Homework 4 Chem 636, Fall 2008

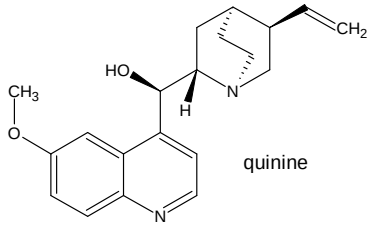
due at the beginning of the 5th week lab (week of Sept 29)

^{1}H 1D NMR: High-Resolution Spectra (& EP mode)

During your lab and HW sessions, refer to **EP** information in the Bruker User Guide (BUG):

4 – Primer on Bruker EP Mode: Most Common Uses

For this lab you will acquire ^{1}H spectra of three samples:



quinine

- 3-heptanone in acetone-d_6
- quinine in benzene-d_6
- ODCB (*ortho*-dichlorobenzene) in acetone-d_6

1. Shim each sample as best you can, and use the standard parameter sets (using, for example, **RJ C6D6.1DJ↵**) to acquire a **DS=0 NS=1** spectrum.

   → Reading in the shim file — e.g., **RSH HOMER.SHIM↵** — is recommended at the start of all sessions on our spectrometers.

   → Note the differences in ^2H relaxations times of the different solvents, as observed by the time required for the lock signal to stabilize following a change in shim value: approx. values for $T_1(^2H)$: ~ 1 sec for DMSO-d_6 and D_2O, 2-4 sec for $CDCl_3$ and benzene-d_6, and 4-8 sec for acetone-d_6 and CD_3CN. For the latter two—which are the most sensitive to shim changes—final adjustments should involve ≤ 5 units for Z2, and ≤ 2 units for Z1.

   → Higher order shims are not "pure". Changes in Z2 will require correction by Z1 (through impurities of Z2), adjusting Z3 will require corrections in both Z2 and Z1, etc. Such "2nd-order" corrections can be required even for pure shims. From a practical perspective, one often has to reduce the lock signal with the higher order shim, and then see if a lower order shim change will produce a better overall line shape to achieve the best resolution.

2. Process the spectrum on the spectrometer. For ^1H spectra, enter **FT↵** , which produces a spectrum without line broadening or phase correction. The full spectral width (**SW**) will be displayed.

3. To inspect the spectrum, enter the expand-and-phase routine by typing **EP↵ . N**ote the change in the display: the text at the top of the screen is removed, and the spectrum color changes from cyan to yellow. To exit EP mode, hit the return/enter key, ↵

   Expand the spectrum—**A** and **B** knobs, followed by [cursor left side] **R** [cursor right side] **R** (use ^B to reactivate the knobs)—so you can see the ^{29}Si doublet on the TMS peak (or the ODCB multiplets directly for that sample).

Use **P** and then the **C** knob to quickly phase the spectrum. You need not be precise (so the D knob, changing the 1st phase correction, is usually not needed), but just enough to inspect the TMS (or other solvent) signal to see the quality of your shim. **M** will memorize (keep) the phase correction.

4. Continue shimming if the ^{29}Si doublet or ODCB multiplet is not well resolved. Be patient in making shim changes (esp. with acetone).

ACQUIRE ROUTINE DATA: For each sample, acquire and save a normal spectrum (**DS**=2 **NS**=8 **SW**=6020 **AQ**=2.7).

5. *Before removing each sample, do the following to acquire a "high-resolution" spectrum on that sample:*

   a) 3-heptanone and quinine sample:

   Resolution is improved by increasing **AQ**:

   acquisition resolution in Hz ≈ 1 / AQ **(1)**

   The simplest method is to increase **AQ** directly. Unfortunately, this cannot be done on a Bruker AC. You must first increase **SI** (the size of the transformed spectrum, in Kbytes), which is limited in size to 128K. Set **SI=128K** (entered as **SI** ↵ **128K** ↵). Be patient! This change will take ~10s as the AC reallocates its memory.

   Now increase **TD** to 128K. **TD** is the number of acquired points, where **TD ≤ SI** . After changing **TD**, the spectrometer will display a new **AQ** setting. **TD**, **SW**, and **AQ** are dependent on each other:

   AQ = TD / (2×SW) **(2)**

   TD is now 4× its previous size, so **AQ** is 4× larger as well: **AQ** = 2.7×4 = 10.9. Thus, the new spectrum can be up to 4× better in resolution; as always, resolution is also limited by shim quality and natural linewidths.

ACQUIRE HIGH-RES DATA ON 3-HEPTANONE & QUININE: Acquire and save a new **DS=2 NS=8** spectrum, with the bigger **SI**, **TD** and **AQ**.

   b) For the ODCB sample:

   *This sample is a standard sample used for testing resolution on NMR spectrometers. You could obtain a good spectrum using the technique specified above. But optimizing the sweepwidth (**SW**) of a spectrum is common in many areas of NMR (esp. in setting up 2D experiments) to improve resolution. The following is a common procedure for optimizing **SW**, and is performed in a similar manner on modern spectrometers.*

   Go back to **DS**=0 **NS**=1 and collect a new FID. One scan spectra will have the best resolution (by limiting the time needed for the data collection, thereby limiting variations that will always occur in sample temp, room temp, etc).

FT and expand the spectrum about the aromatic region in **EP** mode. Apply a rough phase correction. Adjust the expansion such that > 20% of the visible spectrum is baseline on either side of the aromatic multiplets (more baseline is better than too little).

Still in **EP** mode, enter **^O** (CONTROL-O). **SW** (the sweepwidth) and **O1** (the spectrum center) will be changed to match the displayed region.

Because **SW** changed, **AQ** was also changed by the **^O** command, via eq (2) above. Check the value of **AQ**, and reduce if needed to **AQ**=20. Note that this method, which reduces **SW**, makes much longer values of **AQ** accessible.

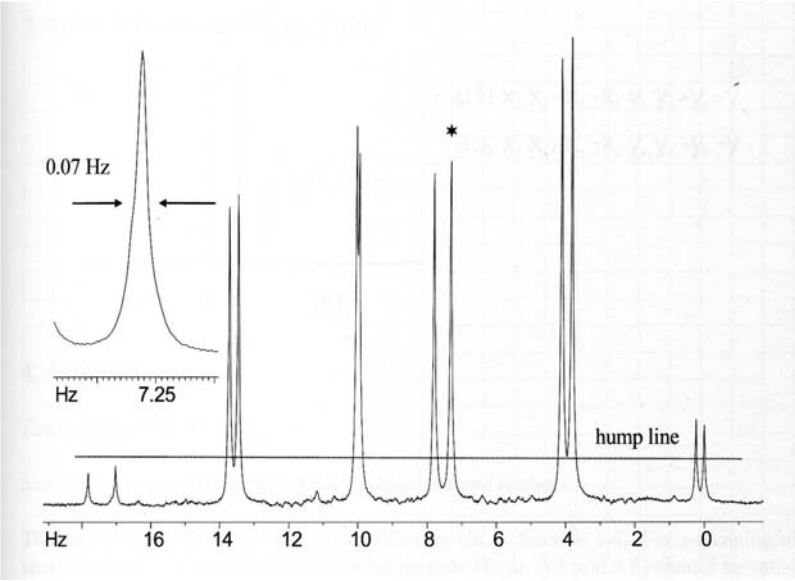
ACQUIRE AND SAVE A ONE-SCAN HIGH-RES SPECTRUM OF ODCB

PLOTS 1,2,3 → Plot the two spectra of each compound using NUTS **BU** (buffer) mode. Make the expansion of the plot for ODCB similar to that shown below (the inset is not needed).

Q1 → You will likely not see improvements in the high-resolution spectra of quinine. TMS and other solvent peaks, on the other hand should improve. Discuss how the three factors that limit resolution—quality of shims, acquisition time, and natural linewidths—affect the resolution observed for solute vs solvent peaks.

Q2 → There should be significant improvements in the high-resolution spectrum of the ODCB spectrum. This sample is degassed, and sealed in acetone-d_6. Discuss the reasons why degassing and use of acetone-d_6 are important for this sample, used for testing spectrometer resolution. Why would DMSO-d_6 have been a poor choice for the solvent?

The figure below shows a very high quality 1H spectrum of ODCB (SW=1ppm, AQ=80). Only the left half of the AA'BB' pattern is shown. ***For this lab, a very good shim will show some splitting of the two peaks at 10Hz. An acceptable shim will show some resolution of three of the four primary "doublets".*** The flatness of the baseline—showing essentially no hump—is exceptional (one of the best I've ever seen); this quality cannot be reproduced on our instruments due to floor-vibration noise [a consequence of our not being located on a ground floor]. Otherwise, the spectrum is a good, but relatively common, example of resolution (peak splitting and shape) *from a 200 MHz spectrometer*. Our 300s do slightly worse than this example due to the higher field strength. NMR users often fail to realize that as field strength increases, resolution degrades. The best resolution of a complex multiplet is always achieved at lower field strength: in this regard, a 200 is better than a 600 or 900 MHz spectrometer! Bigger, (very) expensive magnets provide better *dispersion* and sensitivity, not better resolution.



[From Stefan Berger and Siegmar Braun, 200 and More NMR Experiments (Wiley, 2004), pg 65.]