

Reminder: These notes are meant to supplement, not replace, the laboratory manual.

## Nuclear Magnetic Resonance notes

Nuclear Magnetic Resonance (NMR) is a spectrometric technique which provides information about a particular type of atom contained within a sample. Not all atoms are 'visible' in NMR. The most commonly examined nuclei using NMR are  $^1\text{H}$  (proton) and  $^{13}\text{C}$  (carbon 13). A few of the other routinely examined nuclei include  $^{19}\text{F}$  (fluorine) and  $^{17}\text{O}$  (oxygen 17) and  $^{31}\text{P}$  (Phosphorous 31). In this class we will only use proton NMR and carbon NMR.

In a simplified manner an NMR works because<sup>i</sup> nuclei have a charge and a spin. Spinning charges create a small magnetic dipole. When a sample is placed in a very strong magnetic field, the nuclei align themselves with the strong magnetic field. Then the nuclei are 'bumped' out of alignment by the application of a burst of electromagnetic energy usually in the radio frequency range. When this burst is removed, the nuclei realign themselves and give off a small amount of energy. The characteristics of the energy given off, reveals a great deal about the type, location and quantity of that nuclei. The energy given off is recorded as an NMR spectrum. The proper interpretation of an NMR spectrum can reveal the exact structure of a compound.

The strength of the NMR is determined by the electromagnetic frequency which generates the magnetic field. The higher the frequency the stronger the magnetic field. Within Xavier's chemistry department there is a 60 MHz (megahertz) and a 90 MHz NMR. Plans are underway to install a 300 MHz instrument.

There are four basic pieces of information that can be obtained from standard proton NMR (pmr). These are 1) the number of non-equivalent protons 2) the chemical environment of each type of protons 3) the relative number of each proton present and 4) the number of adjacent protons. The correct interpretation of this information can reveal the chemical structure.

### 1H NMR Interpretation

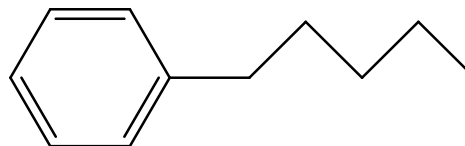
1. Number of signals equals the number of non-equivalent protons.

Proton magnetic resonance only shows the nuclei of the most common isotope of hydrogen,  $^1\text{H}$ . Atoms other than  $^1\text{H}$  do not give signals in the pmr spectrum. Deuterium, an isotope of Hydrogen,  $^2\text{H}$  or D, does not show in the proton NMR. For example, compounds such as water ( $\text{H}_2\text{O}$ ) and table sugar (sucrose,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ) do give a pmr spectrum (from their H's only). Compounds without protons such compounds as NaCl,  $\text{CO}_2$ ,  $\text{D}_2\text{O}$  and  $\text{K}_2\text{Cr}_2\text{O}_7$  do not.

Every proton (that is, every  $^1\text{H}$ ) in a sample can give a signal. If all of the protons in a sample are *equivalent* to one another, their signals will coincide, and chemists say that the spectrum contains one signal. For example, the pmr spectrum of a sample of  $\text{CH}_4$  contains only one signal. When all the protons in the same molecule are *equivalent*, a sample of the compound will give only one signal in the pmr spectrum. Methanol ( $\text{CH}_3\text{OH}$ ) gives two signals in its proton

nmr spectrum. The three protons of the  $\text{CH}_3$  group are equivalent to one another, but the proton of the OH group is not equivalent to the others.

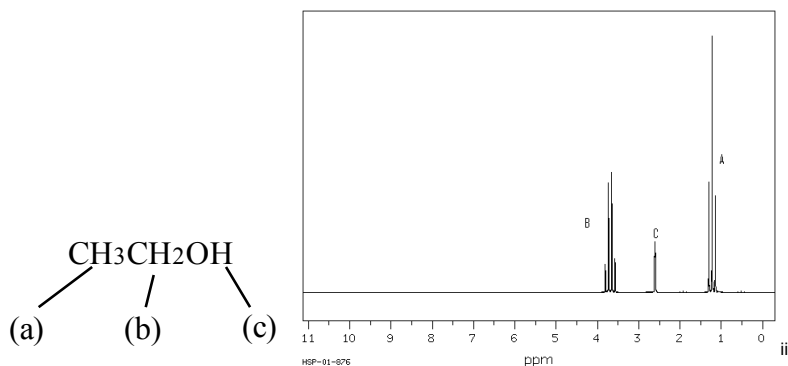
Sample questions: How many signals are there in the proton nmr spectra of each of the following molecules?



- a)  $\text{CH}_3\text{CH}_2\text{OH}$       b)  $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$       c)

Answers:

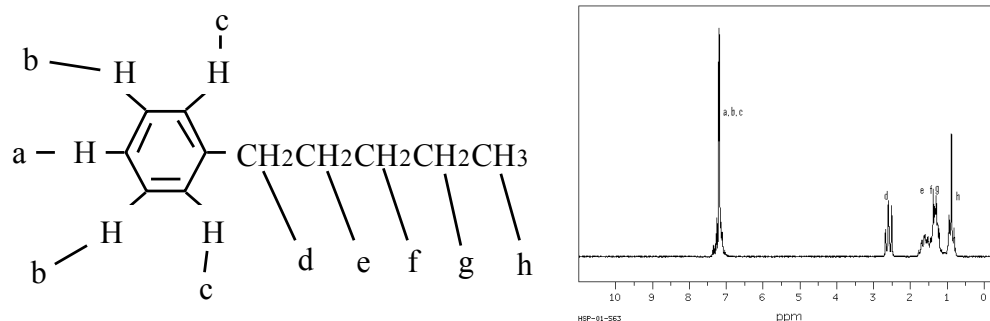
a) The three protons in the  $\text{CH}_3$  group in ethanol are equivalent to one another. The two protons of the  $\text{CH}_2$  group form a second set, and the OH gives a third signal. This compound gives three signals in its proton nmr spectrum, as shown here:



b) This time all six H's in the  $\text{CH}_3$  groups are equivalent to one another. Both of the  $\text{CH}_3$  groups are bonded to  $\text{CH}_2$  groups that are bonded to the O. The  $\text{CH}_2$  group protons are also equivalent. This compound (diethyl ether) gives two signals:

The actual proton nmr spectrum of diethyl ether shows two signals, as predicted. The fine structure of these signals (that is, the fact that they do not consist of single peaks) will be addressed below and in your lab lecture.

c) Remember that molecules represented by bond-line formulas contain hydrogen atoms that are not shown in the formula. This compound (pentylbenzene or n-amylbenzene) gives 8 signals, as indicated here with its actual pmr spectrum following.



The actual proton nmr spectrum of this compound illustrates some of the practical problems chemists encounter when interpreting real proton NMR spectra. The protons labeled e, f and g above are not equivalent to one another, but they are similar enough that their signals overlap in the spectrum. The protons a, b, and c attached to the benzene ring give three signals in theory, but they are so similar to one another that their signals overlap to give one relatively narrow peak. A high field NMR (400 MHz or higher) can resolve or separate these similar proton signals into discrete peaks.

2. Location of signals (chemical shift) is determined by the chemical environment of the proton.

The location of signals on a pmr spectrum is almost always expressed in units of parts per million (ppm) or  $\sigma$ , which is given along the bottom of the spectra shown above. There are three main factors that influence the location of signals, also known as the chemical shift: (1) the presence of electronegative atoms near the proton giving a signal, (2) the presence of  $\pi$  bonds, and (3) the number of bonds between the proton and the electronegative atom or  $\pi$  bond.

(1) Effect of electronegative atoms. Protons that are part of  $\text{CH}_3$  groups far away from atoms more electronegative than carbon or  $\pi$  bonds generally give  $\sigma$  values between  $\sigma$  0.5 and  $\sigma$  1.0. In general, protons that are part of  $\text{CH}_3$ ,  $\text{CH}_2$ , and  $\text{CH}$  groups that are NOT directly attached to an  $\text{sp}^2$  carbon atom or heteroatom (that is, an atom other than C or H) give signals that appear between  $\sigma$  0.5 and  $\sigma$  2.0.

Protons that are attached to carbon atoms that are attached to electronegative atoms such as O, N, and the halogens appear at higher  $\sigma$  values. For example, the proton on chloroform (trichloromethane  $\text{CHCl}_3$ ) has a shift of 7.26 ppm. Protons on groups attached to electropositive atoms give signals at low  $\sigma$  values. The standard compound tetramethylsilane (TMS),  $(\text{CH}_3)_4\text{Si}$ , gives a signal whose location is defined to be  $\sigma$  0.

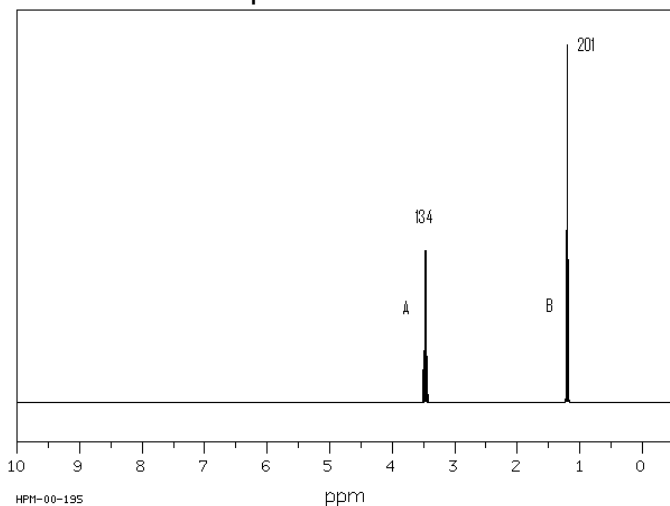
(2) Effect of  $\pi$  bonds. Protons that are attached to  $\text{sp}^2$  carbon atoms (carbon atoms involved in most  $\pi$  bonding) give signals that have high  $\sigma$  values. The benzene ring protons a, b, and c in pentylbenzene, for instance, give a signal at approximately  $\sigma$  7.2.

(3) Effect of distance. The farther a proton is from a  $\pi$  bond or electronegative atom, the lower the value of  $\sigma$  of its signals.

A summary of the shifts of the different environments may be found on the  $^1\text{H}$  NMR guide sheet.

3. Relative size of the signal is proportional to the number of that type of proton

The more of a particular proton type present in a molecule, the larger that signal will be compared to the other signals. If a molecule only has one type of proton such as with ethane, there will only be one signal present of relative size of 1 (100%). The nmr does not know the total number of protons present, so it cannot give an exact number of protons. It gives a relative size of one signal to the other signals. The size is calculated by integrating the area under each peak, so this value is often called the integration value. Diethylether  $\text{CH}_3\text{-CH}_2\text{-O-CH}_2\text{-CH}_3$  has two types of protons. There are 4 methylene protons and 6 methyl protons. The relative size of the two peaks will be 1 to 1.5. The integration values of these two peaks will have this ratio. The absolute integration values may be 1 to 1.5, or 2 to 3, or 4 to 6, or 46 to 69, or 1.86 to 5.58 or any other pair of numbers with a 1 to 1.5 ratio. The absolute values given by the integration have no relation to the actual number of protons. Below is a  $^1\text{H}$  nmr of diethylether.



(a) The compound responsible for the above spectrum does not have 134 of A type protons and 201 of B type. To reduce the number to least whole number increments it may be useful to first divide all integration values by the smallest integration value present. In the above example the smallest integration is 134.  $134/134 = 1.0$  and  $201/134 = 1.5$ . Now the ratio of A to B has been reduced to 1 to 1.5. There cannot be a fraction of hydrogen present, so both sides of the ratio must be multiplied by the same number until a whole number ratio results. If 1:1.5 is multiplied by 2, the ratio becomes 2:3. This does not mean that there are necessarily 2 of A type hydrogen and 3 of B type, but that the RATIO of the two hydrogen types are 2 to 3. This means that the actual number of A and B protons may be 2:3, but also may be 4:6, 6:9, 8 to 12, or any other 2 to 3 combination.

You have to relate the ratio to the actual number of protons in the molecule, which is 4:6 in case of diethyl ether.

4. The pattern of the signal indicates the number of hydrogen on the adjacent carbon.

The protons which produce a signal are influenced by the protons (or other magnetic nuclei) on the adjacent carbon. The adjacent or neighboring protons split the signal of the hydrogen of interest. The formula which describes the splitting pattern is number of neighboring protons ( $n$ ) plus 1 is the pattern ( $n+1 = \text{split}$ ). If no adjacent hydrogen are present, ( $n=0$ ,  $n+1$  is  $0+1=1$ ) no splitting is present and the signal appears as a singlet. If there is one adjacent hydrogen the split will be a ( $n+1$  is  $1 + 1 = 2$ ) doublet. If there are two adjacent hydrogen the split will be a ( $n+1$  is  $2 + 1 = 3$ ) triplet. If there are three adjacent hydrogen the split will be a ( $n+1$  is  $3 + 1 = 4$ ) quartet. The patterns are shown at the top of the  $^1\text{H}$  NMR guide sheet.

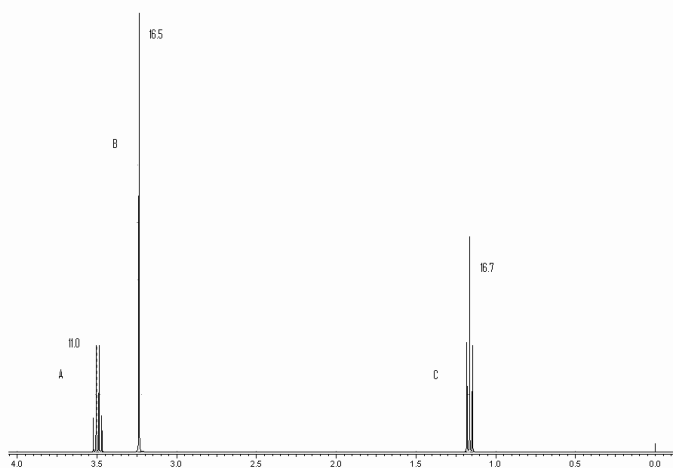
A caveat in this interpretation is the fact that protons on OH, NH, and CHO groups do not act as neighbors and will not bring about a splitting pattern in the adjacent protons.

For example, using the case of diethyl ether from above, the three (A) hydrogens on the methyl group have two protons on the neighboring carbon. Therefore the number of neighbors ( $n$ ) is 2, this means that the A hydrogens will appear as a ( $n+1=2+1=3$ ) triplet.

Similarly the two (B) hydrogens on the Methylene in diethylether have three neighboring protons. This means the B hydrogens appear as a quartet.

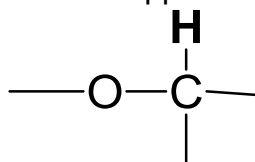
5. The above 4 steps are combined to fully interpret a spectra.

Below is a spectrum of an unknown compound with the empirical formula of  $\text{C}_3\text{H}_8\text{O}$ .



(step 1) There are three different signals therefore there are three types of nonequivalent hydrogen. These three signals were arbitrarily labeled A, B and C.  
(step 2) The shifts of the three different signals are 3.5ppm 3.25ppm and 1.15ppm.

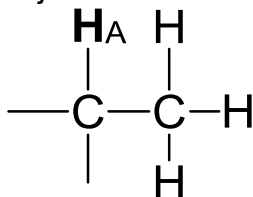
From the  $^1\text{H}$  NMR guide sheet the two signals at 3.5ppm and 3.25 may be from



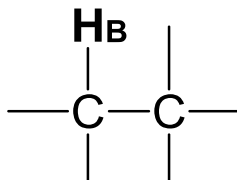
hydrogens on carbons adjacent to oxygen or they may be caused by hydrogen directly attached to an oxygen such as a hydroxyl group. The integration ratio of A:B:C is 11.0:16.5:16.7. If all of these are divided by the smallest number this ratio reduces to 1.0:1.50:1.52. The value of 1.52 is very close to 1.50 so the reduced ratio is simplified as 1.0 to 1.5 to 1.5. Since there cannot be any fractional hydrogen present, the entire ratio is multiplied by 2. The new ratio is 2 to 3 to 3. If this is the actual number of hydrogen then there would be 8 hydrogens present. Comparing with the formula given, this shows a match. If the empirical formula was  $\text{C}_6\text{H}_{16}\text{O}_2$ , then the entire ratio would be multiplied by 2 again.

This means that there are 2 A type hydrogen, 3 B type hydrogen, and 3 C type hydrogen.

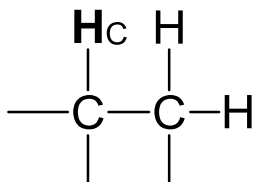
The A signal is a quartet, which means there are three hydrogens on the adjacent carbon.



The B signal is a singlet, which means there are no hydrogens on the adjacent carbon.



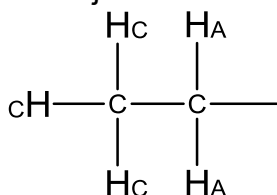
The C signal is a triplet which means there are two hydrogens on the adjacent carbon.



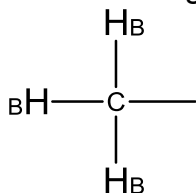
Often at this point it is helpful to draw a grid and to fill in the missing pieces.

Signal	Shift-type	Relative Integration	Splitting= Adjacent H's
A	3.5- CH-O or H-O	11 -> 2	quartet- 3 NDN
B	3.25; CH-O or H-O	16.5 -> 3	singlet- 0 NDN
C	1.2; Alkane	16.7 -> 3	triplet- 2 NDN

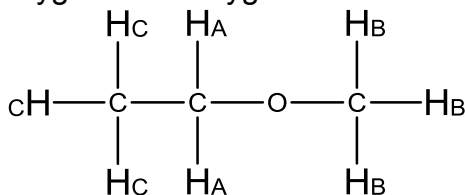
Couple this with what is known from above. There are two A Hydrogens and they are adjacent to a carbon with 3 hydrogens. There are three C hydrogen and they are adjacent to a carbon with two Hydrogen. This means that the A hydrogens are adjacent to the C hydrogens. This partial structure is then known.



It is also known that the three B Hydrogens are on a carbon without an adjacent carbon having any hydrogen.



These partial structures can be subtracted from the chemical formula  $\text{C}_3\text{H}_8\text{O} - \text{C}_2\text{H}_5 - \text{CH}_3 = \text{O}$ . This means the only thing missing is an oxygen. This oxygen can be used to connect these two pieces.



The complete structure is then constructed. The above  $^1\text{H}$  NMR spectrum was made by ethyl methyl ether.

### $^{13}\text{C}$ NMR Interpretation

A typical  $^{13}\text{C}$  NMR spectrum only provides information as to how many non-equivalent carbon atoms are present in a sample, and the environment in which these atoms exist.

The integration of  $^{13}\text{C}$  NMR is not useful due to the low and non-uniform natural abundance of  $^{13}\text{C}$  isotope within molecules.

A guide sheet of how  $^{13}\text{C}$  chemical shift relates to the environment of the carbon will be provided in class.

0-50 ppm = Alkanes  
50-100 = Alkynes and Carbons bonded to oxygens  
100-160= Alkenes and Aromatics  
150-240= Carbons of carbonyl

Additional NMR problem solving skills will be reviewed in your lab class.

## References

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<sup>i</sup> Silverstein, R. M. , Webster, F. X., Kiemle, D. *Spectrometric Identification of Organic Compounds*, 5<sup>th</sup> Ed, 2005  
John Wiley and Sons

<sup>ii</sup> NMR spectra SDBSWeb : <http://riodb01.ibase.aist.go.jp/sdbs/> (National Institute of Advanced Industrial Science and Technology, November 11, 2010)