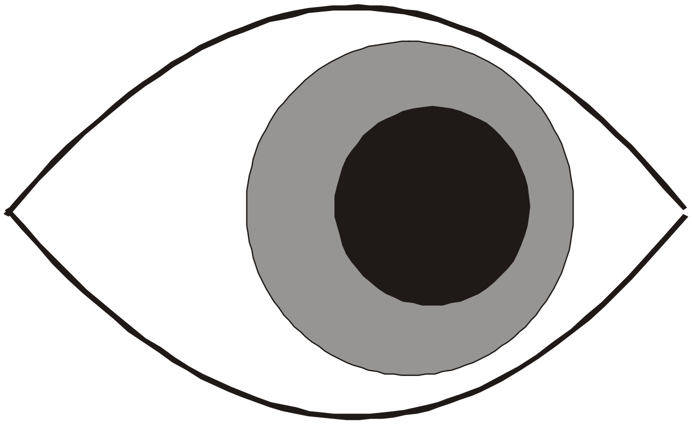


Examination of Proton NMR Spectra

What to Look For –

1) Number of Signals --- indicates how many "different kinds" of protons are present.

2) Positions of the Signals --- indicates something about magnetic (electronic) environment of protons.

3) Intensities (areas) of the Signals --- proportional to number of protons present.

4) Splitting of a Signal Into Several Peaks --- indicates the number of nearby nuclei having magnetic moments (usually protons, sometimes fluorine).

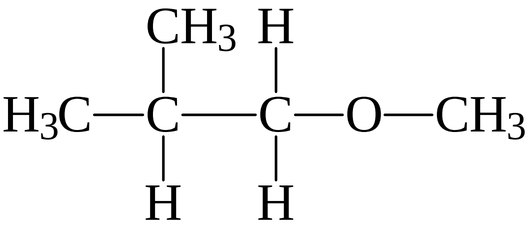
Number of NMR Signals

In a molecule, protons in the same magnetic environment absorb at the same applied magnetic field strength, H_o; different environment – different H_o.

A set of protons with the same magnetic environment are called *equivalent*. Therefore, the number of signals may reveal how many "kinds" of protons are in the molecule. Often, magnetically equivalent protons are chemically equivalent,

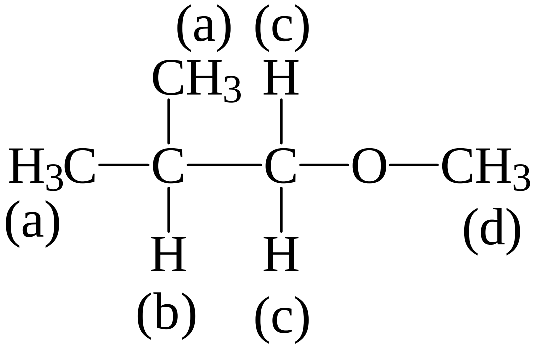
eg CH_3CH_2OH
a b c 3 NMR signals

How many signals?



$$\mathrm{H_3C{-}\overset{CH_3}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}O{-}CH_3}$$

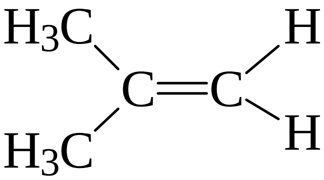
There would be four signals because there are four sets of equivalent protons (sets a, b, c, and d).



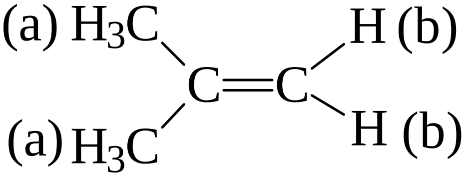
$$\mathrm{\underset{(a)}{H_3C}{-}\overset{\overset{(a)}{CH_3}}{\underset{\underset{(b)}{H}}{C}}{-}\overset{\overset{(c)}{H}}{\underset{\underset{(c)}{H}}{C}}{-}O{-}\underset{(d)}{CH_3}}$$

To be chemically equivalent, protons must be stereochemically equivalent —

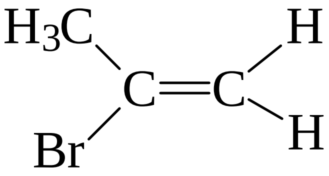
How many NMR signals?



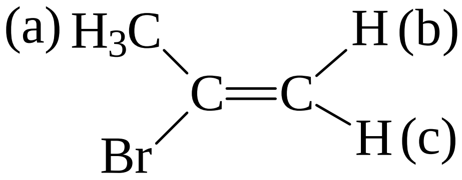
Two signals.



How many NMR signals?



Three signals.



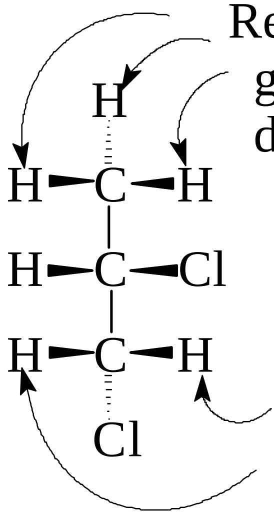
The two vinylic protons, b and c, are not equivalent. One is *cis* to the bromine, the other is *trans*.

Q: How does one unequivocally decide whether or not two protons are equivalent?

A: Read on.

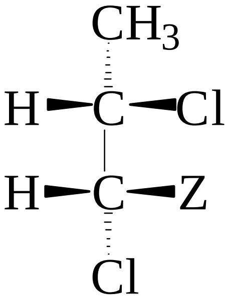
To determine whether protons are equivalent — replace each proton in question, in turn, by Z, where Z is a "dummy" atom, different from any other atom in the molecule. If replacement of either proton by Z gives the same product *or* enantiomeric products, the protons are chemically and magnetically equivalent. Ignore the existence of conformational isomers (except at low temperatures).

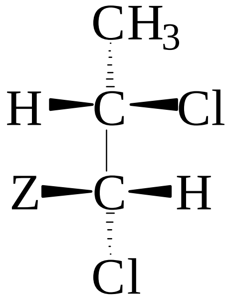
eg



Replacement of any one of these by Z gives the same molecule (the carbon does not become a chiral center).

Replacement of these, in turn, by Z gives a pair of diastereomers:



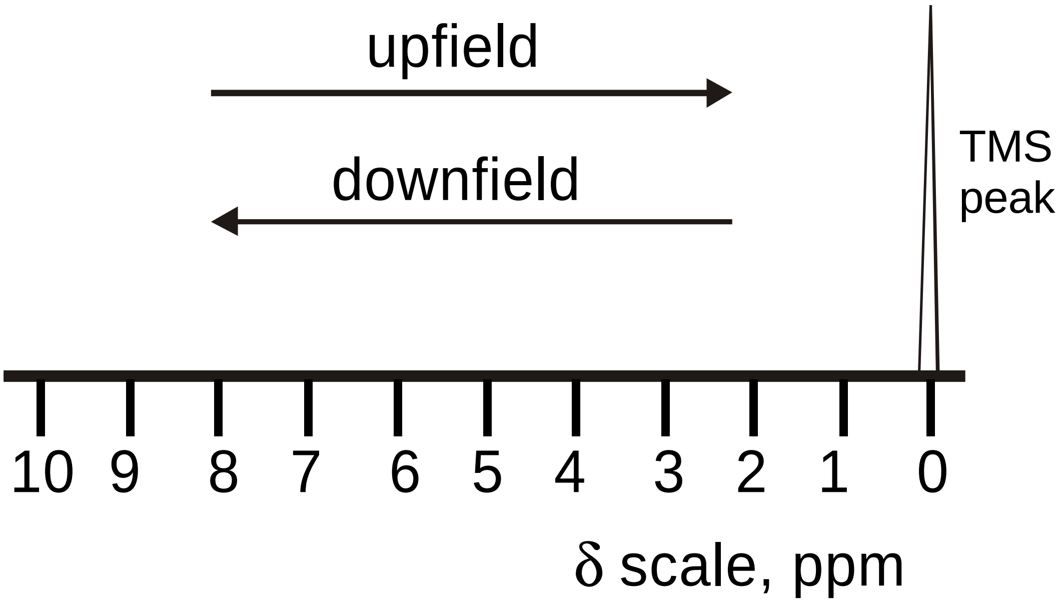


therefore, the hydrogens are <u>not</u> equivalent
(they are *diastereotopic*).

Note: The theoretical number of signals may not equal observed number because of overlap.

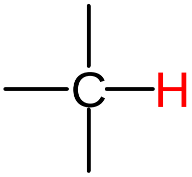
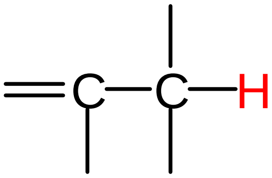
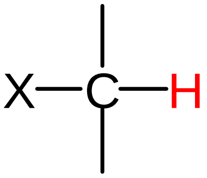
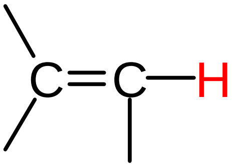
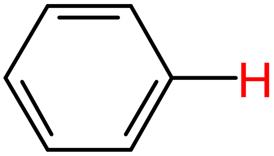
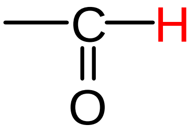
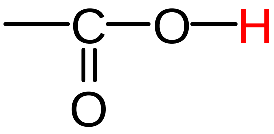
Positions of NMR Signals: Chemical Shift

The position of a signal in the spectrum helps to reveal what "type" of proton(s) gives rise to the signal. The position of a signal – its *chemical shift* – is measured in ppm (parts per million) of H_o relative to the proton signal from tetramethylsilane (TMS), $(CH_3)_4Si$.



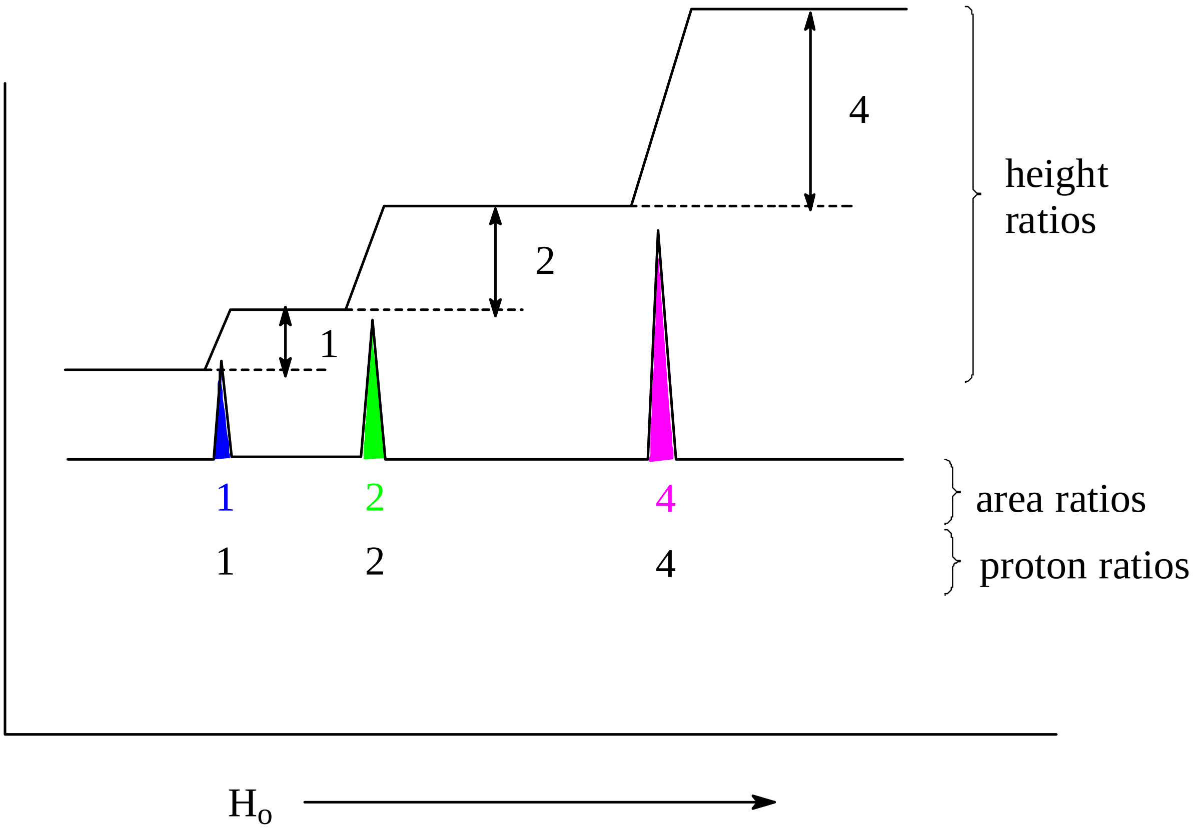
Equivalent protons have the same chemical shift. Also, protons in similar environments, but in different molecules, will absorb at about the same place in the spectrum; hence, NMR chemical shift tables which relate chemical shift to structural features in the molecule near the proton(s) that are giving rise to the signal.

The following is an *incomplete* list of possibilities:

Proton Type	Region, ppm (δ)
	0 - 1.5
	1.5 - 2.5
	2.5 - 4.5 [X is electronegative, *e.g.* N, O, Cl]
	4.5 - 6.5
	6.5 - 8
	9 - 10
	11 - 12

Peak Area and Proton Counting

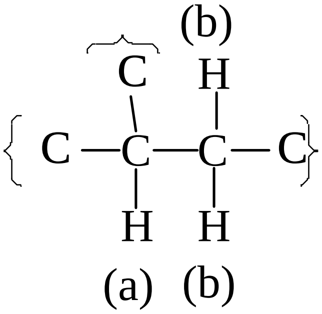
The area under a particular signal is proportional to the number of protons giving rise to the signal. Proton NMR spectrometers sometimes display the integrated area under the signal as a stepped curve --- step height is proportional to area.



Splitting of Signals --- Spin-Spin Coupling

Electrons affect the magnetic environment of a proton. So, also, do nuclei of nearby atoms that have magnetic moments. For organic molecules the most important of these nuclei are those of hydrogen and fluorine. We shall consider hydrogen.

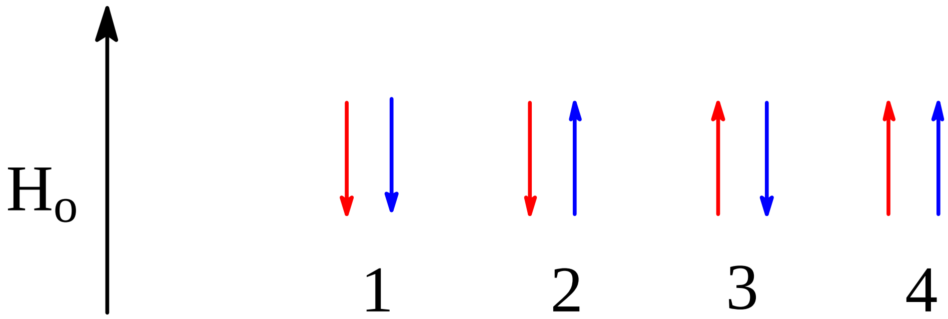
Consider



There are no hydrogens on boldface Carbons.

The magnetic field that protons (b) feel at a given instant is slightly increased or decreased by the magnetic moment (μ) of proton (a): increased if $\mu_{(a)}$ auguments H_o, decreased if $\mu_{(a)}$ opposes H_o. Since about half the molecules have $\mu_{(a)}$ opposing H_o and about half the molecules have $\mu_{(a)}$ augmenting H_o, the absorption by the (b) protons in half the molecules will be shifted upfield (slightly) and in the other half downfield (slightly). Therefore, the signal from protons (b) is split into two peaks, *a doublet*, with virtually equal peak areas.

Consider proton (a): its local magnetic field will be affected by $\mu_{(b1)}$ and $\mu_{(b2)}$.
Possible arrangements, of virtually equal probability of $\mu_{(b1)}$ and $\mu_{(b2)}$:



So, 25% of the molecules will have each arrangement. Two of these, 2 and 3, are equivalent: the (a) proton in molecules with either of these arrangements will give a signal at the same chemical shift. On one side of this signal will be a signal from molecules which have arrangement 1 and equidistant on the other side will be a signal from molecules which have arrangement 4. Therefore, the signal from proton (a) is split into 3 equally spaced peaks called *a triplet.*

The intensities of the peaks in the triplet are 1:2:1 because molecules which have arrangement 2 or 3 give signals at the same place.

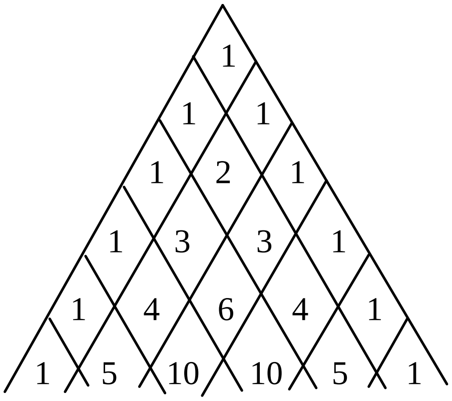
[The area under the triplet (1 proton) will be half the area under the doublet (2 protons).]

The separation between the peaks (*coupling* or *splitting constant*, J) in the doublet must be equal to the separation between the peaks in the triplet. This equality for coupled protons is an aid in analyzing spectra, sometimes, because different *multiplets* (doublets, triplets, quartets, *etc*.) displaying different coupling constants cannot arise from coupled protons.

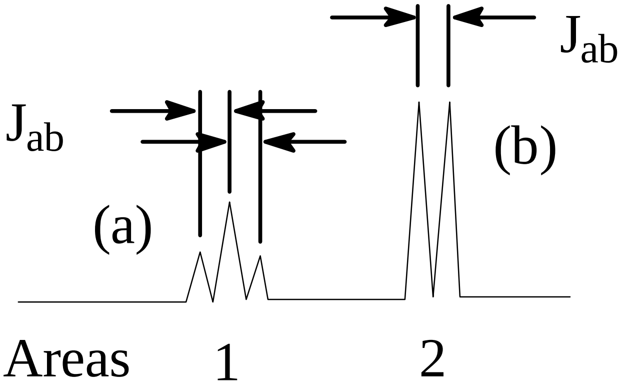
What if there are more than two equivalent protons causing splitting?

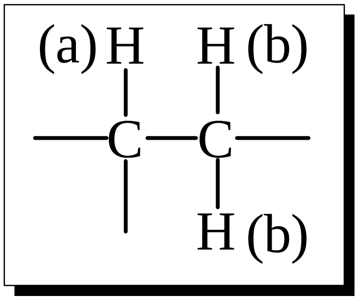
☞ In general, n equivalent protons will split the signal of a proton, or set of protons, coupled to them into n + 1 peaks.

☞ The relative intensities of these peaks may be found from Pascal's triangle.



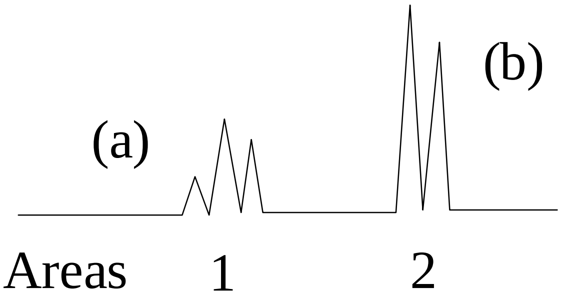
In the case we have been considering, we would expect the spectrum to look like —

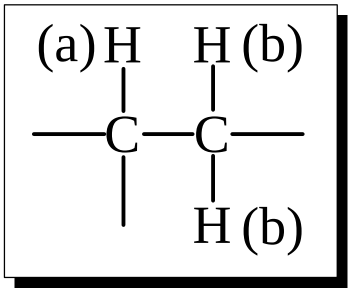




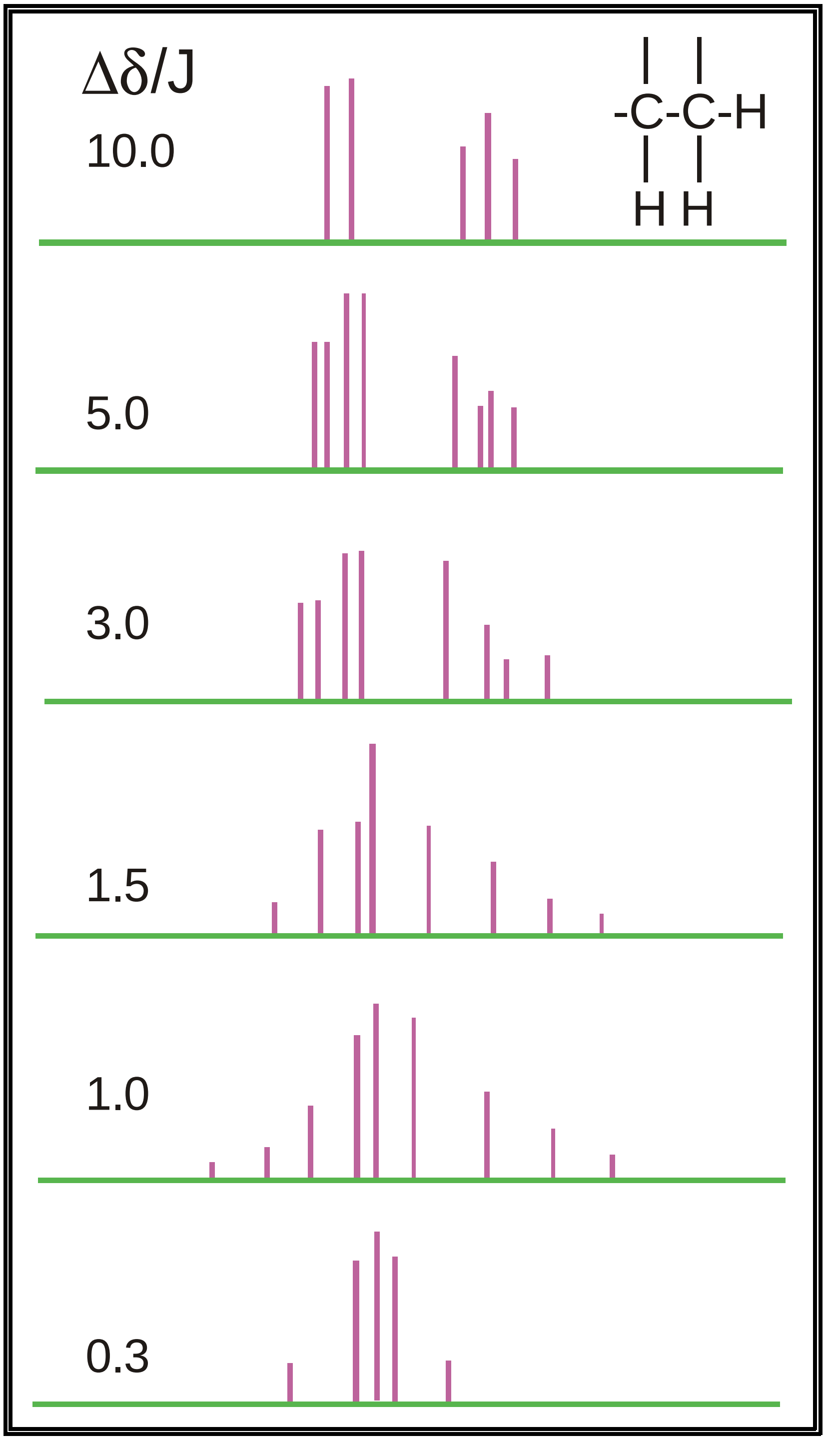
So far, we have been considering the spin-spin splitting in *first order* spectra, where the difference in chemical shift of the coupled protons is at least 40 x the coupling constant, $\Delta(\delta) \geq 40J$.

When $\Delta(\delta) \approx 10J$, the interior peaks of the multiplet grow at the expense of the exterior peaks.





When $\Delta(\delta) < 10J$, the spectrum becomes complex (second order) and difficult (read: impossible) to analyze. This can be seen in the graphic on the next page which shows the spectrum we have been discussing ranging from a situation in which $\Delta(\delta) = 10J$ to one where $\Delta(\delta) = 0.3J$.


Δδ/J
10.0
-C-C-H
H H
5.0
3.0
1.5
1.0
0.3

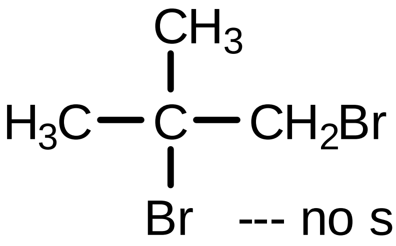
Which protons couple?

Spin-spin splitting is expected only between **non-equivalent** neighboring protons. Non-equivalent means occurring at different chemical shifts. Neighboring usually means protons on adjacent carbons, but may sometimes mean protons further removed from each other, particularly if π-bonds intervene.

If protons on the same carbon are non-equivalent they may couple.

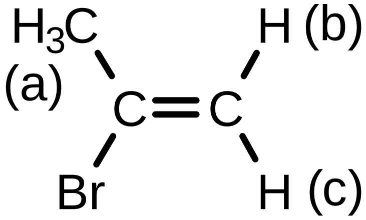
eg CH_3Br ----- no splitting

CH_3CH_3 ---- no splitting



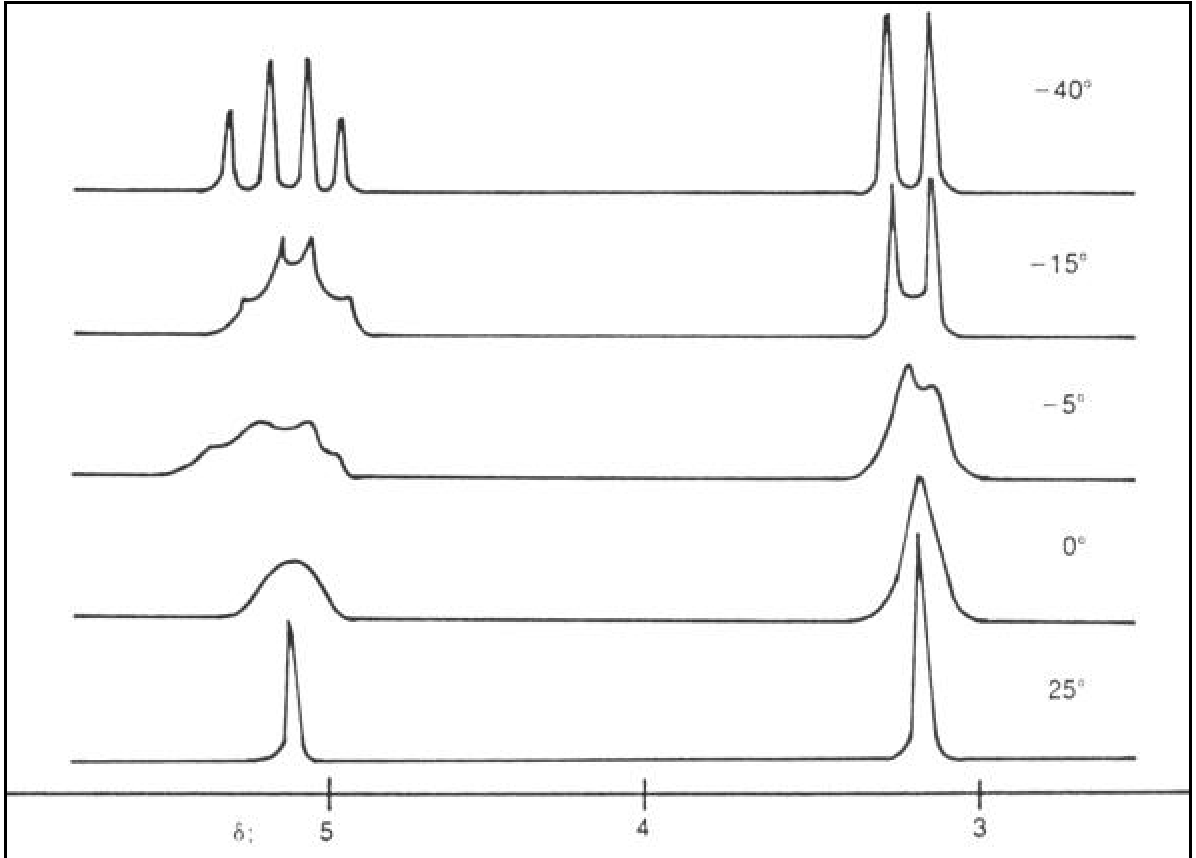
$$H_3C-\overset{\displaystyle CH_3}{\underset{\displaystyle Br}{C}}-CH_2Br$$

--- no splitting



$J_{bc} \neq 0$

Protons on N (*eg* 1^{o} and 2^{o} amines, R-NH$_2$ and R$_2$NH) or O (*eg* alcohols) frequently do not couple because of proton *exchange*. These protons are exchanged between molecules too rapidly for NMR to see anything but an average signal as opposed to a split signal. The spectra of methanol, shown below, were taken at different temperatures. At room temperature proton exchange between -O-H groups is too fast for splitting to be observed. However, at -40^{o}C we see that the CH$_3$ protons split the OH proton into a quartet, while the OH proton splits the CH$_3$ protons into a doublet.



NMR Spectra of Methanol at Various Temperatures

Carbon-13 NMR Spectra

Looking at carbon using NMR is more difficult than looking at hydrogen because carbon-12 does not have a magnetic moment. This means that we have to look at carbon-13, which does have a magnetic moment, but which is only about 1% of carbon as it occurs in nature. So, the instrumentation required is more complex.

On the other hand, analysis of C-13 spectra is considerably easier than analysis of proton spectra. In most cases the analysis of a C-13 spectrum involves noting the number of signals and their chemical shift. Each carbon gives rise to a signal, but if two or more carbons are equivalent, their signals will exactly overlap. As in proton NMR chemical shift may suggest the type of carbon that is giving rise to a particular signal.

Typical C-13 Chemical Shifts, δ from TMS

“Type” of Carbon	Chemical Shift
$-CH_3$	10-40
$-CH_2-$	20-65
≡C	70-90
=C	100-150
aromatic	120-170
C=O	190-200

Signal splitting and peak areas are not usually a feature of these spectra. Furthermore, signal overlap from non-equivalent atoms is much less common in C-13 spectra than in proton spectra.

DEPT-NMR —
Through a technique known as DEPT-NMR it is possible to determine which signals in a carbon-13 NMR spectrum come from carbons with no hydrogens attached, which come from carbons with one hydrogen attached, which come from carbons with two hydrogens attached, and which come from carbons with 3 hydrogens attached.

Step 1
Run an ordinary (*broadband-decoupled*) C-13 NMR spectrum of the compound. A signal will appear for each non-equivalent carbon. (Equivalent carbons will all contribute to the same signal.)

Step 2
Run a DEPT-90 C-13 NMR of the compound. A signal will appear for each non-equivalent carbon that has one hydrogen attached (CH). No peaks will appear for the C, CH_2, or CH_3 carbons.

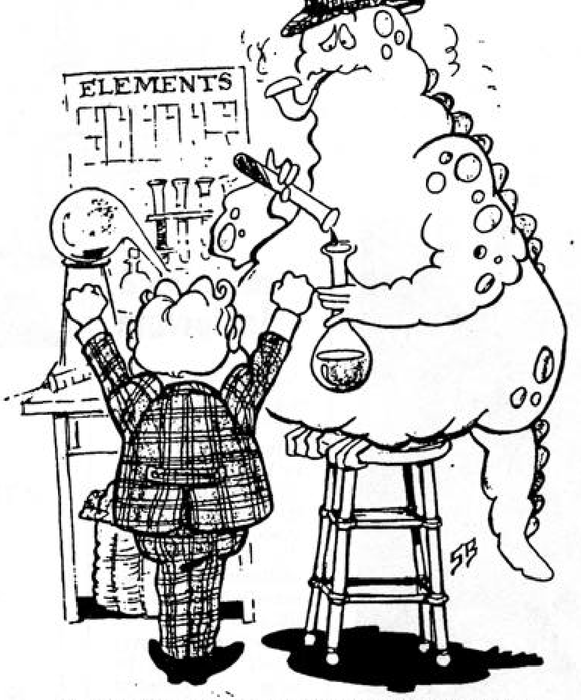
Step 3
Run a DEPT-135 C-13 NMR of the compound. A positive signal (peak) will appear for CH_3 and CH carbons. A negative peak will appear for CH_2 carbons.

To sum up —

Broadband-decoupled	DEPT-90	DEPT-135
C, CH, CH_2, CH_3	CH	CH, CH_3 positive
		CH_2 negative

Based on this information, Sherlock, could you figure out what’s what?

Art in the Blood by Scott Bond



"GREAT SCOTT, HOLMES! THIS TIME THESE INFERNAL CHEMICAL EXPERIMENTS HAVE GONE TOO FAR!"