

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

Introduction to Nuclear Magnetic Resonance

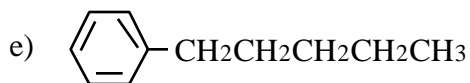
(See also the Gas Chromatography notes, which also apply to today's experiment. Notes for the objectives of the two parts of this lab are in these two separate sections.)

5. Proton magnetic resonance only studies the nuclei of the most common isotope of hydrogen, ^1H . Protons that are part of other nuclei do not give signals in the pmr spectrum. For example, compounds such as water (H_2O) and table sugar (sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$) do give a pmr spectrum (from their H's only); such compounds as NaCl , CO_2 , and $\text{K}_2\text{Cr}_2\text{O}_7$ do not.

Every proton (that is, every ^1H) 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 HCl 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. H_2O is an examples of such a compound; its two H's are equivalent. Others are methane (CH_4) and ethane (CH_3CH_3). Methanol (CH_3OH) gives two signals in its proton nmr spectrum. The three protons of the CH_3 group are equivalent to one another, but the proton of the OH group is not equivalent to the others.

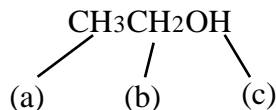
Sample questions: How many signals are there in the proton nmr spectra of each of the following molecules?

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

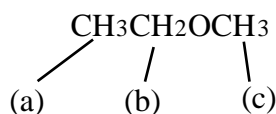


Answers:

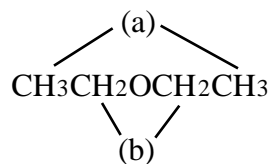
- a) The three protons in the CH_3 group in ethanol are equivalent to one another. The two protons of the CH_2 group form a second set, and the OH gives a third signal. This compound gives three signals in its proton nmr spectrum, as shown here:



- b) The CH_3 groups are not equivalent to each other. One of them is attached to the oxygen atom, and the other is attached to a CH_2 group. This compound gives three signals, as shown here:

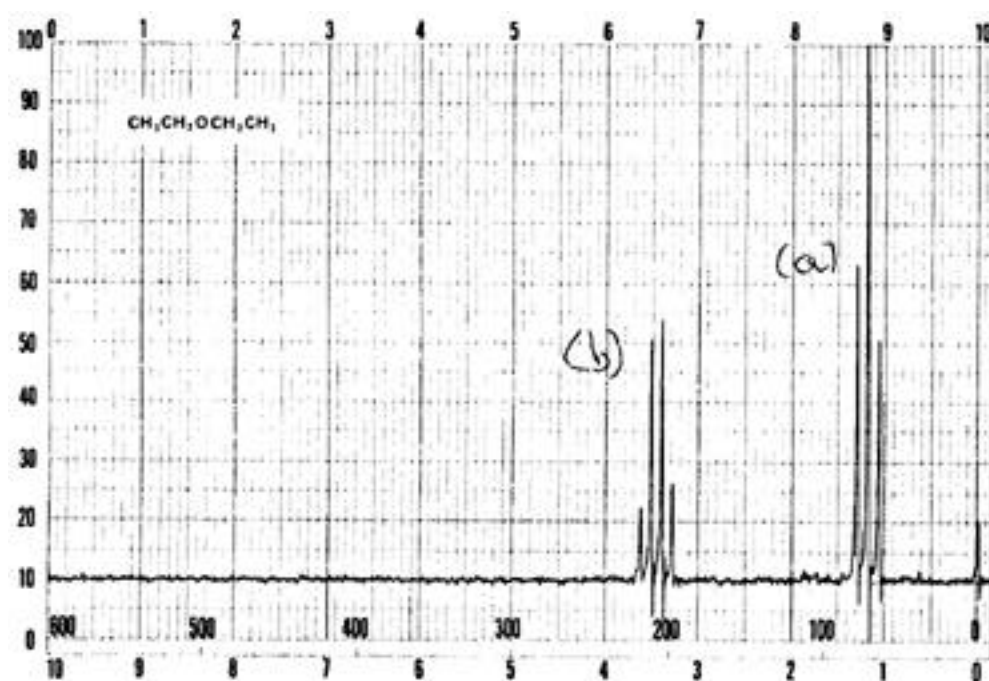


- c) This time all six H's in the CH₃ groups are equivalent to one another. Both of the CH₃ groups are bonded to CH₂ groups that are bonded to the O. The CH₂ group protons are also equivalent. This compound (diethyl ether) gives two signals, as shown here:



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 later in these notes (under #6). Here is the proton nmr spectrum of diethyl ether:

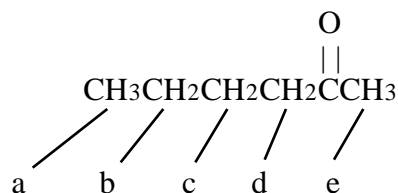
SPECTRUM 1



In addition to the two signals labeled a and b, the sharp-eyed reader will note a small signal directly above the 0 on the scale of units across the bottom. This is a signal from a standard compound (TMS, see below) that was added to the diethyl ether. Ignore this signal when interpreting proton nmr spectra.

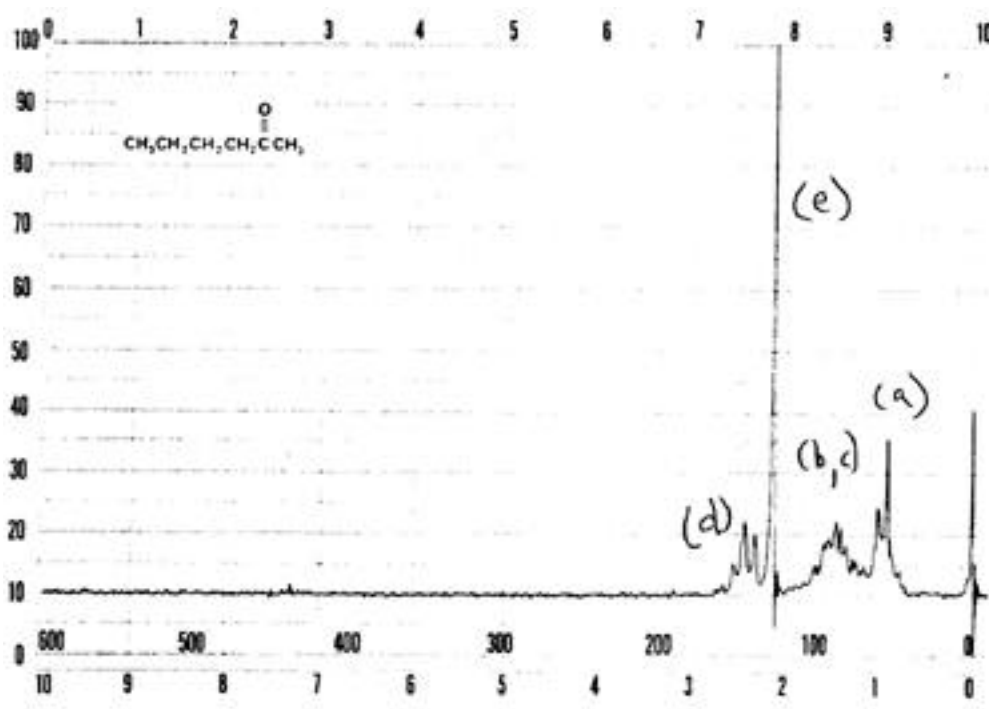
For reasons why the signals fall where they do on the spectrum, see the next section (#6).

- d) This compound, 2-hexanone, is expected to give 5 signals in its proton nmr spectrum, as shown here.



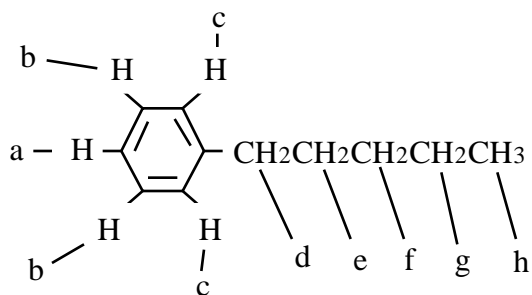
The actual proton nmr spectrum of this compound illustrates some of the practical problems chemists encounter when interpreting real proton nmr spectra. The protons labeled b and c above are not equivalent to one another, but they are similar enough that their signals overlap in the spectrum, which is shown here. The signals for a and d are broad and complex. Only the signal for e is a single narrow peak.

SPECTRUM 2



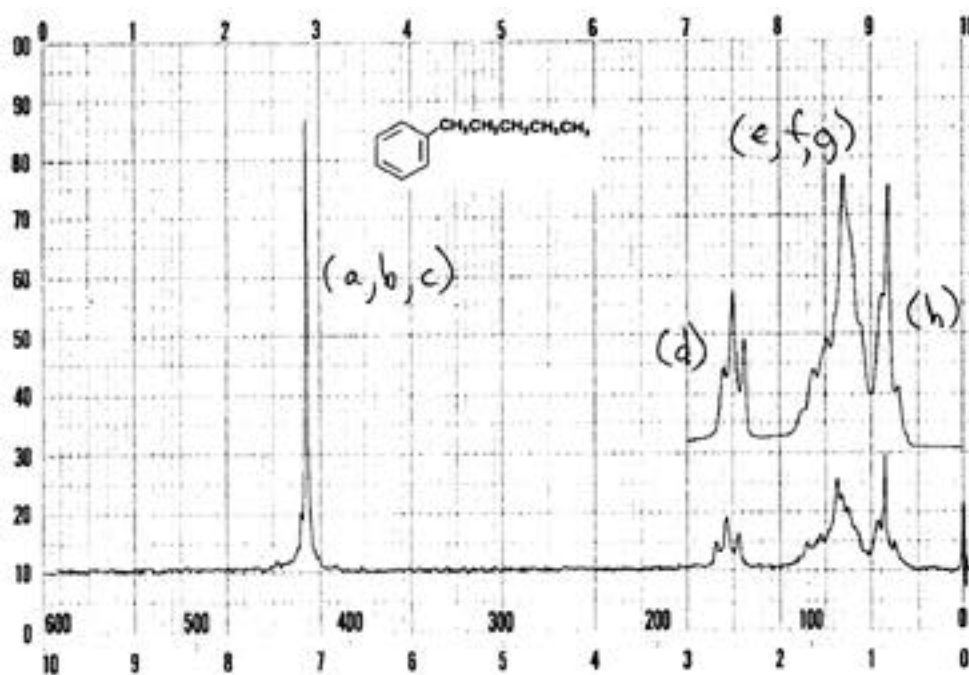
Once again there is a signal at 0; ignore this. For reasons why the signals fall where they do on the spectrum, see the next section (#6).

- e) Remember that molecules represented by bond-line formulas contain hydrogen atoms that are not shown in the formula. This compound (pentylbenzene or n-amyllbenzene) gives 8 signals, as indicated here.



Here is the actual proton nmr spectrum of this compound.

SPECTRUM 3



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. The protons labeled *e*, *f*, and *g* are also similar to one another, and their signals overlap.

6. To identify unknowns from proton magnetic spectra, it is necessary to use three types of information. One is the number of signals (#5 above). The other two are the location of signals (chemical shift in nmr terminology) and the appearance of signals (spin-spin splitting).

A. Location of signals: chemical shift.

The location of signals on a pmr spectrum is almost always expressed in units of parts per million (ppm) on the δ scale, 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 π bonds, and (3) the number of bonds between the proton and the electronegative atom or π bond.

- (1) Effect of electronegative atoms. Protons that are part of CH_3 groups far away from non-carbon atoms or π bonds generally give δ values between 0.5 and 1.0. For examples, see the protons labeled *a* in the spectrum of 2-hexanone above and the protons labeled *h* in the spectrum of pentylbenzene. In general, protons that are part of CH_3 , CH_2 , and CH groups that are NOT directly attached to an sp^2 carbon atom or heteroatom (that is, an atom other than C or H) give signals that appear between 0.5 and 2.0. Other examples of this in the spectra above include the CH_3 group *a* in diethyl ether, the CH_2 groups *b* and *c* in 2-hexanone, and the CH_2 groups *e*, *f*, and *g* in pentylbenzene.

Protons that are attached to carbon atoms that are attached to electronegative atoms such as O, N, and the halogens appear at higher δ values. For example, the protons in the CH_2 group *b* in diethyl ether, which is attached to an O, give a signal at about 3.5. Protons on groups attached to electropositive atoms give signals at low δ values. The standard compound tetramethylsilane (TMS), $(\text{CH}_3)_4\text{Si}$, gives a signal whose location is defined to be 0.

- (2) Effect of π bonds. Protons that are attached to sp^2 carbon atoms (carbon atoms involved in most π bonding) give signals that have high δ values. The benzene ring protons *a*, *b*, and *c* in pentylbenzene, for instance, give a signal at approximately 7.2. Similar protons in alkenes, aldehydes, and carboxylic acids give signals at high values of δ .
- (3) Effect of distance. The farther a proton is from a π bond or electronegative atom, the lower the value of δ of its signals. In pentylbenzene, the benzene ring protons *a*, *b*, and *c* appear at about 7.2. The signal from the protons *d* in a CH_2 group adjacent to the benzene ring, which are called benzylic protons, appears at about 2.6. Similarly, in 2-hexanone, the CH_3 group protons *a* and the CH_2 group protons *b* that are part of groups directly adjacent to the $\text{C}=\text{O}$ group give signals at 2.1 and 2.5 respectively.

B. Appearance of signals: spin-spin splitting

In simple cases the number of signals can be predicted this way: The number of peaks in a signal is equal to the number of neighboring protons plus one. A proton counts as a neighbor when it is (1) not equivalent to the proton you're looking at and (2) three (rarely 2) bonds away from the proton you're looking at. There's another rule: (3) Protons on OH and NH groups usually don't act as neighbors.

C. Identifying unknowns from proton nmr spectra

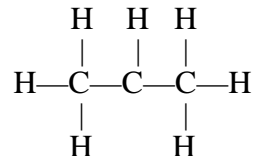
You will sometimes be asked to identify unknowns from real nmr spectra (or copies of them). Sometimes you'll be given abbreviated lists of peaks, especially on quizzes. You'll also be given the molecular formula of the unknown.

There is no set algorithm for identifying an nmr unknown from its proton nmr spectrum. You look through the data you were given and find information that gives you ideas about parts of the structure. Then you put the parts together and identify the whole. The most fundamental information you need is something you already know. Carbon forms four bonds, nitrogen forms three bonds (with one pair of nonbonded electrons), oxygen forms two bonds (with two pairs of nonbonding electrons), halogens form one bond (with three pairs of nonbonding electrons), and hydrogen forms one bond only (no nonbonding electrons).

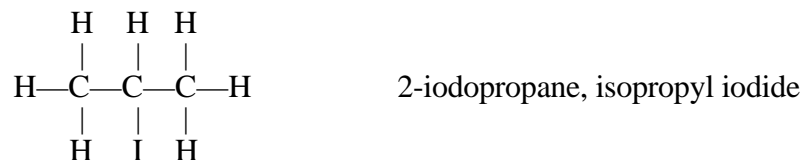
Here are two simple examples.

- a) An unknown compound has the formula C_3H_7I . Its proton nmr spectrum consists of a doublet, 1.9, 6H, and a septet, 4.3, 1H. What is the structure of this unknown?

The formula is a clue. The index of hydrogen deficiency is zero, which means that the compound contains no rings or double bonds. Looking at the spectrum, one of the signals is a doublet given by 6H. Six equivalent hydrogens almost always means two methyl groups. This is a doublet, so the 6H have one neighboring H. This makes sense because the other proton in the spectrum is a septet (seven peaks, 6H neighbors). This gives you the following partial structure.

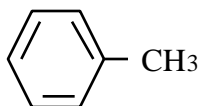


This partial structure and the formula tell you that there's something missing, the I. There's only one place to put it, and here's the answer:



- b) An unknown compound has the formula C_7H_8 . Its proton nmr spectrum consists of a singlet, 2.3, 3H, and a narrow multiplet, 7.2, 5H. What is the structure of this unknown?

The index of hydrogen deficiency is 4. Most often this means that there is a benzene ring in the unknown—3 bonds, 1 ring. The spectrum tells you the same thing. A peak at 7.2 almost always comes from a benzene ring. The ring has 5H on it (the spectrum tells you that). Since benzene itself has 6H, there is one group other than H on our benzene ring. The other group has 3H, so it's almost certainly a methyl group. This unknown is toluene:



A useful check: Does this fit the formula of the unknown? Yes, it does; the formula of toluene is C₇H₈.

- * The key to identifying compounds from proton nmr spectra is practice. You will find proton nmr information in your lecture notes, your drill manual, your lecture textbook, and other sources. Work problems.
- 7. The type of C-13 nmr spectrum you will see in this course shows only singlets, with no spin-spin splitting information. This gives you information about the carbon skeleton, information you don't get from proton nmr. The number of signals is equal to the number of sets of equivalent carbon atoms, and the location (chemical shift) of the signals gives you information about the environment of these atoms. You will be given a table of chemical shifts to help you solve any C-13 nmr problems; a copy is given on this web site.

Infrared spectra give you information about functional groups. This is review; there are notes about IR spectra elsewhere on this web site.