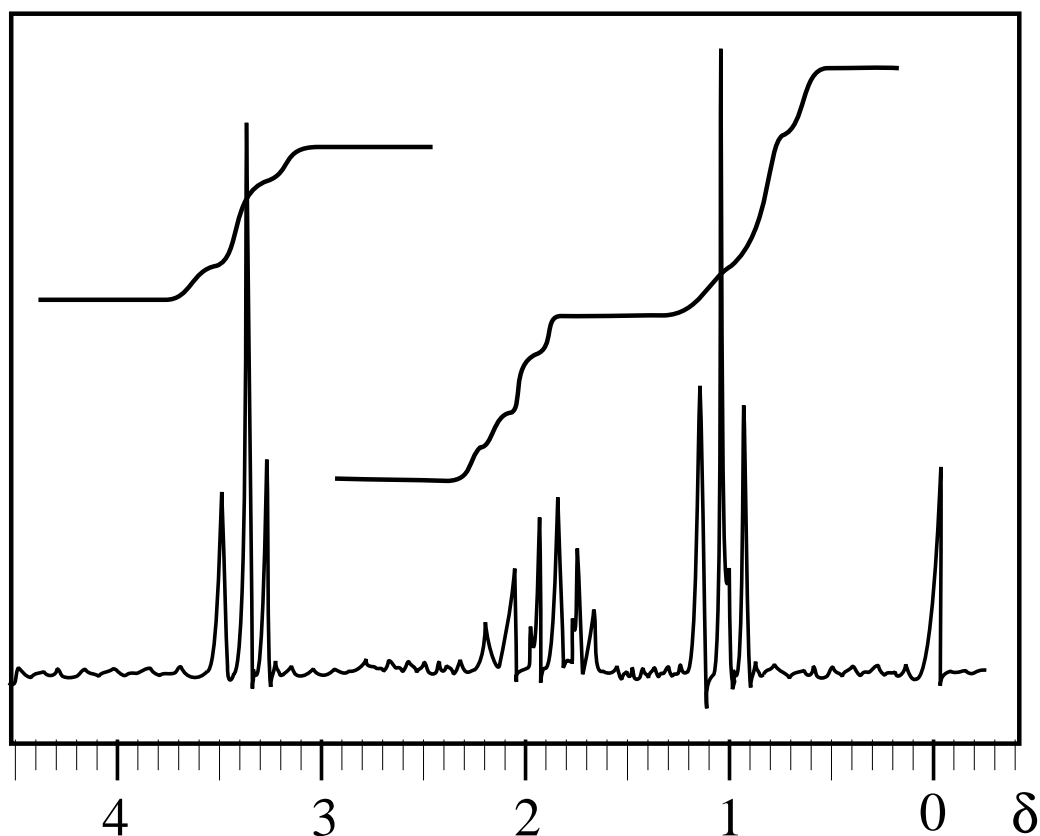


AN INTRODUCTION TO ...

NMR SPECTROSCOPY

NUCLEAR MAGNETIC RESONANCE



— *Self-study booklet* —



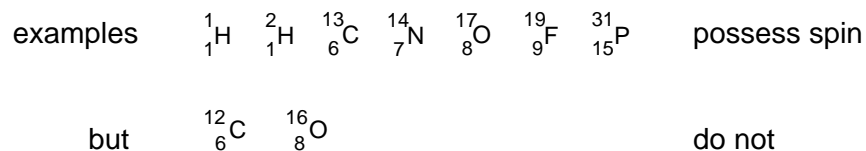
KNOCKHARDY
PUBLISHING

NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Origin of Spectra

Theory

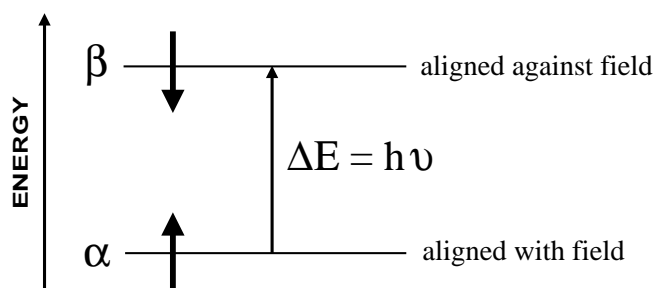
All nuclei possess charge and mass. However, those with either an odd mass number or an odd atomic number also possess spin. This means they have angular momentum.



A nucleus with spin can be detected by nuclear magnetic resonance (nmr) spectroscopy.

A spinning nucleus such as ${}^1\text{H}$ behaves as a spinning charge and generates a magnetic field. It can be likened to a bar magnet.

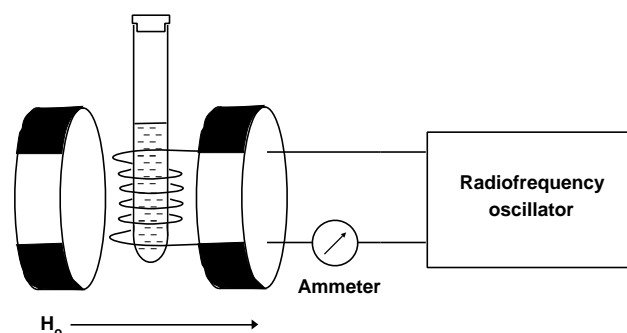
When it is placed in an externally applied field it can align with, or against, the field.



The energy difference between the two states (ΔE) depends on the applied field.

The sample is placed in the field of a large electromagnet and a radio-frequency (RF) field is applied. The magnetic field is increased and the excitation or “flipping” of nuclei from one orientation to another is detected as an induced voltage resulting from the absorption of energy from the RF field.

The basic arrangement of an nmr spectrometer



An nmr spectrum is the plot of the induced voltage against the sweep of the field. The area under a peak is proportional to the number of nuclei “flipping”

Not all hydrogen nuclei absorb energy at the same field strength at a given frequency; the field strength required depends on the environment of the hydrogen.

By observing the field strength at which protons absorb energy, one can deduce something about the structure of a molecule.

INTERPRETATION OF SPECTRA

Introduction NMR spectra provide information about the structure of organic molecules from the ...

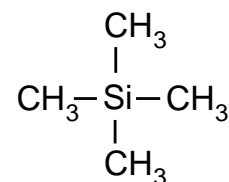
- number of different signals in the spectrum
- position of the signals (chemical shift)
- splitting pattern of the signals
- intensity of the signals

Running spectra

- a liquid sample is placed in a long thin tube which spins in a magnetic field
- solids are dissolved in solvents which won't affect the observed spectrum - CCl_4 , CDCl_3
- a small amount of **tetramethylsilane, $(\text{CH}_3)_4\text{Si}$** , is added to provide a reference signal
- when the spectrum has been run, it can be integrated to find the relative peak heights

TMS

- it produces a single intense peak
- signal is just outside the range shown by most protons
- it is inert, non-toxic and has a low boiling point
it can be distilled off if required



TETRAMETHYLSILANE

Chemical shift

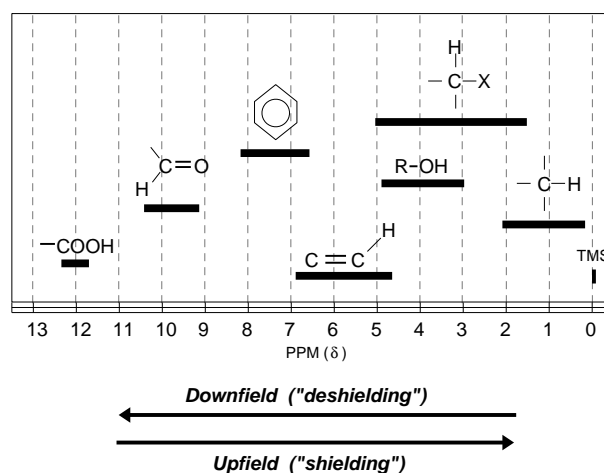
- each proton type is said to be **chemically shifted** relative to a standard (usually TMS)
- the chemical shift is the difference between the field strength at which it absorbs and the field strength at which TMS protons absorb
- the delta (δ) scale is widely used as a means of reporting chemical shifts

$$\delta = \frac{\text{Observed chemical shift (Hz)} \times 10^6}{\text{Spectrometer frequency (Hz)}} \quad \text{ppm} \quad (\text{parts per million})$$

- the chemical shift of a proton is constant under the same conditions (solvent, temp)
- the **TMS** peak is assigned a value of ZERO ($\delta = 0.00$)
- all peaks of a sample under study are related to it and reported in parts per million
- H's near to an electronegative species are shifted "downfield" to higher δ values

Approximate chemical shifts

the actual values depend on the environment



Multiplicity This occurs because the spin of one nucleus affects that of a **chemically different nucleus on an adjacent atom**.

- also known as coupling or spin-spin splitting
- low resolution nmr gives 1 peak for each environmentally different group of protons
- high resolution nmr gives more complex signals - doublets, triplets, quartets, multiplets
- the signal produced indicates the number of protons on adjacent carbon atoms

Number of peaks = number of H's on adjacent chemically different atoms + 1

Ratio of peak sizes for	2 peaks	"doublet"	1:1
	3 peaks	"triplet"	1:2:1
	4 peaks	"quartet"	1:3:3:1
	5 peaks	"quintet"	1:4:6:4:1

Theory

Splitting patterns are worked out by considering the effect **adjacent, chemically different protons** have on another signal in a given environment. The spin of the proton producing the signal is affected by each of the two forms of the adjacent proton. One orientation augments/enhances its field and the other opposes/reduces it. This is done by calculating the various **possible combinations** of alignment of adjacent protons.

1 adjacent H can be aligned either with (α) or against (β) the field
only two equally probable possibilities
the signal is split into **2 peaks** of **equal intensity**

Fig. 1

2 adjacent H's more possible combinations - the signal is more complex
get **3 peaks** in the ratio **1 : 2 : 1**

Fig. 2

3 adjacent H's even more possible combinations
get **4 peaks** in the ratio **1 : 3 : 3 : 1**

Fig. 3

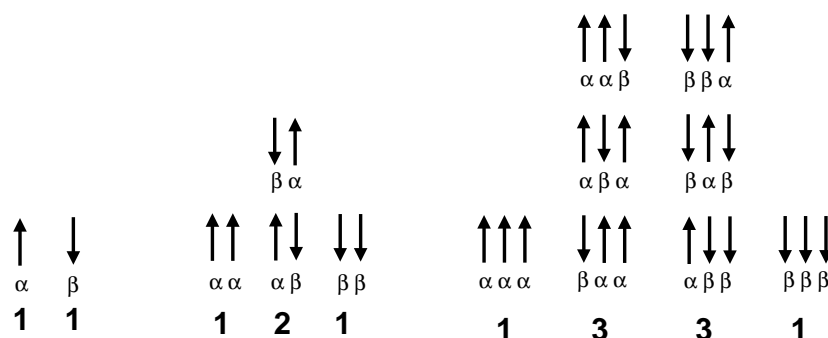


Fig. 1

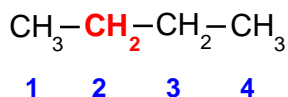
Fig. 2

Fig. 3

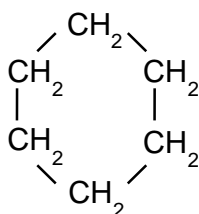
Q.1 Explain the splitting pattern when there are four adjacent protons.

Chemically different?Coupling only **takes place with** chemically different protonsIt **does not take place with** chemically similar protons or H atoms on OH groups

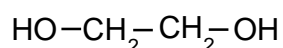
To see if a hydrogen is chemically different you need to look at the whole structure of the molecule, not just the neighbouring atom(s).

Example 1You see **two sets of signals**A triplet due to the CH₃ groups - 2 adjacent H's +1A quartet due to the CH₂ groups - 3 adjacent H's +1

- the signal due to the H's on carbon 2 is not a hexet (5 + 1 = 6)
- the 2 H's on carbon 3 are CHEMICALLY IDENTICAL to those on carbon 2
- **chemically identical hydrogens do not affect the splitting pattern**

Example 2You get just **one signal** - a singlet

- all the hydrogen atoms are chemically equivalent
- there are no chemically equivalent hydrogens on adjacent atoms
- the signal will be a singlet - 0+1 = 1

Example 3

You see two sets of signals

A singlet due to the CH₂ groups

A singlet due to the OH groups

- **signals due to H's on OH groups are always singlets**
- the H's on the CH₂ give rise to a singlet because...
- the H atoms on the adjacent CH₂ are chemically equivalent so don't couple and **H's on adjacent OH groups do not couple**

Q.2

Why are the signals due to the CH₂ hydrogens in BrCH₂CH₂Br singlets not triplets ?

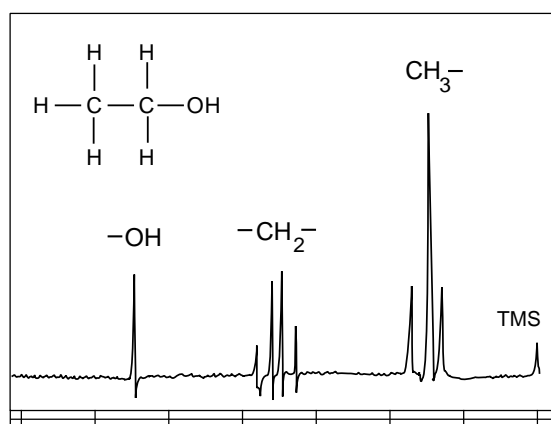
- Special note **Signals for the H in an O-H bond**
- are not affected by hydrogens on adjacent atoms
 - are not split (see later)

A spectrum of a typical alcohol (ethanol) is shown below. One would expect a triplet signal (3 peaks) for the H in O-H but there is only one.

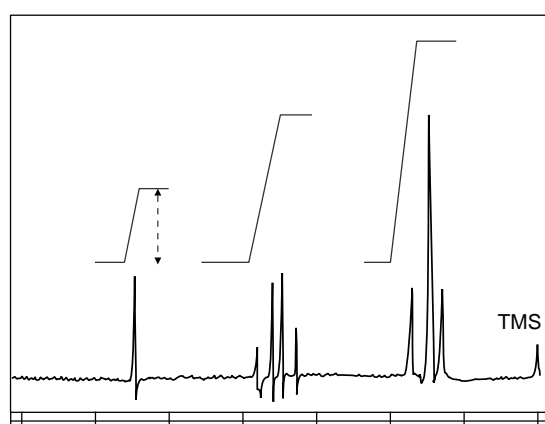
- Integration**
- the area under a signal is proportional to the number of hydrogen atoms present
 - is achieved using an integration device which scans the peaks
 - lines on the spectrum show the **relative abundance** of each hydrogen type

By measuring the distances between the integration lines (dotted line on the spectrum below) one can work out the simple ratio between the various types of hydrogen.

The nmr spectrum of ethanol



(i) before integration



(ii) after integration

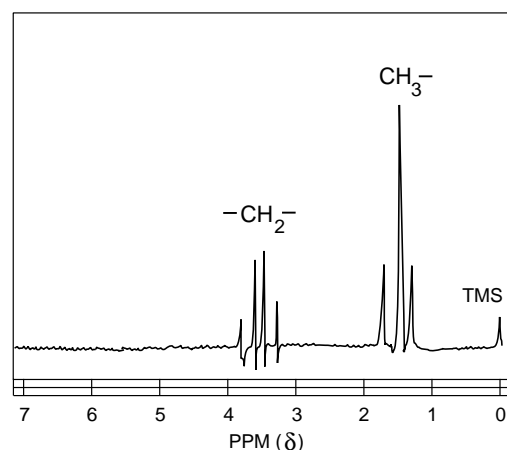
Q.3 Measure the ratio of the heights of the integration lines in the ethanol spectrum. Does it correspond to the actual ratio of protons in the structure?

D₂O shake The signal due to the hydroxyl (OH) hydrogen is seen as a singlet ... there is no splitting

This arises because proton on the OH, rapidly exchanges with protons on other molecules and is not attached to any particular oxygen long enough to register a splitting signal.

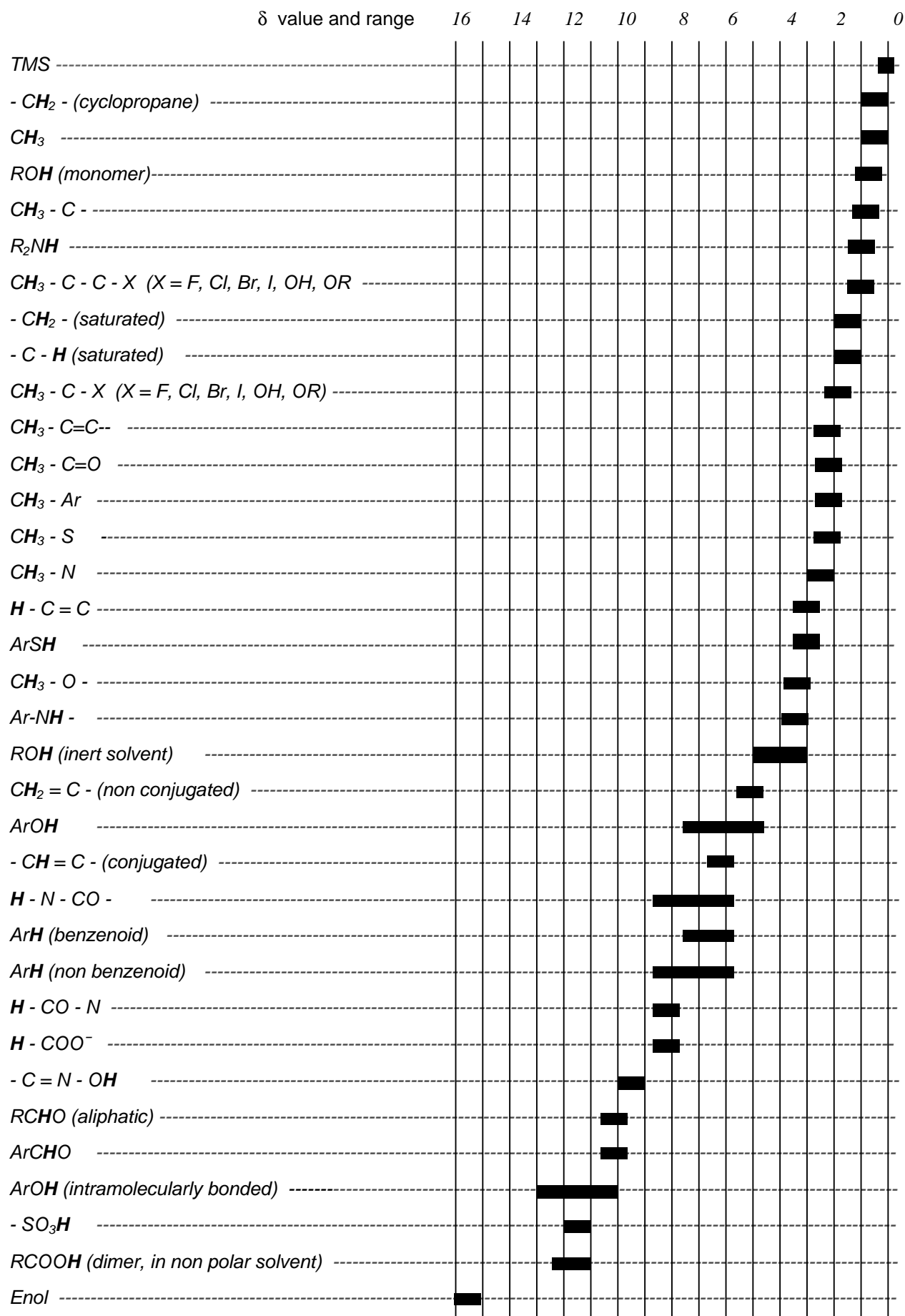
It is possible to exchange the H for deuterium, ²H or D. The usual source is deuterium oxide, D₂O, a form of water.

Deuterium doesn't exhibit nuclear magnetic resonance under the conditions used for proton nmr so the signal is removed to another part of the spectrum.

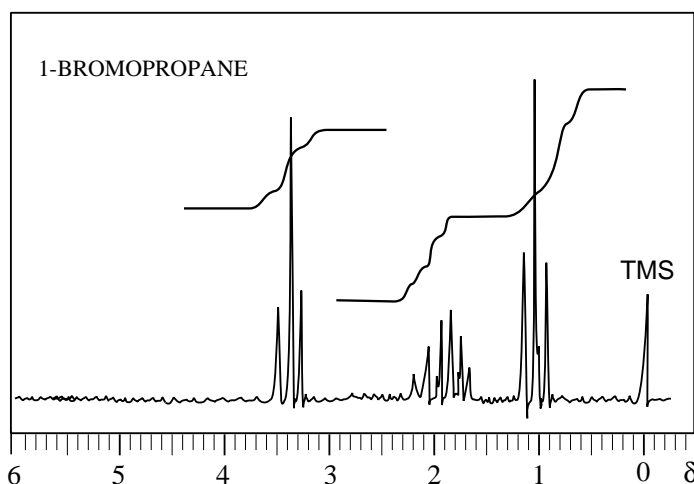


nmr spectrum of ethanol after a D₂O shake

SOME TYPICAL PROTON CHEMICAL SHIFTS



INTERPRETING THE NMR SPECTRUM OF 1-BROMOPROPANE



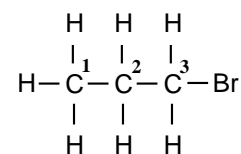
Analysis

Peaks There are three different signals so there are three chemically different protons.

Position The further the signals are shifted from TMS signal, the nearer they are to the halogen.

Splitting The signals include a

triplet	($\delta = 1.0$)
sextet	($\delta = 1.8$)
triplet	($\delta = 3.4$)



The signals due to the protons attached to carbon ...

C ¹	triplet	($\delta = 1.0$)	coupled to the two protons on carbon C ²	(2+1 = 3)
C ²	sextet	($\delta = 1.8$)	coupled to five protons on carbons C ¹ and C ³	(5+1 = 6)
C ³	triplet	($\delta = 3.4$)	coupled to the two protons on carbon C ²	(2+1 = 3)

Integration The integration lines show that the ratio of protons is 2:2:3

Summary An nmr spectrum provides several types of information :-

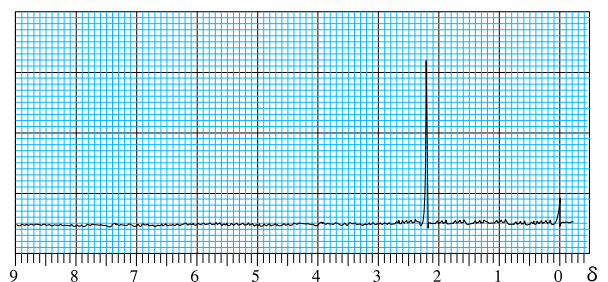
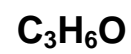
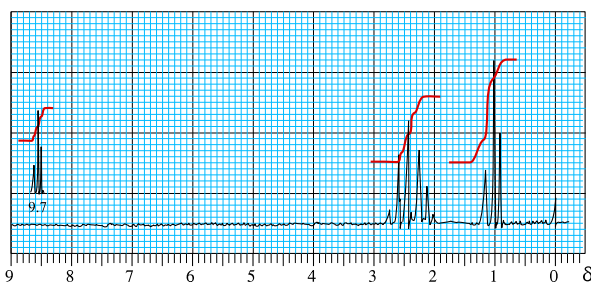
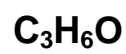
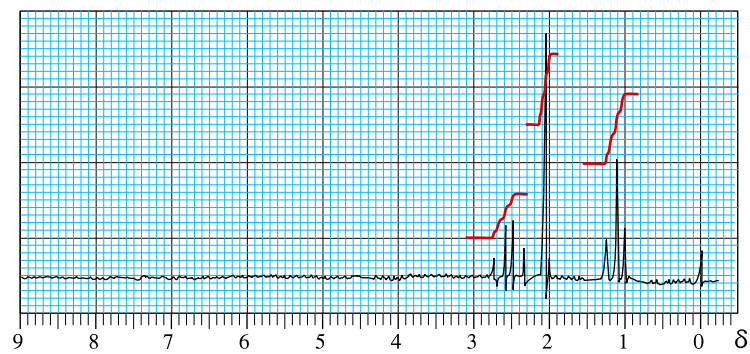
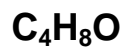
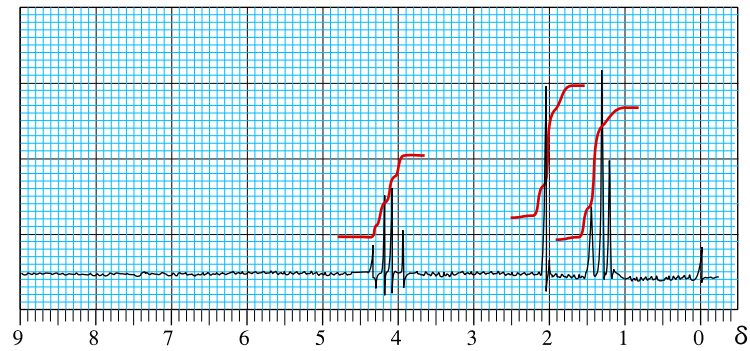
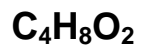
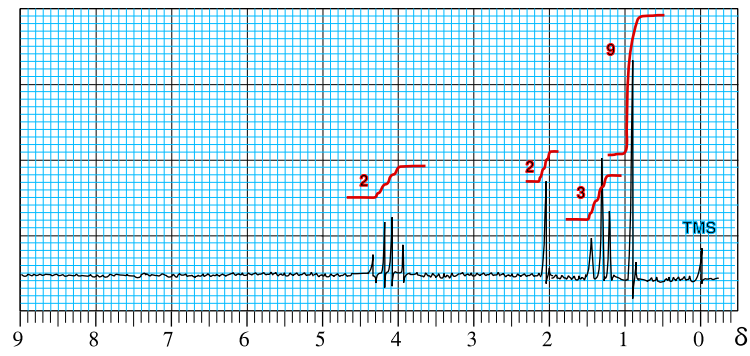
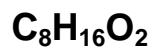
- | | | |
|---------------------------|---------------|---|
| • number of signal groups | tells you ... | the number of different proton environments |
| • chemical shift | | the general environment of the protons |
| • multiplicity | | how many protons are on adjacent atoms |
| • peak area | | the number of protons in each environment |

In many cases this information is sufficient to deduce the structure of an organic molecule.

Q.4 What would you expect the spectrum of 2-bromopropane to be like ?
 Explain your answer in terms of

- a) the chemical shift
- b) the splitting pattern
- c) integration

SAMPLE SPECTRA



Carbon-13 magnetic resonance

Theory After hydrogen, the next most useful atom providing useful information to organic chemists is carbon-13. Natural carbon only contains about 1% of this isotope so the instruments for its detection need to be sensitive and the time taken to obtain a spectrum will be longer. Only the chemical shift is important in this technique as each spectrum gives only single lines for each chemically equivalent carbon. Carbon-13 nmr has wide applications in the study of natural products, complex biological molecules and polymers.

SUPPLEMENTARY QUESTIONS

1. Why is proton nmr more useful for the investigation of organic rather than inorganic compounds ?
2. What other nucleus found in organic compounds is commonly investigated using nmr ?
3. What compound is used as the internal reference for proton nmr chemical shifts ?
How many peaks does it produce on a spectrum and at what delta (δ) value does it appear ?
4. Interpret the spectrum of compound (A) of formula $C_2H_3Cl_3$. Deduce its structure.
5. Which structural isomer of C_4H_8 has an nmr spectrum similar to spectrum (B) ?
6. Three isomeric carbonyl compounds have the molecular formula C_4H_8O . Identify two of them from the nmr spectra (C) and (D). What would the spectrum of the third isomer look like ?
7. What uses have been made of nuclear magnetic resonance in other scientific areas ?

