

Chemistry

Teach Yourself Series

Topic 3: NMR

Contents

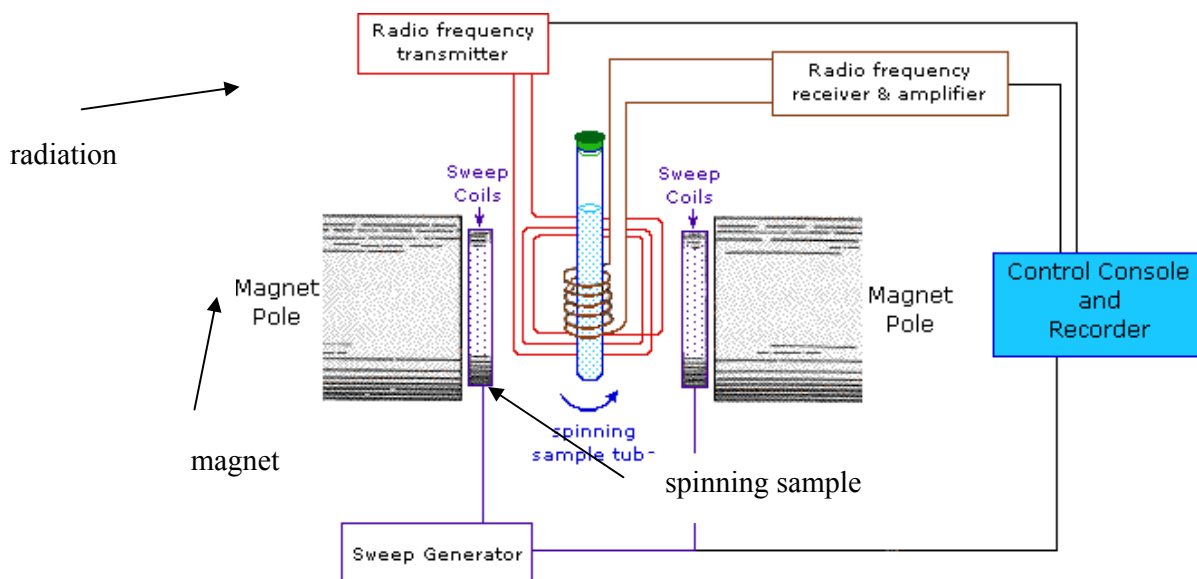
NMR	3
What is it?	3
As it appears in Unit 3	3
Interpreting ^1H NMR (Low resolution).....	5
As it appears in Unit 3	5
Review Questions	6
High resolution splitting.....	7
As it appears in Unit 3	7
Review Questions	8
Carbon-13 NMR	9
As it appears in Unit 3	9
Solutions to questions	10

NMR

What is it?

As it appears in Unit 3

Nuclear Magnetic Resonance is a form of spectroscopy that provides valuable information of the structure of organic molecules.

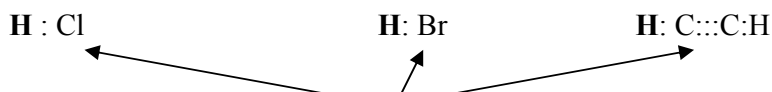


Sample is – placed in a magnetic field, where the intensity of the field is varied.

- spun rapidly
- bombarded by radiation

The nuclei of many elements have a spin. Under the influence of the magnetic field, and the radiation, these nuclei can 'resonate'. Scientists choose to study hydrogen, (^1H or **proton NMR**), and carbon-13 (^{13}C), nuclei more than other elements.

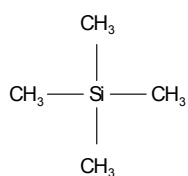
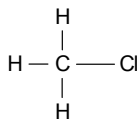
The secret to proton NMR is that the atoms surrounding a hydrogen nucleus shield the nucleus and cause a 'shift' in the magnetic field required for resonance.



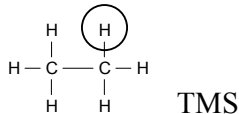
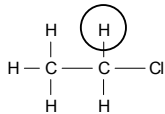
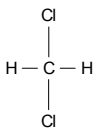
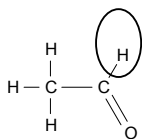
Note that each hydrogen atom in bold print above has different neighbours. It has different electron arrangements surrounding it. The electrons shield the hydrogen nuclei from the magnetic field. The amount of shielding is different in each molecule because the electron arrangement is different. There is a different 'shift' in resonating field strength in each. This shift can be used to identify the atoms present.

Tetramethylsilane, TMS is chosen as a standard (and given a value of 0) and shifts are reported relative to TMS.

Chloromethane – hydrogen atoms have a shift of 3.0 compared to TMS.



The more polar the functional groups, usually the greater the shift. Relative shifts are available from your data book.



TMS



increasing shift in circled hydrogen

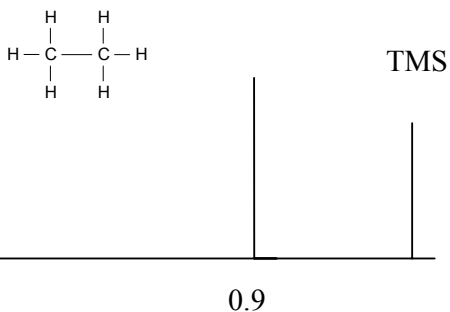


Interpreting ^1H NMR (Low resolution)

As it appears in Unit 3

Example 1 - ethane

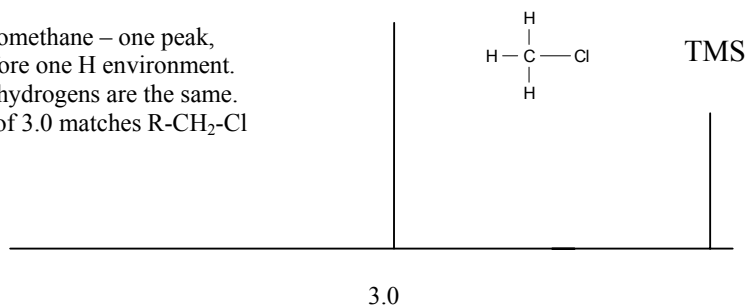
ethane – has 6 H atoms. All have equivalent environments, hence there is only 1 peak. Shift is 0.9, matching R-CH_3



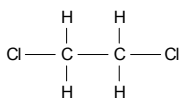
The number of peaks tells you how many different hydrogen environments a molecule has. Ethane – 1 peak, hence all hydrogen atoms same. Shift of 0.9 confirms it is R-CH_3 .

Example 2 - chloromethane

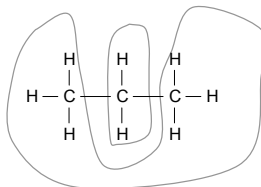
Chloromethane – one peak, therefore one H environment. All 3 hydrogens are the same. Shift of 3.0 matches $\text{R-CH}_2\text{-Cl}$



Note – equivalent hydrogen and non equivalent hydrogen atoms

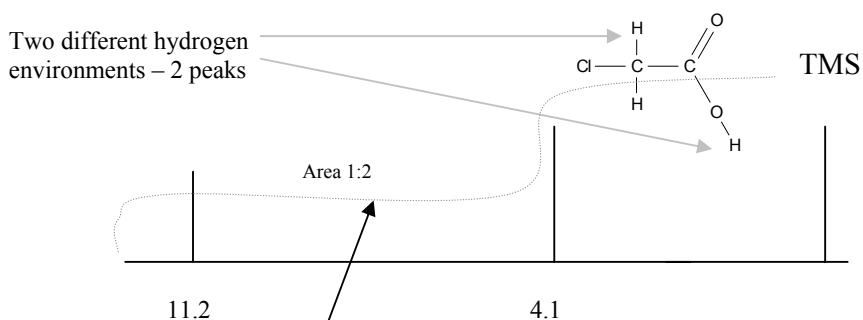


First molecule – all hydrogen atoms equal.
- one NMR peak only



Second molecule – two different hydrogen environments
- two NMR peaks
- 6 end hydrogen atoms equal;
2 middle hydrogen atoms equal

Example 3 chloroethanoic acid



NMR also **integrates the area of each peak**.

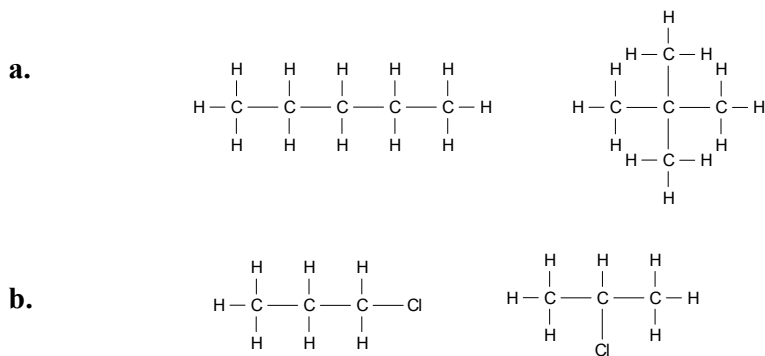
Area under left peak: area under right peak is 1:2, therefore the second peak represents twice as many hydrogen atoms, in this case 1 vs 2, due to O – H vs –CH₂–

Summary: low resolution proton NMR tells us

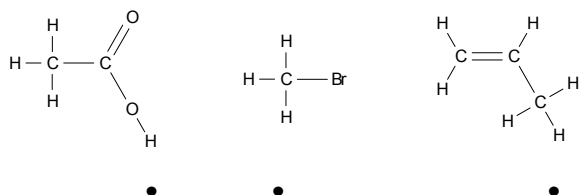
- the number of different hydrogen environments (from the number of peaks)
- the possible identity of atoms in that environment (shift compared to TMS)
- the likely number of hydrogen atoms (from the ratio of peak areas)

Review Questions

1. Explain how NMR would quickly distinguish the following molecules



2. What is the likely chemical shift of each of the marked hydrogen atoms?

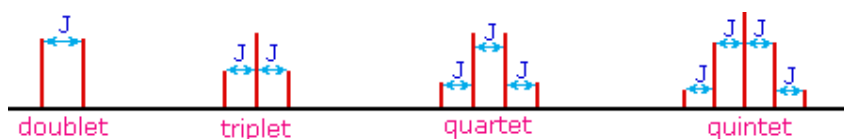


High resolution splitting

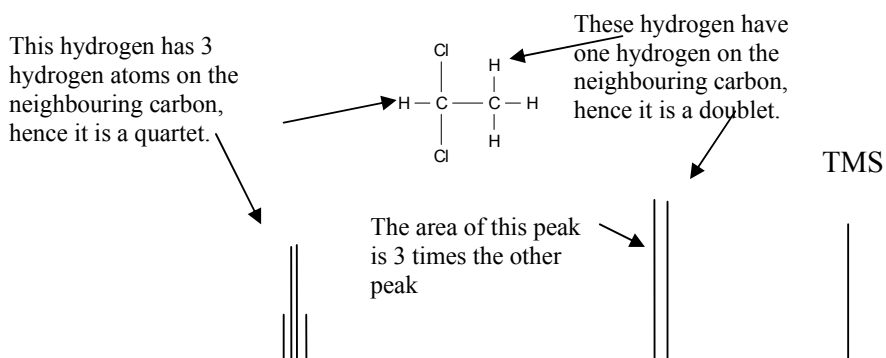
As it appears in Unit 3

Proton NMR peaks will be more complicated than presented so far if the neighbouring carbon atoms also have hydrogen atoms bonded to them. The neighbouring hydrogen atoms cause peaks to split, the more neighbours, the more splits.

A (n+1) rule applies: 1 neighbour = 1 + 1 = 2 peaks, doublet
2 neighbours = 2 + 1 = 3 peaks, triplet
3 neighbours = 3 + 1 = 4 peaks, quartet etc



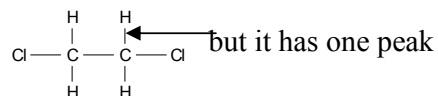
Example: 1,1-dichloroethane



Rather than splitting being a nuisance, it actually helps provide structural information about the molecule. A quartet might mean that the adjacent carbon is a methyl group, CH₃.

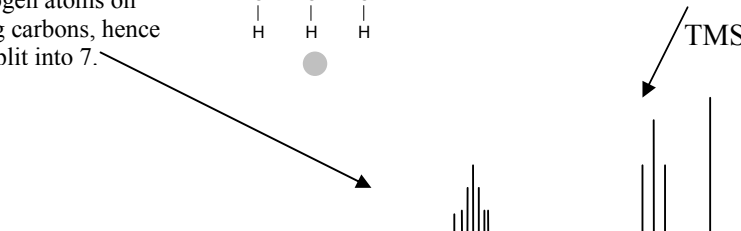
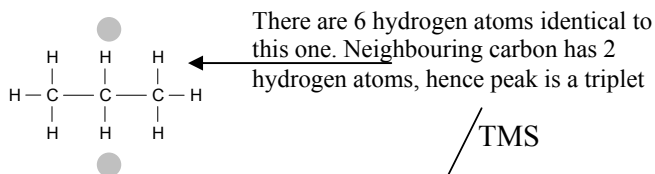
It is easy to use NMR to distinguish 1,1-dichloroethane, above, from 1,2-dichloroethane.

The second molecule is a structural isomer of the molecule above only, as all 4 hydrogen atoms have identical environments.



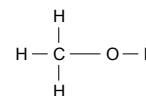
Example: propane

The 2 hydrogen atoms marked are identical. They have 6 hydrogen atoms on neighbouring carbons, hence the peak is split into 7.

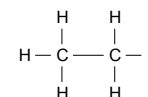


Notes:

1. Splitting does **not** occur if hydrogen atoms are attached to a neighbouring oxygen atom, instead of carbon i.e. methanol.
The hydroxyl hydrogen atom does not cause any splitting on the methyl peak. The oxygen atom shields the hydrogen atoms.

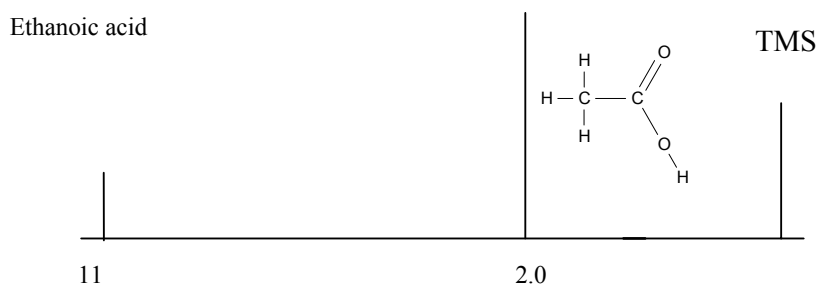


2. Ethane will have one NMR peak only. All hydrogen atoms have identical environments and splitting does not occur between the equivalent methyl groups.



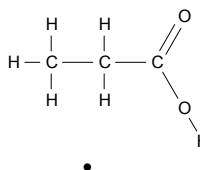
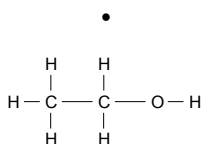
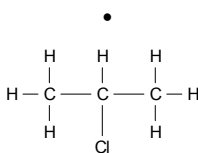
Review Questions

3. The proton NMR for ethanoic acid is shown below

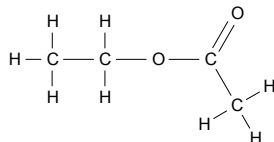


Explain which peak is which part of the molecule.
What will the ratio be between the areas of the two peaks?

4. How many splits will each marked peak have in the molecules drawn below?



5. An ester molecule is drawn below



For this molecule, answer the following

- How many peaks will it have?
- Describe the splitting pattern for each peak
- Compare the areas of each peak.
- Look up the likely shift of each peak
- Draw the NMR spectrum.

Summary

High resolution proton NMR peaks can be split if neighbouring carbon atoms have hydrogen atoms bonded to them. The (n+1) rule governs splits. No splitting occurs if the neighbouring atom is an oxygen atom.

Carbon-13 NMR

As it appears in Unit 3

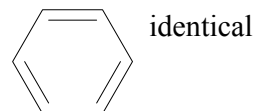
Some organic molecules contain segments with very few hydrogen atoms, hence proton NMR is not very helpful. ^{13}C NMR may be used instead (^{12}C has no spin).

The principle is similar to proton NMR

- there is a separate peak for each different carbon environment.
- there is a shift depending upon the neighbouring atoms and functional groups.

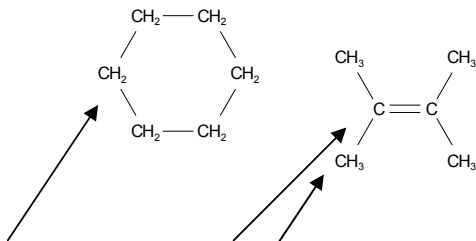
Example: benzene

The benzene molecule has 6 carbons; each of these carbons has an environment. Benzene therefore has one peak only in carbon NMR.



Example: cyclohexane vs 2,3,dimethylbut-2-ene

These two molecules are structural isomers of each other



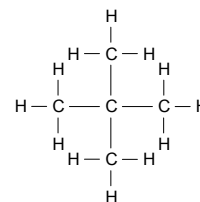
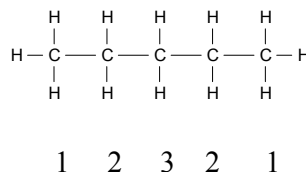
All carbon atoms identical, one peak.

Two carbon environments, two peaks.

Solutions to questions

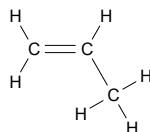
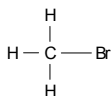
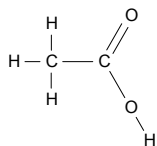
1.

- a. The first molecule will have 3 peaks as there are three different hydrogen environments. In the second molecule there will be one peak only – every hydrogen atom is identical.



- b. The first molecule will have 3 peaks as the hydrogen atoms on each carbon are different. The second molecule will have 2 peaks, as there are two different hydrogen environments.

2.

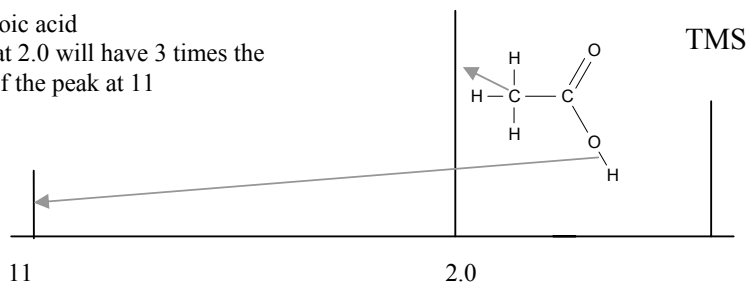


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$$\text{R} - \text{COOH} = 11.5 \quad \text{R} - \text{CH}_2 - \text{X} = 3-4 \quad \text{RCH} = \text{CHCH}_3 = 2$$

3.

Ethanoic acid
peak at 2.0 will have 3 times the
area of the peak at 11

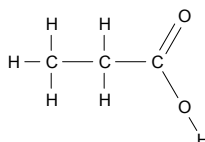
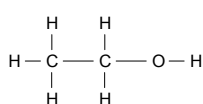
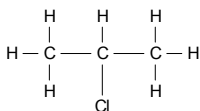


4.

6 H neighbours = 7 split

3 H neighbours = 4 split

no H neighbour on O-H = no split



5.

