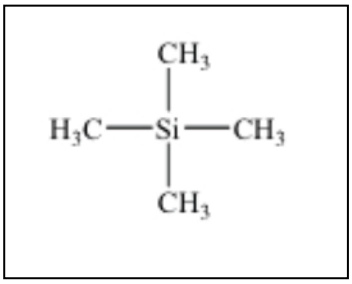
Lesson 1 HNMR

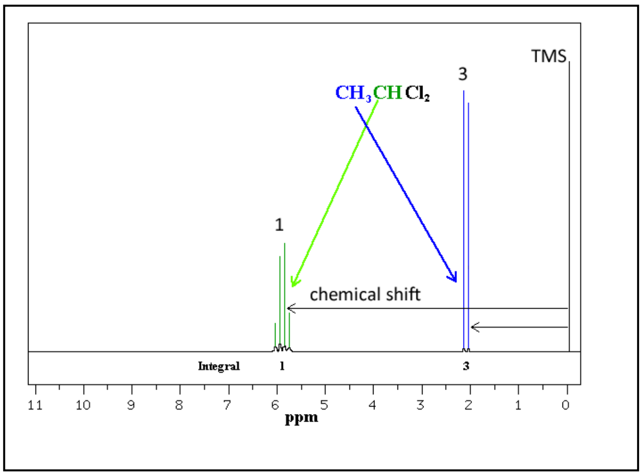
Click to revise $^1$HNMR

There is a *basic vocabulary when dealing with $^1$HNMR spectra. Below are a few terms that you should be familiar with.*

**Tetramethylsilane (TMS)**— TMS has 12 protons which are all equivalent and four carbons, which are also all equivalent. TMS, therefore, gives a strong, single signal in the spectrum and is used as a reference point for all other signals in the spectrum.




**Chemical Shift**—the position of a signal in an $^1$HNMR spectrum relative to the TMS signal, which is at 0. This is determined by surrounding atoms and is explained more under ***shielding.*** Consider the $^1$HNMR of 1,2-dichloroethane, shown on the right. Two signals are produced that relate to the two different hydrogen nuclei present in the molecule, the hydrogen nucleus in the CHCl$_2$ end group is chemically shifted more than the hydrogen nuclei in the CH$_3$ group.

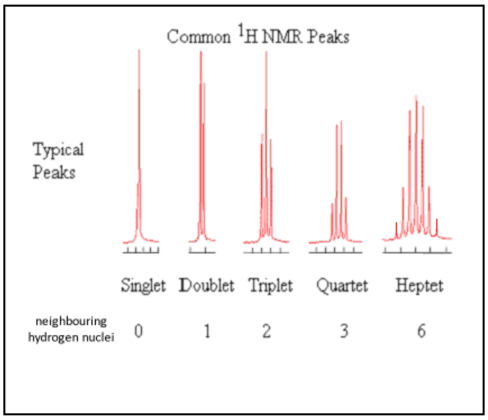



**Shielding**— Electrons surrounding hydrogen nuclei (protons) shield the nucleus from the applied magnetic field, the greater the electron density the greater the shielding. Hydrogen nuclei which are close to electronegative atoms, such as oxygen or chlorine, experience much lower shielding than hydrogen nuclei which are further away from an electronegative atom. Lesser shielding causes the signal from a hydrogen nucleus to move further over to the left on the spectrum, greater chemical shift.

**Integration**—Is the process of measuring the area of an $^1$HNMR signal to determine the relative number of hydrogens that correspond to that signal.

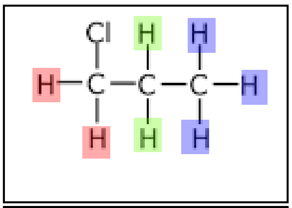
**Ppm**—The horizontal scale of an HNMR spectrum is shown as (**ppm**). It is called the chemical shift and is measured in **parts per million** - **ppm**. It increases as we go from right to left and a peak at a chemical shift of, say, 3.0 means that the hydrogen atoms which caused that peak need a magnetic field three millionths less than the magnetic field needed to produce the TMS signal.

**Signals** — Each hydrogen that is present in a unique chemical environment within the molecule produces its own signal at a certain ppm, this is known as the chemical shift. The signal, however, can be split into different patterns, depending on the neighbouring non-equivalent hydrogen nuclei, as shown on the right.

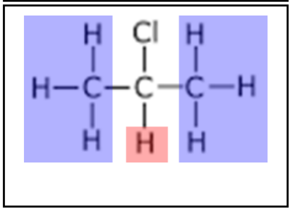


***Equivalent protons*** — hydrogen atoms with a chemical environment that is **identical** in every way and can't be distinguished from each other based on relative position.

Consider the molecule 1-chloropropane shown on the right. It has three chemically different hydrogens. These hydrogens find themselves in totally different chemical environments.



2-chloropropane, on the other hand, has only two chemically different hydrogens.
In this course it is important to be able to identify chemically different hydrogens.



1) Consider the electronegativity of the elements shown on the right.

**F= 4.0**

**O=3.5**

**N= 3.0; Cl=3.0**

**Br=2.8**

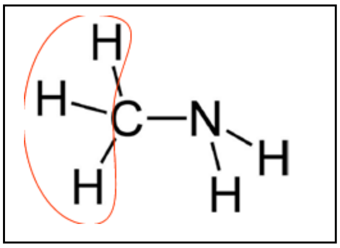
**I= 2.5; S=2.5; C= 2.5**

**P=2.2**

**H=2.1**

a) i. Name the molecule shown on the right.
methanamine

ii. Circle the hydrogen nuclei that are more shielded.



iii. Consider the following protons attached to different non-metal atoms.

a. H-O b. H-C c. H-F d. H-Br e. H-P

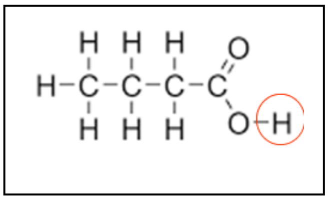
i. Which proton *highest* electron density? *e*

ii. Which of the following attaching protons is *the most shielded*? *e*

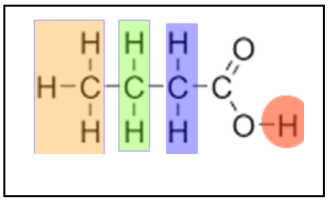
iii. Which of the following attaching protons has the highest chemical shift? *c- the electronegativity of fluorine is far greater and hence reduces the shielding causing a greater chemical shift than all the others.*

iv. Consider the structural formula of butanoic acid

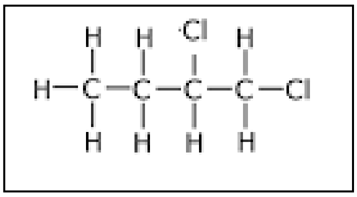
i. Circle the hydrogen(s) that is/are least shielded



ii. How many non-equivalent hydrogens are present? *4 non-equivalent hydrogens are present and shown in different colours on the right.*

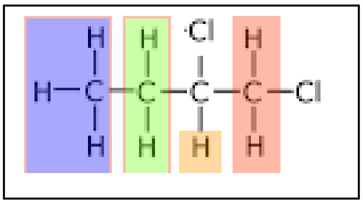


v. Draw the structural formula of 1,2-dichlorobutane.



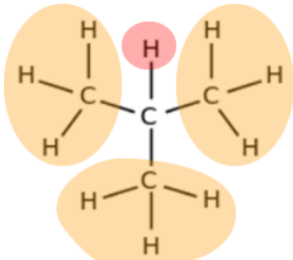
i. How many equivalent hydrogens are present?

*4 non-equivalent hydrogens are present and shown in different colours on the right.*



vi. Name the molecule shown on the right.

*2-methylpropane*



i. How many equivalent hydrogens are present?

*2 non-equivalent hydrogens are present and shown in different colours on the right.*

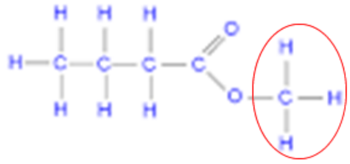
vii. Name the molecule on the right.

*methyl butanoate*

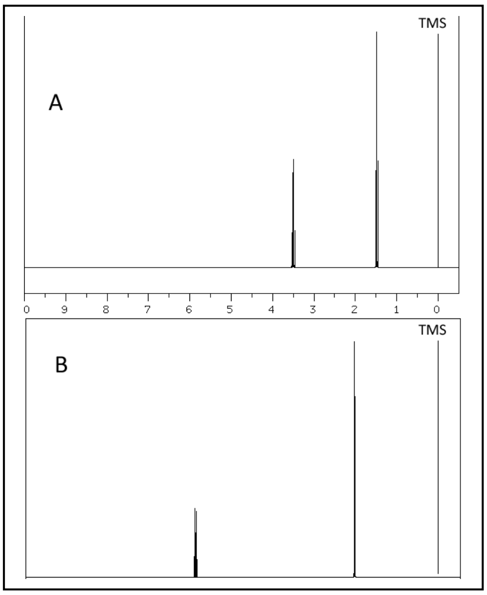
i. How many equivalent hydrogens are present?

*4 non-equivalent hydrogens are present and shown in different colours on the right*

ii. Circle the group of hydrogen atoms that will have the greatest chemical shift on the $^{1}$HNMR spectrum.



viii. Consider the two $^{1}$HNMR spectra shown on the right. They represent 1,1-dichloroethane and 1-chloroethane.




i. Identify which spectrum belongs to each compound. Justify your selection.

*Both compounds have 2 non-equivalent hydrogens so each should have two signals. Spectrum B, however, shows a greater chemical shift than spectrum A. This is due to the presence of two highly electronegative chlorine atoms.*

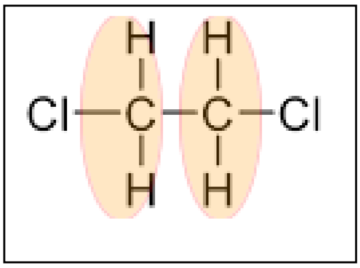
*Spectrum B = 1,1-dichloroethane*

ii. How many non-equivalent hydrogens are present in each molecule. Justify your answer.

*See answer above.*

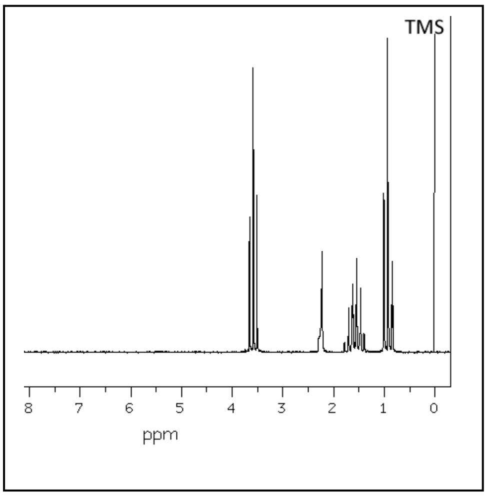
iii. Give one difference between the ¹HNMR spectrum of 1,2-dichloroethane and those shown on the right.

*The spectrum of* 1,2-dichloroethane *should have only one signal as all the hydrogens are equivalent*

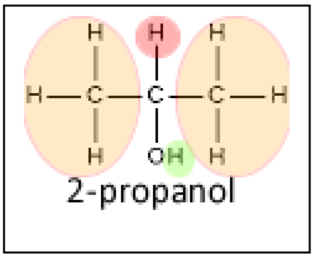



ix. Consider the ¹HNMR sectrum shown on the right.

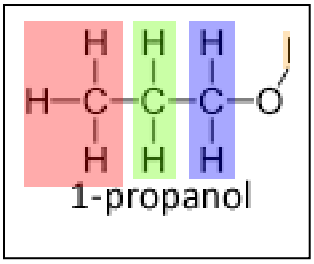
Chemists analysed a bottle filled with an unknown alcohol. They are confident that the alcohol is a propanol but are unsure as to whether it is 1-propanol or 2-propanol. Identify the alcohol and justify your answer.




*2-propanol has 3 equivalent hydrogens while*




*1-propanol has 4 equivalent hydrogens. Since the spectrum shows four signals the compound must be 1-propanol.*



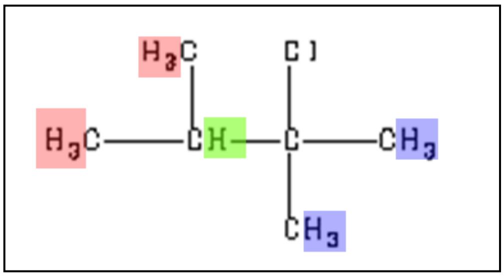

2) Consider the molecule shown on the right.

i. Name the compound

*2-chloro-2,3-dimethylbutane*

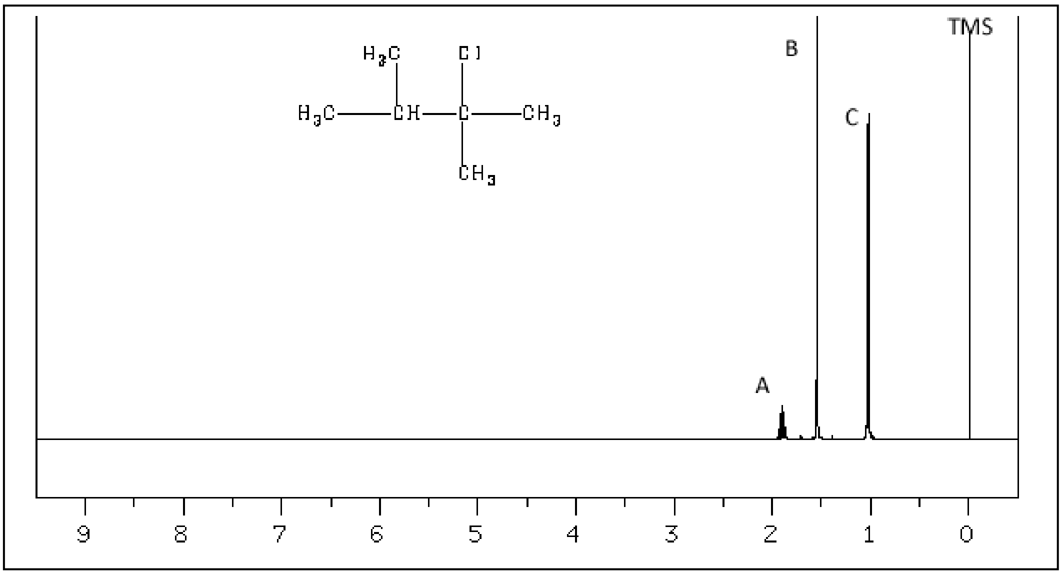
ii. How many equivalent hydrogens are present?

*3*



iii. Below is the $^1$HNMR of this compound.

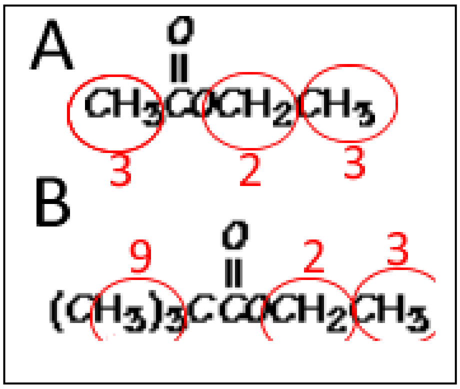
The relative area under each peak is represented by A, B and C. Assign values to A, B and C. *A = 1, B = 6 , C = 6*




3) Consider the semi-structural formulae of the compounds shown on the right.

i. How many equivalent hydrogens are present in each?

*A = 3 , B = 3*




ii. Circle each equivalent set of hydrogens and indicate the integrals for each