CHEMISTRY 344 - Organic Chemistry Laboratory II – Spring 2012
Lab #5: NMR Predictions and Trends

You will use ChemDraw to draw structures, name molecules, and predict NMR spectra. You will learn the limitations and benefits of the predictions. You will read an article that correlates the pKa of para-susbtituted benzoic acids with carbon-13 data and will visit the SDBS to search for spectroscopy data.

Pre-Lab Notebook Preparation: You are expected to read the Journal of Chemical Education article (Wang, H. *J. Chem Ed.* 2005, 82, 1340-41.)

***Laboratory Book*: The following should be completed before leaving lab, initialed and dated by you.**

VII. Data and Observations: Summarize the key observations that you make during the lab exercise.

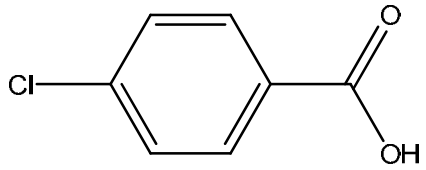
VIII. Discussion and Conclusions: A brief, but critical evaluation of your results and success

You will work independently on this exercise and should not be having small group discussions. This lab must be completed in the lab period and is due at the end of the lab period.

The quality of your answers is important. **Any question that requires an explanation should warrant a full answer from you.** You will lose points for not writing full arguments comprised of several complete sentences or a short paragraph. (This is for parts B to E)

PART A (use your personal super computer –yep your brain)

1) Name this compound using IUPAC nomenclature (use the ortho, meta, or para prefix)



2) Count the total number of each atom and write a molecular formula:

3) Determine the molecular weight:

4) How many carbon signals do you expect to observe in the ^{13}C NMR?

5) How many proton signals do you expect to observe in the (200 to 400MHz) ^{1}H NMR? Write the splitting pattern of each proton set on the structure above.

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PART B

You are now going to search a *Spectral Data Base System* abbreviated **SDBS** that has a large number of spectral data for organic compounds. The database although large is not comprehensive and there is variance in the quality and manner in which the data has been acquired. For example, the NMR spectra quality is affected by a spectrometer's strength, the solvent used, and the acquisition time. Our spectrometer (when functional) is capable of producing much more detailed/resolved spectra than what is generally available in the SDBS database. (FYI the typical forward and back buttons for surfing the web work within the database)

6) Get online and search for the SDBS. How quickly did you find the site?

7) Once found, explain what is present in the disclaimer before scrolling down and hitting I agree to the disclaimer on the SDBS website.

You can search the compound entries in a number of ways. For today, you will be searching for the compound from part A using its molecular formula.

8) Type in the molecular formula that you determined earlier (part A) and write down how many hits correspond to this molecular formula in the database:

Find the correct entry that corresponds to your molecules name. For this molecule, you will review each type of spectroscopy in the database and address the questions below: (all using the SDBS website)

9) Select the MS. How many major mass fragments do you see in the MS data?
(Hit peak data and write down any mass fragment that shows up higher than 25 to 100% of the base peak height)

10) Select the ^{13}C NMR. Does the ^{13}C NMR spectrum appear as you expect it to? (Y/N) explain your answer

11) Select the ^{1}H NMR. Does the ^{1}H NMR spectrum appear as you expect it to? (Y/N) explain your answer

12) Spend a few minutes searching the database and reviewing the results that you attain. What is your general opinion of the database?

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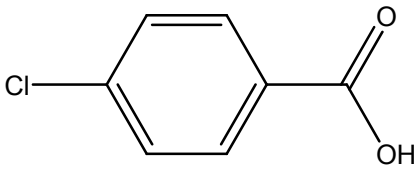
Part C

You will now be using **ChemDraw** to draw a molecule and determine the molecules name, chemical formula, mass spec (ms) fragments, predict carbon-13 NMR, and predict proton NMR.

13) Draw the molecule below using ChemDraw. Then lasso the molecule and right click on the highlighted structure. Select analysis and all. Now write in the information next to the structure below (only some of the information is relevant to the exercise):



Name =

Chemical Formula =

Exact Mass =

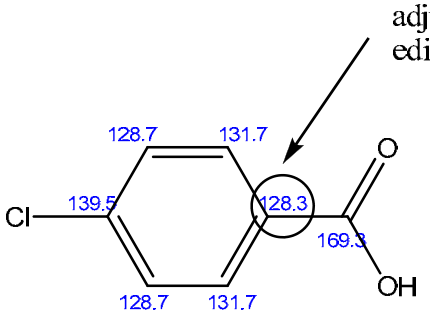
m/z =

If you were to search this molecule using the SDBS database using the name given by ChemDraw, you would not find it. Later in part E there are four compounds that you will be working with. Only one of these compounds is present in the SDBS database. We need a way to predict the proton and carbon spectra of any compound quickly even if it is not perfect.

Part D

14) Draw your molecule from part C. Lasso the structure and select copy, then at the top menu select structure (4th from the left) and select predict proton NMR spectra. The proton NMR spectra appears and the molecule is labeled with chemical shifts in ppm. Use the mouse and hover over a peak in the spectrum or over a proton in the structure. Explain what happens:

15) Then at the top menu choose edit then select all and then hit the backspace on your keyboard to clear the worksheet. Then paste your structure (you copied it earlier), lasso it, then at the top menu select structure (4th from the left) and select predict carbon NMR spectra. The structure should have chemical shifts on it and the carbon NMR should appear below it. The circled carbon will be a key resonance for part E



adjustment to be in line with the previous ChemDraw edition data (have to add 0.4ppm to everything)

128.3ppm + 0.4ppm =

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Part E

Read the first page twice of the JCE article handed out in class that explains an exercise in which there is a correlation between ChemDraw ^{13}C chemical shifts and the pKa values of para-substituted benzoic acids.

16) What is the Hammett σ value as described in the article? Explain in your own words:

17) Review the last paragraph on this page and summarize in your own words the content of this paragraph.

18) Review table 1. Does it appear as though activators or deactivators make the para-substituted benzoic acid more acidic? Explain why?

19) You will be using the pKa equation (lower right of figure 1) for the solid line (ChemDraw chemical shifts). Write down this equation below and use a chemical shift from the table to calculate a pKa and verify the calculation works. Show your work below:

The following four compounds are not present in the table. If we want to estimate their respective pKa's we could use the described pKa chemical shift correlation. First we need to get the carbon NMR shifts.

20) Using procedures in ChemDraw discussed earlier, draw each of the following four compounds then complete a, b, and c for each. You will need to refer to the correct equation in figure 1 to calculate the

pKa for each acid. (We have a new version of ChemDraw, so add 0.4ppm to each shift (for the carbon of interest) ChemDraw gives you prior to insertion into the equation) Show your work.

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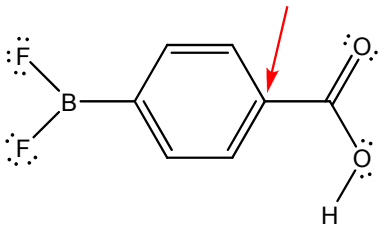
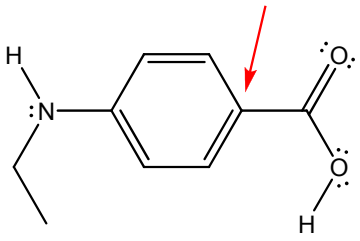


a) chemical name =

b) exact mass =

c) ^{13}C NMR shift of carbon # 1 in ppm =
d) calculated pKa value =
using equation from figure1
(show your work)



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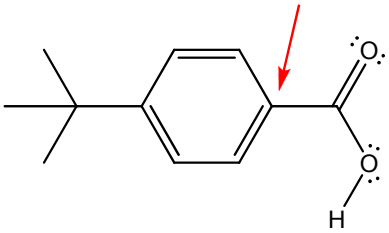
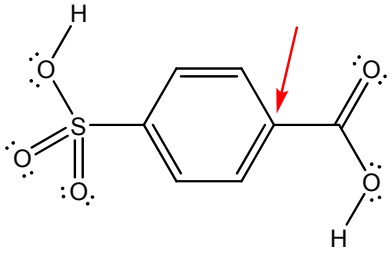


a) chemical name =

b) exact mass =

c) ^{13}C NMR shift of carbon # 1 in ppm =
d) calculated pKa value =
using equation from figure1
(show your work)



a) chemical name =

b) exact mass =

c) ^{13}C NMR shift of carbon # 1 in ppm =
d) calculated pKa value =
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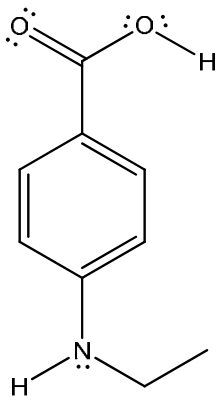
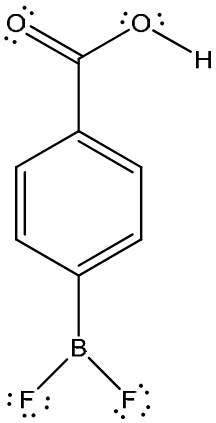
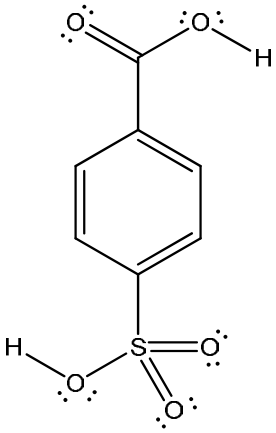
21) Write in the estimated pKa values that you just determined



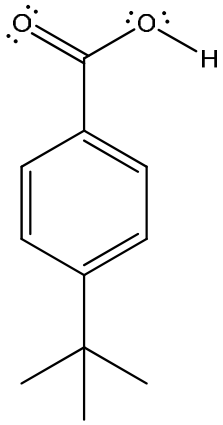
estimated
pKa value =



estimated
pKa value =



estimated
pKa value =



estimated
pKa value =

22) Circle the strongest carboxylic acid and explain if you agree with the overall relative acidity trend determined from this method. This should be a well-written thorough explanation.

23) Visit the instrument room on the third floor and conduct a search using the NIST software on the GC-MS. Your instructor can assist you on this