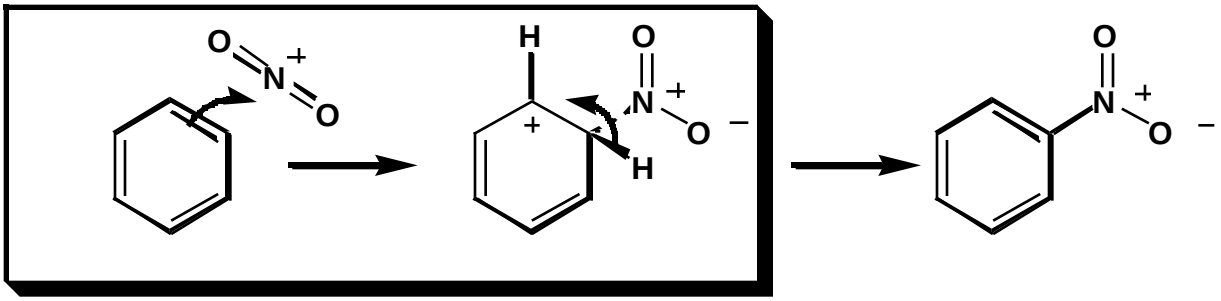
Nitration of Methyl Benzoate:
An Experimental and Computational Investigation

Vince Rotello, Department of Chemistry, University of Massachusetts

The rate-limiting step in nitration of an aromatic species involves the addition of an electrophile to an aromatic ring:

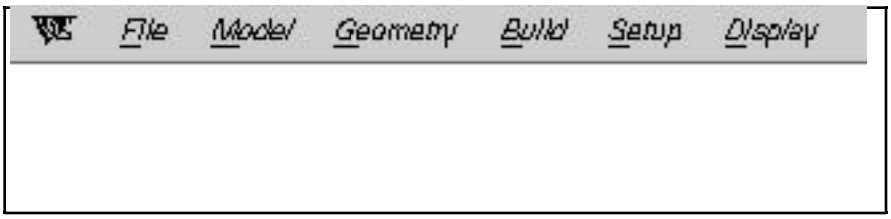


For monosubstituted benzenes three products are possible (ortho, meta, and para). Since the rate-limiting step involves nucleophilic addition of the aromatic species to the nitronium cation, if we can determine which position on the aromatic ring is most nucleophilic, we can predict the regiochemistry of the product. Since nucleophilicity is determined by the availability of electrons, a good predictor of this property is electron density, with addition predicted for the position that has the highest electron density

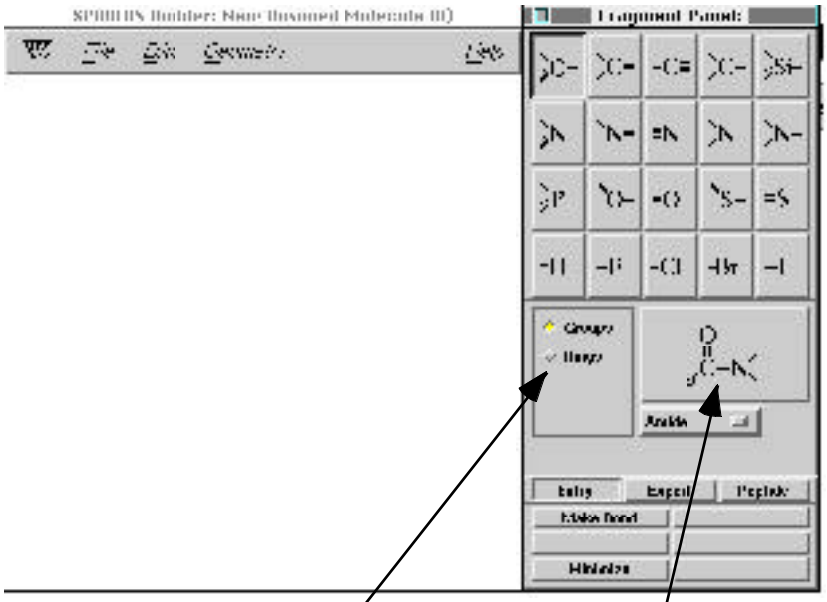
In this experiment we will be using a semi-empirical calculation (**AM1**) to predict electron density. In semiempirical calculations, the forcefield techniques you used last semester are combined with quantum mechanical calculations. We will determine electron density by calculating the **electrostatic potentials** at carbons in methyl bezoate. Electrostatic potentials are derived from the attraction (or repulsion) a point charge would feel to a nucleus.

Getting Started:

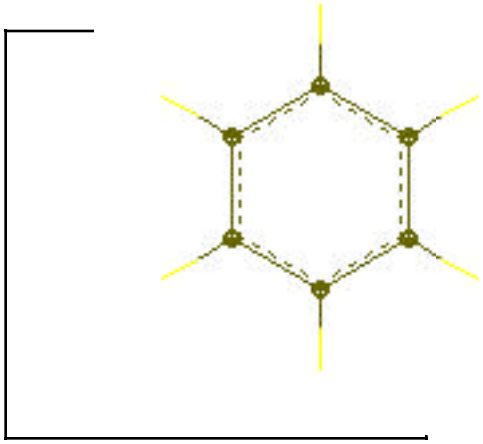
1) Login to the workstation as instructed by your TA. In the blue window Type **spartan**. After you do this you should get a screen that looks like: (next page)



2) pull down on the **File** bar, giving: click on New. This will give you a window to build your structure

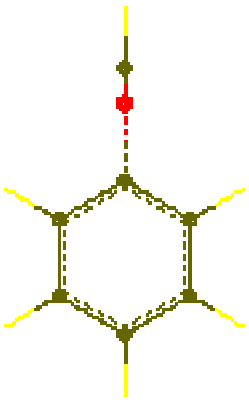


3) Click on Rings button. In the small window you will see a benzene. Click on the main screen, and a benzene will appear in the builder screen:

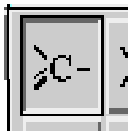


4) Add the ester functionality: Click on groups, and pull down, then click the end of the ester function you want to attach to the benzene. You should have a window that looks like:

5) Click on one of the (yellow) hydrogen atoms of the benzene ring. This will give you a structure that looks like:

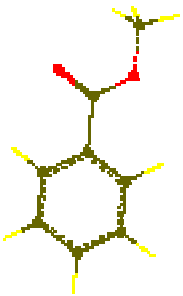


6) Add a methyl group to the ester by clicking on the tetrahedral **C** button, and then clicking on the proton attached to the oxygen atom.

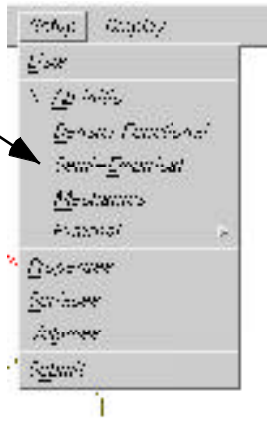


7) **Save** the structure as **throwout**. Ignore overwrite warning, then **Quit** builder

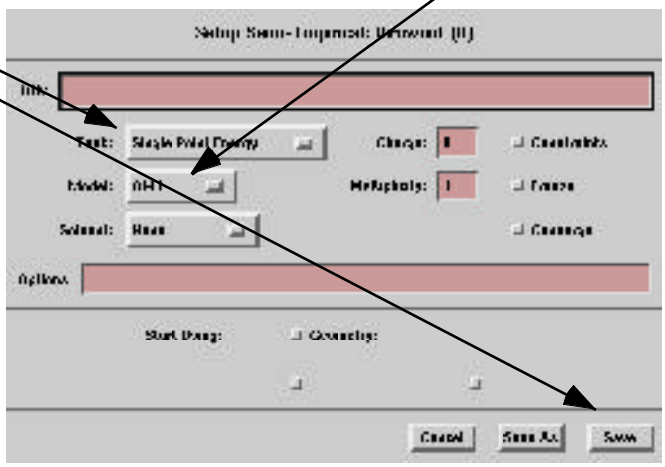
8) Your structure will now appear in the main window.



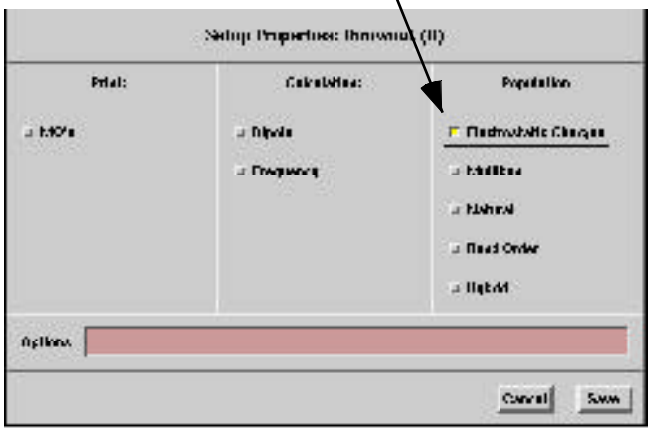
9) You are now ready to calculate the structure, and determine the electronic properties of your structure. Pull down the **Setup** menu, and select **Semi-Empirical**



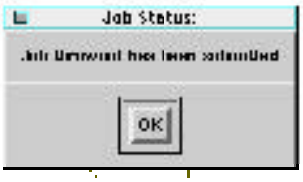
10) This will give you a dialogue box: Select **Geometry Optimization** (to determine the structure), and **AM1**, the semiempirical method you will be using. After you are finished click **Save**.



11) pull down the **Setup** menu again, this time select **Properties**. Click on **electrostatic potential**, then **Save**.

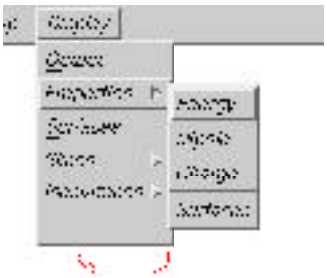


12) Click on Setup one more time, this time selecting **Submit**. you will see a confirmation:



13) The job is now running. After a while, you will see a box indicating that the job is complete. If you get a message saying that the optimization has failed, repeat the **submit** command of **12**

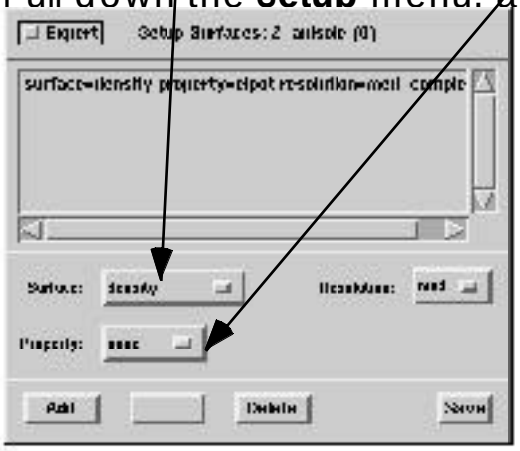
14) Pull down the **Display** menu, This will give you a box that looks like:
Select **Energy** to show the calculated heat of formation of your structure. Record this value.
Next select **Charge** from this same menu.
You can then click on individual atoms to determine their charges. Record these numbers.



15) Pull down the **File** menu, and select **Quit**.
16) C'est Finis! (You are done)

Extra-neat stuff:

Before you logoff, go to the **Setup** dialogue box, select **Surfaces.** In the Dialogue box select **Surface**: **Density**. In property, select **elpot**. Click **Add**, and then **Save**. Pull down the **Setup** menu, and click **Submit**



After seeing the "Job is submitted" notice and "Job is completed" prompt, pull down the **Display** menu, and select **Surfaces**. Click on the line of dialogue in the large box (surface=density.....) click on **Display Surface** Button and **Map Property** button, then click **OK**. You will now see a brightly colored blob corresponding to your molecule. In this blob, red corresponds to areas of highly negative electrostatic potentials, and blue denotes highly electropositive regions. You can play with the **Range** values to see subtler effects more easily.

p,s. If this all seems fascinating and you would like to learn more, the author of this manuscript can be reached at:

rotello@cisco.chem.umass.edu

or stop by 1317 in the tower.