Compound Identification by NMR

Required prelab readings: Ege, sections 5.4 and 5.7A; Mohrig, sections 19.3-19.5.

In this experiment you will be given a small sample of an unknown organic compound, obtain its ^{1}H- (and time permitting its ^{13}C-) NMR spectra, and determine the structure of the unknown using this information.

NMR is a nuclear phenomenon. It was discovered jointly by E. M. Purcell (at Harvard) and Felix Block (at Stanford) in the early 1940's. They shared the 1952 Nobel Prize (in physics) for their discovery. Three additional Nobel Prizes have been awarded to people for work on NMR (or its medical application, MRI). The first commercial NMR's were sold in the early 50's by Varian Corporation.

Only certain nuclei (^{1}H, ^{2}H, ^{13}C, ^{14}N, ^{19}F, ^{29}Si, ^{31}P, …etc.) exhibit NMR. Note that the most abundant isotope of carbon (^{12}C) does not exhibit NMR.

Important Concepts

1. Chemically-equivalent nuclei (i. e., the two methyl groups in propane) are chemical-shift-equivalent (they give only one chemical shift in the NMR).
2. The total number of signals in the NMR represents the total number of sets of chemically-equivalent nuclei in the molecule. Therefore propane, with three carbons and eight hydrogens, exhibits just two signals in both its ^{13}C- and ^{1}H-NMR's.
3. The chemical shift of each signal provides information about the environment around each set of chemically-equivalent nuclei.
4. In ^{1}H-NMR, the area under each peak is proportional to the number of hydrogens in each set.
5. the splitting of ^{1}H-NMR signals into multiplets (doublets, triplets, etc.) reflects the number of neighboring, non-equivalent hydrogens (Ege, Chapter 11).

Sample Preparation for NMR

NMR's are taken as dilute solutions in solvents in which all of the hydrogens have been replaced by deuterium ($CDCl_3$, CD_2Cl_2, C_6D_6, acetone-d_6, etc.) You will use $CDCl_3$. Deuterium does exhibit NMR but at a resonance frequency different from protium, ^{13}C, *etc.*.

Obtain a very CLEAN, DRY, DUST-FREE small test tube (or vial). **NEVER** use the air lines in the lab to dry glassware. Add to the test tube ca. 1 mL of $CDCl_3$ using the pasteur pipette provided. Stopper the container. **It is imperative that you avoid contaminating the stock bottle of $CDCl_3$.** Use only the Pasteur pipet provided and notify your instructor if you think it has been contaminated. Now add to the test tube two or three drops (using a new Pasteur pipet) of your unknown, replace the stopper, and **gently** agitate the test tube until a solution is achieved. Transfer the solution to an NMR tube to a height of *ca.* 50 mm and cap it. (NMR tubes are fragile. Treat them with care.) Place the NMR tube in a 125 mL erlenmyer flask and always keep the NMR tube upright in order to prevent contamination from the cap. You are now ready to take your NMR's.

Clean up of NMR Tubes

Remove cap and pour contents of the NMR tube into the waste container. Fill the NMR tube about half way with acetone using the acetone squirt bottle provided. Empty into the waste container.

Repeat two more times. Clean the outside of the tube with acetone if it appears to be dirty. Now place the NMR tube **upside down** in the beaker provided. Leave the cap in a second beaker. If you think some of your NMR solution has come in contact with the cap, wash the cap with acetone.

NMR
DATA SHEET

NAME: _____

NAME: _____

Section Number: _____

Unknown number: _____

Draw the proposed structure of your unknown below with labeled C's (a, b, etc.) for NMR identification.

^{13}C NMR Spectrum:

δ (ppm)	identification	δ (ppm)	identification

Attach the ^{13}C-NMR spectrum with the proposed structure and assignments.

Find an example of an *Experimental Section* in an article from the *Journal of Organic Chemistry* that contains ^{13}C experimental data. Turn in a ***single page*** (from a pdf file) with a sample of reported ^{13}C data highlighted. Be certain that the chemical shifts reported in your data table are to the same significance those reported in your literature example.