i.e if the no. of equivalent protons in the neighbouring group is "n", then the nmr signal will split into (n+1) lines or peaks.

Thus if n=0 in the neighbouring group, i.e if there is no proton, we will get a singlet. If there is one proton, in the vicinity, (n=1), we will get a doublet.

The intensities of the lines can be given by the Pascal triangle.

| | | |
|---|---|---|
| n=0 | 1 | (singlet) |
| n=1 | 1 1 | (Doublet) (1:1) |
| n=2 | 1 2 1 | (triplet) (1:2:1) |
| n=3 | 1 3 3 1 | (quadrate) (1:3:3:1) |
| n=4 | 1 4 6 4 1 | (quintet) (1:4:6:4:1) |

This triangle can be obtained by summing up the two numbers to its right and left in the line intermediate above. and putting '1' in both end.

e.g. For triplet intensity ratio.

is 1 2 1

i.e. from the line intermediate above (1+1)=2 in the middle. Putting 1 in the two ends 1 2 1.

For quadrate (n=3).

From the line above

(2+1) (2+1)

left right.

1 3 3 1

and so on.

(2) Chemical shift :— The position of the NMR signals help us to tell us what kind of protons they are — aromatic, aliphatic, primary, secondary, benzylic, vinylic etc. These different kind of protons have different electronic environments, and it is the electronic environment that determines just where in the spectrum a proton absorbs.

The separation in the position of the spectral signals of hydrogen atoms in different chemical environments from that of some arbitrarily chosen standard is called the Chemical shift. The shift can be conveniently reported by means of the difference in magnetic field necessary for absorption by the sample compared to that necessary for absorption by the reference compound. This difference is usually reported as the chemical shift, $\delta$, defined as

$$\delta = \frac{B_0 \text{ sample} - B_0 \text{ (reference)}}{B_0 \text{ reference}} \times 10^6.$$

where the reference chosen is usually tetramethyl silane, $(CH_3)_4Si$ abbreviated as TMS.

[Since hydrogen atoms in different samples show resonance or absorption at fields that differ by the order of milligauss when the magnetic field is 14,000 gauss the $\delta$ values are made of convenient magnitude by the inclusion of the factor $10^6$]

Chemical shift is also represented by $\tau$ (Tau). The two Scales are related by the expression ($\tau = 10 - \delta$.)

On the $\tau$ scale, Low value of $\tau$ represents low field absorption and a high value of $\tau$ represents high field absorption. $\tau = 10$ for TMS. On the $\delta$ scale $\delta = 0$ for TMS.

The chemical shift arises due to the shielding and deshielding of proton by electrons.

## What is shielding and deshielding of protons.

When a molecule is placed in an magnetic field, electrons circulate and generate a secondary magnetic field. called induced magnetic field. The induced magnetic field may either oppose or reinforce the applied magnetic field.

(i) If the induced field opposes the applied field, effective field strength decrease, this is called shielding.

(ii) If the induced field reinforce the applied field, effective field strength increase, this is called deshielding.

Compared with a naked proton, a shielded proton requires a higher applied field strength and a deshielded proton requires a lower applied field strength. Thus the shielded proton absorbs upfield, while the deshielded proton absorbs down field.

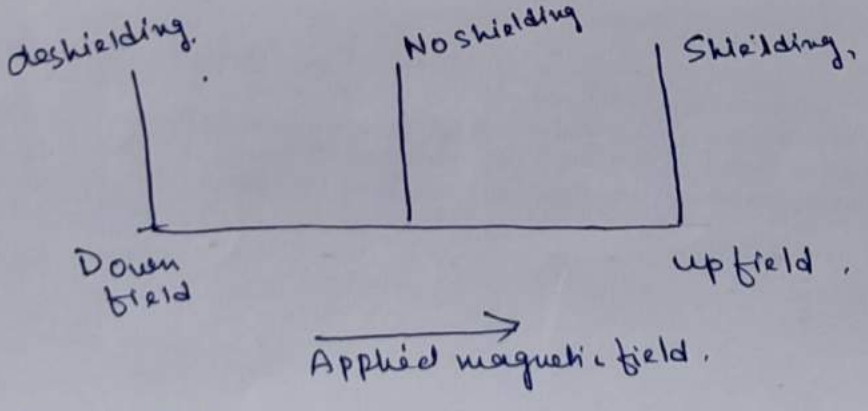


Fig-1 Effect of shielding & deshielding on position of resonance of nuclei.

## Why TMS is used as standard.

TMS has several advantages over other substances which have been used as standards.

(1) Its resonance is sharp and intense since all twelve hydrogen nuclei are equivalent and hence absorb exactly at the same position.

(2) Its resonance position is to high field of almost all other hydrogen resonces in organic molecule (τ value high)

(3) It is a low boiling point liquid (b.p 27°C), so can be readily removed from most sample after use.

## Factors affecting the chemical shift.

(i) Inductive effect.
(ii) Isotopic effect.
(iii) hydrogen bonding

**Inductive effect :-** A proton is said to be deshielded when it is attached to an electronegative atom.

example $CH_3-CH_2-F$

Here electrons are attracted by the fluorine atom (-I effect) and electron density decreases around the proton. As the electronegativity of the atom increases, degree of deshielding also increases. e.g deshielding is more in case of $CH_3-CH_2-F$ than in $CH_3-CH_2-Br$.

**Isotopic effect :-** When the proton is attached to electron donating group (+I effect), then there will be shielding.