→ Nuclear Magnetic Resonance (NMR) spectroscopy :→

- Introduction :→
- This technique was developed by Edward M. Purcell and Felix Bloch in 1940's.
- NMR spectroscopy is a technique which gives us information about the number and types of atoms of a particular element in the molecule.
- NMR spectroscopy which gives the information about hydrogen atom in a molecule is called ^1H-NMR spectroscopy or proton magnetic resonance (PMR) spectroscopy.
- NMR spectroscopy which gives the information about carbon atom in a molecule is called ^{13}C-NMR spectroscopy.
- NMR gives a deeper information about the carbon-hydrogen framework of organic molecules.

- Principle :→
- The nuclei (positively charged particles) of certain atoms or their isotopes possess propery of spinning along their axis, like electron.
- These charged nuclei generates a magnetic moment along the axis of spin. Thus nuclei behave as tiny magnet.

- Only those nuclei possess such magnetic moment (quantized spin angular momentum) which have -

ⓐ odd atomic number and odd mass number <u>OR</u>

ⓑ odd atomic number and even mass number <u>OR</u>

ⓒ even atomic number and odd mass number

- All nuclei possess either half integral $\left(\frac{n}{2}\right)$ or full integral (n) spin quantum number (I). i.e. atomic nuclei having $I = n$ or $I = \frac{n}{2}$ will have magnetic properties.
- The atomic nuclei which have even mass number and even atomic number do not possess a nuclear spin and hence do not have magnetic properties.
- The no. of allowed spin state for a nuclei is

$$\boxed{2I+1}$$

here I = spin quantum no. of nuclous

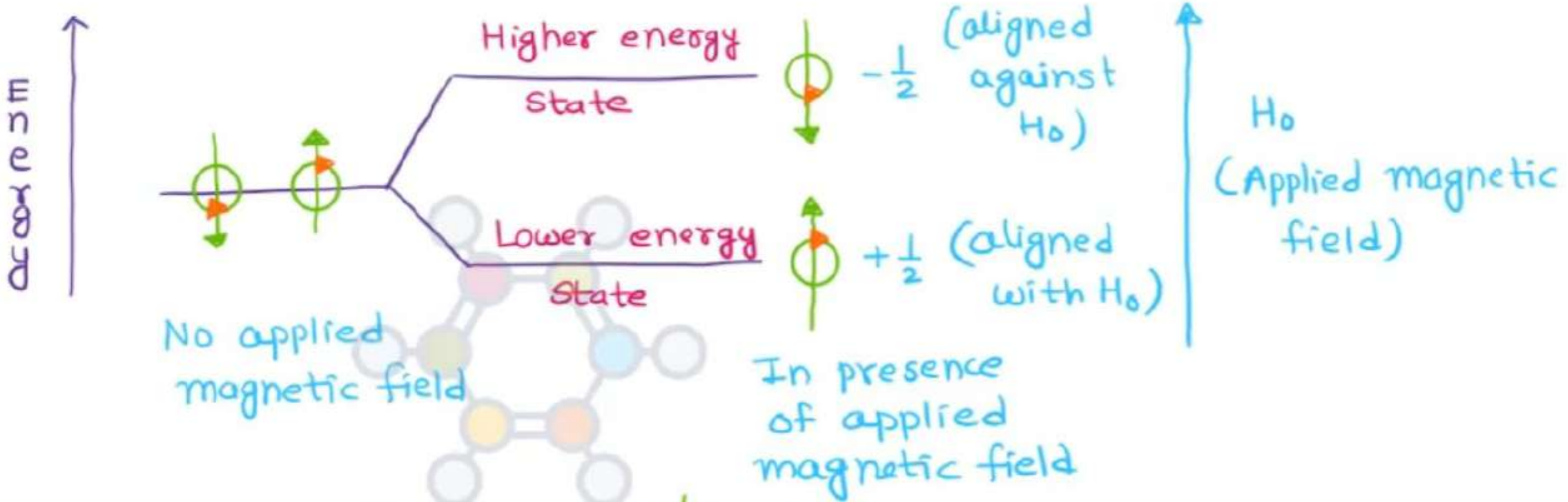
<u>Example</u>:- $^{1}_{1}H$ Mass no. → 1 Atomic no. → 1 spin quantum no. $(I) \rightarrow \frac{1}{2}$

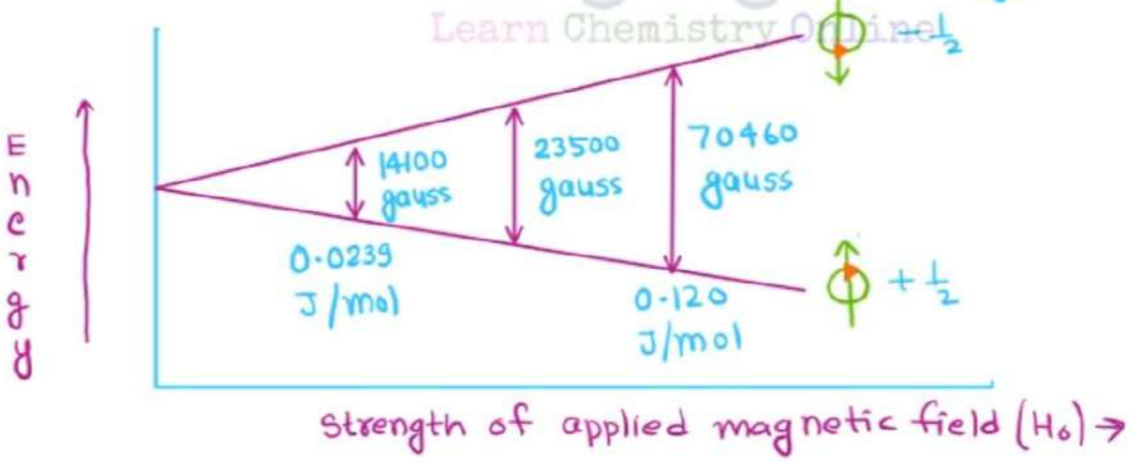
$$= 2 \times \frac{1}{2} + 1$$

Allowed spin state = 2

Element	Mass Number	Atomic Number	Spin Quantum Number (I)	Allowed Spin States (2I + 1)
${}^{1}_{1}H$	Odd	Odd	$\frac{1}{2}$	2
${}^{2}_{1}H$	Even	Odd	1	3
${}^{11}_{5}B$	Odd	Odd	$\frac{1}{2}$	2
${}^{12}_{6}C$	Even	Even	0	0
${}^{13}_{6}C$	Odd	Even	$\frac{1}{2}$	2
${}^{14}_{7}N$	Even	Odd	1	3
${}^{16}_{8}O$	Even	Even	0	0
${}^{17}_{8}O$	Odd	Even	$\frac{5}{2}$	6
${}^{18}_{8}O$	Even	Even	0	0
${}^{19}_{9}F$	Odd	Odd	$\frac{1}{2}$	2
${}^{31}_{15}P$	Odd	Odd	$\frac{1}{2}$	2
${}^{32}_{16}S$	Even	Even	0	0
${}^{35}_{17}Cl$	Odd	Odd	$\frac{3}{2}$	4

- In the absence of applied magnetic field all the allowed spin states of a nucleus are randomly oriented, degenerate and are also equally populated.





- In the presence of strong external magnetic field (H_0), the different spin states of nuclei no more remain random and degenerate.
- For example, in case of hydrogen nucleus, there are two spin states, $+\frac{1}{2}$ and $-\frac{1}{2}$. In the presence of applied magnetic field (H_0), the two energy states will be generated. In lower energy state nuclear magnetic moment will be aligned with applied field $(+\frac{1}{2})$ and in the higher energy state it will be aligned against the applied field $(-\frac{1}{2})$.
- The difference in energy b/w two states is very small when the strength of of applied magnetic field is low. Because of small difference, the two energy stated are nearly equally populated.

- However, calculations show that there is always slight excess of nuclei in the lower energy state.
- The excess of nuclei in lower energy state is responsible for the absorption of energy in the radio frequency region of the spectrum.
- The transition from one energy state to other is called flipping of the proton.

- The difference in energy of two states $\propto$ strength of applied magnetic field
- The frequency of absorbed radiation (ν) is given by

$$\boxed{\nu = \frac{\mu H_0}{hI} \text{MHz}}$$

here μ = magnetic moment
H_0 = Strength of applied magnetic field
h = Planck's constant
I = Spin quantum number

- A second effect of applied magnetic field on the nucleus is that it begins to "Wobble" or "precess" and traces a conical surface in the same manner as a spining top or a gyroscope traces under the influence of gravitation force.

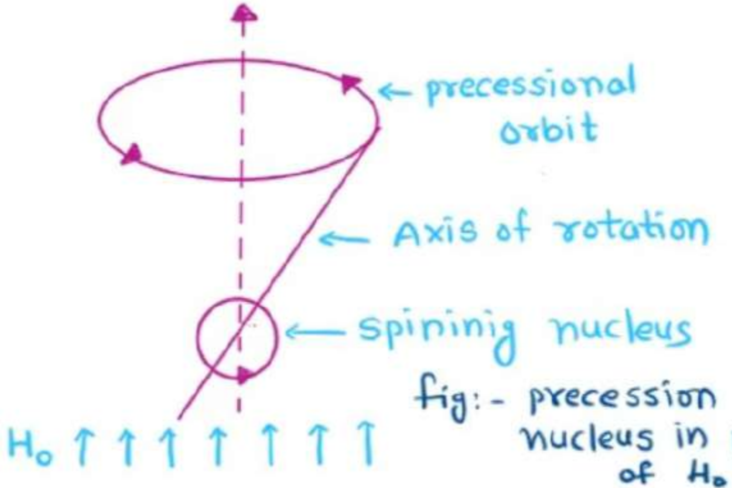


fig:- precession of nucleus in presence of H_0

- The precession of nucleus, generates an oscillating electric field of the same frequency (ω) as the frequency of precessing nucleus (ω)
- Now when such a nucleus is irradiated with electromagnetic radiation also of the same frequency (ω), the two frequencies couple and the nucleus attain the state of resonace and absorb energy. The nuclear spin is flipped from spin state $+\frac{1}{2}$ to $-\frac{1}{2}$. (fig.)
- The instrument detects and records this as a signal to give a spectrum called NMR spectrum.

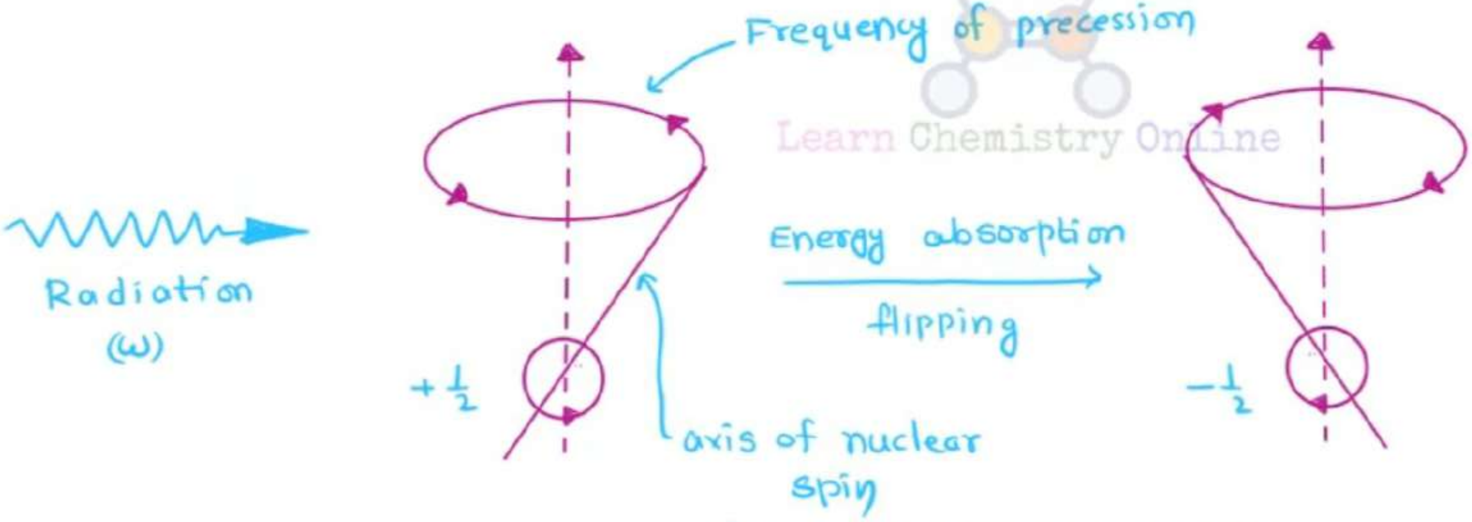


fig:- Resonance process

→ Nuclear shielding and deshielding :→

- In a molecule protons are surrounded by the electron cloud. This electron cloud starts circulating under the influence of applied magnetic field. The circulation of electrons is called diamagnetic current, which induces a local magnetic field (also called secondary or Induced magnetic field). This induced magnetic field opposes the applied magnetic field near the nucleus. As a result, the field strength actually felt by the nucleus (H_{eff}) is always less than the strength of applied field (H_0). such a nucleus is said to be shielded and the phenomenon is called nuclear shielding.
- As this shielding is due to diamagnetic current, it is also called diamagnetic shielding.

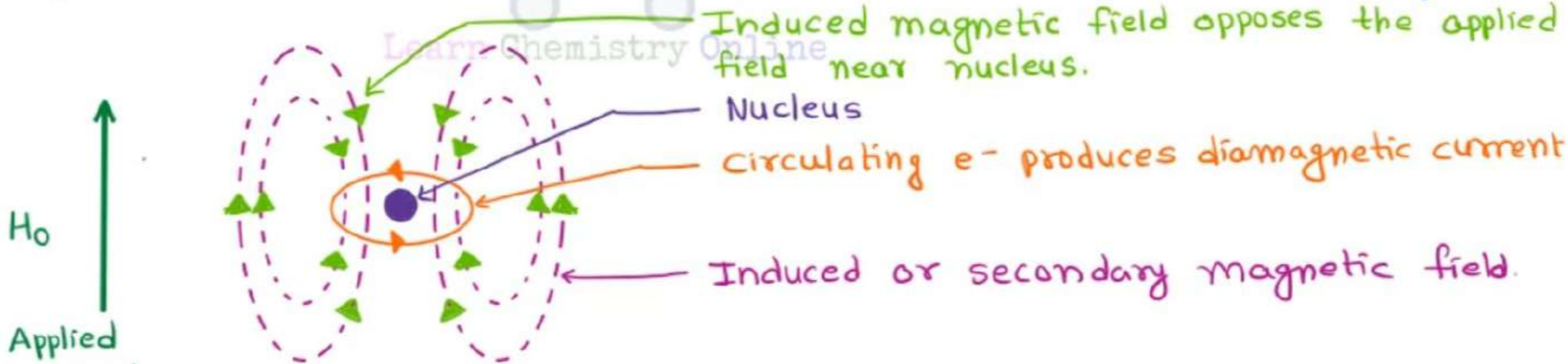


fig:- diamagnetic shielding of proton

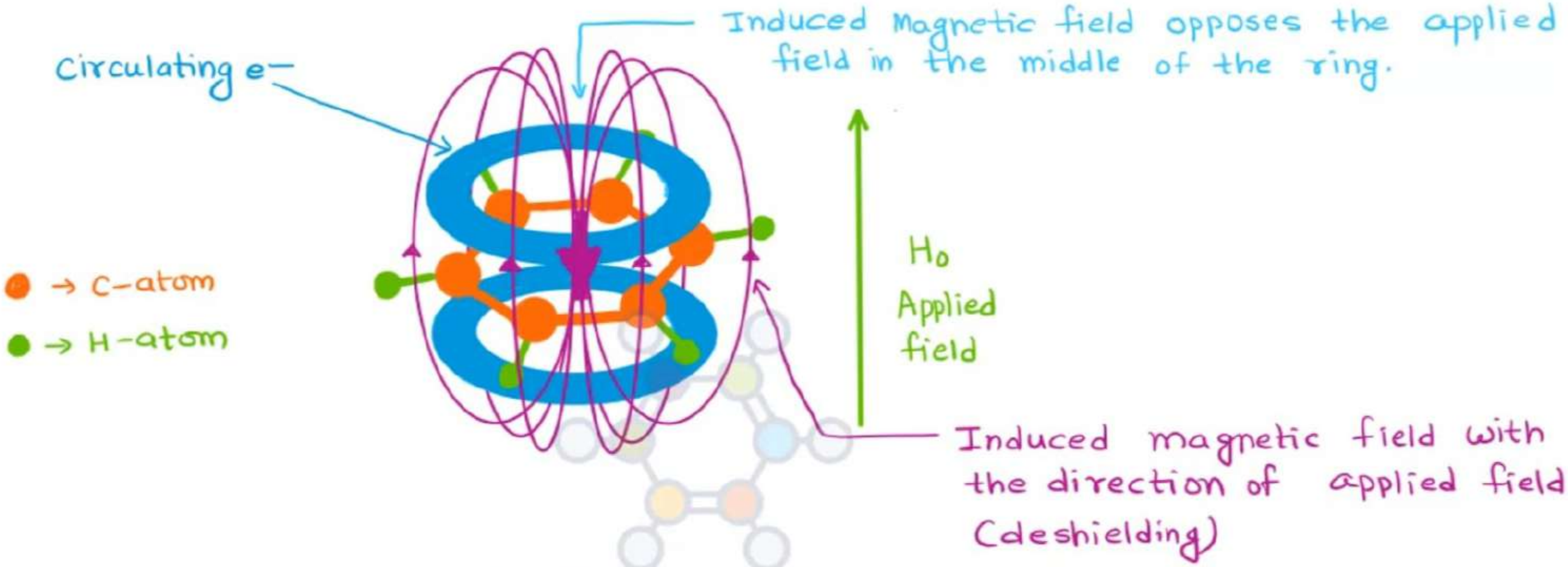
- Greater is the electron density around nucleus greater will be induced magnetic field which opposes the applied magnetic field. thus greater applied magnetic field is required for absorption.
- When absorption occurs, the field H felt by the proton is given by

$$\boxed{H = H_0(1-\alpha)}$$

here H_0 = Applied magnetic field strength.

α = shielding parameter which shows extent of shielding.

- Greater the value of α, greater will be the value of applied field strength which has to be applied to get effective field required for absorption and vice versa.
- If the induced field reinforces the applied field, the proton (nucleus) feels a higher field strength and thus, such a nucleus is said to be deshielded and the phenomenon is called nuclear deshielding.
- Example:→ The π e⁻ in the benzene molecule are delocalised. when a molecule of benzene is placed under the influence of applied magnetic field, it orients itself at 90° to the applied magnetic field and circulating e⁻ generate the induced magnetic field which is diamagnetic in the centre of ring and paramagnetic in the region of protons.



- Presence of e− releasing group (+I) casues shielding of proton because it will increase the e− density around proton while presence of e− withdrawing group (-I) causes deshielding of proton because it will decrease e− density around the proton.
- In case of nuclear shielding, strength of magnetic field should be increased while in case of nuclear deshielding it should be decreased.

→ Chemical shift :→

- The number of signals in a NMR spectrum tells the number of the sets of equivalent protons in a molecule.
- The position of signals in the spectrum help us to know the nature of protons viz. aromatic, aliphatic, acetylenic, vinylic etc.
- chemical shift represent the position of signals.
- If the induced field oppose the applied field, then the proton (nucleus) is said to be shielded. But if the induced field reinforces the applied field, the proton feels a higher field strength and thus, such a proton is said to be deshielded.
- shielding shifts the absorption upfield and deshielding shift the absorption downfield to get an effective field strength necessary for absorption.
- such shifts (compared with a standard reference) in the positions of NMR absorptions which arises due to the shielding or deshielding of protons by the electrons is called chemical shifts.
- For measuring of chemical shift for various protons in a molecule, the signal for tetramethylsilane $(CH_3)_4Si$ (TMS) is taken as reference.
- The difference in absorption position of the proton with respect to TMS signal is called chemical shifts.

→ Units and scale of chemical shift :→

- The chemical shift can be measured in Hz which is directly proportional to the strength of applied magnetic field.
- Since a number of instruments operating at different field strength (i.e. 60 MHz, 100MHz, 200 MHz etc.) are available, the chemical shift, measured in Hz, will be different with different instruments.
- To overcome this problem a field independent scale, was developed.
- The unit used for this is δ (delta) which is the ratio of observed chemical shift (Hz) to the radio frequency used (MHz)
- Since resulting number is too small, it is multiplied by 10^6.

$$\boxed{\delta = \frac{\text{observed chemical shift from TMS (Hz)}}{\text{Spectrometer freq. (MHz)}} \times 10^6}$$

- For example :- First instrument

$$\delta = \frac{120\text{ Hz}}{60\text{ MHz}} \times 10^6 = 2.0$$

Second instrument

$$\delta = \frac{200\text{ Hz}}{100\text{ MHz}} \times 10^6 = 2.0$$

- The δ value assigned to TMS is 0 and chemical shifts of majority of protons fall between $\delta 0$ to $\delta 10$ on a ten point scale.
- A small δ value indicates upfield shift (higher field strength) and the proton is said to be shielded.
- A large δ value indicates downfield shift (lower field strength) and the proton is said to be deshielded.
- Chemical shift also measured using another scale called τ (Tau) scale. on this scale the chemical shift of TMS is assigned the value τ as 10.
- The both δ and τ values are related to each other as follows:

$$\boxed{\delta + \tau = 10}$$

or $$\boxed{\delta = 10 - \tau}$$

or $$\boxed{\tau = 10 - \delta}$$

- The protons having same value of δ are called equivalent protons.
- The protons having different value of δ are called non equivalent protons.

- The relationship b/w two scales, position of TMS signal and correlation of shielding and deshielding effects with magnetic field are shown in fig.

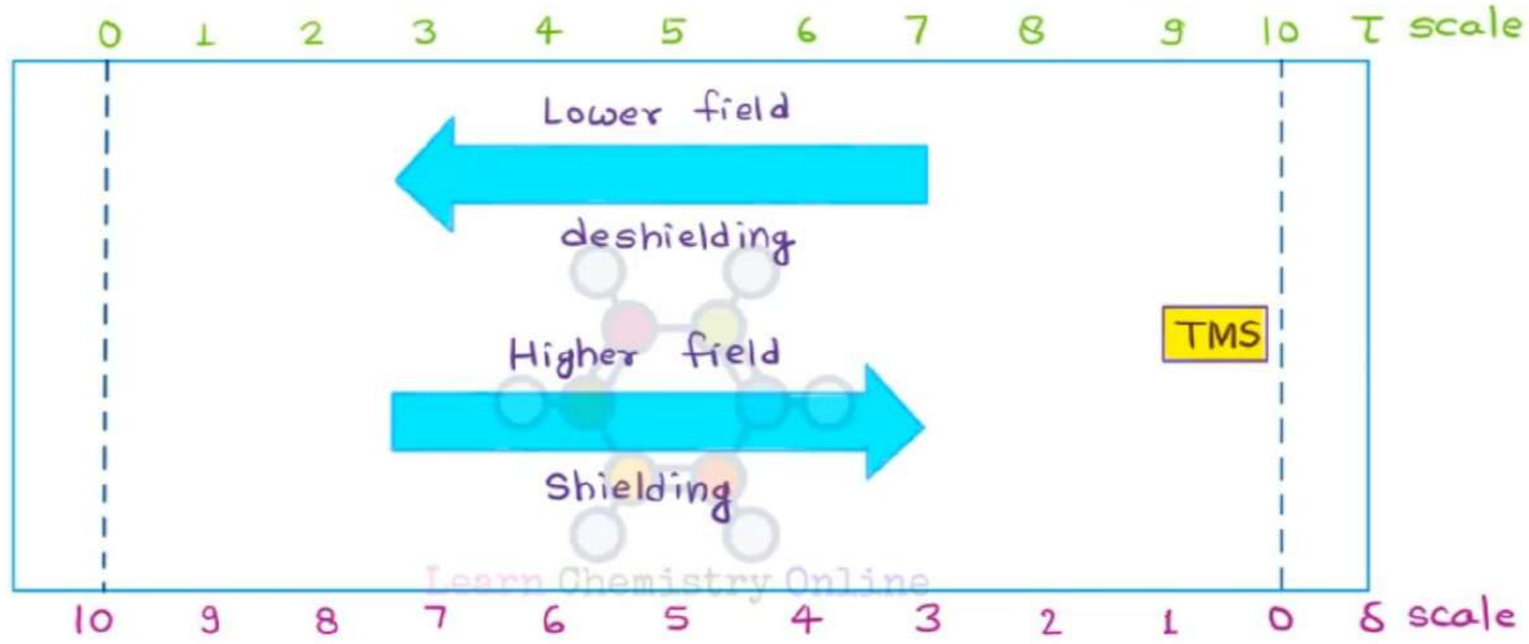
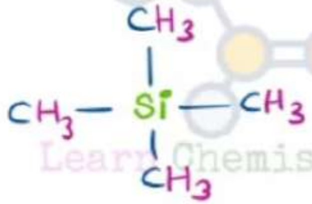


fig:- Scales of NMR spectra

→ TMS as reference compound in NMR spectroscopy :→

- It has been observed that the difference in resonance frequencies of different types of proton due to shielding and deshielding is generally very small. so it is extremely difficult to measure such a small difference accurately.
- To overcome this difficulty, a suitable reference compound is chosen and resonance frequency of the given proton is measured relative to a resonance frequency of proton of this standard compound.
- The most commonly used reference compound is tetramethylsilane (abbreviated as TMS)



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{Si}}}}-CH_3 \quad OR \quad (CH_3)_4Si$$

- The choice of TMS as a reference compound is associated with the following advantages –

① It is relatively inert as it has no polar group.

② It is a highly volatile liquid (b.p. 299.5 K) and, therefore can be easily removed after use thereby making the recovery of the sample (in pure condition) easily.

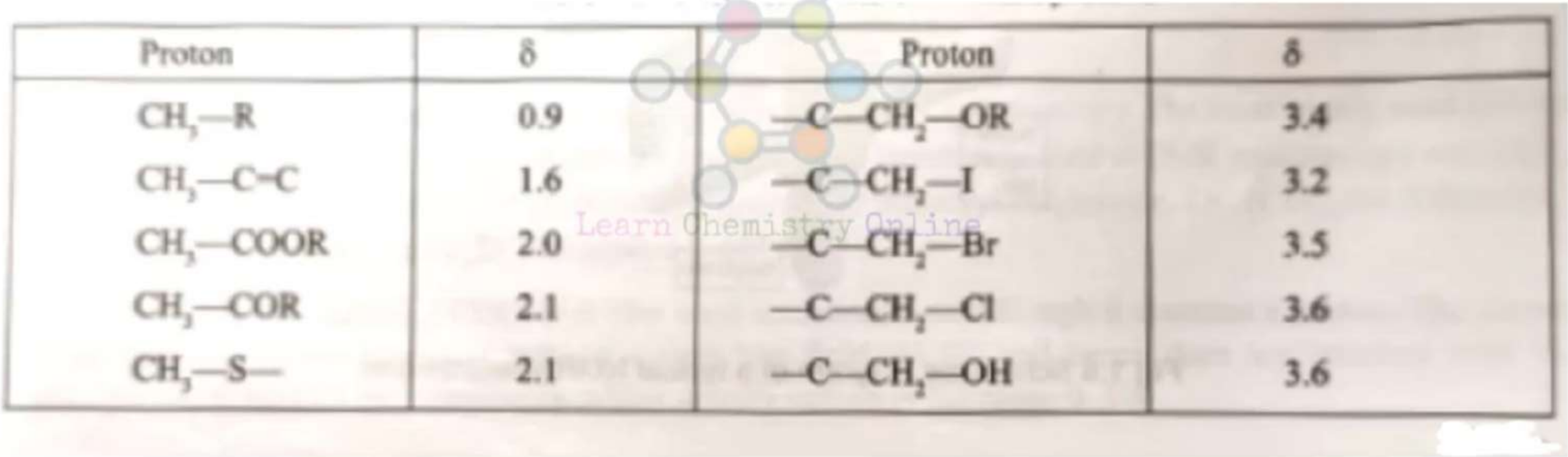
③ It is miscible with most of the organic solvents and does not form any type of complexes with them.

④ It has only one type of protons, so it exhibits one sharp single peak. (a singlet).

⑤ Due to presence of silicon atom, which is more electropositive than carbon, the chemical environment of all the protons of TMS is quite different than that of most of the protons. Hence the signal due to protons of TMS appears outside the normal range of protons of majority of organic compounds. In fact the protons of TMS are highly shielded so change of overlapping of the signal due to these protons with other protons is vary rare.

→ Factors affecting chemical shift:→

- The chemical shift of different types of proton are affected by local environments. so the values of chemical shifts can be used for the characterisation of different types of proton and playing a major role in determination of structure of unknown comp.
- The values of chemical shifts of different types of protons given in table.



Proton	δ	Proton	δ
CH_3-R	0.9	$-C-CH_2-OR$	3.4
$CH_3-C=C$	1.6	$-C-CH_2-I$	3.2
CH_3-COOR	2.0	$-C-CH_2-Br$	3.5
CH_3-COR	2.1	$-C-CH_2-Cl$	3.6
CH_3-S-	2.1	$-C-CH_2-OH$	3.6

① Electronegativity of Nearby atoms or Groups : The inductive effect :→

- The atom or group having −I effect will reduce the electron density around the proton and will result in the deshielding of the proton.
- The atom or group having +I effect will increase the electron density around the proton and will result in the shielding of the proton.

Example :-

(i) The approx. value of δ of methyl protons in different electronic environments are given below-

CH_3-C	CH_3-N	CH_3-O	CH_3-I	CH_3-Br	CH_3-Cl	CH_3-F
δ 0·9-1·0	δ 2·30	δ 3·30	δ 2·16	δ 2·70	δ 3·05	δ 4·26
E.N. 2·5	E.N. 3·0	E.N. 3·5	E.N. 2·5	E.N. 2·8	E.N. 3·05	E.N. 4·0

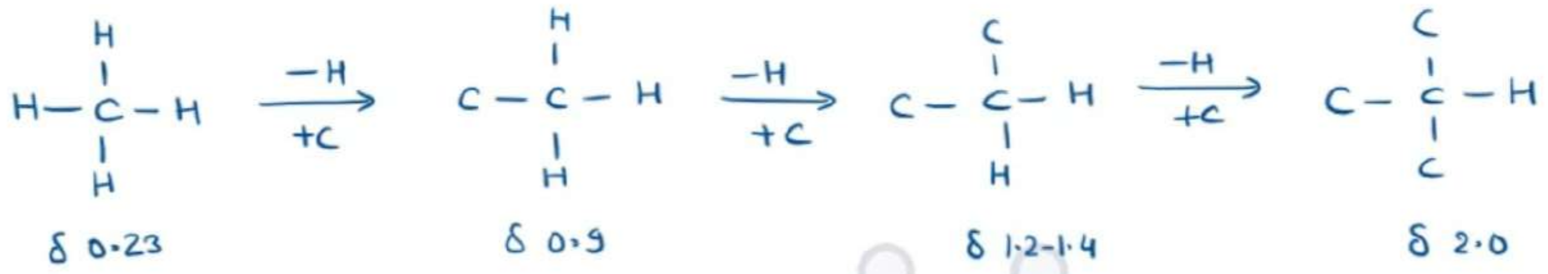
(ii) In case of haloalkanes multiple substition brings about more deshielding.

CH_3-Cl	CH_2-Cl_2	$CH-Cl_3$
δ 3·50	δ 5·30	δ 7·27

(iii) The deshielding effect halogen decreases with increase in distance

$-CH_2-Br$	$-CH_2-CH_2-Br$	$-CH_2-CH_2-CH_2-Br$
δ 3·50	δ 1·69	δ 1·25

(iv) Deshielding effect is increases when hydrogen atom (E.N 2.1) is replaced by carbon atom(E.N 2.5)



(v) Deshielding effect is also increase when hydrogen of methane is replaced by phenyl group

CH_4	$C_6H_5-CH_3$	$(C_6H_5)_2CH_2$	$(C_6H_5)_3-CH$
δ 0.23	δ 2.34	δ 3.92	δ 5.63

(vi) Deshielding of proton due to methine resonance in diphenyl methyl cation

$(C_6H_5)_2-\overset{+}{C}H$

② state of hybridisation :→

(i) $C^{sp^3}-H$:- δ 0.00 - 2.00

1° δ 0.9 - 1.3
2° δ 1.2 - 1.7
3° δ 1.4 - 2.0

s-character of C^{sp^3} = 25 % ∝ E.N ∝ deshielding

(ii) $C^{sp^2}-H$:- Called olefinic or vinylic protons

δ 4.5 - 7.0 (aliphatic)

s- character of C^{sp^2} = 33.3 % ∝ E.N. ∝ deshielding

δ 7.0-8.0 aromatic proton
δ 9.0-10.0 aldehyde proton
} (higher than expected δ value) This is due to magnetic anisotropy

(iii) $C^{sp}-H$:- Called acetylenic protons

δ 2.0 - 3.0

s- character of C^{sp} = 50 %

δ value lower than expected due to deshielding (This is due to magnetic anisotropy)

③ Hydrogen bonding:->

- protons involved in hydrogen bonding resonate downfield compared to non-hydrogen bonded one.
- This shift is due to the fact that in hydrogen bonding there is a shift of electron cloud from the hydrogen atom to the attached hetero atom (F,O,N etc).
- This electron withdrawal decreases the electron density around proton and hence causing downfield shift (deshielding).

Example:- concentrated ethyl alcohol δ 5·28 (hydrogen bonded –OH)

Very dilute solution δ 4·80 (free –OH)

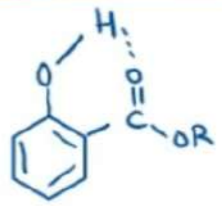
This behaviour of proton is useful in distinguishing b/w inter and intramolecular hydrogen bond

Intermolecular

Concentrated CH_3-CH_2-OH (bonded –OH) δ 5·28

Very dilute CH_3-CH_2-OH (free –OH) δ 4·80

Intramolecular



δ_{OH} 10–12

No change on dilution

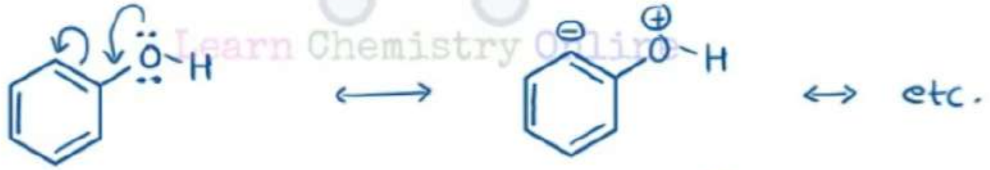
④ Acidic hydrogen :→

- Proton of carboxylic acid	δ 10.6-12.0
Proton of Phenol	δ 4.0-7.0
proton of Enol	δ >15.0

- The deshielding of these protons is due to following reasons-
  - (i) Greater electronegativity of oxygen
  - (ii) Electron-withdrawal from acidic protons due to resonance.

Carboxylic acid

Phenols



Enols

⑤ van der Waals deshielding :→

- when two non-vicinal protons comes near each other in the space, due to steric crowding, their e⁻ clouds undergo unsymmetrical distrotion resulting in mutual deshielding of such protons.

⑥ Magnetic anisotropy :→

- Anisotropy (Greek - different in different directions)
- In same molecule, there may be shielding of proton in one region of the molecule and deshielding in the other. this is called magnetic anisotropy.

Example :-

ⓐ Alkenes :-

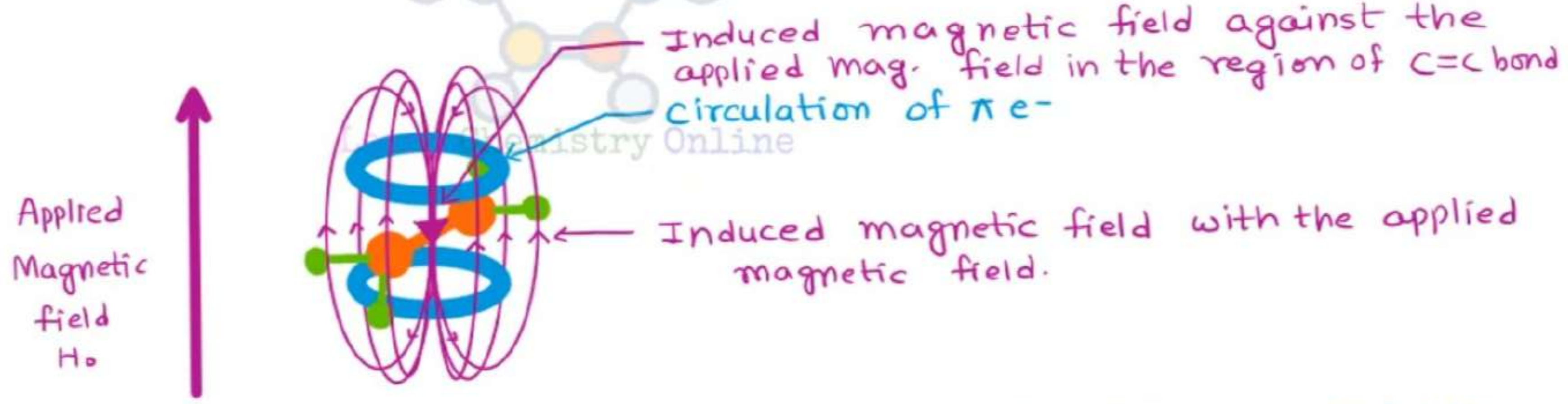


fig:- deshielding of olefinic protons by the induced magnetic filed generated by Circulation of π e⁻

- when a molecule of an alken is placed in external magnetic field, it orients itself in such a manner that π e- cloud is perpendicular to the applied magnetic field and its π e- start circulating in the plane of double bond and generates induced magnetic field.
- This induced magnetic field opposes the applied field in the region of double bond and with the applied field in the region of proton. The net result is the deshielding of protons.

ⓑ Aldehydes :-

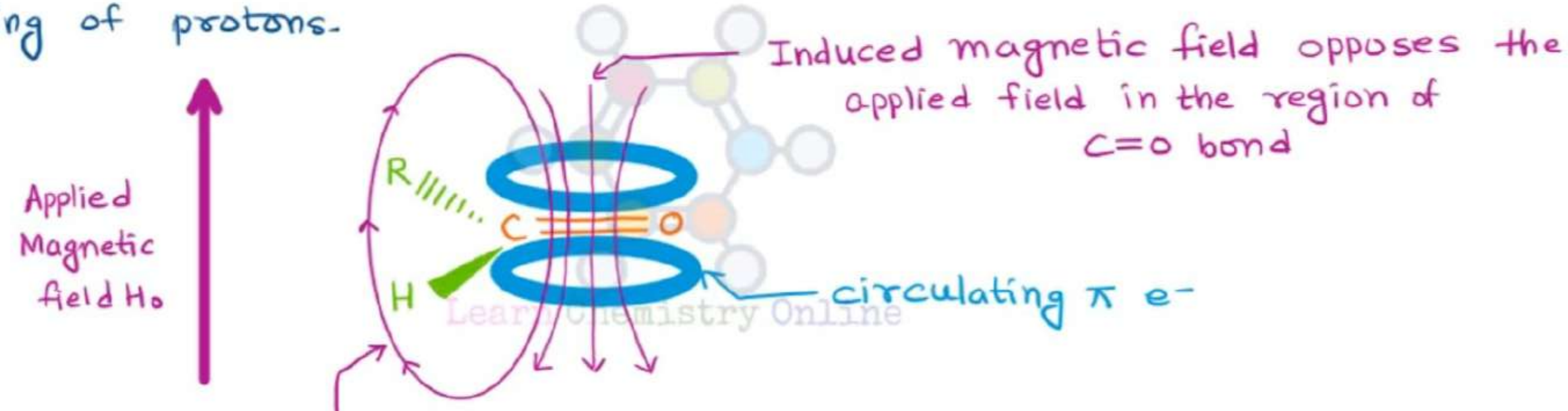


fig:- deshielding of aldehydic protons by induced magnetic field generated by circulation of π e-.

- When aldehyde is placed in external magnetic field, it orients itself perpendicular to the external or applied magnetic field.
- The induced magnetic field generated by the π e⁻ is with the applied magnetic field in the region of aldehydic proton (deshielding) and oppose the applied magnetic field in the region of C=O double bond.
- The extensive deshielding of aldehydic proton is due to magnetic anisotropy and strong electronegativity of carbonyl carbon.

ⓒ Aromic compounds:-

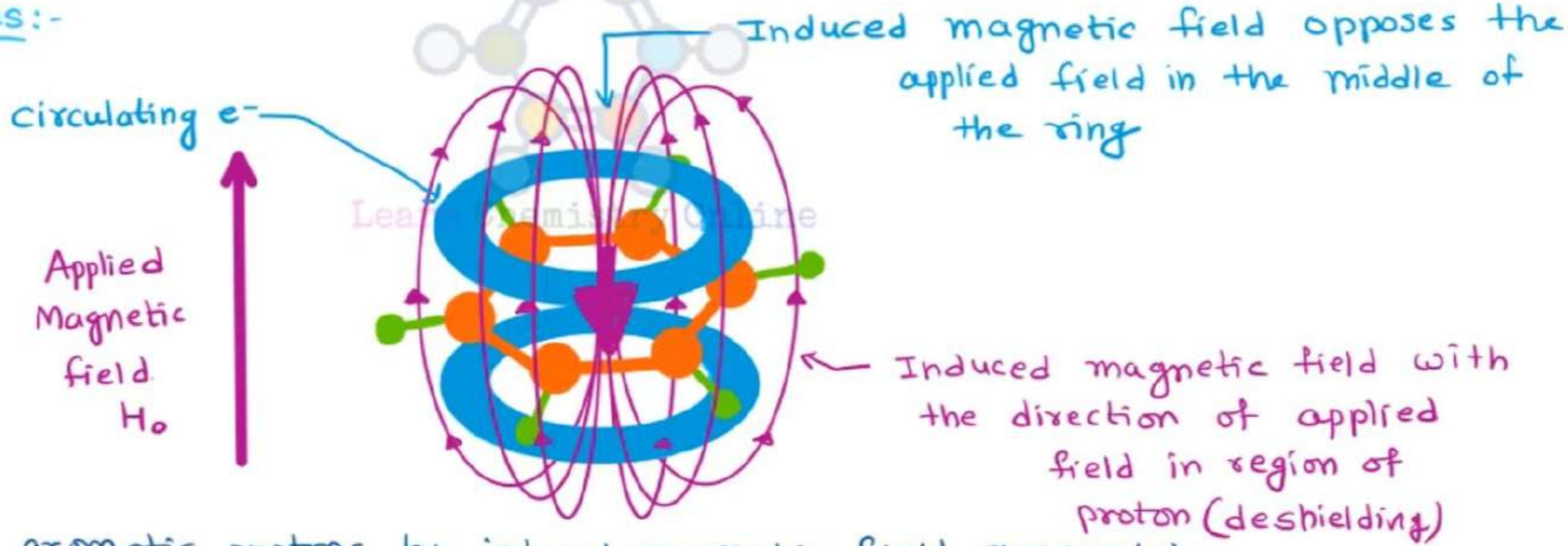


fig:- Deshielding of aromatic protons by induced magnetic field generated by circulating π e⁻ of benzene

- The π e- in benzene molecule are delocalised. when a molecule of benzene is placed under the influence of applied magnetic field, it orients itself perpendicular to the applied field and circulating e- generate induced magnetic field, which is para-magnetic in the region of protons and diamagnetic in the centre of ring.

ⓓ Alkynes:- ✓

- when a molecule of acetylene is placed under the influence of applied magnetic field it orients itself in such a way that molecular axis is parallel to the applied magnetic field.
- The π e- circulating in the plane orthogonal to the applied field, generate the induced magnetic field which opposes the applied field in the region of proton thus causing shielding effect on them.
- The molecule of acetylene also oriented itself at 90° to the applied field the protons would have been deshielded. but the probability of this orientation is almost negligible because π e- are not free to circulate.

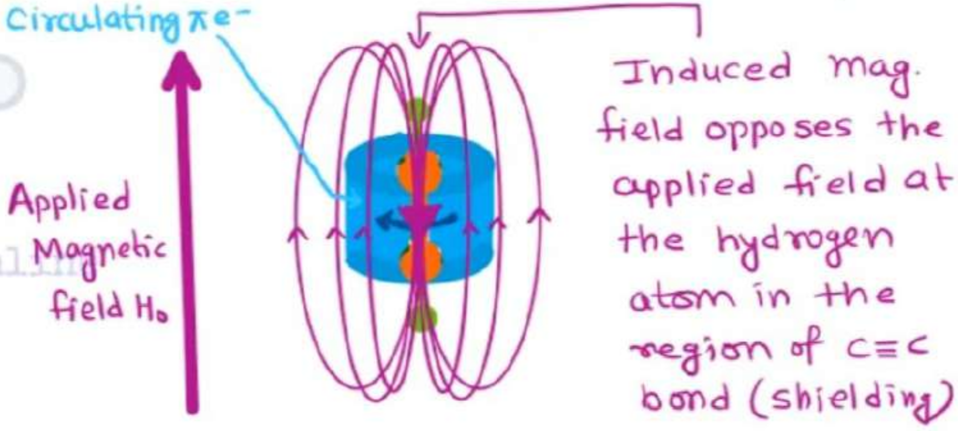


fig:- circulation of π e- of acetylene generates an induced field which opposes the applied field at proton (shielding)

→ Number of signals :→

- Protons having same chemical shift value, i.e. same e- density and same environment, are called chemically equivalent protons or chemical shift equivalent protons.
- All equivalent proton will give the same signal.
- If a molecule has one set of equivalent protons, it will give only one resonance signal.
- In other words, the number of NMR signals will be equal to the number of different types of protons in a compound.
- In some cases, it is easy to decide whether two protons are equivalent or not by just having a look at the formula.

Example

① Acetone :→

$CH_3-\underset{\underset{O}{\|}}{C}-CH_3$

- All six protons are equivalent because each $-CH_3$ group is attached to same group i.e.

$-\underset{\underset{O}{\|}}{C}-CH_3$.

- so this compound gives only one NMR signal.

② <u>Nitroethane</u> :→ $CH_3-CH_2-NO_2$

- The protons of $-CH_3$ group (attached to $-CH_2-NO_2$) are different from those of $-CH_2-$ group (attached to $-CH_3$ and $-NO_2$).
- So this compound gives two NMR signals.

③ Butanone :→

$CH_3-\underset{\underset{O}{\|}}{C}-CH_2-CH_3$

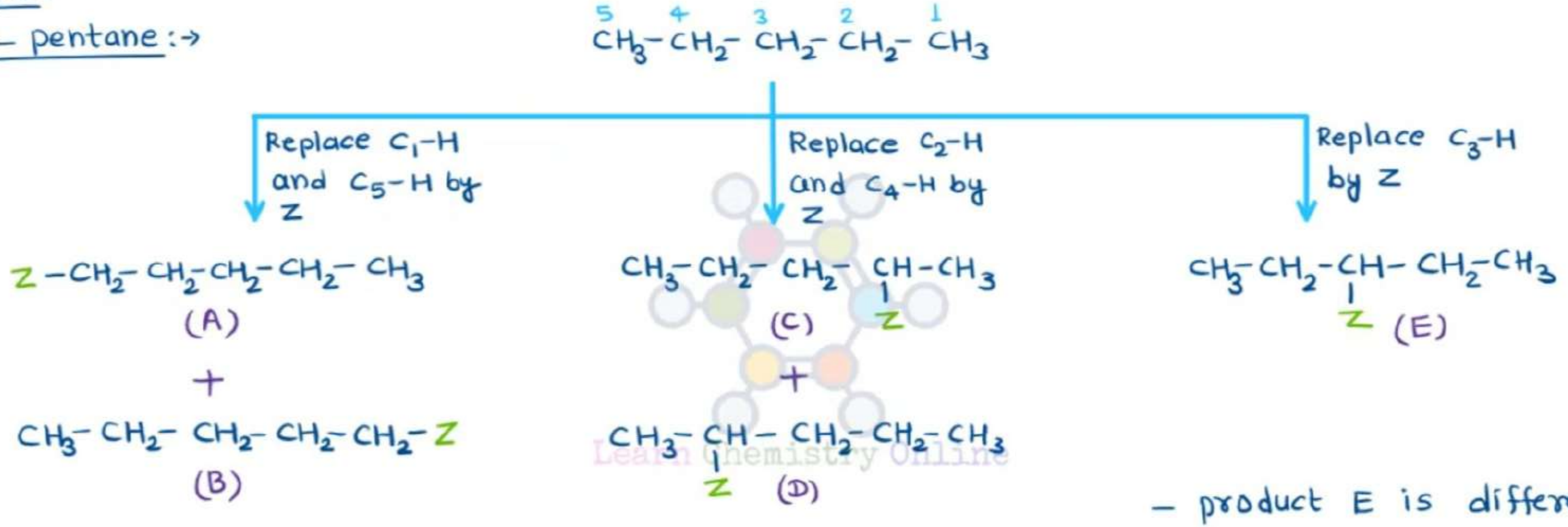
- The protons of $-CH_2-$ are different from those of both $-CH_3$ groups.
- The protons of two $-CH_3$ groups are also different. one is attached to $-CH_2-\underset{\underset{O}{\|}}{C}-CH_3$ and other is attached to $-\underset{\underset{O}{\|}}{C}-CH_2-CH_2$.
- So this compound gives three NMR signals.

- In some cases it is not easy to recognise set of equivalent protons by a simple look at the structure.
- In such cases the procedure of isomer number is used.
- This procedure involve imaginary replacement of each hydrogen atom by a group x.
- If replacement of two protons gives same product or a pair of enatiomers, the two protons are equivalent and will give only one signal.

- If replacement of two protons gives different products or a pair of diastereomers, the protons are non-equivalent and will give two NMR signals.

Example :-

① n- pentane :→



$CH_3-CH_2-CH_2-CH_2-CH_3$

$Z-CH_2-CH_2-CH_2-CH_2-CH_3$ (A) + $CH_3-CH_2-CH_2-CH_2-CH_2-Z$ (B)

$CH_3-CH_2-CH_2-\underset{Z}{CH}-CH_3$ (C) + $CH_3-\underset{Z}{CH}-CH_2-CH_2-CH_3$ (D)

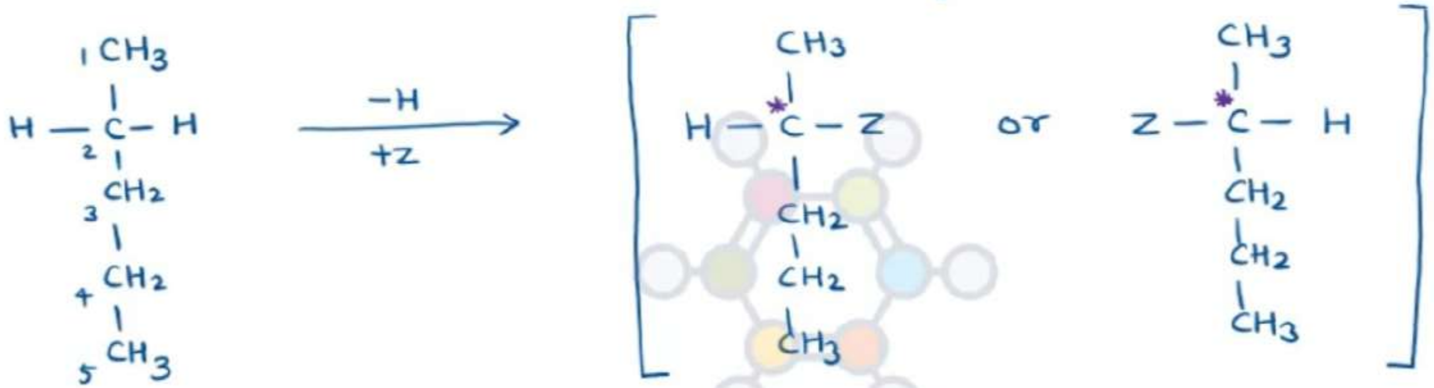
$CH_3-CH_2-\underset{Z}{CH}-CH_2-CH_3$ (E)

- A and B → same product
- hydrogen of both CH_3 groups are equivalent
- one NMR signal

- C and D → Same product
- hydrogen of both $-CH_2-$ groups are equivalent
- one NMR signal

- product E is different from C and D
- hydrogen of this $-CH_2-$ is are equivalent but different from other $-CH_2-$ groups.
- one NMR signal

- Therefore, the protons of n-pentane give three signals (three sets of equivalent protons).
- The replacement of two hydrogens of 2-CH_2 and 4-CH_2 produce a pair of enantiomers. Such protons are called enantiotopic protons. Such protons are magnetically equivalent because of their environments are mirror image of each other.

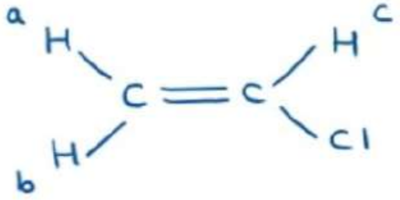


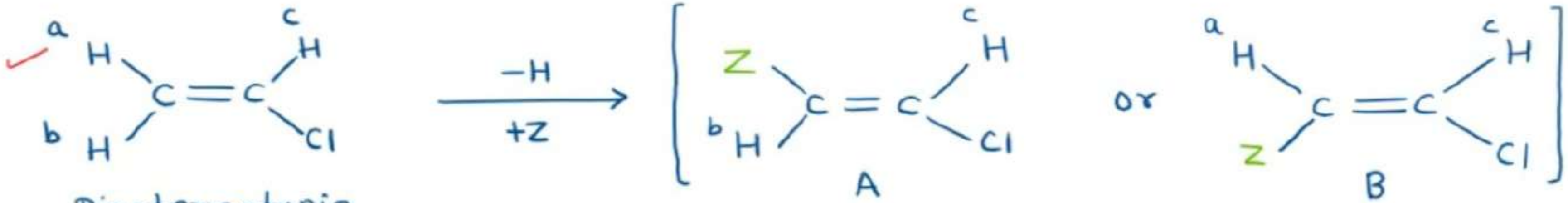
Enantiotropic protons

Enantiotropic products

✯ NMR cannot differentiate enantiotropic protons. becase it is a achiral probe.

② <u>chloroethene</u> :- ($CH_2=CH-Cl$)





Diastereotopic protons

(Three signal)

Diastereomeric products

(The protons H_a and H_b are diastereotopic)

- The environment of H_a and H_b is different and hence they are non-equivalent and hence produce 2 signals.
- So the molecule of chloroethene gives three NMR signals.

→ Intensity of signal and proton counting (Integration) :- / Peak area and proton counting :→

- The intensity of ^{1}HNMR signal represents the size of peak or area under the peak which give useful clue about the number of protons responsible for each of these signals.
- The area under each peak is proportional to the number of protons responsible for the peak.
- The peak area is measured with the help of an automatic electronic integrating device which traces vertically rising lines superimposing on the original spectrum in the form of stepped curves over each signals.
- The hight of these steps are proportional to the areas under the peaks.
- The chart paper of ^{1}HNMR spectrum is cross-hatched. Therefore, the heights of the steps can be easily measured by counting the number of squares.
- The ratios of hights of the steps, in term of number of squares, is the same as that of the number of proton of different types.
- These numbers are converted into smallest whole number by dividing each number with the smallest number and rounding up the fraction to whole numbers by multiplying with the smallest integer.

- If the total number of protons in a molecule (molecular formula) is known we can calculate the number of protons responsible by each signal by the total number of protons in the same ratio as determined above.

Example:- The ^{1}HNMR spectrum of phenylacetone ($C_6H_5-CH_2-\underset{O}{\overset{}{\underset{\|}{C}}}-CH_3$)

- The hight of integral line

$\delta = 7.2 \rightarrow 44.3$ divisions

$\delta = 3.6 \rightarrow 17.5$ divisions

$\delta = 2.1 \rightarrow 26.1$ divisions

Dividing each by smallest number

$$\frac{44.3}{17.5} : \frac{17.5}{17.5} : \frac{26.1}{17.5}$$

$$2.53 : 1.00 : 1.49$$

multiply each by 2 to get simplest whole no.

$$5 : 2 : 3$$

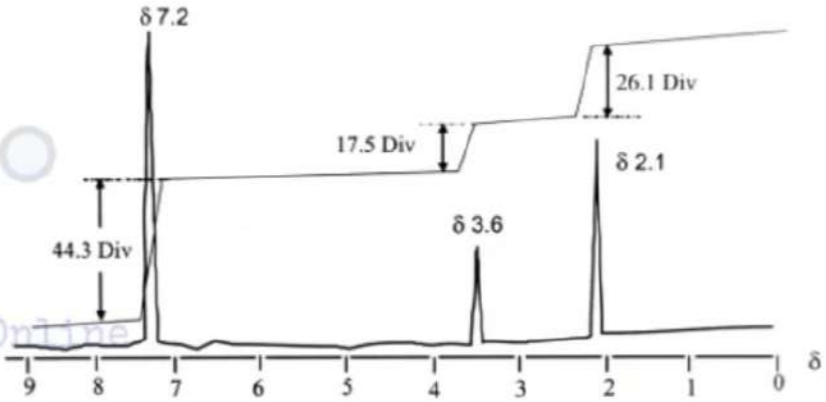


fig:- ^{1}HNMR spectrum of phenylacetone

Looking at the molecular formula $C_9H_{10}O$

(i) five protons resposible for signal at δ 7.2 (C_6H_5) (ii) two protons responsible for signal at δ 3.6 ($-CH_2-CO$)

(iii) three protons responsible for signal at δ 2.1 ($-CO-CH_3$)

→ spin-spin splitting / spin-spin coupling:-

- The analysis of NMR spectrum revealed that the number of peaks in the spectrum of a given compound is equal to the number of different types of protons in it.
- In other words, there will appear one peak (singlet) for each set of equivalent protons.

Example:- NMR spectrum of phenylacetone shows three peakes (three singlet peaks)-

δ 2.2 (3 protons, $-CH_3$)
δ 2.6 (2 protons, $-CH_2-$)
δ 7.2 (5 protons, $-C_6H_5$)

- But this is not true in all the cases. In majority of compounds all the signals do not appear as singlets. They appears as-

two peaks → doublet
three peaks → triplet
four peaks → quartet
five peaks → quintet
six peaks → sextet
seven peaks → septet

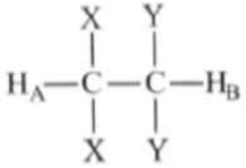
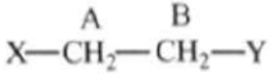
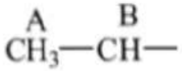
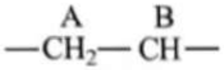
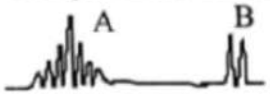
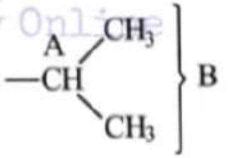
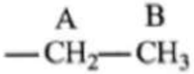
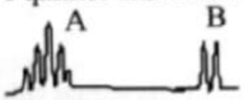
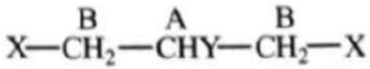
- This example shows that the individual signal which we expect for a set of equivalent protons may not necessarily appear as a single peak but as a group of peaks. This phenomenon is called spin spin splitting.
- spin-spin splitting is defined as the splitting of a signal into a set of peak under the influence of neighbouring non-equivalent protons.
- The pattern of splitting can be explained on the basis of an empirical rule called as n+1 rule.
- According to this rule, if a proton has n protons non-equivalent to it but equivalent among themselves on the same or adjacent carbon atom, its signal is split into n+1 peaks

Example :-

for these protons n=2
their signal splits into
(2+1)= 3 peaks:
a triplet (1:2:1)

Cl_2CH-CH_2Cl

for these protons n=1
their signal splits into
(1+1) = 2 peaks:
a doublet (1:1)

Splitting patterns		**Structural clue**
1. Two doublets of equal intensity		$\mathrm{H_A{-}\overset{X}{\underset{X}{C}}{-}\overset{Y}{\underset{Y}{C}}{-}H_B}$ (X≠Y)
2. Two triplets of equal intensity		$\mathrm{X{-}\overset{A}{CH_2}{-}\overset{B}{CH_2}{-}Y}$ (X≠Y)
3. A doublet and a quartet		$\mathrm{\overset{A}{CH_3}{-}\overset{B}{CH}{-}}$
4. A doublet and a triplet		$\mathrm{{-}\overset{A}{CH_2}{-}\overset{B}{CH}{-}}$
5. A septet and a doublet		
6. A quartet and a triplet		$\mathrm{{-}\overset{A}{CH_2}{-}\overset{B}{CH_3}}$
7. A quintet and a doublet		$\mathrm{X{-}\overset{B}{CH_2}{-}\overset{A}{CHY}{-}\overset{B}{CH_2}{-}X}$

→ Splitting of signals in other cases:→

- If the protons responsible for spin-spin coupling are not in exactly similar environment, the number of lines for a particular multiplet will be equal to

$$(n+1)(n'+1)(n''+1)$$

where $n, n' n''$ = no. of protons in different environments.

Example:- 1,1-dibromo-3,3- dichloropropane

$$Br_2-\overset{a}{CH}-\overset{b}{CH_2}-\overset{c}{CH}-Cl_2$$

In this compound, protons 'a' and 'c' are non-equivalent and thus will, influence the methylene ($-CH_2-$) protons differently.

Thus signal for $-CH_2-$ protons appears as multiplet and consist four lines (quartet)

$(n+1)(n'+1)$ n = no. of protons of type a

$(1+1)(1+1) = 4$ n' = no. of protons of type c

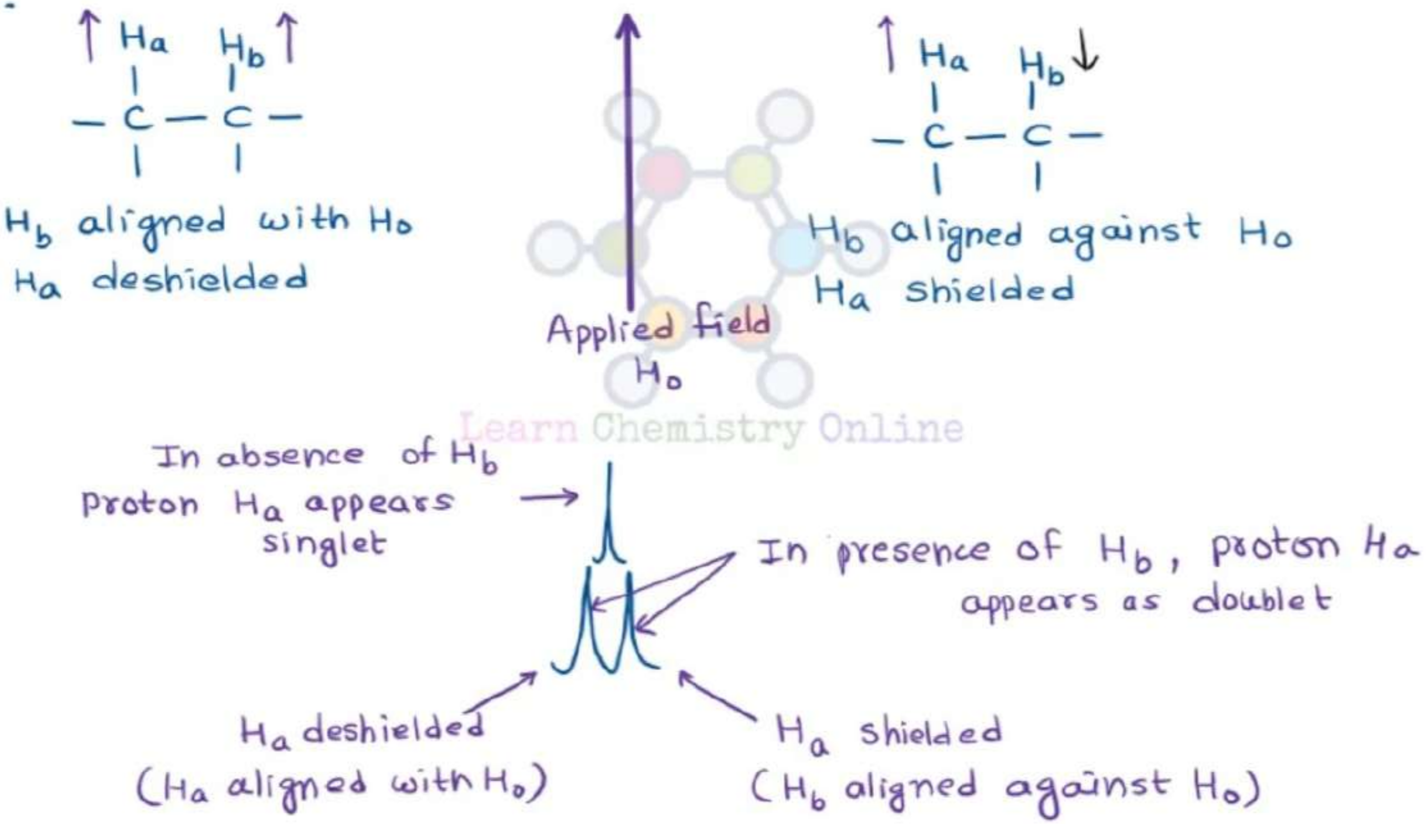
→ Physical basis of spin-spin splitting :→

- The splitting in NMR signals is due to spin-spin coupling or spin-spin splitting between neighbouring non-equivalent protons.
- Protons are behave as tiny bar magnets and generates the local or secondary magnetic field. this local magnetic field influence the magnetic field strength felt by the neighbouring protons.
- consider a molecule having two non-equivalent protons H_a and H_b. since they have different environment, they resonate at different field strength. The signals due to these protons do not appear as singlet. They rather appears as two doublets.
- Such a splitting is due to fact that the chemical environment of a given proton (H_a) depends upon the total magnetic environment, which includes the local environment due to neighbouring proton (H_b)
- The nuclear magnetic moment of H_b can either align with or align against that of H_0 (applied magnetic field). Thus proton H_b can-

ⓐ increase the net field being felt by H_a thus causing deshielding effect. (H_b aligned with)

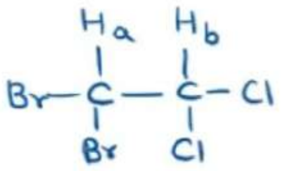
ⓑ decrease the net field being felt by H_a thus causing shielding effect (H_b aligned against)

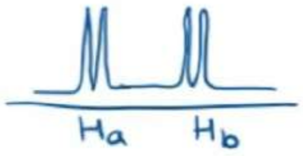
- In fact H_b causes both deshielding and shielding simultaneously. In solution one half of the molecules of H_b causes deshielding of H_a and other half causes shielding of H_a. As a result this H_a resonates twice and give rise to two signals (doublet) one downfield and one upfield compared to the position of signal in the absense of H_b(singlet).



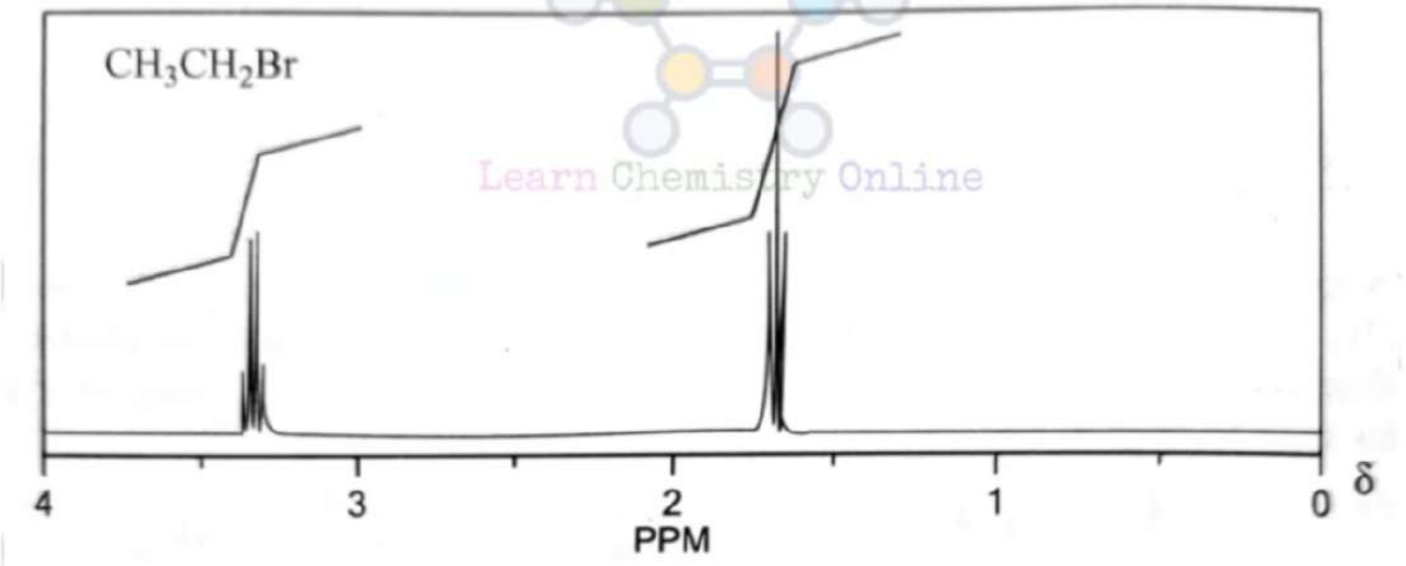
- for similar reasons, the signal of H_b is also split into a doublet by H_a.

Example:- ① NMR spectrum of 1,1- dibromo-2,2- dichloromethane





② NMR spectra of ethylbromide

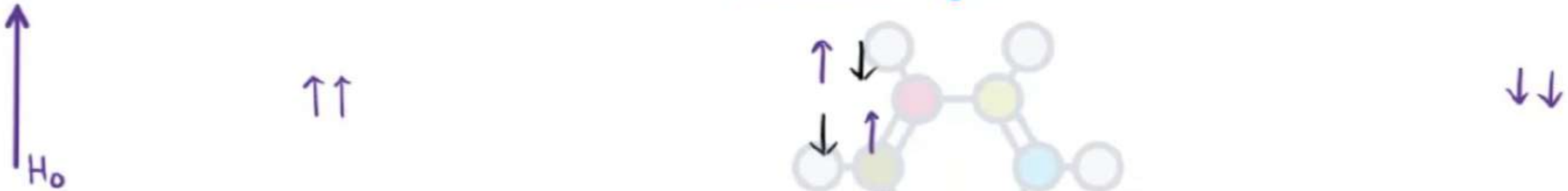


- The cause of splitting

ⓐ Appearance of a triplet for methyl protons :-

- The two protons of $-CH_2-$ can have four equally probable spin alignments as shown below -

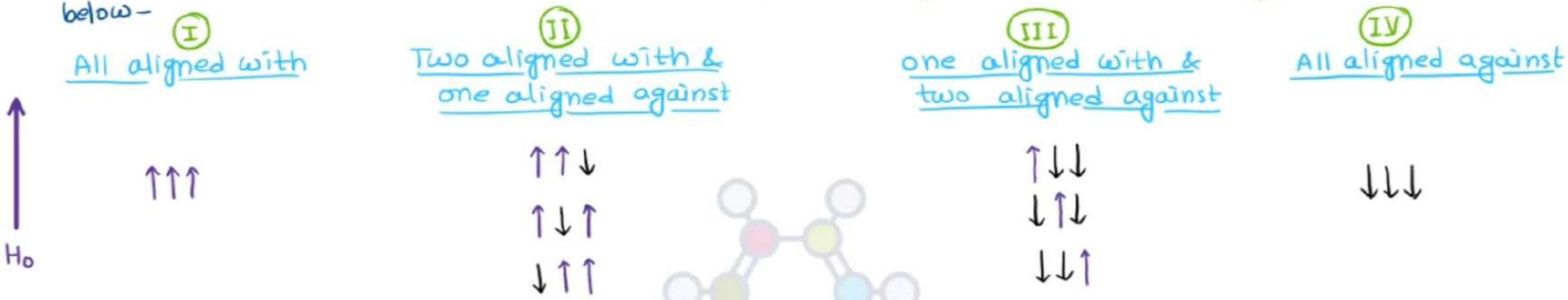
Both aligned with | one aligned with and another against | Both aligned against



- two middle alignments are equivalent. Thus there are three different spin states which influence the chemical shift of CH_3 thereby splitting its signal into a triplet.
- the probability of first and third spin is equal but that of second is twice, so the relative intesities of the three peaks will be 1:2:1

ⓑ Appearance of a quartet for methylene protons:→

- The three protons of $-CH_3$ can have eight equally probable spin alignments as shown below-



- Three combinations of set II and set III are equivalent. Thus there are four effective spin states, with statistical probability 1:3:3:1, which affect the chemical shift of $-CH_2-$ whose signal is split into a quartet with relative peak intensity of 1:3:3:1

→ The relative intensities of peak :→

- The relative intensities of the various peaks of multiplet can be calculated using the binominal expansion, $(a+b)^n$. where n = number of vicinal protons

for $n=1$, $(a+b)^1 = a+b$, the relative intensities of a line of a doublet are 1:1
for $n=2$, $(a+b)^2 = a^2+2ab+b^2$, " " " " " " triplet are 1:2:1
for $n=3$ $(a+b)^3 = a^3+3a^2b+3ab^2+b^3$ " " " " " " quartet are 1:3:3:1

- These relative intensities can also be determined by Pascal triangle in which each entry is the sum of two entries above on the left and other on the right

Singlet	1
Doublet	1 : 1
Triplet	1 : 2 : 1
Quartet	1 : 3 : 3 : 1
Quintet	1 : 4 : 6 : 4 : 1
Sextet	1 : 5 : 10 : 10 : 5 : 1
Septet	1 : 6 : 15 : 20 : 15 : 6 : 1

→ Coupling constant :→

- The distance between two adjacent peaks of a multiplet is called coupling constant.
- It is denoted by J.
- It is measured in Hz or cps (cycle per second).
- It generally ranges between 0-18 Hz.
- Unlike chemical shift, The value of J is constant for a particular arrangement of protons. Thus when the NMR spectra of the same compound are scanned at different field strength, the chemical shift (in Hz) will be different but, coupling constant will be the same.
- Example:- CH_3-CH_2-Br contains two sets of non-equivalent protons, these both sets have same value of coupling constant.

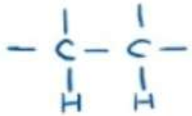
    The protons of $-CH_2-Br$ are coupled with $-CH_3$ protons and appears as quartet at J = 7.0 Hz

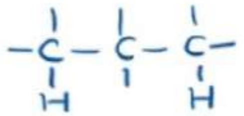
    Similarly the protons of $-CH_3$ coupled with $-CH_2-Br$ protons and appears as triplet at J = 7.0 Hz

- This relationship of coupling constant is quite useful in telling that protons of which two sets are coupled with each other.
- This is a very useful structural information provided by coupling constant.

- Usually a shorthand notation is used to express the coupling constant depending upon the number of intervening covalent bonds between the coupling nuclei.

$^2J_{H,H}$, represents geminal protons , 2 means two intervening covalent bonds, 

$^3J_{H,H}$, represents vicinal protons , 3 means three interening covalent bonds, 
$-\underset{H}{\overset{|}{C}}-\underset{H}{\overset{|}{C}}-$

$^4J_{H,H}$, coupling in system, 4 means four intervening covalent bonds, 
$-\underset{H}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-\underset{H}{\overset{|}{C}}-$

- Magnitude of coupling constant $\propto \dfrac{1}{\text{No. of intervening covalent bonds}}$

- Magnitude of coupling constant is almost negligible if more than three bonds intervene between the coupling protons. Thus $^3J_{H,H}$ is obsered, whereas $^4J_{H,H}$ is not observed.
- In addition to number of intervening bonds, the magnitude of coupling constant also depends upon the dihedral angle (α) between planes of two σ C–H bonds.

if α is 0° or 180° → J is maximum
α is 90° → J is minimum

- The relationship between coupling constant and dihedral angle is given in the form of Karplus curve.

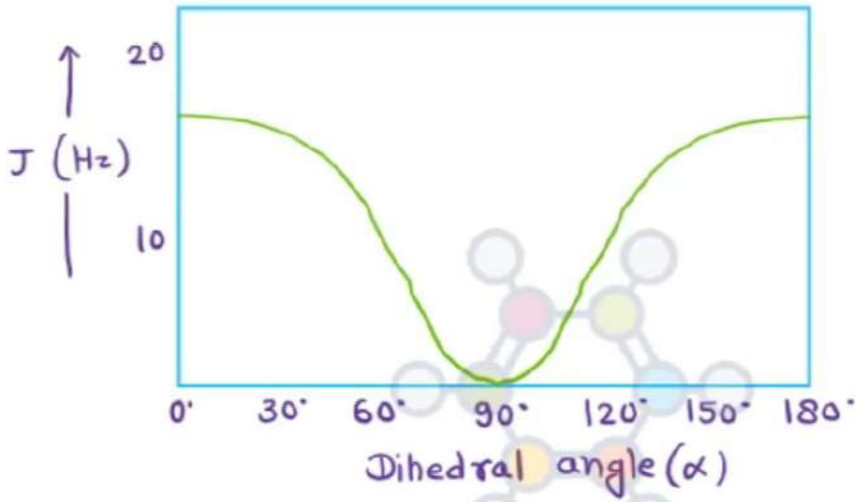
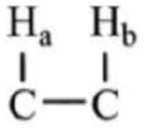
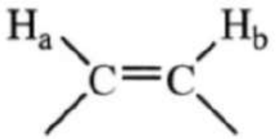
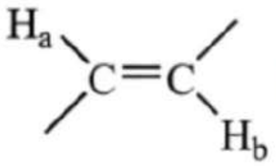
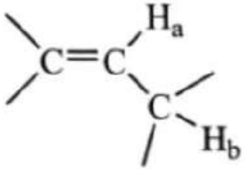
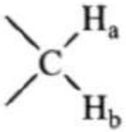
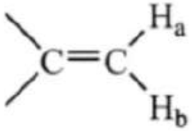
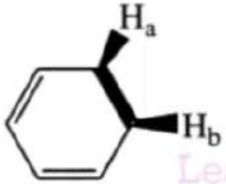
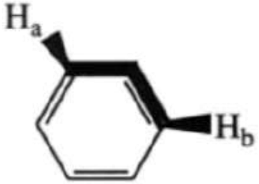


fig:- Karplus curve

-The coupling constants of some typical structural units are give in following table-

S. No.	Structural Unit	Designation	Value
1.	 $\overset{H_a}{\underset{\mid}{C}}-\overset{H_b}{\underset{\mid}{C}}$	$^{3}J_{H,H}$, vicinal	6 – 8 Hz
2.		$^{3}J_{H,H}$, vicinal, *cis*	7 – 11 Hz
3.		$^{3}J_{H,H}$, vicinal, *trans*	13 – 18 Hz

4.		$^3J_{H,H}$, vicinal, *allylic*	4 – 10 Hz
5.	(a) 	$^2J_{H,H}$, geminal	0 – 20 Hz
	(b) 	$^2J_{H,H}$, geminal	0 – 7 Hz
6.		$^3J_{H,H}$, *ortho*	6 – 10 Hz (usually 9 Hz)
7.		$^4J_{H,H}$, ω coupling, *meta*	1 – 4 Hz (usually 2.5 Hz)
8.		$^5J_{H,H}$, *para*	0 – 1 Hz (usually not seen)

→ Chemical exchange or proton exchange reaction :→

① The –OH group :→

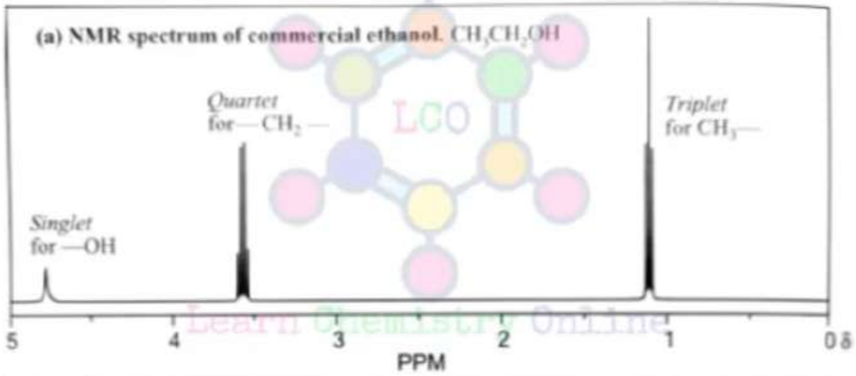
- When the NMR spectrum of commercial sample of an alcohol is scanned in $CHCl_3$ or CCl_4 solution, the signal due to –OH appears as singlet.
- In other words it does not show any coupling with the adjacent protons. because in commercial alcohol the protons of –OH groups of different molecules undergo chemical exchange at a rate of 10^5 protons per second. (10^{-5} second for a proton to move to other molecule.)
- This rate of exchange is too rapid as compared to intrument (10^{-2} to 10^{-3} s). so the instrument records an average situation in which the coupling with adjacent proton is not visible.

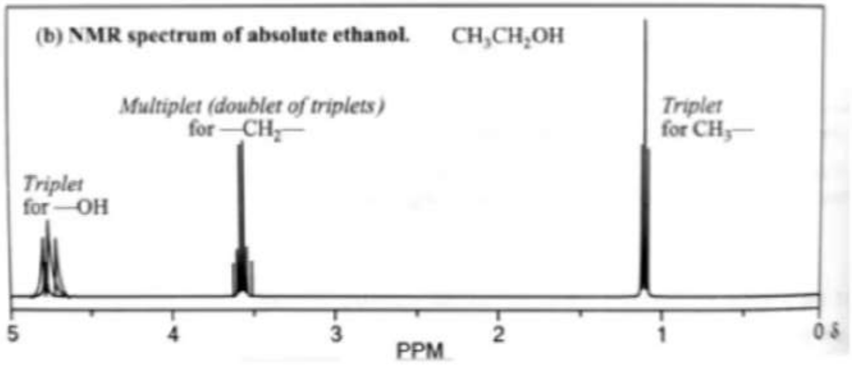
$$R-O-H + R-O-H \underset{}{\overset{10^{-5}s}{\rightleftharpoons}} R-O-H + R-O-H$$

(The exchange is much faster than NMR time scale of 10^{-2} – 10^{-3} s)

- Reason of proton exchange :→
- Commercial alcohol contains acidic impurity which catalyses the exchange reaction thereby enhancing the exchange rate.

- In case of pure alcohol or solution in dimethyl sulphoxide, the -OH proton appears as triplet in primary alcohol and as a doublet in secondary alcohol.
- This is due to the fact that in both cases the exchange process is slowed. i.e.
  ⓐ in case of pure liquid the acid catalyst is absent.
  ⓑ in dimethyl sulphoxide the formation of complex is takes place.
- In such cases the -OH showing coupling with adjacent protons with J = 4-7 Hz.


(a) NMR spectrum of commercial ethanol. CH_3CH_2OH


(b) NMR spectrum of absolute ethanol. CH_3CH_2OH

② The –S–H group :→

- In case of proton attached to sulphur, the exchange rate is much slower (compare to –OH) and falls within the NMR scale. hence it shows coupling with neighbouring protons with J ≃ 8 Hz.

③ The –N–H group :→

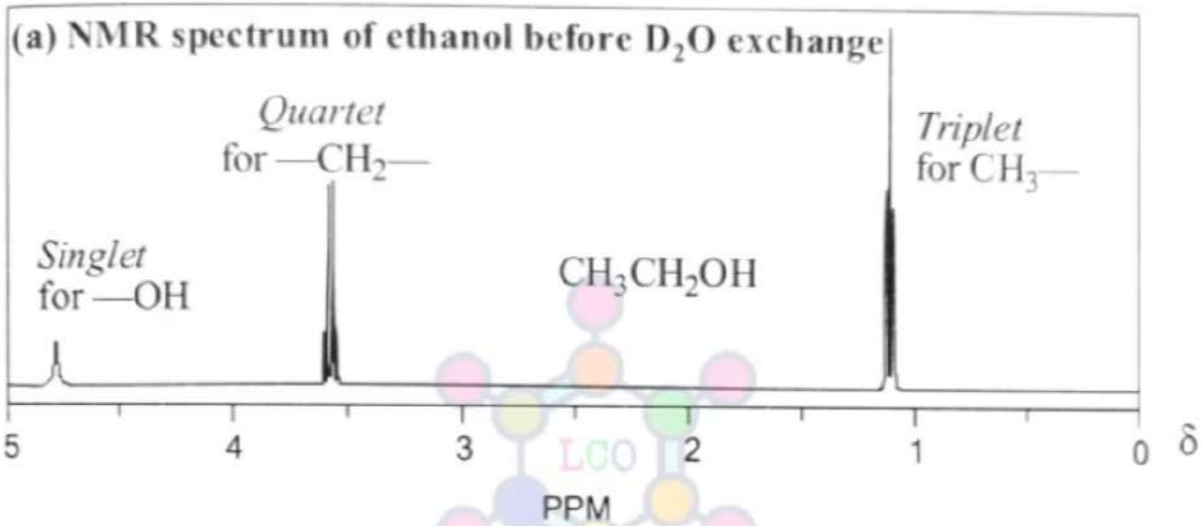
- Like –OH in this case also the exchange rate is much rapid compared to NMR time scale. Hence no coupling with adjacent protons is seen.

→ Duetrium exchange :→

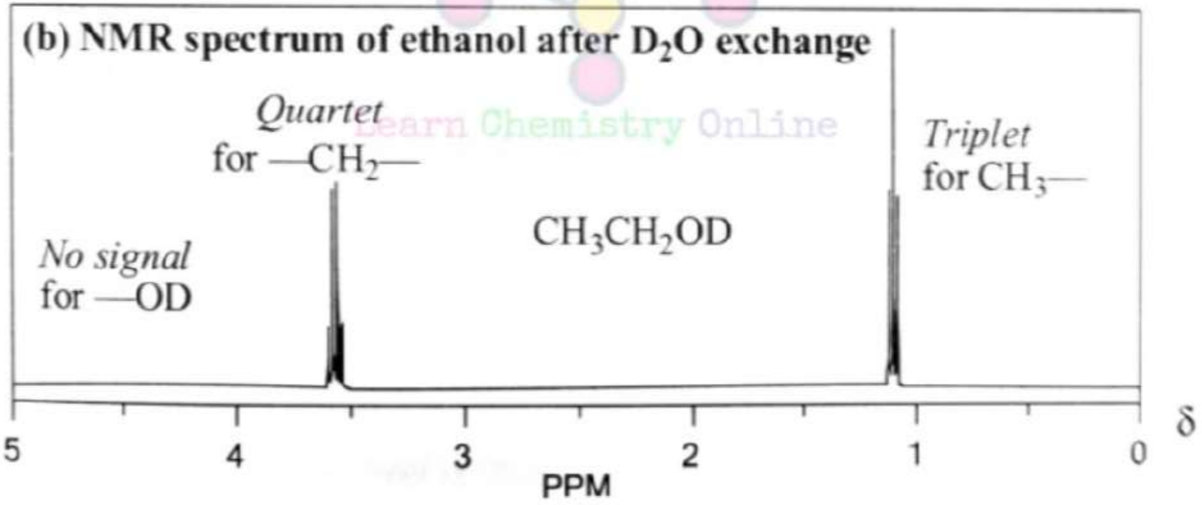
- In a number of cases the position of signal due to –X–H proton are variable. The easiest way to locate these proton is to rescan the spectrum after shaking the sample with 2 drops of D_2O.
- By doing so the signal of such a proton disappears due to deuterium exchange. because D is NMR inactive at the frequency of proton absorption.

$$R-X-H + D_2O \longrightarrow R-X-D + HOD$$ X = Electronegtive element

- The NMR spectra of ethanol before and after D_2O shaking are as follows -



(a) NMR spectrum of ethanol before D_2O exchange



(b) NMR spectrum of ethanol after D_2O exchange

→ Interpretation of NMR spectra :→

- NMR spectrum of compound provide very important about its molecular structure. This information is gathered as follows:-

① The Number of signal represents many kinds of protons in different chemical environments present in the molecule.

② The position of signal represents the electronic environment of each type of proton.

③ The intensities of signal represents the relative number of protons of different kinds.

④ The splitting of signal represents the environment of absorbing proton with respect to the environment of the neighbouring protons.

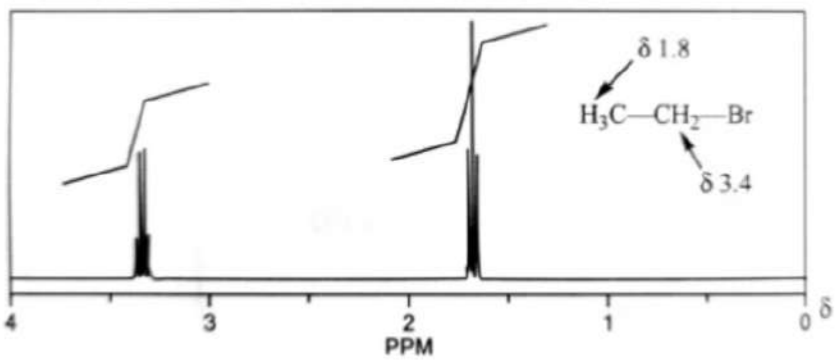


fig:- NMR spectrum of Ethyl brom[illegible]e

→ Limitations of NMR spectroscopy :->

① NMR cannot be used to distinguish between the enatiomers.

② The sample should be in liquid state, i.e. either pur liquid or the solution of the substance in the suitable solvent.

③ The instrument is quite costly.

④ Interpretation of the complex spectra is often a very boring job.

→ NMR spectra of some simple compound :→

① Ethyl bromide CH_3-CH_2-Br

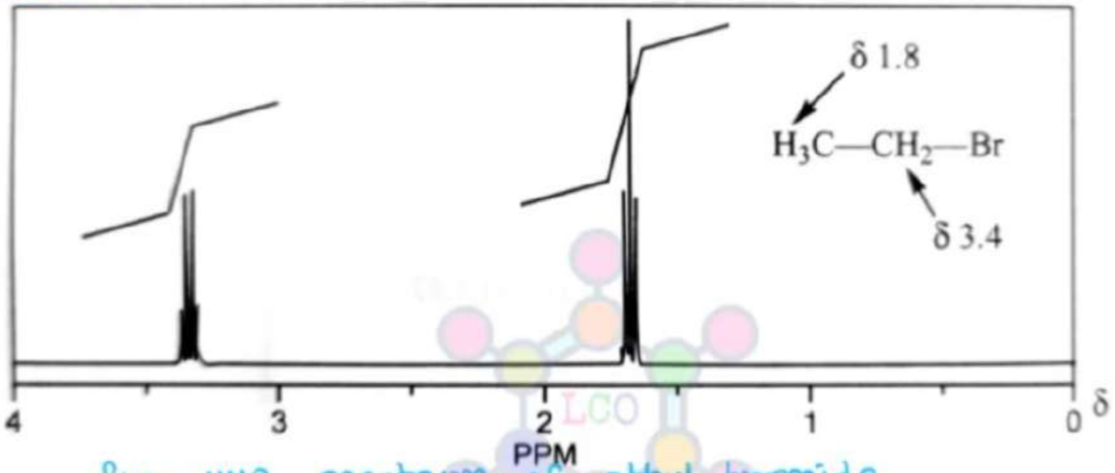


fig:- NMR spectrum of ethyl bromide

- A look at the spectrum of CH_3-CH_2-Br reveals the following signals.

  ⓐ A 3H triplet (1:2:1) centered at δ 1·80 , J = 7·0 Hz

  ⓑ A 2H quartet (1:2:2:1) Centered at δ 3·40 , J = 7·0 Hz

- Explanation :→

  ⓐ The 3H Triplet centered at δ 1·80 is due to three magnetically equivalent methyl protons which are coupled with two methylene protons. (CH_3-CH_2-)

ⓑ The 2H quartet centered at δ 3.40 is due to two magnetically equivalent protons of a methylene group which are coupled with three methyl protons (CH_3-CH_2-)

ⓒ Integration reveals that the integral ratio of two signal is 3:2 (upfield : downfield). as the molecule has only 5 protons, the upfield signal is due to 3 protons and down field signal is due to 2 protons.

ⓓ As the coupling constant of the two multiplets is the same (7.0 Hz), therefore, the CH_3 and CH_2 protons are coupled with each other.

② 1,1,2-tribromoethane $Br-CH_2-CH-Br_2$:→

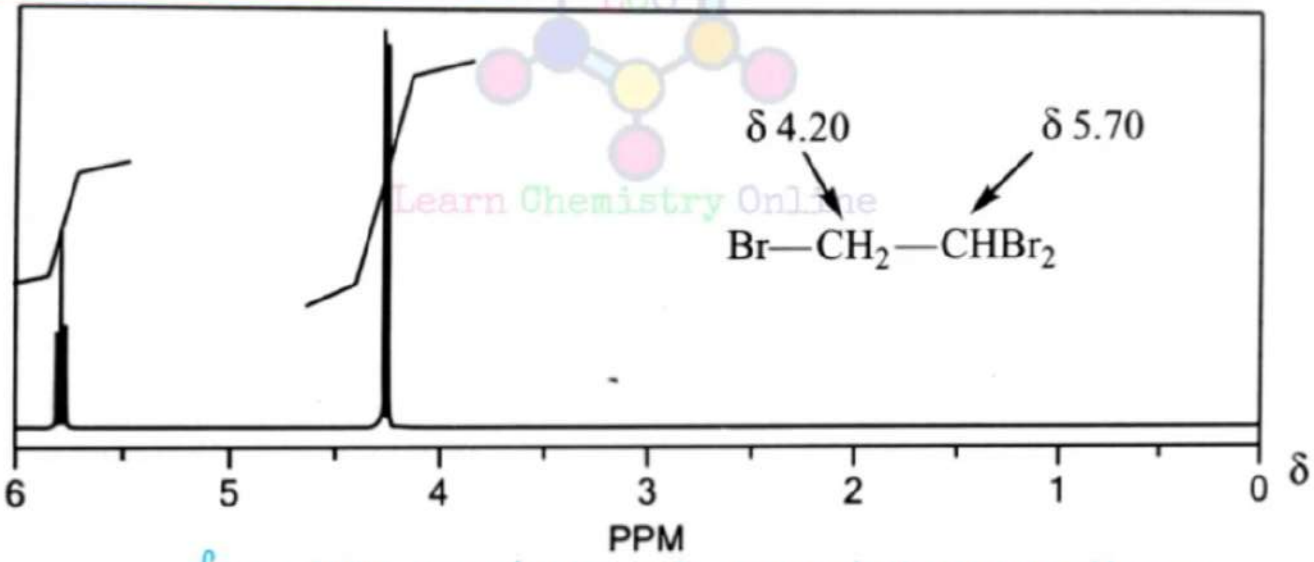


fig:- NMR spectrum of 1,1,2-tribromomethane

- A look at the spectrum reveals the following signals:-

ⓐ A 2H doublet (1:1) centered δ 4.20, J = 7.0 Hz

ⓑ A 1H Triplet (1:2:1) centered δ 5.70, J = 7.0 Hz

Explanation:→

ⓐ The 2H doublet centered at δ 4.20 is due to two equivalent methylene protons which are coupled with one methine proton. ($-CH_2-CH-$)

ⓑ The 1H triplet centered at δ 5.70 is due to one methine proton which is coupled with two methylene protons. ($-CH_2-CH-$)

ⓒ Integration reveals that integral ratio of two signal is 2:1 (upfield : downfield). As the molecule has only three protons, the upfield signal is due to two methylene protons and the downfield signal is due to one methine proton.

ⓓ The same coupling constant of two multiplets (7.0 Hz) further proves that CH_2 and CH protons are coupled with each other.

→ NMR spectra of some simple compounds :→

① Toluene $C_6H_5-CH_3$:→

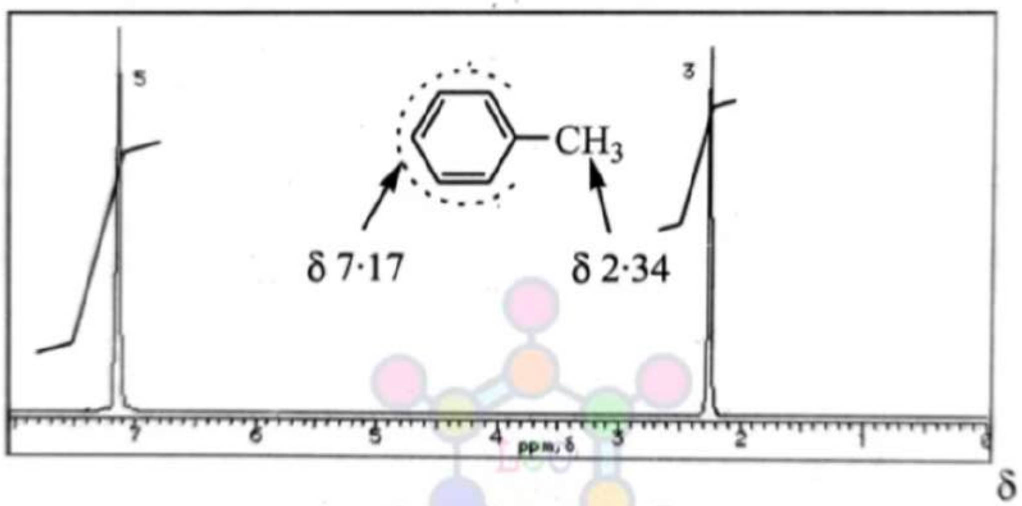


fig:- NMR spectrum of Toluene

A look at the spectrum reveals the following signals :-

ⓐ A 3H singlet at δ 2·34

ⓑ A 5H singlet at δ 7·17

Explanation:→

ⓐ The 3H singlet at δ 2·34 is due to methyl group attached to aromatic ring ($Ar-CH_3$)

ⓑ The 5H singlet at δ7·17 is due to five protons of phenyl group ($C_6H_5-CH_3$)

- In case of high resolution instrument the five aromatic protons show a complex splitting pattern showing up as a multiplet.

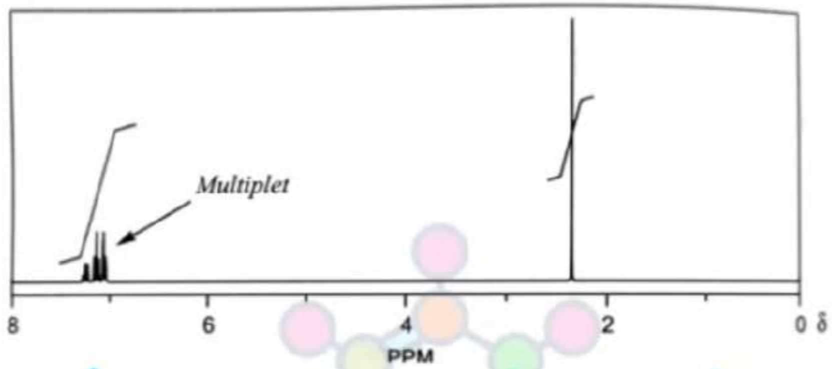


fig:- NMR spectrum of Toluene (High resolution)

② Acetophenone  $C_6H_5-\underset{O}{\underset{\|}{C}}-CH_3$

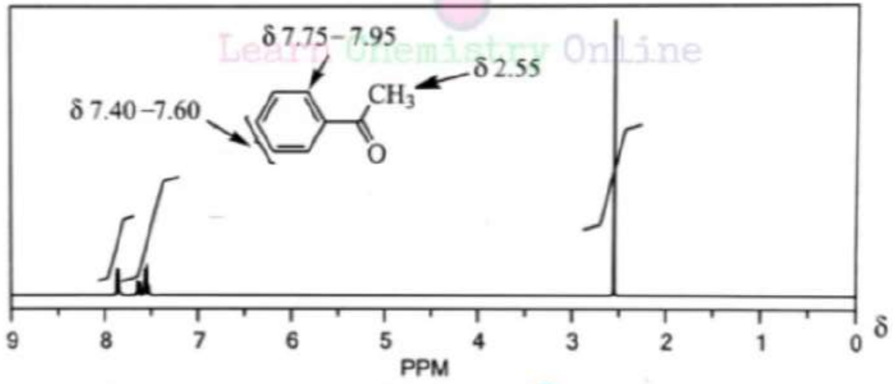
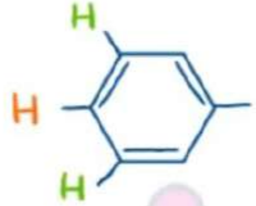


fig:- NMR spectrum of acetophenone

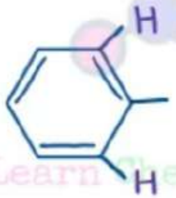
A look of the spectrum reveals the following signals :-

ⓐ A 3H singlet at δ 2.55 is due to methyl protons of acetyl group (CH_3-CO)

ⓑ The 3H multiplet at δ 7.40 – 7.60 is due to two meta and one para proton of benzene ring.



ⓒ The 2H multiplet at δ 7.75 - 7.95 is due to two ortho protons of benzene ring.



✱ The excessive downfield shift of ortho protons is attributed to additional anisotropy of the carbonyl group i.e. the ortho protons fall in the deshielding zone of the carbonyl group.

→ NMR spectra of some simple compounds :→

① Acetaldehyde CH_3-CHO

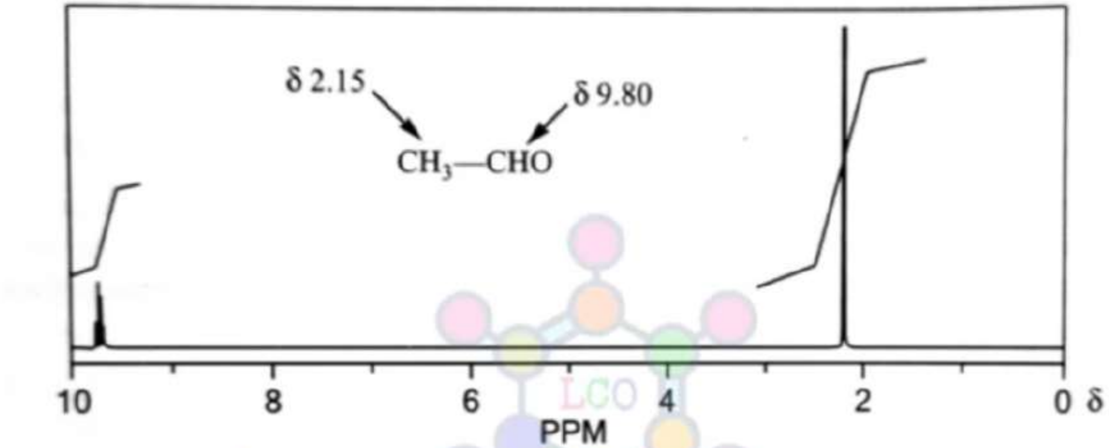


fig:- NMR spectrum of Acetaldehyde

A look at the spectrum reveals the following signals :→

ⓐ A 3H doublet (1:1) centered at δ 2·15 , J = 2·8 Hz

ⓑ A 1H quartet (1:3:3:1) centered at δ 9·80 , J = 2·8 Hz

Explanation :→

ⓐ The 3H doublet centered at δ 2·15 is due to three magnetically equivalent protons of CH_3 group which are coupled with methine proton of $-CHO$ group (CH_3-CHO). The position of signal at δ 2·15 also shows presence of CH_3-CO moiety.

ⓑ The 1H quartet centered at δ 9·80 is due to methine proton of aldehyde group, which is coupled with methyl protons (CH_3-CHO)

The typical position of (δ 9·80) of proton clearly indicate the presence of $-CHO$ group.

② Ethyl acetate 

$CH_3-\underset{\underset{O}{\|}}{C}-O-CH_2-CH_3$

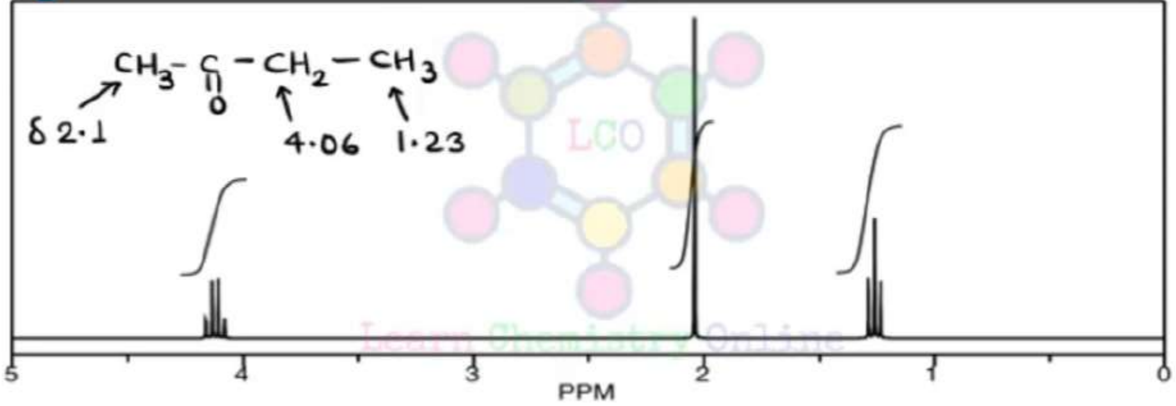


fig:- NMR spectrum of Ethyl acetate

A look at the spectrum reveals the following signals:-

ⓐ A 3H singlet centered at δ 2·1

ⓑ A 3H Triplet centered at δ 1·23 J = 7·0 Hz

ⓒ A 2H quartet centered at δ 4·06 J = 7·0 Hz

Explanation :→

ⓐ A 3H singlet at δ 2.1 due to methyl protons of methyl group ($CH_3-\underset{\underset{O}{\|}}{C}-O-CH_2-CH_3$)

ⓑ A 3H Triplet at δ 1.23 due to methyl protons of methyl group ($CH_3-\underset{\underset{O}{\|}}{C}-O-CH_2-CH_3$) which are coupled with two methylene protons.

ⓒ A 2H quartet at δ 4.06 due to methylene protons ($CH_3-\underset{\underset{O}{\|}}{C}-O-CH_2-CH_3$) which are coupled with three methyl protons.

→ NMR spectra of some simple compounds :→

① Ethanol C_2H_5-OH

ⓐ commerical alcohol :→

- In case of commercial alcohol, the signal due to −OH appears as singlet. It is due to phenomenon of chemical exchange or proton exchange.

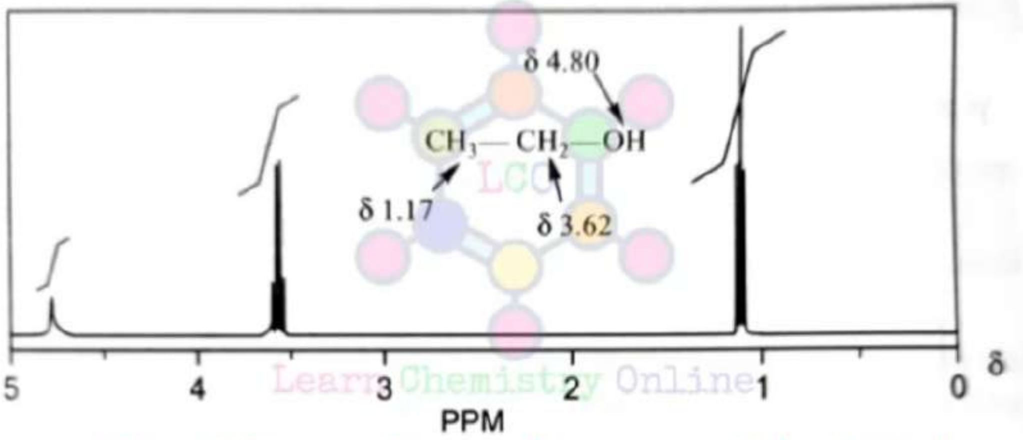


fig:- NMR spectrum of commercial alcohol

A look at the spectrum of commercial alcohol reveals the following signals.

ⓐ A 3H Triplet (1:2:1) centered at δ 1.17, J = 7.0 Hz

ⓑ A 2H quartet (1:3:3:1) centered at δ 3.62, J = 7.0 Hz

ⓒ A 1H singlet centered at δ 4.80

Explanation:->

ⓐ + ⓑ The 3H triplet centered at δ1.17 and the 2H quartet centered at δ 3.62 both having the same coupling constant (7.0 Hz) clearly proves the presence of an ethyl group (CH_3-CH_2-)

ⓒ The downfield singlet at δ4.80 is due to −OH proton.

ⓑ Absolute alcohol or pure alcohol:->

- In case of pure alcohol, the signal due to −OH proton appears as triplet. it is due to slow chemical exchange or proton exchange reaction.

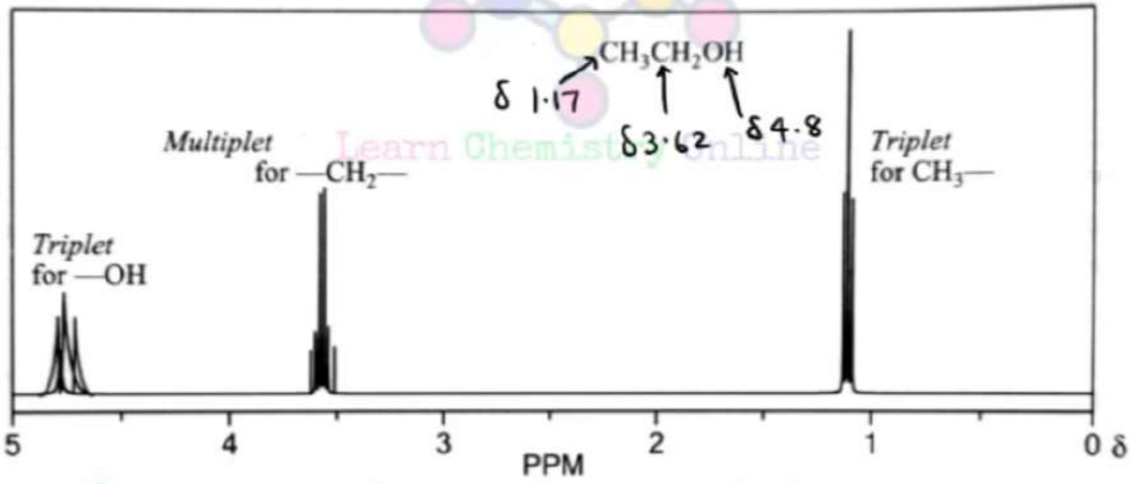


fig. NMR spectrum of pure alcohol

A look at the spectrum of pure alcohol reveals the following signals -

ⓐ A 3H triplet (1:2:1) centered at δ 1.17

ⓑ A 2H multiplet centered at δ 3.62

ⓒ A 1H triplet centered at δ 4.80

Explanation:→

ⓐ A 3H triplet centered at δ 1.17 is due to three methyl protons (CH_3-CH_2-) which are coupled with two methylene protons.

ⓑ A 2H multiplet centered at δ 3.62 is due to two methylene protons (CH_3-CH_2-) which are coupled with three methyl proton and one proton of -OH group.

ⓒ A 1H Triplet centered at δ 4.80 is due to -OH proton which is coupled with two methylene protons.

→ Applications of NMR Spectroscopy :→

1 Identification of an unknown compound:→

- Like fingerprit region of the IR spectra, the NMR spectrum can also be used as a fingerprint of a compound.
- In other words, if NMR spectrum of unknown compound is superimposable on the NMR spectrum of compound of known structure then the unknown must be identical with the known substance. i.e. it must have the same structure as that of the known.

2. Determination of structure:→

- The characteristic pattern of splitting (doublet, triplet, quartet etc.) alongwith their coupling constant and integral ratio clearly tell us which protons are coupled with which, thereby helping us in establishing the structure.

3. Distinction between geometric isomers:→

- NMR spectroscopy is quite useful in distinguishing between cis- and trans- isomers on the basis of the values of coupling constant. For cis- J=7-11 Hz and for trans J=13-18 Hz.

4. Identification of reaction compounds:-

- If in a reaction two or more isomeric products are possible, the NMR spectroscopy can be used to identify the actual products.
- These products can be easily distinguished on the basis of their NMR spectra.

5. Distinction between inter and intramolecular hydrogen bond:-

- If chemical shift value or δ value of a proton shifts upfield on dilution then hydrogen bonding is intermolecular hydrogen bonding and if δ value remains unchanged on dilution then hydrogen bonding is intramolecular hydrogen bonding.

6. Determination of relative amounts of tautomers:-

- Quantitative determination of percentage of keto and enol forms in the equilibrium mixture can be easily done using NMR spectroscopy.
- The NMR spectra of such molecules exhibit different signals due to $-CH_2-$ protons of keto form and $-CH=$ proton of enol form.
- By comparing area under these signal (integral areas), the percentage of keto and enol forms can be easily calculated using following formulas.

$$\boxed{\text{Percentage of keto form} = \frac{K}{K+E} \times 100} \qquad \boxed{\text{Percentage of enol form} = \frac{E}{K+E} \times 100}$$

here K = Integral area of $-CH_2-$ protons of keto form

E = Integral area of $-CH=$ protons of enol form

→ Problems pertaining to the structure elucidation of some simple organic compounds using UV, IR and NMR spectroscopic techniques:-

Problem ① - An organic compound with molecular formula C_4H_8O shows the following spectral data :

UV : 275 nm ε_{max} 17

IR : 2941-2857 (m), 1715 (s) and 1460 cm^{-1} (m).

NMR : (i) Quartet 2.48 δ (2H)
(ii) Singlet 2.12 δ (3H)
(iii) Triplet 1.07 δ (3H)

Determine the structure of the compound.

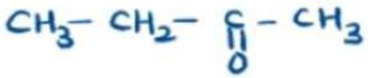
Solution:-

(i) The absorption at 275 nm ε_{max} 17 is a characterstic of carbonyl group due to $n-\pi^*$ transition.

(ii) 2941 -2857 (m) is due to C-H stretching, 1715 (s) is due to saturated ketonic group, 1460 (m) is due to C-H bending.

(iii) NMR spectra reveals three types of protons
- Presence of triplet at 1.07 δ and quartet at 2.48 δ is characteristic of CH_3-CH_2-
- Singlet at 2.12 δ is due to $-CH_3$ group adjacent to carbonyl carbon.

- Hence the probable structure of compound is



$CH_3-CH_2-\underset{\underset{O}{\|}}{C}-CH_3$ 2-butanone

Problem ② - An organic compound with molecular formula C_4H_8 shows the following spectral data :

UV : Transparent above 210 nm

IR : 3022(m), 1676(m) and 965 cm^{-1} (s)

NMR : (i) Quartet 5.55 δ (1H)
(ii) Doublet 1.60 δ (3H)

Determine the structure of the compound.

Solution:-

(i) Since the UV spectrum is transparent above 210 nm, it shows the absence of conjugation and carbonyl group.

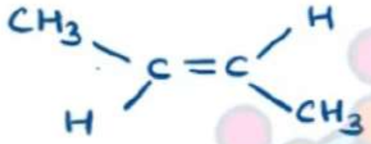
(ii) IR, 3022 (m) is due to C-H stretching. Since carbonyl group is absent, the band at 1676 cm^{-1} (m) may be due to C=C stretching. Thus the compound must be unsaturated.

(iii) NMR, Doublet at 1.60 δ is due to methyl group $-CH_3$
Quartet at 5.55 δ is due to one proton of $-CH=$ group
Both signals are due to $CH_3-CH=$ group.

- The molecular formula (C_4H_8) of the compound is just double of $CH_3-CH=$ group (C_2H_4). hence the structure of compound is

$$CH_3-CH=CH-CH_3$$

- IR band at 965 cm⁻¹ is characteristic of trans alkene. Thus the exact structure of the compound is


Trans 2-butene

Problem-③ – A compound with molecular mass 69 is transparent above 200 nm. The absorption bands in infra-red spectrum are (i) 2941 cm⁻¹ (m) (ii) 2273 cm⁻¹ (m) and (iii) 1460 cm⁻¹ (m). In NMR, two signals are formed. one is septet at 2.72 δ (J = 6.7 cps, 4.2 squares) and another is doublet at 1.33 δ (J = 6.7 cps, 25.8 square).

Solution:-

(i) Since, UV spectrum is transparent above 200 nm, it shows absence of conjugation and carbonyl group.

(ii) The ratio of two proton set :-

$$= 4.2 : 25.8$$

$$= \frac{4.2}{4.2} : \frac{25.8}{4.2}$$

$$= 1 : 6$$

- Two absorption bands - septet and doublet with the same values of J suggest the presence of


$$\begin{matrix} CH_3 \\ CH_3 \end{matrix} \!\!> CH-$$

- The molecular mass of $(CH_3)_2CH$ is 43.

Molecular mass of compound = 69

" " of $(CH_3)_2CH-$ = 43

Remaining. 26

(iii) IR band at 2273 cm^{-1} shows presence of nitrile ($-CN$) group by $-C\equiv N$ stretching.

Thus the structure of compound is -

$(CH_3)_2CH-C\equiv N$

- one proton septed ($\delta = 2.72$) slightly downfield (deshielded) due to the presence of $-C\equiv N$ group directly linked to it

Problem ④ – An organic compound contains 66·6% carbon, 11·1% hydrogen and 22·3% oxygen and have following spectral data :-

UV : 275 nm ε_{max} 17

IR : 2941-2857 (m), 1715 (s) and 1460 cm^{-1} (m).

NMR : (i) Quartet 2·48 δ (2H)
(ii) Singlet 2·12 δ (3H)
(iii) Triplet 1·07 δ (3H)

Determine the structure of the compound.

Solution :- (i) Determination of Molecular formula of compound.

– Consider 100 g of compound :-

$$\text{Mass of Carbon} = \frac{66{\cdot}6\,g}{12{\cdot}01\,g} = 5{\cdot}545$$

$$\text{Mass of hydrogen} = \frac{11{\cdot}1\,g}{1{\cdot}008\,g} = 11{\cdot}01$$

$$\text{Mass of oxygen} = \frac{22{\cdot}3\,g}{16\,g} = 1{\cdot}394$$

C : H : O

5·545 : 11·01 : 1·394

divide by smallest number

$$\frac{5{\cdot}545}{1{\cdot}394} : \frac{11{\cdot}01}{1{\cdot}394} : \frac{1{\cdot}394}{1{\cdot}394}$$

4 : 8 : 1

Thus molecular formula of compound is C_4H_8O

–Remaining solution of problem ④ is similar to problem ①