculation to do, and which set of calculations to use.
- Next, you need to setup the calculation of the density surface potential. Click: Setup \rightarrow Surfaces. In the Surfaces List dialog, click: Add. In the Add Surface dialog, select: Surface: density; Property: potential. Resolution: medium. Click OK. Then close the Surfaces List window.
- Now all of the calculations have been set up. To start the calculation, click: Setup: Submit. Spartan will ask you to save the file. (You might want to give it a name that is representative of the molecule, the basis set, and you. For example, I might call a file acetylene_3-21G_Caran.) Click OK.
- After the calculation is complete, Spartan will let you know. (This may take seconds, minutes, or hours, depending on the complexity of the calculation. For all of the molecules you will be doing, they should take less than a minute each.)
- To display the electrostatic surface potential, click: display \rightarrow surfaces. In the Surfaces List dialog, you will notice that the status of your calculation is now “completed”. Click on the yellow box next to the surface you wish to display. The Electrostatic potential map shows up on your molecule. You can close the Surfaces List dialog.
- To change the appearance of the density potential map, click on it. A small box will appear on the surface. You can change the appearance from solid (the default) to mesh, transparent, or dots.
- To measure the calculated surface potential at a specific point along the surface, click: Display \rightarrow properties. This will open up the Properties dialog. Clicking on
the surface of the molecule will toggle this dialog between “Molecule Properties” (which shows energy, HOMO/LUMO energy, dipole, point group, area, volume, etc) and “Surface Properties”. In the Surface Properties dialog, the number displayed after “Value” is the calculated electrostatic surface potential at the point where you placed the box in the surface of the molecule. Try clicking on different areas of the molecule to see how the potential changes.

- The numbers in the Property Range boxes show the minimum and maximum values for the surface potential for the molecules of interest. The color red is defined as the lower limit, and the color blue as the upper limit. In this assignment, we will be comparing the electrostatic of hydrogens on various molecules. When comparing potentials on different molecules, we need to display our electrostatic surface potential maps on the same scale so that we can get a clear visual representation of the relative potentials. To change the Property Range (as you will be asked to do in the problems below), simply highlight the value in the property range number in the Surface Properties box, type in a new number, and hit return. (Note that you need to hit return for each new value that you type in. Notice how the appearance of the potential map changes when you hit return.

In this assignment, we will be attempting to answer the question: To what extent do the electrostatic charges on hydrogens in molecules predict the ease at which they will donate a proton (i.e. their acidity)?

1. Relative Acidities of Hydrogens on sp³, sp² and sp Hybridized Carbons.

Hydrogens attached to sp-hybridized carbons (i.e. in terminal alkynes) are more acidic than those attached to sp²-hybridized carbons (i.e. in alkenes), which are more acidic than those attached to sp³-hybridized carbons (i.e. in alkanes). Typically, this is explained by comparing the relative energies of the conjugate bases of these compounds: The acetylene anion is sp hybridized (50% s-character); the ethylene anion is sp²-hybridized (33% s-character); and the ethane anion is sp³-hybridized (25% s-character). The greater the s-character, the closer the electrons are held to the carbon (since an s-orbital is closer to the nucleus than a p-orbital), and thus the more stable the anion (lower energy). Let’s find out if the order of acidities is correctly predicted by the electrostatic potentials near the acidic hydrogen.

a. Build ethane, ethylene, and acetylene and optimize using a 3-21G(*) calculation.

b. For each molecule generate the electron density surface, onto which has been mapped the electrostatic potential.

c. Display all three surfaces simultaneously in Spartan (as solid surfaces). To do this, build the molecules one at a time, and then

d. Change the Property Range on each of the molecules, so it is consistent for all of the molecules. The range of the scale should be set so that the minimum equals the lowest minimum of any of your molecules, and your maximum equals the highest maximum of any of your molecules. Report the scale you are using to display your potential surfaces.

e. Measure the electrostatic potential of each of the molecules in the region of the hydrogens. (In the molecules in this assignment, this will typically be the region of highest positive surface potential, so you may want to click around to find the largest number. Report these values to 1 significant figure past the
decimal place (i.e. to the tenths place). Copy the electrostatic potential maps into Word (as solid surfaces). You should leave the marker (the small square box) on each of the electrostatic potential maps to show the point at which you are measuring.

f. Which molecule contains the most electron-poor hydrogen? Which contains the least electron-poor hydrogen? Are these results consistent with the known order of acidity?

2. Effect of Ring Strain on Acidity

We can also use a hybridization argument when comparing the acidities of hydrogens on strained ring systems with their acyclic counterparts. There are several ways to explain this phenomenon. Ring strain forces tetra-coordinate carbons away from ideal tetrahedral geometries, thus imparting the C-C bonds with more p-character (i.e. partial sigma, partial pi character), and the C-H bonds with more s-character than unstrained systems (sp^3 carbons have 75% p character). The Coulson-Moffit model of cyclopropane considers the C-C bonds to be sp^5 (83% p) while the C-H bonds are considered sp^{2.3} (70% p). Weird, eh? The C-C bonds are “bent” 22º away from the imaginary line between the two carbons as shown below. Alternatively, the Walsh model considers the carbons to be sp^2 hybridized, and constructs the C-C bonds out of a mixture of sp^2 orbitals pointing radially towards the center of the ring (Ψ_1), and unhybridized p orbitals (Ψ_2 and Ψ_3).

Using either model, we would expect hydrogens on strained ring systems to be more acidic than those on unstrained molecules. In this problem, we will compare cyclopropane, cyclobutane, propane and butane.

a. Build cyclopropane, cyclobutane, propane and butane and optimize using a 3-21G(*) calculation.
b. For each molecule generate the electron density surface, onto which has been mapped the electrostatic potential.
c. Display all four surfaces simultaneously in Spartan (as solid surfaces), all on the same scale. (The range of the scale should be set so that the minimum equals the lowest minimum of any of your molecules, and your maximum equals the highest maximum of any of your molecules.) Report the scale you are using to display your potential surfaces.
d. Measure the electrostatic potential of each of the molecules in the region of the methylene (CH_2) hydrogens. Report these values to 1 significant figure past the decimal place. Copy the electrostatic potential maps into Word (as
solid surfaces). You should leave the marker on each of the electrostatic potential maps to show the point at which you are measuring.

e. Compare the electrostatic potential of cyclopropane to propane. Do the potentials lead to the correct ordering of the acidities of these two molecules?
f. Compare the electrostatic potential of cyclobutane to butane. Which of these two is predicted to be more acidic from these calculations? Is the difference greater or less than the difference calculated for the 3-carbon analogs? Does this make sense in terms of the relative ring strains of cyclopropane and cyclobutane? Explain.

3. Acidity of Hydrogen Halides

The order of acidities of hydrogen halides increases in the following order: HF < HCl < HBr < HI. Let’s see if the calculated electrostatic potential predicts this trend.

a. Build HF, HCl, HBr and HI. Optimize using a 3-21G(*) calculation.
b. For each molecule generate the electron density surface, onto which has been mapped the electrostatic potential.
c. Display all four surfaces simultaneously in Spartan (as solid surfaces), all on the same scale. (The range of the scale should be set so that the minimum equals the lowest minimum of any of your molecules, and your maximum equals the highest maximum of any of your molecules.) Report the scale you are using to display your potential surfaces.
d. Measure the electrostatic potential of each of the molecules in the region of the hydrogens. Report these values to 1 significant figure past the decimal place. Copy the electrostatic potential maps into Word (as solid surfaces). You should leave the marker on each of the electrostatic potential maps to show the point at which you are measuring.
e. Compare the electrostatic potential of the four molecules. Do they correctly predict the relative acidities? Clearly explain why they do or do not. (i.e. If they do not correctly predict the trend, what is responsible for the trend we observe empirically? How can we account for the calculated values?)

4. Substituent Effects on Acidity

Electron-withdrawing substituents will increase acidity, because they stabilize (decrease the energy) of a conjugate base by delocalizing the charge. Electron-donating substituents have the opposite effect. Let’s

a. Build the following five molecules and optimize using a 3-21G(*) calculation.

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\begin{align*}
\text{MeO} &= \text{C} \equiv \text{C} \equiv \text{H} \\
\text{Me} &= \text{C} \equiv \text{C} \equiv \text{H} \\
\text{Me} &= \text{O}_2\text{N} \\
\text{C} \equiv \text{C} &= \text{N} \\
\text{C} \equiv \text{C} &= \text{F}_3
\end{align*}
\]

b. For each molecule generate the electron density surface, onto which has been mapped the electrostatic potential.
c. Display all five surfaces simultaneously in Spartan (as solid surfaces), all on the same scale. (The range of the scale should be set so that the minimum equals the lowest minimum of any of your molecules, and your maximum
equals the highest maximum of any of your molecules.) Report the scale you are using to display your potential surfaces.

d. Measure the electrostatic potential of each of the molecules in the region of the hydrogens bound to the sp-hybridized carbons. Report these values to 1 significant figure past the decimal place. Copy the electrostatic potential maps into Word (as solid surfaces). You should leave the marker on each of the electrostatic potential maps to show the point at which you are measuring.

e. Compare the electrostatic potential of the five molecules. For each molecule, would you predict it to be more or less acidic than acetylene (from question 1)?

f. Arrange the 5 substituents (-NO₂, -OMe, -Me, -CN, -CF₃) in order of increasing electron-withdrawing ability, according to your calculations.

5. Strong and Weak Acids

a. Build ethanol (a weak acid), acetic acid (a moderately strong acid), and nitric acid (a strong acid), and optimize using a 3-21G(*) calculation.

b. For each molecule generate the electron density surface, onto which has been mapped the electrostatic potential.

c. Display all three surfaces simultaneously in Spartan (as solid surfaces), all on the same scale. (The range of the scale should be set so that the minimum equals the lowest minimum of any of your molecules, and your maximum equals the highest maximum of any of your molecules.) Report the scale you are using to display your potential surfaces.

g. Measure the electrostatic potential of each of the molecules in the region of the most acidic hydrogens of each molecule. Report these values to 1 significant figure past the decimal place. Copy the electrostatic potential maps into Word (as solid surfaces). You should leave the marker on each of the electrostatic potential maps to show the point at which you are measuring.

h. Compare the electrostatic potential of the three molecules. Do they correctly predict the relative acidities?

Directions for pasting structures into Word:

a. Orient the molecule(s) so that all atoms are clearly visible.

b. Increase the size of the molecule (or group of molecules) so that it is approximately as large as the window. [hold shift, and hold down the right mouse button while dragging up until the you reach the desired size.]

c. Set the background color to white. [click on the background, then select: options → color, set all to 100%]

d. Copy the molecules and paste it into Word.

e. Resize it to an appropriate size once in Word. (If you right-click on the picture, it will allow you to select “format picture”. From this dialog box, if you click on the “layout” tab and chose “square”, you may then move your image around in Word. If you right-click and choose “show picture toolbar”, this toolbar will allow you to manipulate your image in a variety of ways.)