**11.4 Spectroscopic identification of organic compounds (HL)**

**Learning objectives**

• Understand how chemical shifts can provide information about the structure of organic molecules

• Use high-resolution 1H NMR to determine the structure of molecules

• Understand how to use information from a combination of spectroscopic techniques to determine the structure of molecules.

**Chemical shift**

The horizontal scale on a nuclear magnetic resonance spectrum is the **chemical shift**, which is given the symbol δ and has units of parts per million (ppm). Chemical shift data provide information about the environments that protons (hydrogen nuclei) are in – protons in different chemical environments have different chemical shifts.

The standard for measurements of the chemical shift

Chemical shift values are measured relative to tetramethylsilane (TMS)



The protons in TMS are assigned an arbitrary chemical shift of 0.00 ppm and all chemical shifts are measured relative to this.

**Why TMS is chosen as the standard**

* has 12 protons all in the same environment and so gives a strong signal when only a small amount is added.
* chemical shift of the protons in TMS is at a lower value than the protons in virtually all organic molecules
* TMS signal does not overlap with the protons signals that we are interested in.
* it is non-toxic and inert.

TMS molecule

**TMS is a reference standard used to fix the chemical shift scale. A small amount of TMS is added to the sample before the NMR spectrum is recorded**

The chemical shift for a particular hydrogen depends on the number of alkyl groups that are attached to the carbon to which it is bonded.

Example of chemical shift for C=O group in aldehyde and ketones:



**Exam tip**

IB Chemistry data booklet gives the chemical shifts. You should practice using them.

When using a table of chemical shift values, you must try to find the best match to the proton environments in the molecule you are analysing.

**Spectrum of propanal example:**

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This shows the three chemical shifts and low resolution NMR spectrum of propanal – CH3CH2CHO.

**High-resolution NMR spectra**

The low- and high-resolution NMR spectra of 1,1,2-trichloroethane are shown in Figure below.



There are two peaks in the low-resolution spectrum because there are two different chemical environments for protons

The splitting in the high resolution NMR is due to the hydrogen atoms on adjacent carbon atom(s).

This results in the signal due to H1 being split into three (a triplet), because there are two Hs on the adjacent carbon atom. The signal due to H2 and H3 is split into two (a doublet), because there is one H on the adjacent carbon atom. This **splitting** is called spin– spin splitting or spin– spin coupling.

**Multiplicity** of a peak is the number of smaller peaks it is split into. The multiplicity of a triplet is 3 and that of a doublet is 2.

In general, if there are *n* protons (hydrogen atoms) on an adjacent atom, the signal for a particular proton will be split into (*n* + 1) peaks. Another way of saying this is that if the multiplicity of a peak is *x* then the number of hydrogen atoms on the adjacent atom is *x* − 1.

**Exam tip**

When a signal due to two hydrogen atoms is split into a quartet and the signal due to three hydrogen atoms is split into a triplet, this indicates the presence of an ethyl group (CH3CH2) in a molecule – well worth remembering!

**Example of high resolution NMR spectrum of chloroethane:**

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The signal at δ 3.5 ppm is split into a quartet – and therefore, has a multiplicity of 4. Now, 4 − 1 = 3 and so we can deduce that there are three hydrogen atoms on the adjacent carbon atom.

The signal at δ 1.5 ppm is split into a triplet – this has a multiplicity of 3. Now, 3 − 1 = 2 so there must be two hydrogen atoms on the adjacent carbon atom.

**Summary diagram and pascals triangle**

The intensities of the lines in a splitting pattern are given by Pascal’s triangle. So we talk about a 1 : 1 doublet (the areas under the peaks are equal) or a 1 : 2 : 1 triplet etc, 2 being higher in the middle.

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**‘Rules’ for spin–spin coupling**

• Protons on the same atom (e.g. CH3, CH2) do not split each other – they are **chemically equivalent** and behave as a group.

• Splitting generally only occurs with protons on adjacent atoms – see below.

• Protons attached to oxygen atoms do not usually show or cause splitting – this is because the protons exchange with each other and with the solvent and experience an ‘average’ environment.

 

Ha protons couple only with Hb protons – Hc and Hd are too far away.

These examples are from Cambridge by Steve Owen.





**Single crystal X-ray crystallography**

Further evidence for the structures of molecules can be obtained from **single crystal X-ray crystallography**. This involves irradiating a crystal with X-rays and looking at the positions and intensities of the diffracted beams.It gives a three-dimensional picture of the molecule with bond lengths and bond angles.

If a single crystal can be grown, X-ray crystallography usually provides the final word on the structure.

**Using combined spectroscopic techniques to determine the structure of a molecule**

In practice, information from more than one spectroscopic technique is often used to determine the structure of a molecule.

**See example on Cambridge by Steve Owen pp 545-547**