A Primer on ^{1}H Nuclear Magnetic Resonance Spectroscopy (^{1}H NMR)

This is a very brief introduction to a subject that will be covered in more detail in the 59-235 course, and in much more detail in the 59-330 course. It's designed to help you get through the Experiment #5 in the laboratory.

Nuclei with either odd atomic mass or odd atomic number have a nuclear spin. The most well studied case is the nucleus of the most abundant isotope of the hydrogen atom, the proton (^{1}H). In a magnetic field, the spins will orient either with the magnetic field (the lower energy situation) or against it (the higher energy situation). If one then applies the correct amount of energy to the system (about FM radiofrequency level) the nuclei will absorb that energy to go from the lower to higher energy situation, and that energy absorption can be detected.

Fortunately, for protons, the energy range over which this can occur is pretty narrow, is only based upon a few properties of the environment around the proton, and are very characteristic of that local environment. For reasons of simplicity, this energy is relative to a standard compound that is arbitrarily called 'zero'. *That* compound is tetramethylsilane, ($Si(CH_3)_4$). The units used aren't frequency or energy units as you might expect, but parts per million (**ppm**, essentially a fraction of the applied frequency), so that the place at which absorption occurs (referred to as **δ**, or the **chemical shift**) does not change with the strength of the magnetic field applied.

Most of the protons in compounds you will see in organic chemistry undergo this energy absorption (we normally use the term '**resonate**') somewhere between 0.5 and 8 ppm. There are a few types of protons that resonate at above 8 ppm, while there *are* some inorganic compounds (but *very* few organic ones) that resonate at <0 ppm. I'm sure Dr. Macdonald would <u>love</u> to tell you about those.

As was mentioned before, the chemical shifts for certain environments around hydrogen atoms/protons are quite diagnostic. Hydrogen atoms near electronegative atoms tend to resonate at higher chemical shift (**downfield**), whereas those not near electronegative atoms tend to resonate at lower chemical shift (**upfield**). Hydrogen atoms on sp^2 and sp hybridized carbon atoms have some <u>additional</u> effects not attributable *only* to electronegativity; that is material for future courses. The following list is a good starting point, though:

δ 0 - 1 methyl groups ($-CH_3$'s) not shifted by electronegative atoms

δ 1 - 2 methyl groups β- to (2 atoms away from) O or N atoms, attached to C=C or attached to aromatic rings; methylene groups ($-CH_2-$'s)

δ 2 - 3 methyl and methylene groups next to carbonyls (ketones, aldehydes, esters, etc.) or attached directly to nitrogen of amines

δ 3 – 4.5 methyl and methylene groups attached to oxygen or halogens (Br, Cl).

δ 4.5 - 6.5 hydrogens on sp^2 hybridized carbons of alkenes (not aromatics)

δ 6.8 - 8.5 aromatic protons (those directly substituted on benzene rings)

δ 9 - 10 aldehyde protons

-O**H**'s and N**H**'s tend to move around a lot, to be dependent on concentration of your sample, and to often be broad. The key one for this laboratory is the OH of a carboxylic acid. It resonates well above 10 ppm (it's probably the only common group that does, at about 12 ppm), and is so broad that you often don't see it.

There are two useful additional points which helps diagnose structures:

1) The area underneath the absorption (called the **integral**) is directly proportional to the number of hydrogen atoms it represents. For that reason, it's quite easy to tell a –CH group from a $-CH_2$ group from a $-CH_3$ group in the same molecule.

2) If everything works out ideally, the protons of a resonance are made to show splitting by the number of protons on the *next* carbon to it. The splitting follows an **N+1** rule; one gets a singlet if the are no protons on the next carbon over, one gets a doublet if there is one proton on the next carbon, a triplet if there are two protons on the next carbon, and a quartet if there are three protons on the next carbon over. This can get more complex, because sometimes protons on carbon atoms further away can cause smaller sized couplings, and because I have given you the 'ideal' situation. Again, though, these details are for future courses.

Finally, you may see a small 'peak' in your spectrum at about 7.27 ppm. That is from the solvent that the samples are dissolved in, trichloromethane (chloroform) with the hydrogen atoms replaced by the heavier isotope, deuterium ($CDCl_3$). In the form we buy it, there is still about 1% of undeuterated $CHCl_3$ present; that's the small 7.27 ppm resonance that you (may) see.

I've included the chemical shift ranges of some common functional groups more graphically on the next page. There is definitely more information on it than you need to complete the lab.

^{1}H NMR Chemical Shift Ranges for Common Functional Groups