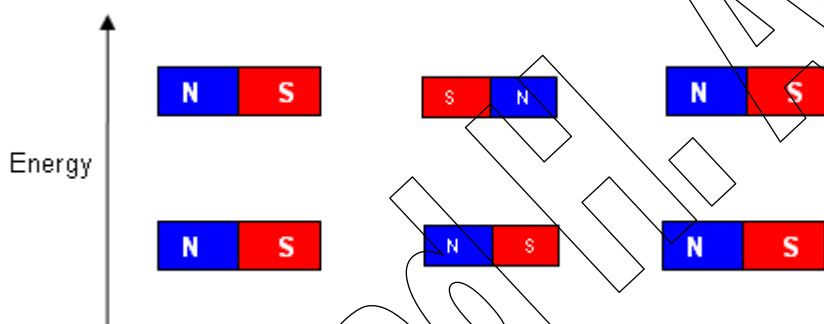


Nuclear Magnetic Resonance (N.M.R.) Spectroscopy

The basis of N.M.R.

- Nuclear magnetic resonance spectroscopy is an extremely useful technique for organic chemists.
- N.m.r. provides chemists with detailed information about the nuclei of hydrogen atoms; the nuclei behave differently in different environments, thus n.m.r. can tell us what the environments are and how many hydrogen atoms are within them.
- N.m.r. can be used to find out about any nuclei that has an odd number of protons + neutrons; in addition to ^1H nuclei, ^{13}C , ^{19}F and ^{31}P are also used for n.m.r.
- When nuclei are placed in a strong magnetic field, they act like small magnets; they can either align themselves with the magnetic field, or against it (requiring more energy).

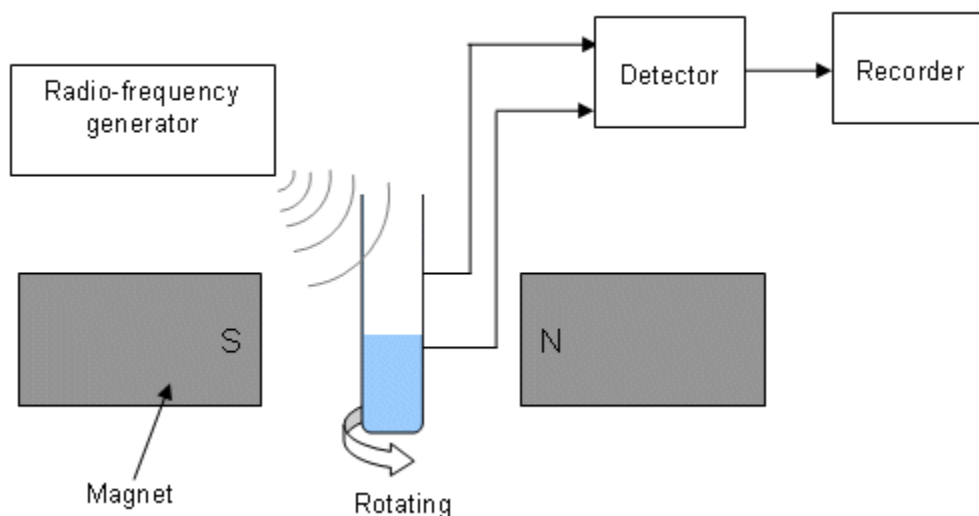


- More than 50% of the nuclei align themselves with the magnetic field (lower energy).
- Like when electrons are promoted, it requires a definite amount of energy to move the nuclei up to a higher energy level (aligned against the magnetic field); this amount of energy is different for the hydrogen nuclei in different environments.
- The energy that is needed to move the nuclei up to a higher energy level corresponds to that of radio waves.
- The energy required depends upon the strength of the overall magnetic field on the nuclei.
- The strength of the magnetic field not only corresponds to the strength of the instrument's magnetic field, but it also depends upon the magnetic fields of the groups surrounding the hydrogen nuclei.
- The electrons associated with neighbouring atoms have a small magnetic field themselves, which usually opposes the external magnetic field. The overall field that is experienced by the proton is therefore smaller than the external field; the small change associated with the value of the local field from the surrounding part of the molecule.
- This means that for every different kind of molecular environment, there is a different magnetic field.

- Thus in different molecular environments, the energy gap between the lower and higher energies of the nuclei changes; therefore in different environments the hydrogen nuclei absorb different frequencies of radiation.

The N.M.R. Machine

- The n.m.r. machine comprises of a magnet (produces strong magnetic field), a radio-frequency source, a detector and a recorder.



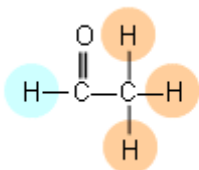
- The samples are dissolved in solvents which contain no hydrogen atoms (e.g. CCl_4) or that have the hydrogen atoms replaced with deuterium (e.g. $\text{CD}_3\text{CD}_2\text{OH}$).

How it works:

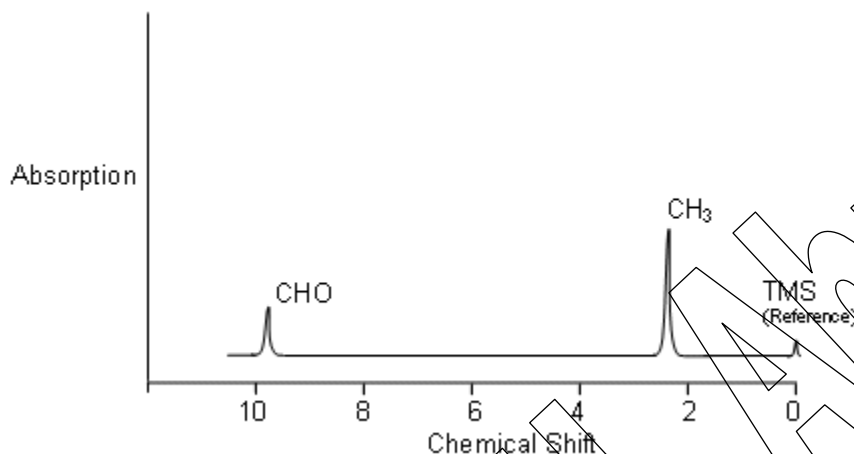
1. The magnetic field is held constant while a band of frequencies is applied as a pulse to the sample.
2. The radio-frequency results in the nuclei energy level increasing; immediately after this increase, there will be a greater than normal amount of protons at the higher energy level. Some of these emit radiation as they move down to the lower energy level.
3. This radiation is measured by the detector and sent to the recorder.
4. The radiation is weak and the process is over very quickly, so it is repeated many times to ensure that a valid result is returned.
5. A graph of absorption against frequency (referred to as chemical shift) is produced.

Interpreting the Spectra

- As afore mentioned, the n.m.r. can distinguish between ^1H atoms in different environments.
- If we analysed a molecule of ethanal, there would be two different peaks, as there are two different environments (represented by different colours below):



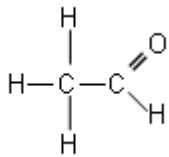
- It will require more energy, thus a higher frequency to move the ^1H nucleus attached to the $\text{C}=\text{O}$ group, as it is within the magnetic field of the oxygen atoms lone pair of electrons. (The chemical shift values can be found in the data booklet).
- The n.m.r. spectrum for ethanal is shown below:



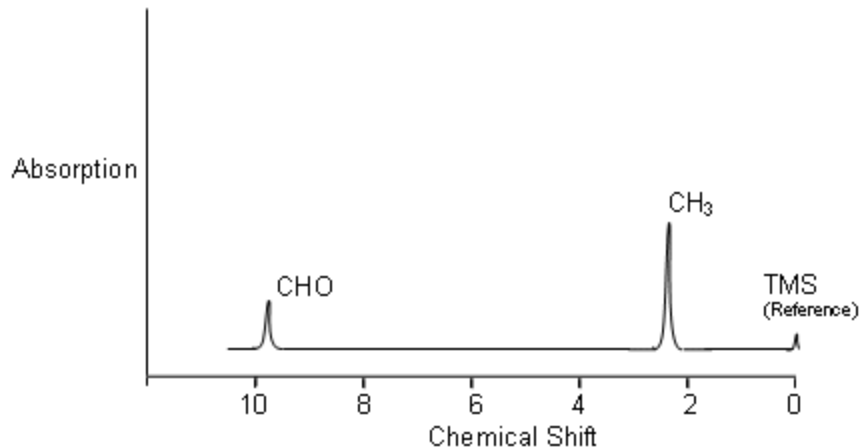
- The area under the peaks is proportional to the number of protons absorbing each time; i.e. there are three times as many protons in the CH_3 group than the CHO group, thus the area under the CH_3 peak is three times the area under the CHO peak.
- Tetramethylsilane (TMS) is the standard reference (gives a sharp signal well away from the ones of interest to chemists, and is relatively inert) which all the other absorptions are compared with. The extent to which a signal differs from TMS is called the **chemical shift**.
- NB. On the chemical shift axis, the scale is reversed.
- The n.m.r. machine actually produces a signal which is far more detailed than the ethanal example (above).

High Resolution N.M.R

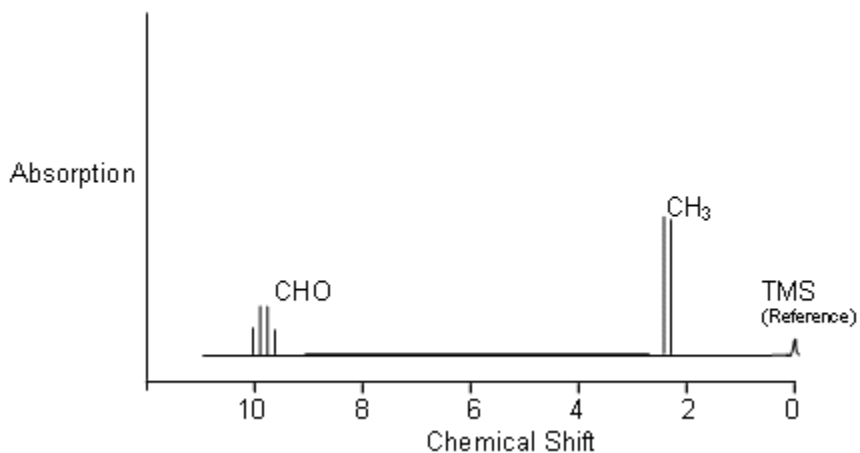
- High resolution n.m.r spectrographs have much more detail than the low resolution n.m.r explained previously.
- The extra detail arises because the ^1H nuclei, which behave like small magnets, can be in one of two orientations depending upon whether they are in a low or high energy level.
- Therefore, some of the ^1H nuclei will be spinning with the external field and the others will be spinning against it. The probability of each event is equal.
- The extra detail can provide us with more information about the molecule.
- For example, take for instance a molecule of ethanal:



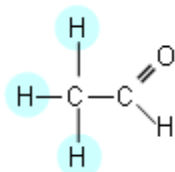
- There are two different proton environments (the CH₃ group and the CHO group); the low resolution spectrum would look like the following:



- However, the high resolution graph looks like the following:



- The CHO peak is split into four peaks (a quartet) and the CH₃ group is split into two peaks (a doublet).
- This is due to the effect of the ¹H nuclei on the adjacent carbon atom acting like small magnets.
- Looking closer at this idea, the separate peaks can be accounted for.



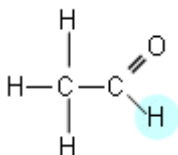
- If we focus first on the ¹H nuclei within the CH₃ group.
- There are two different peaks for the CH₃ group, and these are brought about by the effect of the CHO group.

- As mentioned previously, the hydrogen nuclei have an equal probability of spinning with or against the external field. There is only one ^1H nuclei and therefore there are two possible spins:

S-N (aligned with external field)

N-S (aligned against external field)

- Therefore there are two different magnetic effects on the protons within CH_3 group when the absorbance is being read; there are two peaks.



- Now looking at the CHO group.
- The four peaks are brought about by the hydrogen nuclei in the CH_3 group.
- The arrangements of the spins (against or with external field) can be:

S-N S-N S-N All with

S-N S-N N-S
S-N N-S S-N } 2 with, 1 against.
N-S S-N S-N

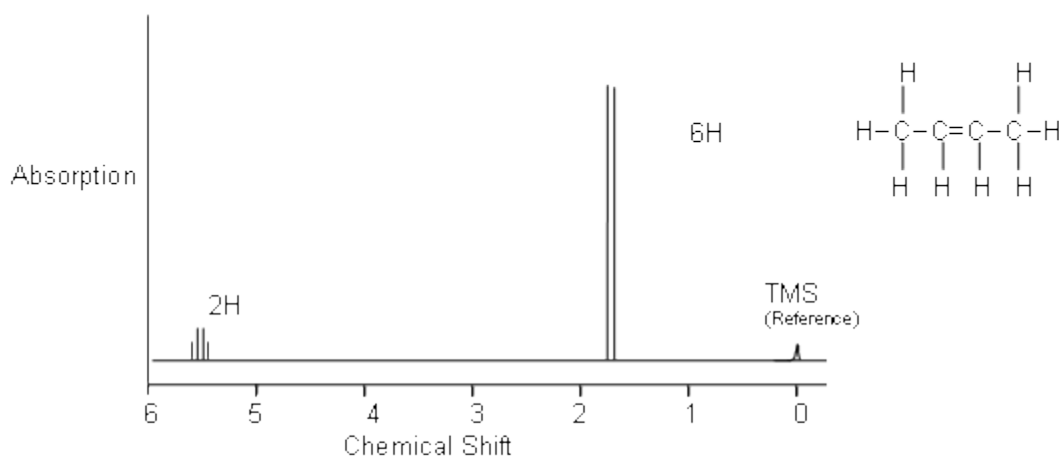
N-S N-S S-N
N-S S-N N-S } 1 with, 2 against
S-N N-S S-N

N-S N-S N-S All against

- There are four different arrangements, hence four peaks. The ratio of the heights of the peaks is 1:3:3:1 as there are three times as many arrangements of "2 with, 1 against" and "1 with, 2 against" compared to "all against" and "all with".
- Therefore counting the number of peaks allows you to work out the number of hydrogens attached to the adjacent carbon atom (if there were 2 peaks, the adjacent carbon would have 3 hydrogen atoms attached to it; if there were n peaks, the adjacent carbon would have n-1 hydrogen atoms attached to it)*
- *When referring to the adjacent carbon- the next hydrogen in a different environment (attached to a carbon).

Example:

But-2-ene



Chemical Shift	Relative Number of Protons	Type of Protons
1.6	3	CH_3
5.6	1	$\text{H}-\text{C}=\text{C}-\text{H}$

The difference between high and low resolution spectra

What a low resolution NMR spectrum tells you

Remember:

- The number of peaks tells you the number of different environments the hydrogen atoms are in.
- The ratio of the areas under the peaks tells you the ratio of the numbers of hydrogen atoms in each of these environments.
- The chemical shifts give you important information about the sort of environment the hydrogen atoms are in.

High resolution NMR spectra

In a high resolution spectrum, you find that many of what looked like single peaks in the low resolution spectrum are split into clusters of peaks.

For A'level purposes, you will only need to consider these possibilities:

1 peak	a singlet
2 peaks in the cluster	a doublet
3 peaks in the cluster	a triplet
4 peaks in the cluster	a quartet

You can get exactly the same information from a high resolution spectrum

as from a low resolution one - you simply treat each **cluster of peaks** as if it were a single one in a low resolution spectrum.

But in addition, the amount of splitting of the peaks gives you important extra information.

Interpreting a high resolution spectrum

The n+1 rule

The amount of splitting tells you about the number of hydrogens attached to the carbon atom or atoms **next door** to the one you are currently interested in.

The number of sub-peaks in a cluster is **one more** than the number of hydrogens attached to the next door carbon(s).

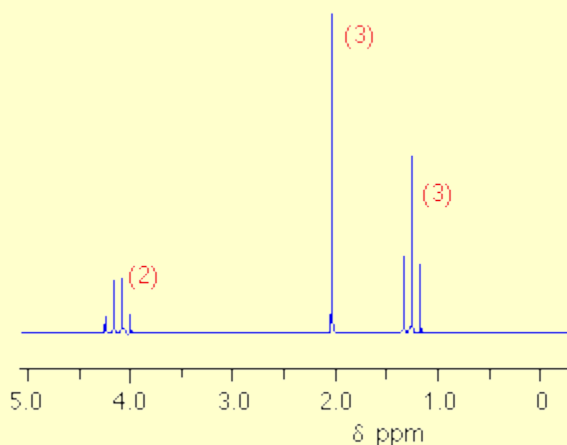
So - on the assumption that there is only one carbon atom with hydrogens on next door to the carbon we're interested in (usually true at A'level!):

singlet	next door to carbon with no hydrogens attached
doublet	next door to a CH group
triplet	next door to a CH ₂ group
quartet	next door to a CH ₃ group

Note: You probably won't need to know the origin of the n+1 rule, but if you are interested there is a page on [the reasons for splitting](#) which you could look at.

Using the n+1 rule

What information can you get from this NMR spectrum?



Note: The nmr spectra on this page have been produced from data taken from the Spectral Data Base System for Organic Compounds ([SDBS](#)) at the National Institute of Materials and Chemical Research in Japan.

Any small errors that I've introduced during the process of converting them for use on this site won't affect the argument in any way.

Assume that you know that the compound above has the molecular formula $C_4H_8O_2$.

Treating this as a low resolution spectrum to start with, there are three clusters of peaks and so three different environments for the hydrogens. The hydrogens in those three environments are in the ratio 2:3:3. Since there are 8 hydrogens altogether, this represents a CH_2 group and two CH_3 groups.

What about the splitting?

The CH_2 group at about 4.1 ppm is a quartet. That tells you that it is next door to a carbon with three hydrogens attached - a CH_3 group.

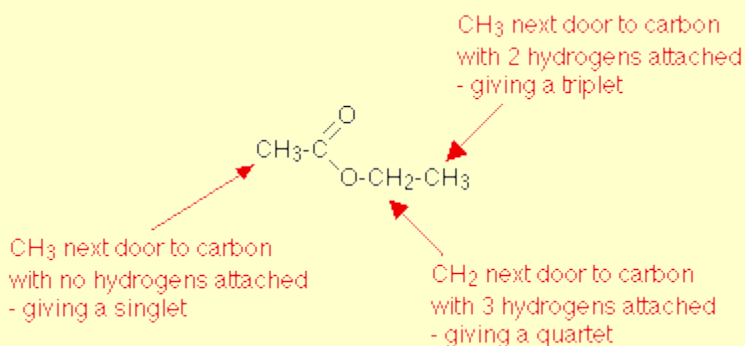
The CH_3 group at about 1.3 ppm is a triplet. That must be next door to a CH_2 group.

This combination of these two clusters of peaks - one a quartet and the other a triplet - is typical of an ethyl group, CH_3CH_2 . It is very common. Get to recognise it!

Finally, the CH_3 group at about 2.0 ppm is a singlet. That means that the carbon next door doesn't have any hydrogens attached.

So what is this compound? You would also use chemical shift data to help to identify the environment each group was in, and eventually you would come

up with:



Note: You now know how to get the information you need from NMR spectra, but it often isn't easy to fit all that information together into a final formula. You simply need to practise! Go through all the examples in past papers from your Exam Board. How complicated they are will vary markedly from Board to Board. Some of the compounds you will come across may be very unfamiliar. Don't forget to use the information in chemical shift tables - if your examiners include some obscure group, it's almost certain you will need to use it. Take all the hints that are going!

Two special cases

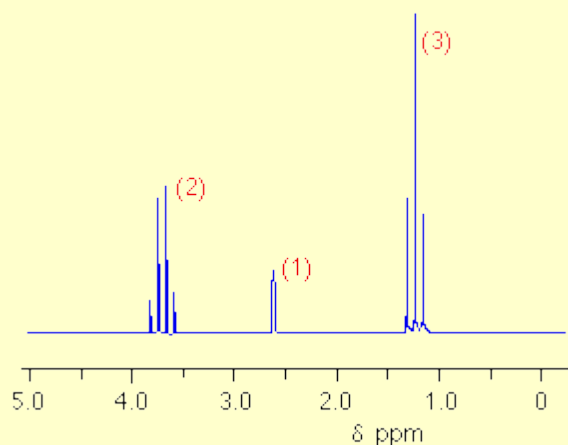
Alcohols

Where is the -O-H peak?

This is very confusing! Different sources quote totally different chemical shifts for the hydrogen atom in the -OH group in alcohols - often inconsistently. For example:

- The Nuffield Data Book quotes 2.0 - 4.0, but the Nuffield text book shows a peak at about 5.4.
- The OCR Data Sheet for use in their exams quotes 3.5 - 5.5.
- A reliable degree level organic chemistry text book quotes 1.0 - 5.0, but then shows an NMR spectrum for ethanol with a peak at about 6.1.
- The SDBS database (used throughout this site) gives the -OH peak in ethanol at about 2.6.

nmr spectrum for ethanol, $\text{CH}_3\text{CH}_2\text{OH}$ - source SDBS



The problem seems to be that the position of the -OH peak varies dramatically depending on the conditions - for example, what solvent is used, the concentration, and the purity of the alcohol - especially on whether or not it is totally dry.

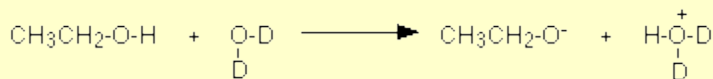
Help! Do you need to worry about this? Not really - you can assume that in an exam question, any NMR spectrum will be consistent with the chemical shift data you are given.

A clever way of picking out the -OH peak

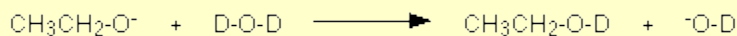
If you measure an NMR spectrum for an alcohol like ethanol, and then add a few drops of deuterium oxide, D_2O , to the solution, allow it to settle and then re-measure the spectrum, the -OH peak disappears! By comparing the two spectra, you can tell immediately which peak was due to the -OH group.

Note: Deuterium oxide (sometimes called "heavy water") is simply water in which all the normal hydrogen-1 atoms are replaced by its isotope, hydrogen-2 (or deuterium).

The reason for the loss of the peak lies in the interaction between the deuterium oxide and the alcohol. All alcohols, such as ethanol, are very, very slightly acidic. The hydrogen on the -OH group transfers to one of the lone pairs on the oxygen of the water molecule. The fact that here we've got "heavy water" makes no difference to that.



The negative ion formed is most likely to bump into a simple deuterium oxide molecule to regenerate the alcohol - except that now the -OH group has turned into an -OD group.



Deuterium atoms don't produce peaks in the same region of an NMR spectrum as ordinary hydrogen atoms, and so the peak disappears.

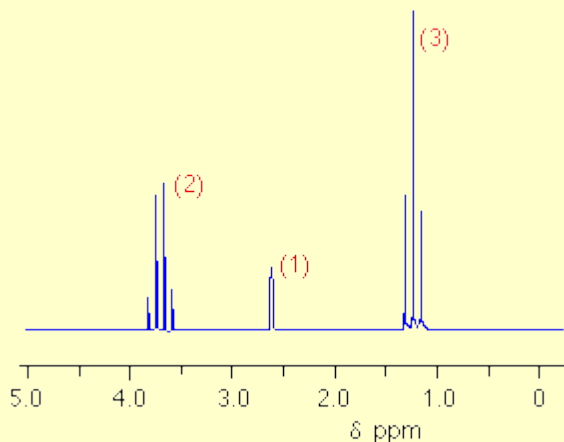
You might wonder what happens to the positive ion in the first equation and the OD⁻ in the second one. These get lost into the normal equilibrium which exists wherever you have water molecules - heavy or otherwise.



The lack of splitting with -OH groups

Unless the alcohol is absolutely free of any water, the hydrogen on the -OH group and any hydrogens on the next door carbon don't interact to produce any splitting. The -OH peak is a singlet and you don't have to worry about its effect on the next door hydrogens.

nmr spectrum for ethanol, CH₃CH₂OH - source SDBS



The left-hand cluster of peaks is due to the CH₂ group. It is a quartet because of the 3 hydrogens on the next door CH₃ group. You can ignore the effect of the -OH hydrogen.

Similarly, the -OH peak in the middle of the spectrum is a singlet. It hasn't turned into a triplet because of the influence of the CH₂ group.

Note: The reason for this is quite complex, and certainly goes beyond A'level. It lies in the very rapid interchange that occurs between the hydrogen atoms on the -OH group

and either water molecules or other alcohol molecules. To find out about it you will have to read either a degree level organic chemistry book or one specifically about NMR.

For A'level purposes just accept the fact that -OH produces a singlet and has no effect on neighbouring groups!

If you are interested, you can read more about the OH group in NMR in two articles from Michigan State University:

[NMR1](#) Look under "Hydroxyl Proton Exchange and the Influence of Hydrogen Bonding"

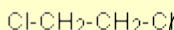
[NMR2](#) Look under "Hydrogen Bonding Influences"

Don't expect these to be easy reading though - this is university level stuff.

Equivalent hydrogen atoms

Hydrogen atoms attached to the same carbon atom are said to be **equivalent**. Equivalent hydrogen atoms have no effect on each other - so that one hydrogen atom in a CH₂ group doesn't cause any splitting in the spectrum of the other one.

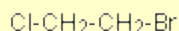
But hydrogen atoms on neighbouring carbon atoms can also be equivalent if they are in exactly the same environment. For example:



These hydrogens are in exactly the same environment and so are said to be **equivalent**.

These four hydrogens are all exactly equivalent. You would get a single peak with no splitting at all.

You only have to change the molecule very slightly for this no longer to be true.



These hydrogens aren't in exactly the same environment and so **aren't** equivalent.

Because the molecule now contains different atoms at each end, the

hydrogens are no longer all in the same environment. This compound would give two separate peaks on a low resolution NMR spectrum. The high resolution spectrum would show that both peaks subdivided into triplets - because each is next door to a differently placed CH_2 group.

A comment about NMR and benzene rings

At this introductory level, all you can safely say about hydrogens attached to a benzene ring is how many of them there are. If you have a molecular formula which has 6 or more carbon atoms in it, then it could well contain a benzene ring.

Look for NMR peaks in the 6.0 - 9.0 range. If you are given a number like 5 or 4 alongside that peak, this just tells you how many hydrogen atoms are attached to the ring.

If there are 5 hydrogens attached to the ring, then there is only one group substituted into the ring. If there are 4 hydrogens attached, then there are two separate groups substituted in, and so on. There should always be a total of 6 things attached to the ring. Every hydrogen atom that is missing has been replaced by something else.

Splitting patterns involving benzene rings are far too complicated for this level, generally producing complicated patterns of splitting called multiplets.

Note: If you are unfortunate enough to have examiners who ask about splitting in benzene rings at this level (for 16 - 18 year old chemistry students), look carefully at the question and mark scheme so that you can see exactly what they want, and just learn that. But it may well be that all they want is for you to notice the number of hydrogen atoms involved in the ring (see above).
