PMR spectroscopy:- (^1H NMR).

(proton magnetic Resonance spectroscopy)

Introduction & principle of NMR spectroscopy:-

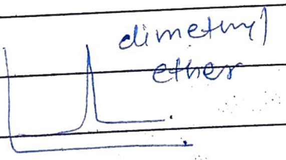
Nuclear magnetic resonance (NMR) spectroscopy as is implied ~~by~~, ~~these~~ involves the change of the spin state of a nuclear magnetic moment when the nucleus absorbs electromagnetic radiation in a strong magnetic field.

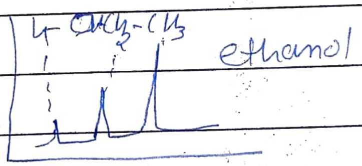
study of the compound by proton NMR spectroscopy (PMR), ~~one~~ ~~co~~

1) The relation between the number of signals (or peak) in the spectrum and the number of different kinds of hydrogen atom in the molecule

2) The area underneath each signal are in the same ratio as the number of hydrogen atom causing each signal.

e.g. CH_3-O-CH_3





1 : 2 : 3

3) The principale signal may get split into smaller peak. i.e. spin-spin splitting may be observed. The type of spliting pattern observed (doublet, triplet, quartet) depends on the number of neighbouring non-equivalent protons.

predict the splitting pattern with ~~a~~ the n+1 rule, where n is the number of neighbouring proton.

④ The spacing between the peak (as a result of spin-spin splitting) is labelled J, which is given the units of cycles per second or (Hz)
J - is the coupling constant of two protons.

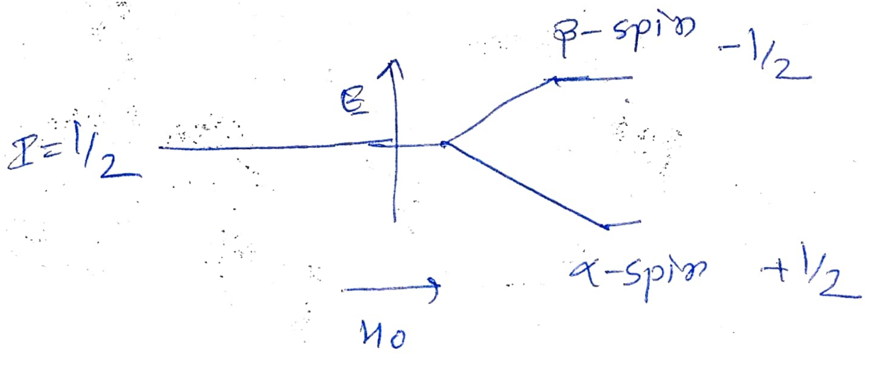
* orientation of hydrogen nucleus :-

In quantum mechanical terms the spin quantum number determines the number of orientation by using $(2I+1)$ formula.

spin quantum number of proton is $- I - 1/2$

$$2 \times 1/2 + 1 = \boxed{2}$$

The influence of external magnetic field, proton can take up two orientation. i.e. energy level. one of lower energy (α-spin) & another of higher energ (β-spin)

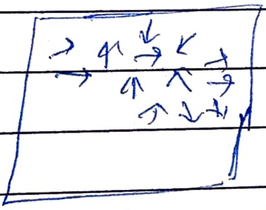


Two energy level for proton in a magnetic field H_0.

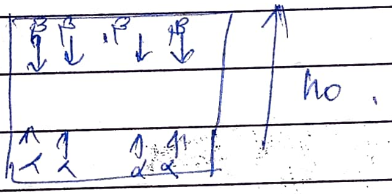
In the absence of external magnetic field, the magnetic moments of protons of a given sample are randomly oriented.

when a compound containing hydrogen (proton) is placed in an applied external magnetic field. the proton may assume one of two possible orientations with respect to external magnetic field.

The magnetic moment of proton may be aligned with the external magnetic field (α-spin) or against it (β-spin). These alignments correspond to the two spin states of proton.



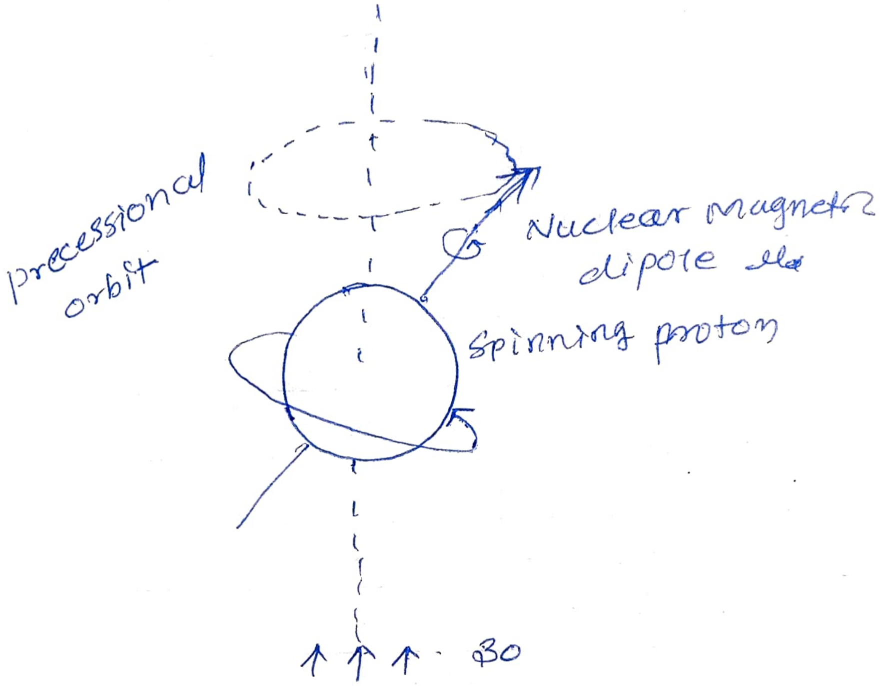
Randomly orientated proton in the absence of external magnetic field



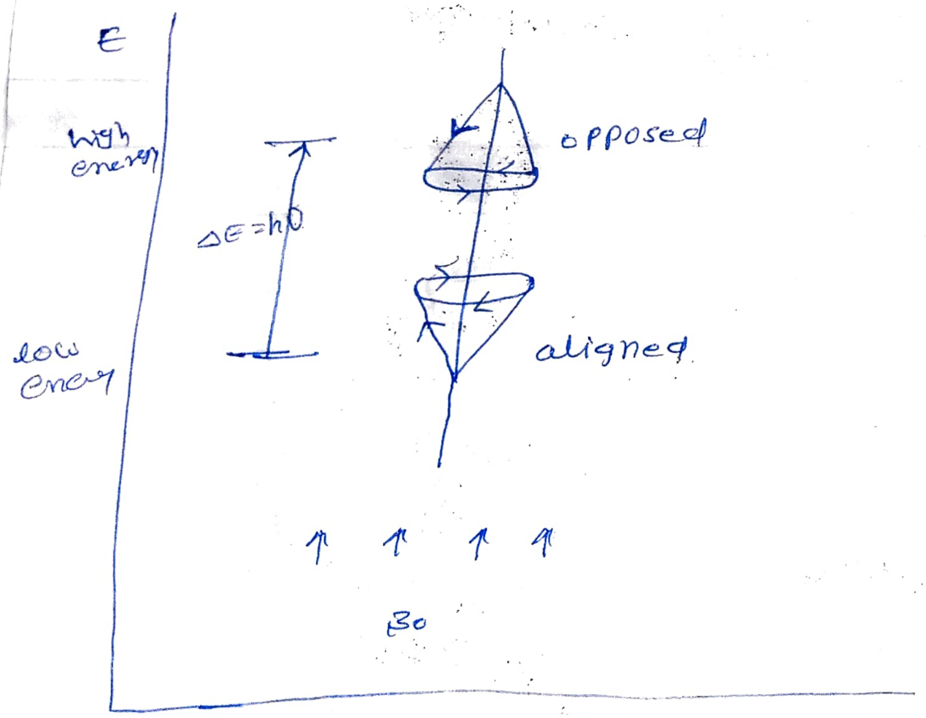
* pressional Motion of nucleus:-

The proton is behaving as a spinning magnet ont only can it align itself with or oppose an external magnetic field,

consider the behavior of a spinning top. as well as describing its spinning motion, the top will (unless absolutely vertical) also perform a slower waltz like motion, in which the spinning axis of the top moves slowly around the vertical. This is precessional motion & the top is said to be precessing around the vertical axis of the earth's gravitation field

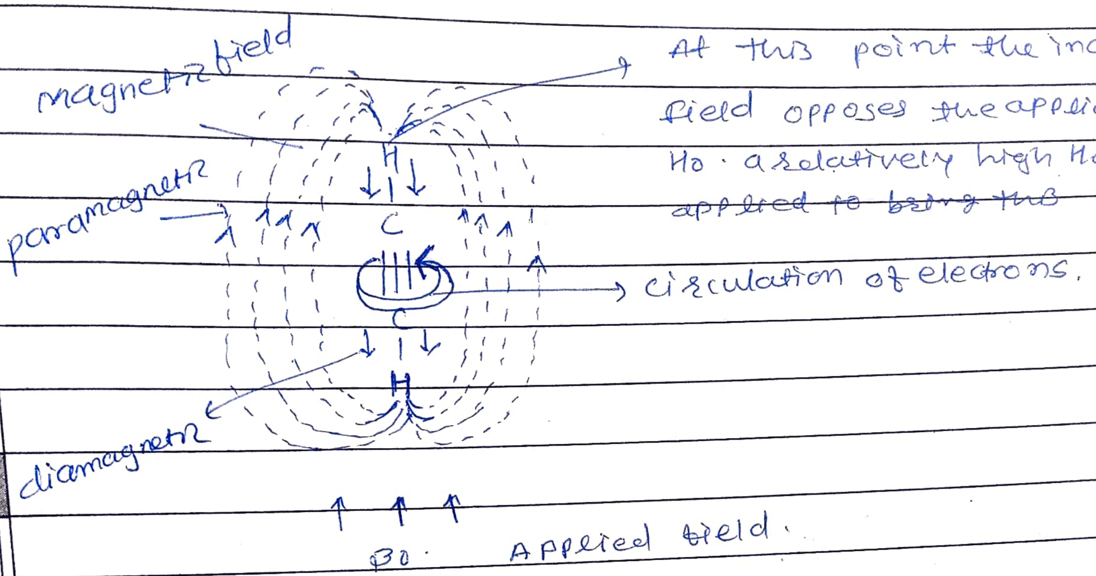


classical representation of a proton precessing in a magnetic field of magnitude B_0 in analogy with a precessing spinning top.



Representation of precessing nuclei & the ΔE transition between the aligned & opposed conditions.

Shielded proton in acetylene :-



At this point the induced magnetic field opposes the applied field H_0. a relatively high H_0 will have to be ~~applied to bring this shielded H-atom~~

The shielding of acetylenic protons by π electron circulation.

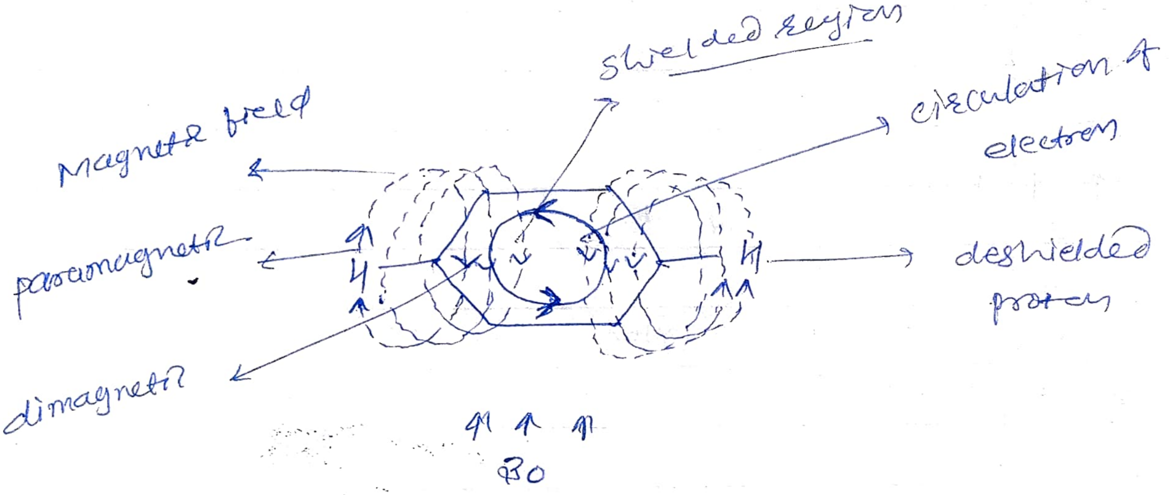
The Induced magnetic field opposes the applied field, electrons are said to be diamagnetic & the effect on the nucleus is called diamagnetic shielding.

The acetylenic proton, the induced magnetic field opposes the applied field H_0. Thus a higher applied field is required to bring this proton into resonance & the induced field in this acetylene is an effective shielding of the ~~alkyne~~ ~~pro~~ acetylene proton.

* Deshielded proton of Benzene :-

The induced magnetic field is reinforce or alinged with applied magnetic field, electron are called as paramagnetic deshielding.

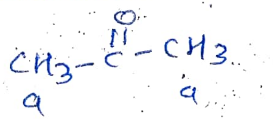
Benzen rings display strong magnetic anisotropy. Above & below the ring, there is a strong shielding region (induced magnetic field is in opposition to the applied field) while in the plane of the ring there is a strong deshielding region (induced magnetic field is in the same direction as the applied field).



Anisotropic shielding & deshielding associated with the aromatic ring current. ~~The moleculecule are constantly tumbling~~.

* Numbers of signals (equivalent & non-equivalent protons) in following compounds.

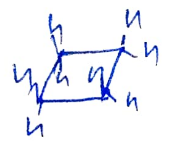
① Acetone



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

one pmR signal.

Acetone shows one pmR signal.

② cyclobutane  one pmR signal.

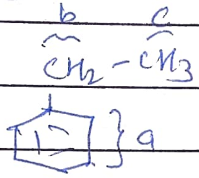
cyclobutane shows one pmR signal.

③ Methanol

$\underset{a}{CH_3}-\underset{b}{OH}$ Two pmR signal.

methanol shows one CH_3 signal + one OH signal ~~two~~ tota
give two pmR signal.

④ Ethyl benzene



Three pmR signal.

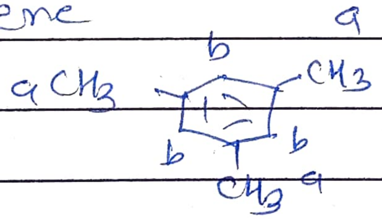
ethyl benzene shows three pmR signal.

⑤ Ethyl amine

$\overset{a}{CH_3}-\overset{b}{CH_2}-\overset{c}{NH_2}$ Three pmR signal,

ethyl amine shows Three pmR signal.

⑥ Mesitylene



Two pmR signal.

⑦ Diethyl ether.

$\overset{a}{CH_3}-\overset{b}{CH_2}-O-\overset{b}{CH_2}-\overset{a}{CH_3}$ Two pmR signal.

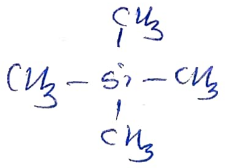
* chemical shift :⇒

The chemical shifts is defined as the difference between the absorption position of a particular proton & the absorption of a reference proton.

The shielding, shifts the absorption position upfield, whereas deshielding shifts the absorption position downfield and these effects are termed as shielding & deshielding effect respectively. such shifts in the NMR absorption position. are called as chemical shifts.

The chemical shift are commonly expressed in δ unit

Tetramethyl silane (TMS) $(CH_3)_4Si$, is the most commonly used internal reference compound.



$$CH_3-\underset{CH_3}{\overset{CH_3}{Si}}-CH_3$$

T.MS.

$$\delta = \frac{\Delta\nu}{\nu} \times 10^6 \text{ ppm}$$

where δ = chemical shift of nucleus, ppm.

Δν = difference in resonance frequency (Hz) betn standard TMS & the peak being measured (observed shift)

ν = spectrophotometer frequency in megacycles.

$$\delta = 10 - \tau.$$

$$\tau = 10 - \delta.$$

spin - spin coupling & coupling constant :-

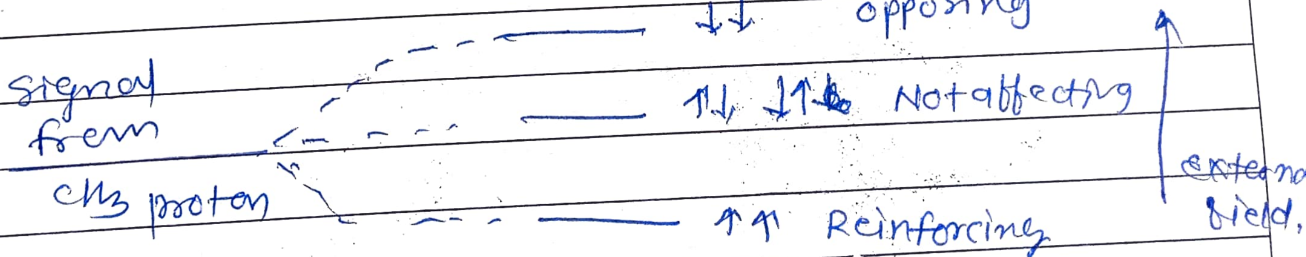
PMR signal consisting single peak (singlet) double peak (doublet), three peak (triplet) four peak (quartet), a group of peak (a multiplet) is observed in PMR spectrum. This is called the splitting of NMR signals or the spin-spin splitting.

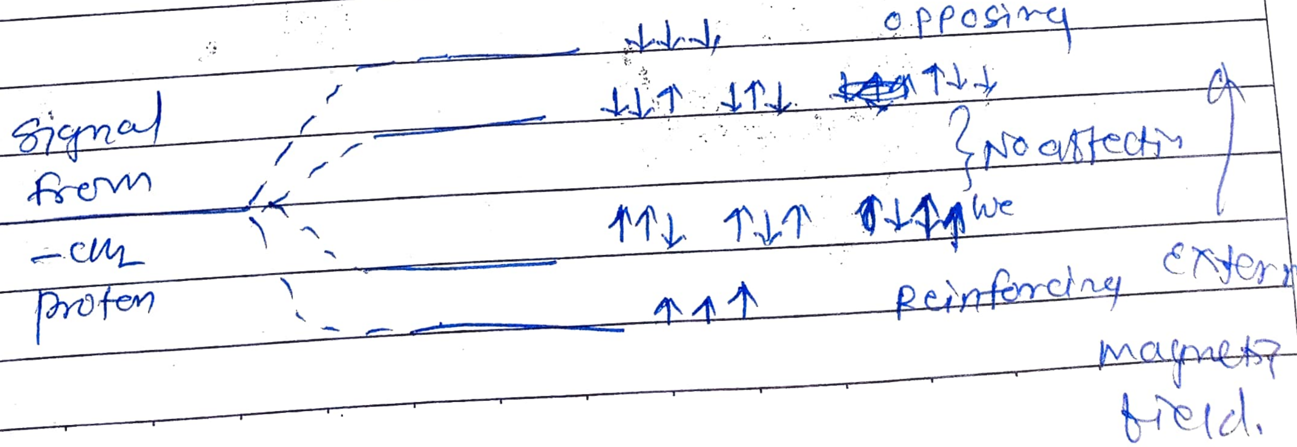
The splitting of NMR signals is caused by spin-spin coupling which is indirect coupling of proton spins through the intervening bonding electrons.

e-g.

CH_3-CH_2-Br.

In CH_3-CH_2-Br molecule, the spin of two proton ($-CH_2-$) can couple with the adjacent methyl ($-CH_3$) in three different ways relative to external magnetic field. The three different ways of alignment are as follows.





CH_3-CH_2-Br
b a

by using (n+1) rule
n- No. of neighbouring protons.

CH_2 - shows - quartet (3+1=4) four line

CH_3 - show triplet. (2+1)=3 three line

Relative intensities of various multiplet.

No. of proton responsible for splitting, n	multiplet	Relative intensity
0	singlet	1
1	doublet	1:1
2	triplet	1:2:1
3	quartet	1:3:3:1
4	quintet	1:4:6:4:1
5	sextet	1:5:10:10:5:1
6	septet.	1:6:15:20:15:6:1

The splitting of a signal is dueto different enviroment of the absorbing proton with respect to the neighbouring proton but not with respect to electrons. The intensities (areas) of a PMR signals depends up on the number of absorbing protons & the multiplicity of a signal depends up on the number of the neighbouring protons spin- spin splitting (n+1) rules.

The interaction between the spin of neighbouring magnetic nuclei in a molecule may cause the splitting of NMR signal in the spectrum. This is known as spin-spin coupling which occurs through bonds (not space).

By using (n+1) rules.
n = no. of neighbouring protons.

CH_3-CH_2-Br

$\downarrow$ 2 $\qquad$ $\downarrow$

$(2+1) = 3$ triplet $\qquad$ $(3+1) = 4$ quartet

Coupling constant.

The distance bet^n the centres of the two adjacent peak in a simple multiplet is called the coupling constant (J.)

- J is independent of the external field.
- It is expressed in Hertz (Hz) or in cycle per second (cps).

geminal coupling -
vicinal coupling -

TMS .

1) It is chemical inert, magnetically isotropic, volatile (b.p. 300°K), non-toxic, cheap, soluble in most of the organic solvents.

- It gives a single sharp absorption peak & absorbs at higher field than almost all organic proten.

- TMS can be used as an external reference.

peak Area proton counting :.

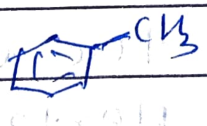
peak represent equivalent sets of protens in an NMR spectrum. The size of each peak tells the number of proten in each set present in the compound under study.

The area under an NMR signal is directly propotional to the number of protons giving rise to signal.

i) CH_3-OH 2 a : b = 3 : 1

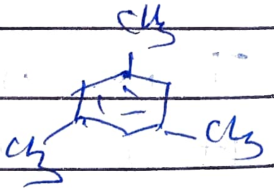
CH_3-CH_2-OH 3 : 2 : 1

$CH_3-CH_2-CH_2-OH$ 3 : 2 : 2 : 1



3 : 5

6 : 4.



9 : 3.

Type of proton	chemical shift δ ppm
1) 1° Alkyl $R-CH_3$	0.8 - 1.0.
2) 2° Alkyl $R-CH_2-R$	1.2 - 1.4.
3) 3° Alkyl $R-\underset{R}{\underset{\vert}{CH}}-R$	1.4 - 1.7
4) Allylic $R_2C=\underset{R}{\underset{\vert}{C}}-CH_3$	1.6 - 1.9.
5) Benzylic $Ar-CH_3$	2.2 - 2.5.
6) Alkyl chloride $R-CH_2-Cl$	3.6 - 3.8
7) $R-\underline{CH_2}-Br$	3.4 - 3.6
8) $R-\underline{CH_2}-I$	3.1 - 3.3.
9) ether $R-O\underline{CH_2}R$	3.3 - 3.9
10) Alcohol $HO\underline{CH_2}R$	3.3 - 4.0
11) ketone $R-\overset{O}{\overset{\Vert}{C}}-\underline{CH_3}$	2.1 - 2.6.
12) Aldehyde $R-\overset{O}{\overset{\Vert}{C}}-\underline{H}$	9.5 - 9.6.
13) Aromatic $Ar-H$	6.0 - 8.0
14) $Ar-OH$	4.5 - 7.7
15) carboxylic $R-COOH$	10 - 11
16) Alcohol hydroxyl $R-OH$	0.5 - 6.0 (1° 3.2, 2° 3.4, 3° 3.8)
17 Amino $R-NH_2$	1.0 - 5.0. (3.8)

18) Ester $R-\overset{O}{\overset{\Vert}{C}}-O-\underline{CH_2}-R-$

dt. 28/5/2021
Time 11.40 to 12.30

Interpretation of pmR spectra of following compounds.

ⓐ Ethyl bromide:

$\overset{a}{CH_3} - \overset{b}{CH_2} - Br$ D.B.E = $x + 1 - \frac{y + \text{no. Halogen}}{2}$

$= 3 - 6/2 = 3 - 3 = 0$ //

↓ ↓

n+1 n+1

2+1 3+1

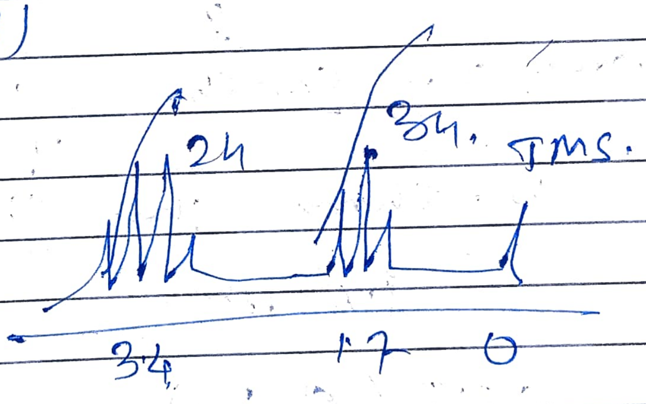
= 3t. 4 q

The proton a shows triplet (t) due to neighbouring two $\underline{CH_3} - CH_2$

δ 1.7 (t, 3H)

b. shows the quartet due $\underline{CH_2} - CH_3$

δ 3.4 (q, 2H)



ⓑ Ethyl alcohols

$\underset{a\,t}{CH_3} - \underset{b\,q}{CH_2} - \underset{c}{OH}$ 5t DBE = 0// 3-3 = 0

3:2:1

a - $\underline{CH_3} - CH_2$ shows the triplet at δ 1.3 ppm.

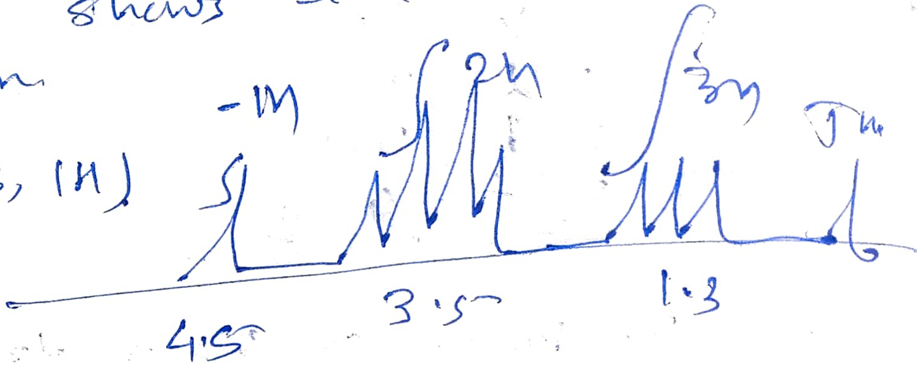
a δ 1.3 (t, 3H)

proton b – shows the quartet $-\underline{CH_2}-CH_3$.
peak appears at δ 3.5 ppm

δ 3.5 (2H, q)

proton c –OH proton shows the singlet at 4.7 ppm

δ 4.7 ppm (s, 1H)



ⓒ

ⓒ Acetaldehyde

D.B.E. 3−2=1

$\underset{d}{\underset{a}{CH_3}} - \underset{q}{\underset{b}{\overset{O}{\overset{\|}{C}}-H}}$

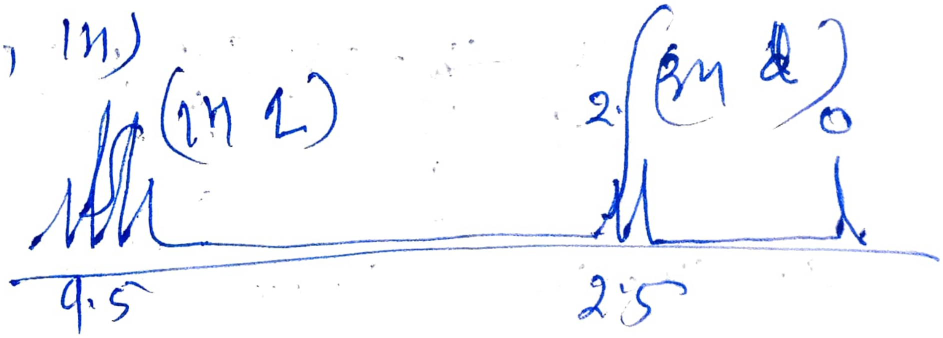
3:1 or 1:3

proton a – $\underline{CH_3}-\overset{O}{\overset{\|}{C}}H$ doublet at δ = 2.5 P

b – shows the $\overset{O}{\overset{\|}{\underline{C}}}H-CH_3$ quartet at δ 9.5 ppm.

δ 2.5 (d, 3H)

δ 9.5 (q, 1H)



(d) 1,1,2- Tribromo ethane :

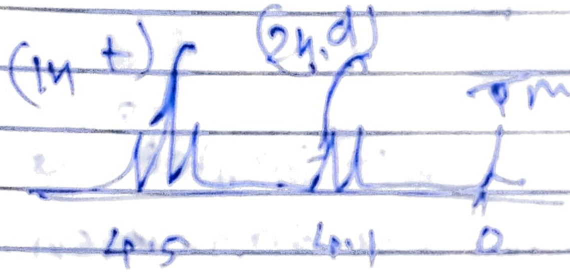
a b

$Br-\underset{Br}{CH}-CH_2-Br$

t d 1:2

a - $C\underline{H}-CH_2$ = triplet at δ = 5.7 ppm

b - $C\underline{H_2}-CH$ = doublet at δ = 4.1 ppm.



(e) Ethyl acetate

$CH_3-\overset{\overset{O}{\|}}{C}-O-CH_2-CH_3$ dBE = 1

a b c

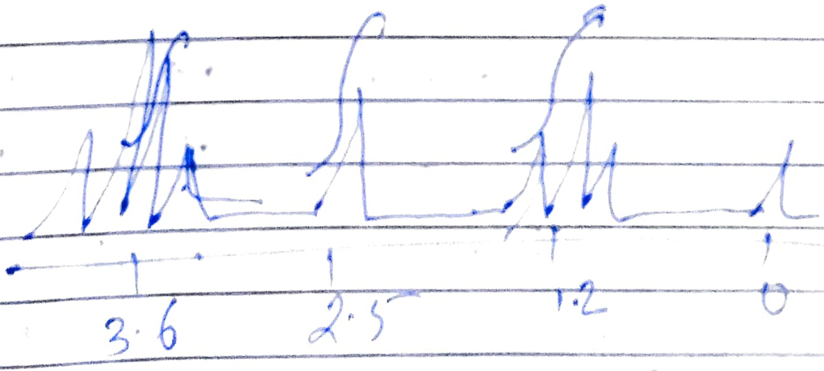
s q t

2 : 3 : 3.

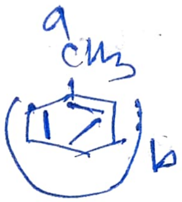
part a shows the singlet at δ = 2.5 ppm

b shows the quartet at δ = 3.6 ppm

c - shows the triplet at δ = 1.2 ppm.

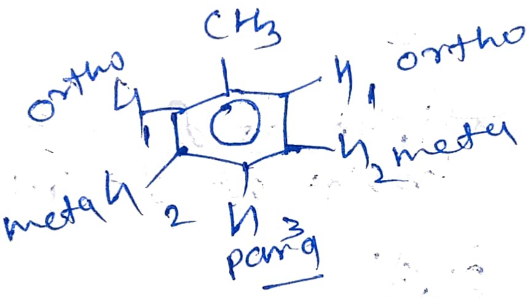


(f) Toluene



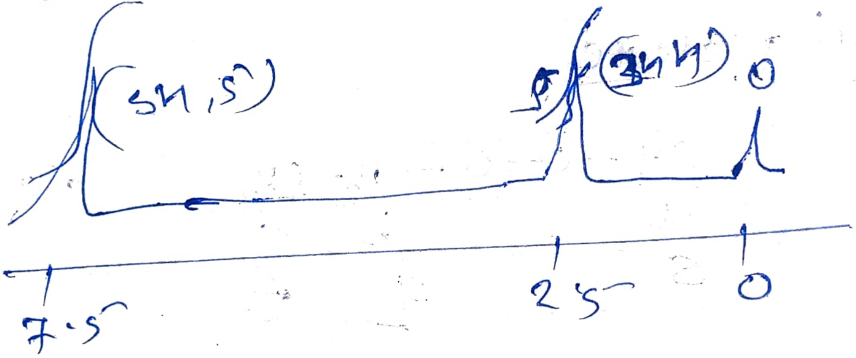
DBE = 4

C7H8 = x+1-y/2
= 8-8/2
= 8-4
= 4



a shows the singlet (3H) at δ = 2.5 ppm.

b - shows the singlet (5H) at δ = 7.5 ppm

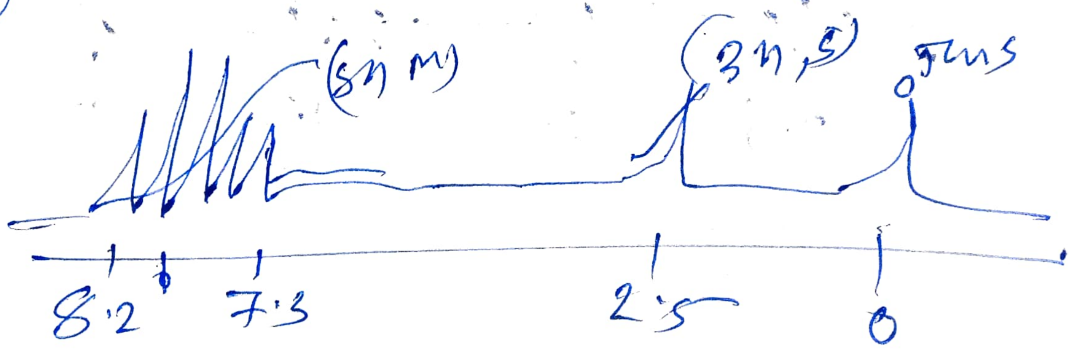


(g) Acetophenone

DBE = 5

a - shows multiplet (5H) at δ = 7.3 - 8.2 ppm

(b) shows singlet (3H) at δ = 2.5 ppm



(h) Ethyl amine

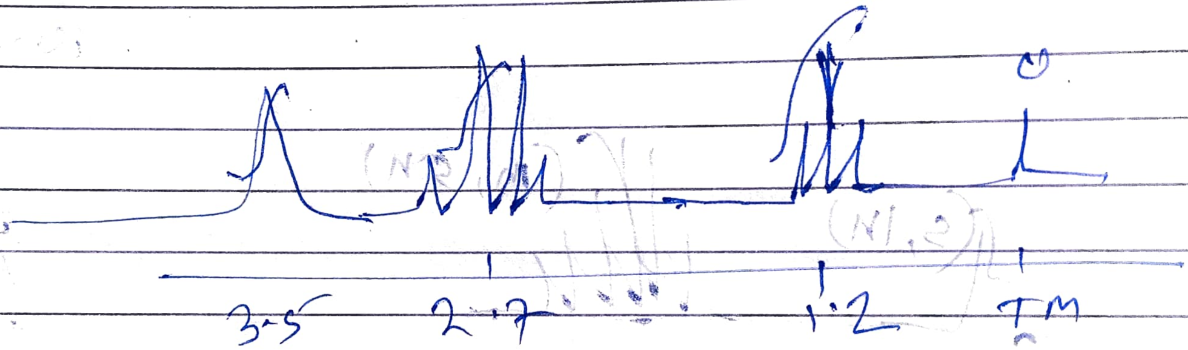
$CH_3-CH_2-NH_2$
a b c s
t q 2:2:3.

$DBE = x+1-\frac{y-\text{No. of N-atom}}{2}$

$= 2+1-\frac{7-1}{2}$

$= 3 - 6/2 = 3-3$
$= \underline{\underline{0}}$

a - δ 1.2 (t, 3H)
b - δ 2.7 (q, 2H)
c - δ 3.5 (s, 2H, " exchangable with D_2O)
broad

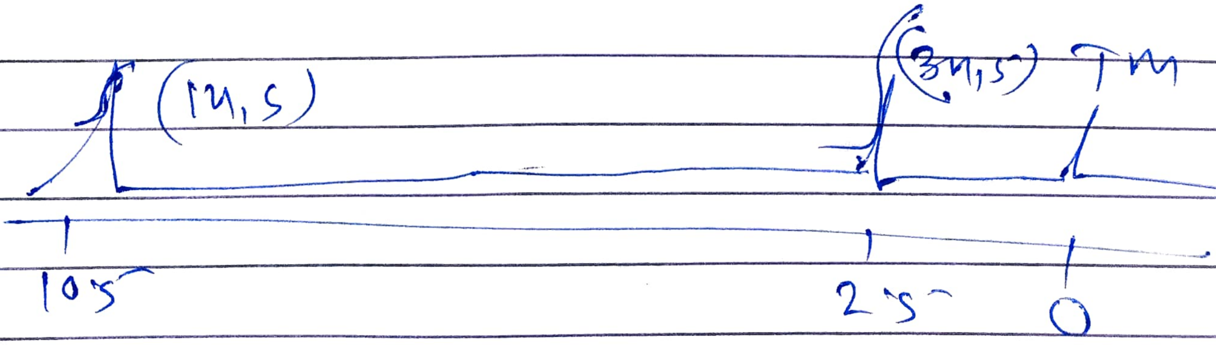


(i) Acetic acid

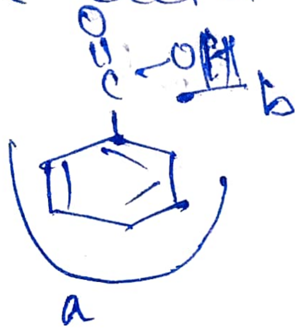
$CH_3-\overset{O}{\overset{||}{C}}-OH$
a b

DBE = $\underline{\underline{1}}$

a shows the singlet at δ 2.5 ppm
b shows the singlet at δ 10.5 ppm.



(i) Benzoic acid



DBE = 5

proton a shows the multiplet a δ = ~~7.1–7.5~~ ppm
7.1 – 7.5 pm

proton b shows the singlet at δ =
10.5 ppm.