Chem 225b

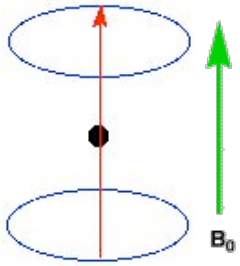
Problem Set 9

Chapter 10

Due: Monday, April 17, 2006

The Novice Level in the NMR module is an interactive exercise that will help you learn about ^{1}H and ^{13}C NMR. The estimated order of complexity is 15, 11, 12, 2, 3, 7, 1, 10, 6, 8, 4, 5, 9, 13, 16, 14, and 17-20. Try to avoid the solutions until you are truly in need. These exercises are important. I hope to do some of them in class.

[Note: If you do not see spectra appear, use Netscape 4.8 available here.]



An α spin nucleus precessing in a magnetic field

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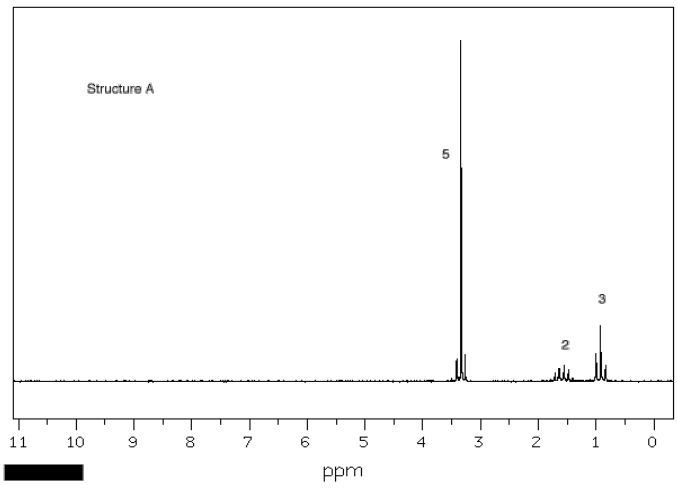
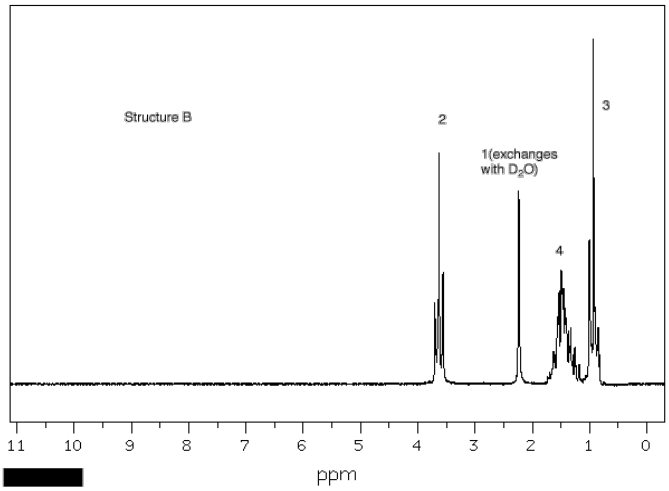
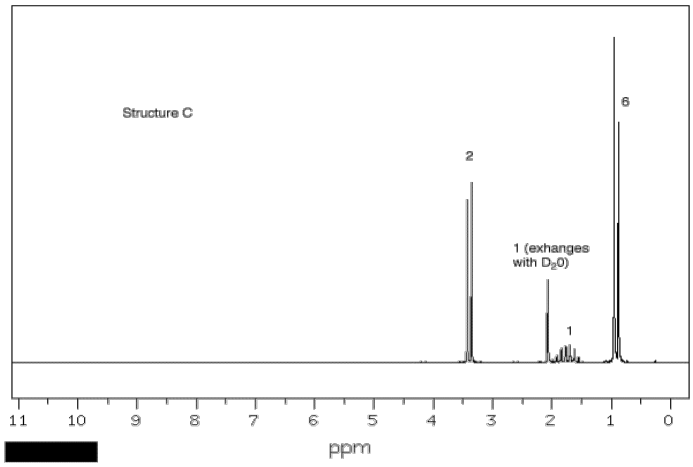
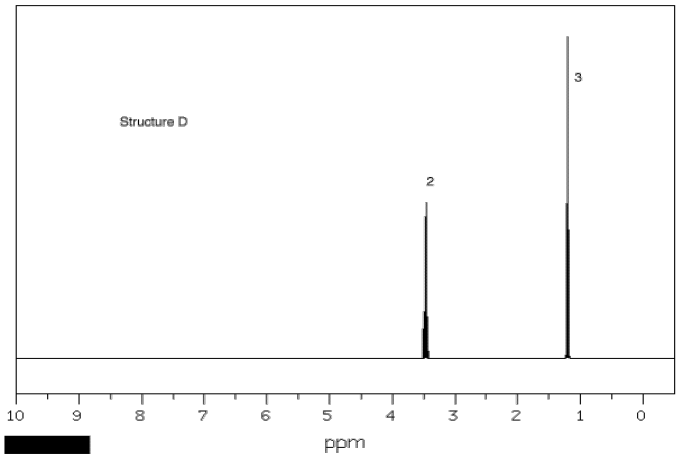
1. Four bottles in a laboratory bear the labels "$C_4H_{10}O$". A student records the ^{1}H NMR spectrum of each one (Spectra **A-D**). Using the areas number by resonances, chemical shifts and the multiplicity (as well as you can discern it), provide the structures of **A-D**. Explain. [Click on the spectra for larger views.] One of the spectra was recorded at 300 MHz, the others at 90 MHz. Explain which is which.

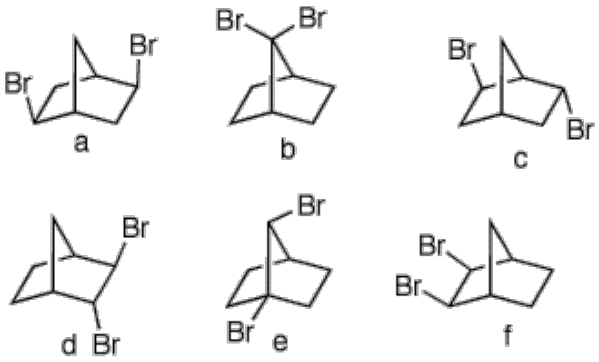








2. Predict the number of singlets in the ^{13}C broadband decoupled NMR spectrum of each of the following dibromides. Explain.



3. The ^{1}H NMR spectra of several compounds are given below in standard line notation. Determine the structure of each one and the number of resonances that are expected in its broadband decoupled ^{13}C NMR spectrum. Show your reasoning. [The first three questions were given on a recent exam in Chem 425b/525b. Degree of Unsaturation is a useful technique in these problems. All compounds are acyclic. s = singlet; d = doublet; t = triplet; q = quartet; dd = doublet of doublets; qd = quartet of doublets.]

A: C_3H_3Br; δ 2.33 (1H, J = 2.70 Hz, t) and 3.82 (2H, J = 2.70 Hz, d)

B: C_3H_3Br; δ 4.82 (2H, J = 5.85 Hz, d) and 5.85 (1H, t, J = 5.85 Hz)

C: C_3H_5NO; δ 3.65 (3H, s) and 4.20 (2H, s)

D: C_3H_6O; δ 1.11 (3H, J = 7.3 Hz, t), 2.46 (2H, J=7.3 and 1.4 Hz, qd) and 9.79 (1H, J = 1.4 Hz, t)

E: $C_4H_{10}O$; δ 0.99 (3H, J = 7.5 Hz, t) and 2.37 (2H, J = 7.5 Hz, q)

F: C_4H_8O; δ 1.27 (3H, J = 7.0 Hz, t), 3.74 (2H, J = 7.0 Hz, q), 6.46 (1H, J = 14.4 and 6.9 Hz, dd), 4.17 (1H, J = 14.4 and 1.9 Hz, dd) and 3.96 (1H, J = 6.9 and 1.9 Hz, dd)

4. This problem needs to be done on-line and the answers recorded on the homework. If you do not see the spectra when you click on the links below, use Netscape 4.8 or go ***here*** to download it. The ancient tree, *Ginkgo biloba*, is claimed to date back to the age of the dinosaurs (65-150 million years ago). My neighbors have a female tree in their yard that drops its rancid fruit during the fall. Butanoic acid (n-butyric acid) has the smell of rancid butter. It is one of the odiferous components of the fruit. Several years ago, I brought some of the fruit into the lab. Dr. Martha Sarpong (a former orgo TA; Yale Ph.D. 2002) crushed the fruit, extracted the pulp with hot water, extracted the cooled aqueous solution with ether, evaporated the ether and isolated a liquid. The ^{1}H NMR spectrum and the ^{13}C NMR spectrum, which were recorded, are provided. Examine the ^{1}H NMR spectrum of the extract and you should be convinced that there is more here than n-butyric acid (butanoic acid) present. Note the two triplets at high field of unequal intensity.

a) Calculate their J values in Hz.

b)What are their chemical shifts?

Expand the region around d 2.25. It contains two triplets for -$CH_2CH_2CO_2H$.

c)What is the J value for each of these signals and what are the two chemical shifts?

Look at the ^{13}C NMR spectrum.

d) How many -CO_2H carbons are there?

The remaining eight signals are upfield. Three of them belong to n-butyric acid.

e) The remaining five belong to what normal chain carboxylic acid? Think about it, then check here and here.

f) Assign each signal to one of the two carboxylic acids. You need not assign the specific carbon atoms. Expand the spectrum and use the cursor to get the chemical shift.

5. In the 1997 Miramax film, Good Will Hunting, [See the commentary by the structure in the previous link!] Minnie Driver's character Skylar did a considerable amount of grousing about organic chemistry in general and ^{1}H NMR spectroscopy in particular. Her complaint about interpreting the proton spectrum of ibogamine has merit. There isn't a lot of information in it. Click here.

a) Look at the downfield region of the spectrum. What is the large singlet? What are the chemical shifts of the sp^2 aromatic protons? How many of each

are there?

b) What is the chemical shift, integral, and multiplicity of the highest field signal in the spectrum? Assign this signal.

c) What is the sign of the optical rotation of ibogamine shown here?

On the other hand, if her assignment had been to interpret the ^{13}C NMR spectrum of ibogamine, she may not have been so bored. It is much more informative. Click here for the ^{13}C NMR spectrum.

d) What is the strong set of signals around 77 ppm? [It is actually 3 signals (triplet) and not 4 signals as the print out at the top of the spectrum indicates.]

e) Are all of the carbons of ibogamine present in the spectrum?

f) Draw the structure of laevorotatory ibogamine.

g) What enantiomer of ibogamine is Will Hunting (Matt Damon) drawing here?

h) Assign the singlets in the region 100-150 ppm to their respective carbons.That is, assign the taller signals (mark them with an "x" in part f.) to the appropriate group of carbons and the shorter signals (mark them with a "y") to their carbons. You will not be able to make a specific assignment of individual carbons.

i) Locate the carbons that absorb at higher field than 40 ppm. Mark them with a "z". How might they be described?

j) How many carbons remain unassigned? Describe the two types of carbons that remain. How many of each are there?