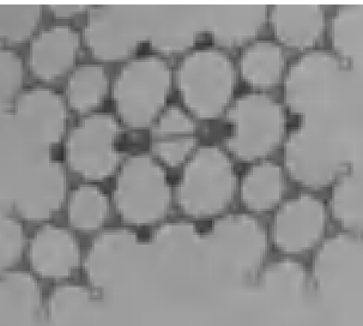


UNIT- VI

^{1}H–NMR Spectroscopy (PMR)

1. Introduction

For past so many years nuclear magnetic resonance spectroscopy, (NMR) has developed as a prominent technique for determining the structure of organic compounds. However, it is the only spectroscopic technique in which a complete analysis and interpretation of the entire spectrum is normally expected among the different spectroscopic methods known like UV, IR, mass spectroscopy etc.

Although instrumentation wise NMR spectroscopic analysis requires large amounts of sample (more than for a mass spectroscopy), NMR is non-destructive. Moreover with modern analytical techniques sufficiently good data may be obtained from samples weighing less than a milligram.

In an atom like electrons, the proton and neutrons also spin on their axis. If the nuclear particles do not have their spin paired, there is a net spin. Thus a charged particle like proton, in spinning state will produce a definite magnetic field and magnetic moment along the axis of spin. Thus a spinning proton (or nucleus) acts like a tiny magnet. Thus a nucleus spinning in the anticlockwise direction will be associated with a magnetic field with magnetic moment working in upward direction and if the nucleus is spinning clockwise the magnetic moment will act downwards. Thus nuclei of atoms having odd mass number such as ^{1}H, ^{17}F, ^{31}P or having odd atomic number and even mass number such as $^2_1$H, $^{10}_5$B, $^{14}_7$N are magnetic in nature because of unpaired spins.

Thus the magnetic properties of the nuclei in most of the organic compounds is the basis of nuclear magnetic resonance NMR spectroscopy.

2. NMR Active Molecules

NMR active molecules are those which have unpaired spins. This is represented in following table.

Atomic Mass	Atomic Number	Spin Number
Odd	Odd or Even	$\frac{1}{2}, \frac{3}{2}, \frac{5}{2}$
Even	Even	1
Even	Odd	0, 1, 2, 3

Some examples of NMR active molecules

Element	Spin number
^1H	1/2
^2H deuterium	1
^3H tritium	1/2
^{13}C	1/2
^{17}O	5/2
^{19}F	1/2
^{29}Si	1/2
^{31}P	1/2

3. Principles of NMR Spectroscopy

Nuclei with an odd number of protons or neutrons have a permanent magnetic moment and quantized nuclear spin states. For example, in case of ^1H (it has only one proton) , it has two nuclear spin states which have equal energies. These energy states are assigned quantum numbers +1/2 and −1/2.

Fig. 1: Two nuclear spin states of proton in H

When a compound is placed in a magnetic field, the hydrogens of the compound align their own field. The alignment can be either with the external magnetic field or against the external magnetic field. In the higher energy state, E_2, the two fields are aligned against each other. Similarly in the lower energy state, E_1, the two fields are aligned with each other.

The difference in energy between these two states – E_1 and E_2 is directly proportional to the external field strength H_0, which in turn corresponds to a frequency of radio waves. It straightaway means that radiowaves can flip hydrogen nuclei from lower to higher energy states, reversing their spins in the process. When such spin flip takes place, the nucleus (or more specifically the proton, in case of hydrogen atom) is said to be in resonance with the applied energy (radio waves). It is because of this reason the whole process is named as nuclear magnetic resonance spectroscopy technique.

Fig. 2: Nuclear spin states in H in an external magnetic field

Importantly, it must be remembered that nuclei having odd number of protons or neutrons give rise to NMR spectrum.

In organic chemistry, proton as the nuclei is studied because hydrogen is a constituent of almost every organic compound. The branch of NMR spectroscopy where the nucleus is a proton is called proton magnetic resonance PMR spectroscopy. However principally, NMR and PMR spectroscopic studies are the same. The relationship between energy difference (ΔE) of the higher and lower energy states of the proton (or nucleus), frequency ν of radiation and strength (H_0) of magnetic field can be given by the following expression:

$$\Delta E = h\nu$$

$$h\nu = \frac{\gamma h H_0}{2\pi}$$

$$\therefore \quad \nu = \frac{\gamma H_0}{2\pi} \qquad \text{...(1)}$$

Here γ is a nucleus constant known as gyromagnetic ratio and h is Planck's constant.

For a proton value of γ is 26750.

From equation (1) it can be concluded that higher the value of applied magnetic field Ho, higher will be the frequency of radiation needed to flip the proton from lower to higher energy state. A typical PMR signal is obtained as shown in fig 3.

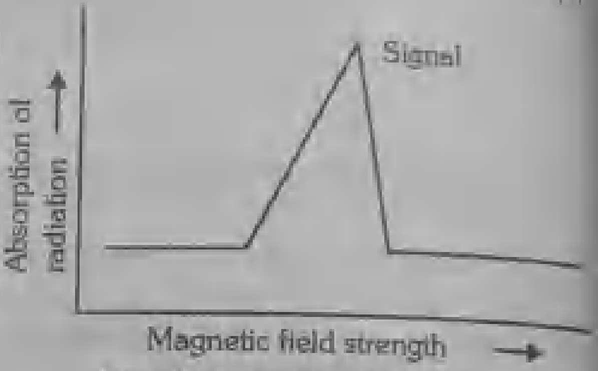
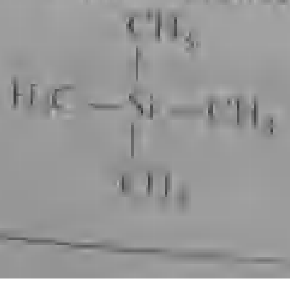


Fig. 3: A typical PMR signal

4. ^{1}H NMR Spectrum

After knowing what is a ^{1}H NMR spectrum, it becomes easier to know how to obtain a ^{1}H NMR spectrum. Some of the important determinants to obtain a ^{1}H NMR spectrum are discussed below;

1. In practice, it is easier and cheaper to keep the frequency constant and gradually change the magnetic field strength (H_0) slowly. When the H_0 value is reached, enabling the proton to absorb the radio waves for a spin flip, a peak or a signal is obtained on a calibrated chart paper (which plots transmittance versus H_0). Interestingly, when the radio waves are removed the excited nuclei turn back to the same lower energy spin state. This enables the same sample to be used for obtaining repeated spectra.
2. **Choice of Solvent:** The sample compound is kept in a proton free solvent such as CCl_4 or $CDCl_3$. Although D is NMR active, but it is non interfering. It is because of the fact that it does not absorb in the frequency range set in the instrument for ^{1}H NMR spectrum. If required a more polar solvent can also be used like hexadeuterated dimethyl sulfoxide- $(CD_3)_2S=O$.
3. The compound which has to be analyzed is kept in a long thin glass tube which is spun in the magnetic field properly so that all the molecules are uniformly exposed to magnetic field.
4. **Internal Standard / Reference Compound:** A small amount of a reference compound in the form of TMS-Tetra Methyl Silane $(CH_3)_4Si$ is added to the sample



$$H_3C-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{Si}}}}-CH_3$$

It is important to know that why TMS is chosen as the reference compound. It is due to the fact :

(i) TMS gives a single peak because it has only one type of proton. More importantly, its H are more shielded than those of majority of compounds, its unique signal is isolated in the high upfield region.

(ii) Since silicon (1.8) is less electronegative than carbon, TMS protons are highly shielded. Signals due to the hydrogen of TMS are assigned as zero. Organic protons absorb downfield (to the left) of the TMS signal.

(iii) TMS is chemically inert and have a low b.p. (300K). It can be easily evaporated after the experiment.

5. Now the spectrum is taken, and when the H_0 value reaches so that proton flip takes place (it is also expressed as that the proton is in resonance at the set frequency), a peak is obtained on a calibrated chart paper as shown in fig. 3.

6. With the exception of water, chloroform and sulfuric acid, which are examined as liquids, all the other compounds are measured for NMR spectrum as gases.

5. Nuclear Shielding and Deshielding of Protons

In the NMR/PMR spectrum of a compound, the electrons around the protons (in orbits) also play their role. When a compound is kept in a magnetic field, the electrons around the protons also generate a magnetic field; this is called as induced magnetic field. This induced field may support (reinforce) or oppose the applied field. Hence following two cases arise :

1. If the induced field opposes the applied field, the proton experiences a decreased effective field strength. Hence for the excitation of protons to higher level, greater applied field is required. Technically, it is expressed as proton absorbs "upfield" and are shielded by electrons.

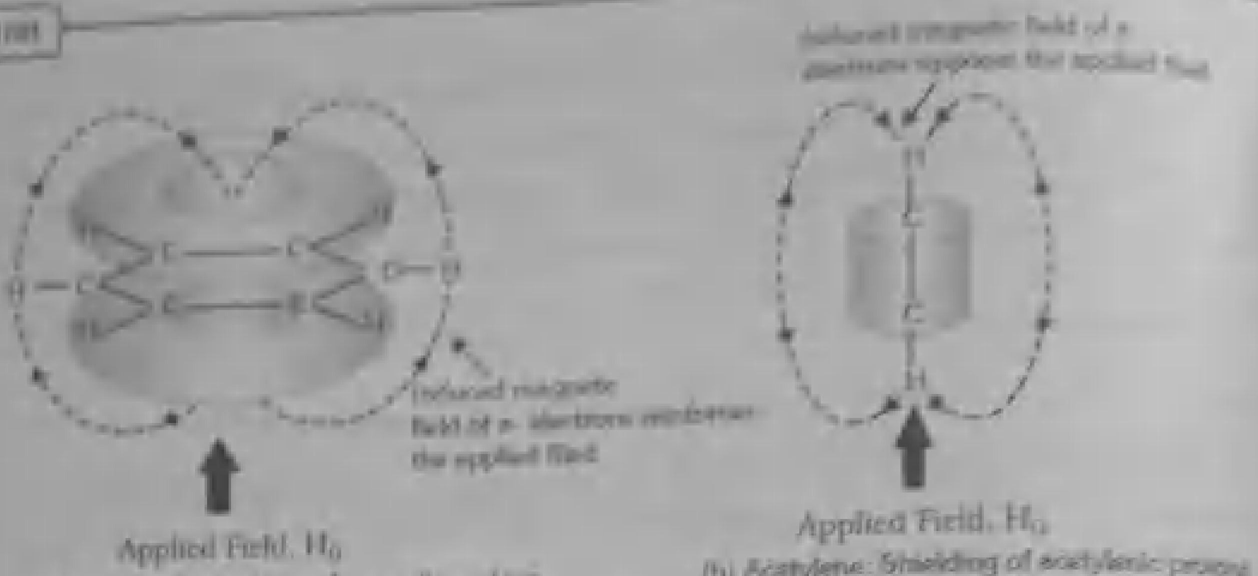
2. If the induced field supports the applied field, the proton experiences an increased field strength. Hence for the excitation of protons to higher level, a smaller applied field is required. This is expressed as proton absorbs "downfield" and are deshielded by protons.

Shielding and deshielding of protons occur due to various factors like the inductive and electromeric effects of groups and hydrogen bonding.

In a case when π electrons are involved, whether the induced field opposes or supports the applied field depends upon the way in which π-electrons circulate under the influence of applied field. For example,

(i) When a benzene derivative is kept in a magnetic field, the delocalised π-electrons of benzene ring circulate in a manner that induced magnetic field supports the applied field. Thus aromatic protons (i.e. H atom attached directly to benzene ring) experience a greater magnetic field strength; thus these are deshielded and absorb downfield as shown fig. 4(a).

(ii) On the contrary, when acetylene molecule is placed in magnetic field, the π-electrons circulate around the axis of molecule in a way that induced field opposes the applied magnetic field. Hence here protons get shielded and absorb upfield as shown in fig.4 (b).



(a) Benzene: Deshielding of aromatic protons

(b) Acetylene: Shielding of acetylenic protons

Fig. 4: Shielding and deshielding of protons

Shielding and deshielding of protons causes a shift in the position of signal.

6. Chemical Shift (δ)

The chemical shift refers to the displacement of a signal or peak from the hypothetical position of maximu shielding (the hydrogens of TMS). It is represented as delta (δ) and measured in ppm or parts per million. The larger the delta (δ) value, the greater is the chemical shift and the more downfield is the signal. The signa obtained from the hydrogens of TMS are conventionally assigned a zero value.

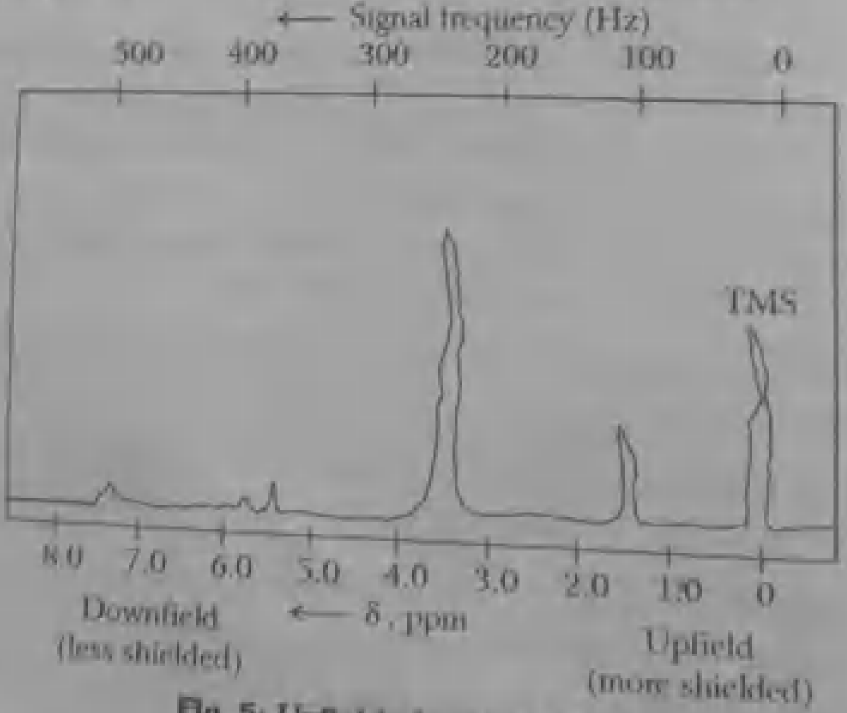
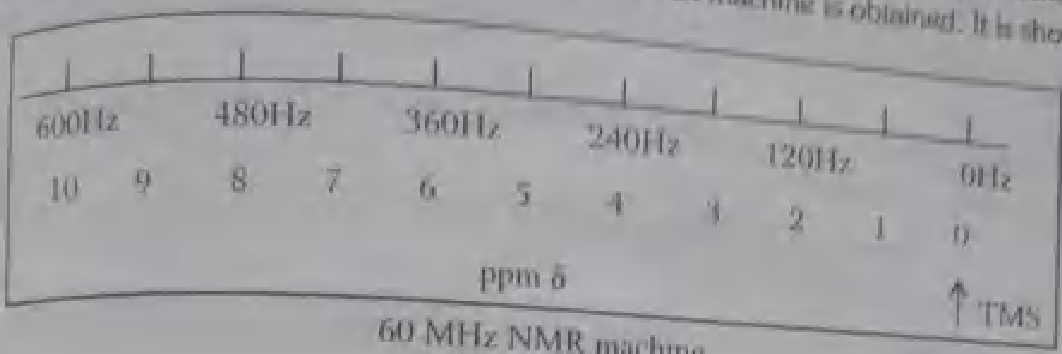


Fig. 5: Upfield, downfield table

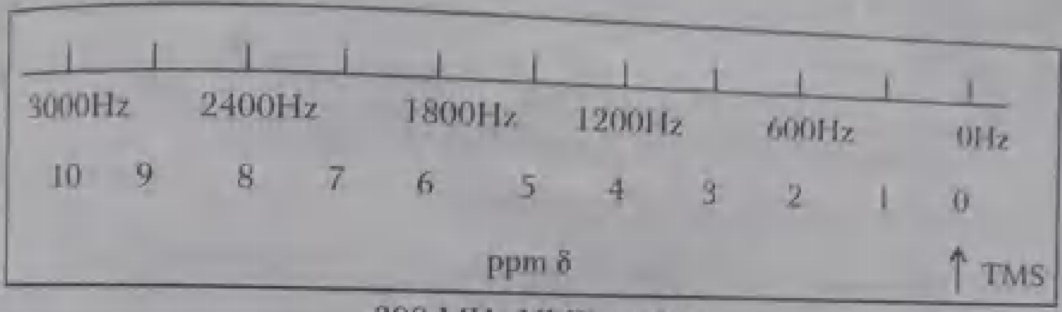
The equation for calculating chemical shift δ is

$$\text{Chemical shift } \delta = \frac{\text{Observed shift from TMS (Hz)}}{\text{Frequency of spectrometer (commonly } 60 \times 10^6 \text{ Hz)}} \times 10^6 \text{ ppm}$$

words, it can also be defined as a ratio of shift downfield from TMS (Hz) to total spectrometer frequency. So, interestingly same δ value for 60, 100 or 300 MHz NMR machine is obtained. It is shown below



60 MHz NMR machine



300 MHz NMR machine

For example, If a signal is obtained at 120 Hz downfield with reference to TMS using 60×10^6 Hz NMR machine, then chemical shift is given by

$$\text{Chemical shift (S)} = \frac{120}{60 \times 10^6} \times 10^6 = 2 \text{ ppm}$$

Chemical shift is expressed using two scales

- δ (delta scale)
- τ (tau) scale

Both of them are in parts per milion.

$$\delta = \frac{\delta\nu \text{ (in cps)} \times 10^6}{\text{Radio frequency used in cps}}$$

and $\tau = 10 - \delta$

Assuming the position of TMS signal as zero ppm, most chemical shifts have values between 0 – 10. A small δ value indicates a small downfield shift while a large δ value indicates a largedown field shift.

On the contrary, on τ scale the positions of the TMS signal is taken as 10.0 ppm and most compounds have chemical shift values between 10 and zero. This can be explained with the help of scale as shown below.

δ and τ scale of shift

Solved Examples

Example 1: **Is the δ value for a given kind of H an inherent constant number or it changes wit the frequency of spectrometer?**

Solution: Yes, it is a constant. It is because as the value of spectrometer frequency changes, there is a du compensatory change in the downfield shift.

Example 2: **Find (i) the δ value and (ii) the observed shift from TMS in Hz of peak in a 100 MH instrument that is 162 Hz in a 60 MHz instrument.**

Solution: (i) Using the equation

$$\delta = \frac{\text{Observed shift from TMS (Hz)}}{\text{Frequency of spectrometer (commonly } 60 \times 10^6 \text{ Hz)}} \times 10^6 \text{ ppm}$$

$$\delta = 162\,\text{Hz} \times 10^6/60 \times 10^6\ \text{Hz} = 2.70\ \text{ppm}$$

(ii) Since δ is constant, 2.70 ppm = Observed shift $\times 10^6/100 \times 10^6$ Hz

From which observed shift = 270 Hz.

6.1 Different Protons have different Chemical Shifts

It is very important to note that all hydrogens in a molecule do not spin-flip at the same applied magnetic fiel at constant frequency, so these have different chemical shift values.

The following example can give us an idea about the different behavior shown by different hydrogens in molecule. Presently, the example of a methanol molecule is considered.

Depending on their chemical environment, protons in a molecule are shielded by different amounts.

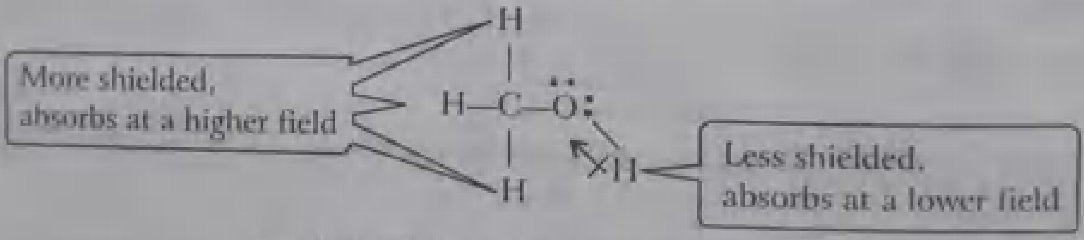


Fig. 6: Shielding of protons in methanol

6.2 Factors Influencing the Chemical Shift δ

There are so many factors which influence the value of chemical shift, δ. Some of these determinants an discussed below:

6.2.1 Influence of Electronegativity on the Chemical Shift

The influence of electronegativity on the chemical shift can be explained from a simple example. We conside a molecule having a structural feature like F-C-H. Due to high electronegativity of F(fluorine) C—H bonded pair is shifted towards C, thereby deshielding H. So, it must be characterized with higher delta (δ) or mor downfield peak. If F is replaced by a Cl atom, again de-shielding takes place but the amount of de-shielding less (with respect to F). Therefore, the delta (δ) value is lesser.

Table-1: Effect of electronegativity of X on δ values

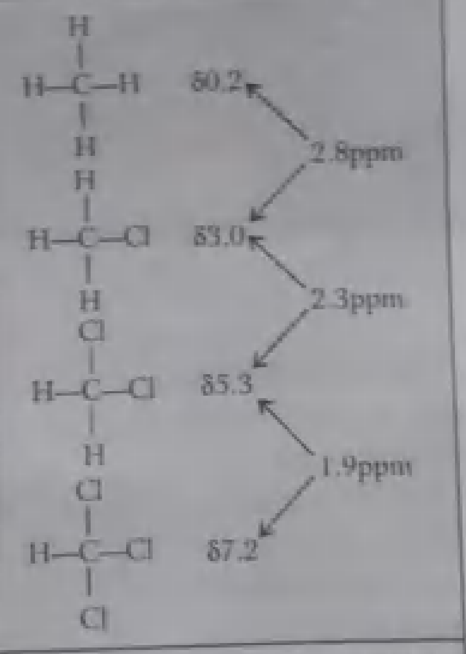
S.No.	X	δ (in ppm)
1	F	4.3
2	Cl	3.1
3	Br	2.7
4	I	2.2

So, conclusively highly electronegative atoms cause greater downfield shift and hence more delta (δ). However the effect of electronegativity decreases with distance.

Additional electronegative atoms cause increase in chemical shift , as shown by the data:

Chemical Shifts of the Chloromethanes

Compound Chemical shift Differences



Note: Each chlorine atom added changes the chemical shift of the remaining methyl protons by about 2 to 3 ppm. These changes are nearly additive

6.2.2 Influence of π Bond on the Chemical Shift

A π bond attached to C-H bond, for example, $C=C-C-H$ will again cause a downfield shift (in comparison to an alkane). Some of the important cases are discussed here.

1 **Aromatic Protons:** It is definitely a matter of concern that the δ value of an aromatic H(6-8.5ppm) is higher than a vinylic H (4.6 –5.9 ppm). The explanation is that the applied magnetic field induces the e^-'s in the aromatic ring to circulate around the ring. This circulation, called a ring current, generates a magnetic field which overshadows the normal shielding of the e^-'s in any C—H bond. The net effect is to deshield the aromatic planar hydrogen atoms external to the ring. This effect, a kind of anisotropy, is called paramagnetic deshielding. The C = C of alkenes also has a deshielding anisotropic effect that, however, is less strong than that of the aromatic ring. As a result, vinylic hydrogen atoms are more upfield than aromatic hydrogen atoms.

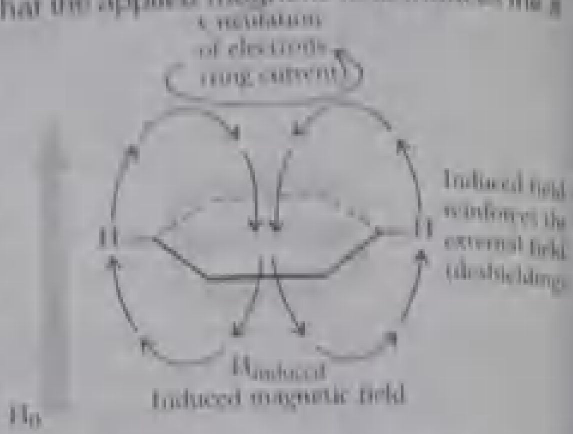


Fig. 7: Chemical shift of aromatic protons

2 **Vinylic Proton**

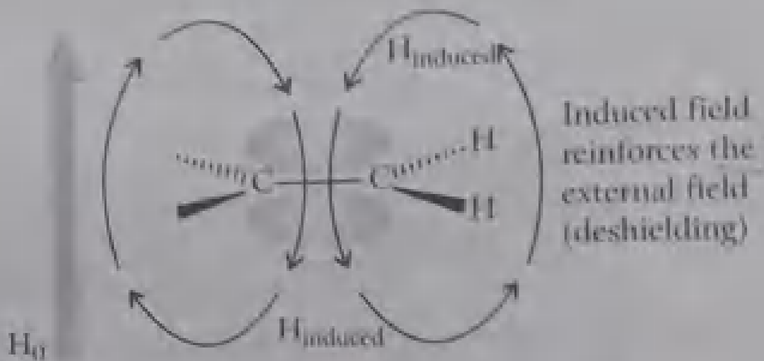


Fig. 8: Chemical shift of vinylic protons

3 **Acetylenic Proton**

It is quite interesting to note that why acetylenic hydrogen atoms (δ =2 to 3 ppm) are more upfield (less downfield) than vinylic hydrogen atoms.

One might expect that acetylenic hydrogen atoms, attached to sp hybridized carbon atom, should give more downfield signals than vinylic hydrogen atoms. This is not the case, because the anisotropic effect of the induced circulation of the π e^-'s shields the linearly disposed hydrogen atoms that lie within the ring current. Were it not for the strong electron-withdrawing effect of the C≡C group, signals for acetylenic hydrogen atoms would be even more upfield.

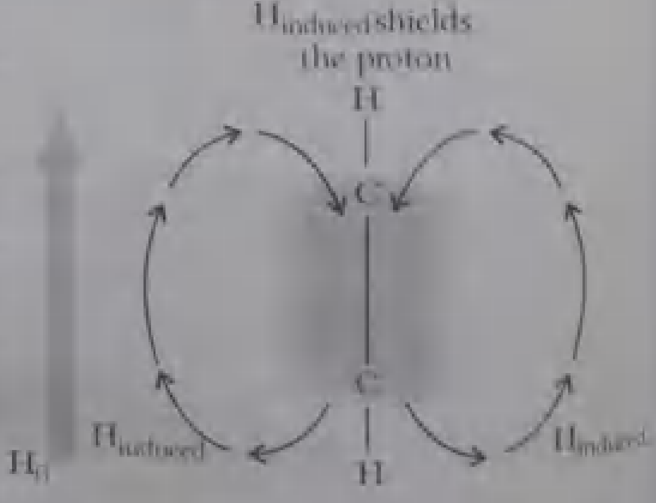


Fig. 9: Chemical shift of acetylenic protons

So, summarily the important factors which influence the chemical shift δ are

1. Electronegative atoms, such as N, O, and X, lessen the shielding of H's and cause downfield shifts. The extent of the downfield shift is directly proportional to the electronegativity of the atom and its proximity to the H.

Table-2: Some important δ values

S.No.	Underlined Proton	δ ppm
1.	$\mathrm{Br-\overset{|}{\underset{|}{C}}-\underline{H}}$	4 – 2.5
2.	$\mathrm{HO-\overset{|}{\underset{|}{C}}-H}$	4 – 3.4
3.	$\mathrm{R-NH_2}$	5.0 – 1.0
4.	$\mathrm{RO-H}$	5.5 – 1.0

2. Hydrogen atoms attached to π-bonded carbon atoms are less shielded than those in alkanes. The order of δ values is

$$\mathrm{H-\overset{|}{C}=O > Ar-H > H-\overset{|}{C}=\overset{|}{C}- > H-C\equiv C- > H-\overset{|}{\underset{|}{C}}-}$$

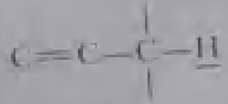
3. Ar, C = O, C = C and C ≡ C are electron-withdrawing by induction and cause a downfield shift of an H on an adjacent C, as in

$\mathrm{O=C-\overset{|}{\underset{|}{C}}-\underline{H}}$

α carbonyl

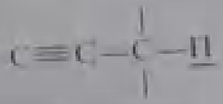
$\mathrm{Ar-\overset{|}{\underset{|}{C}}-\underline{H}}$

Benzylic



$\mathrm{C=C-\overset{|}{\underset{|}{C}}-\underline{H}}$

Allylic



$\mathrm{C\equiv C-\overset{|}{\underset{|}{C}}-\underline{H}}$

Propargylic

For alkyl groups in similar environments, shielding increases with the number of hydrogen atoms on the C. The order for δ values is

$$\mathrm{-\overset{|}{\underset{|}{C}}-H > -\overset{H}{\underset{H}{C}}- > -\overset{H}{\underset{H}{C}}-H}$$

Methine Methylene Methyl

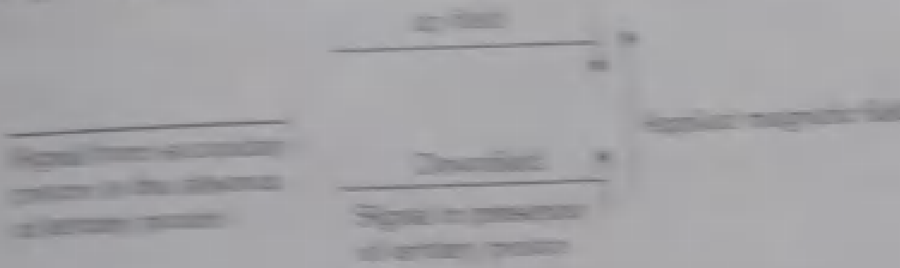
5. Electropositive atoms, such as Si, shield hydrogen atoms; hence the reference property of TMS.

6. Hydrogen atoms which participate in H-bonding like OH and NH, exhibit variable δ values over a wide range, depending mainly on sample concentrations. H-bonding diminishes shielding. Hence, in a non-H-bonding solvent, the OH-signal for ROH (or NH-signal for RNH_2) moves downfield as the sample is concentrated, because H-bonding is enhanced. H-bonding is accompanied by exchange of hydrogen atoms between the ROH molecules which ultimately results into broadening of the signals.

If the magnetic field produced by tertiary proton is oriented along the applied field, the secondary protons will experience increased magnetic field strength and so will absorb at lower applied field (i.e. downfield).

If the magnetic field produced by tertiary proton is oriented against the applied field, the secondary protons will experience decreased magnetic field and so will absorb at higher applied field i.e. at upfield.

Since there is equal probability of both, half of the secondary protons will absorb downfield and the other half upfield and so peak of secondary hydrogen will split into two as shown in following figure.



1:1 Splitting/Doublet formation

(One adjacent proton causes 1:1 splitting)

Now we consider absorption by tertiary proton in presence of two adjacent secondary proton. Two adjacent protons may have three types of spin alignment:

(a) 2 protons are aligned with applied magnetic field.

(b) 2 protons are aligned against applied magnetic field.

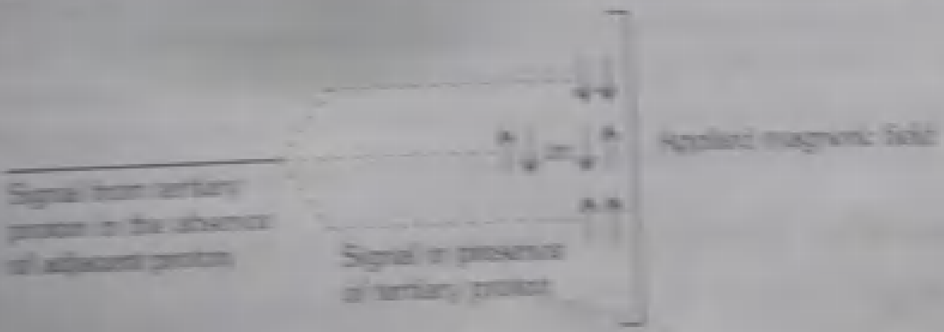
(c) One proton is aligned & one proton is against applied magnetic field so.

First will result in downfield absorption.

Second will result upfield absorption.

In Third position of signal will not change.

result of these alterations, the peak due to tertiary proton will split into three peaks with relative ensities in the ratio 1 : 2 : 1.



nal in presence of secondary proton. Two adjacent proton causes 1 : 2 : 1 splitting (triplet formation).

Total area under the doublet would be twice of the total area under the triplet because the doublet is due to absorption by two protons and triplet is due to absorption by one proton.

The N + 1 Rule: If a signal is split by N equivalent protons, it is split into N + 1 peaks.