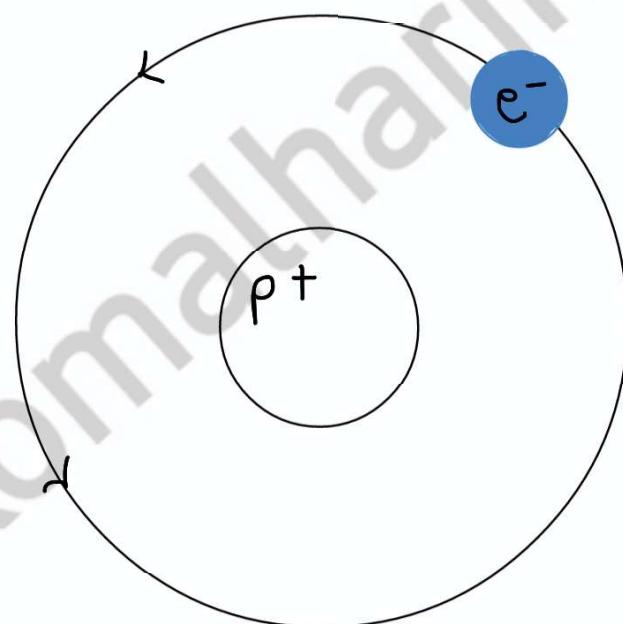


NMR Active atoms

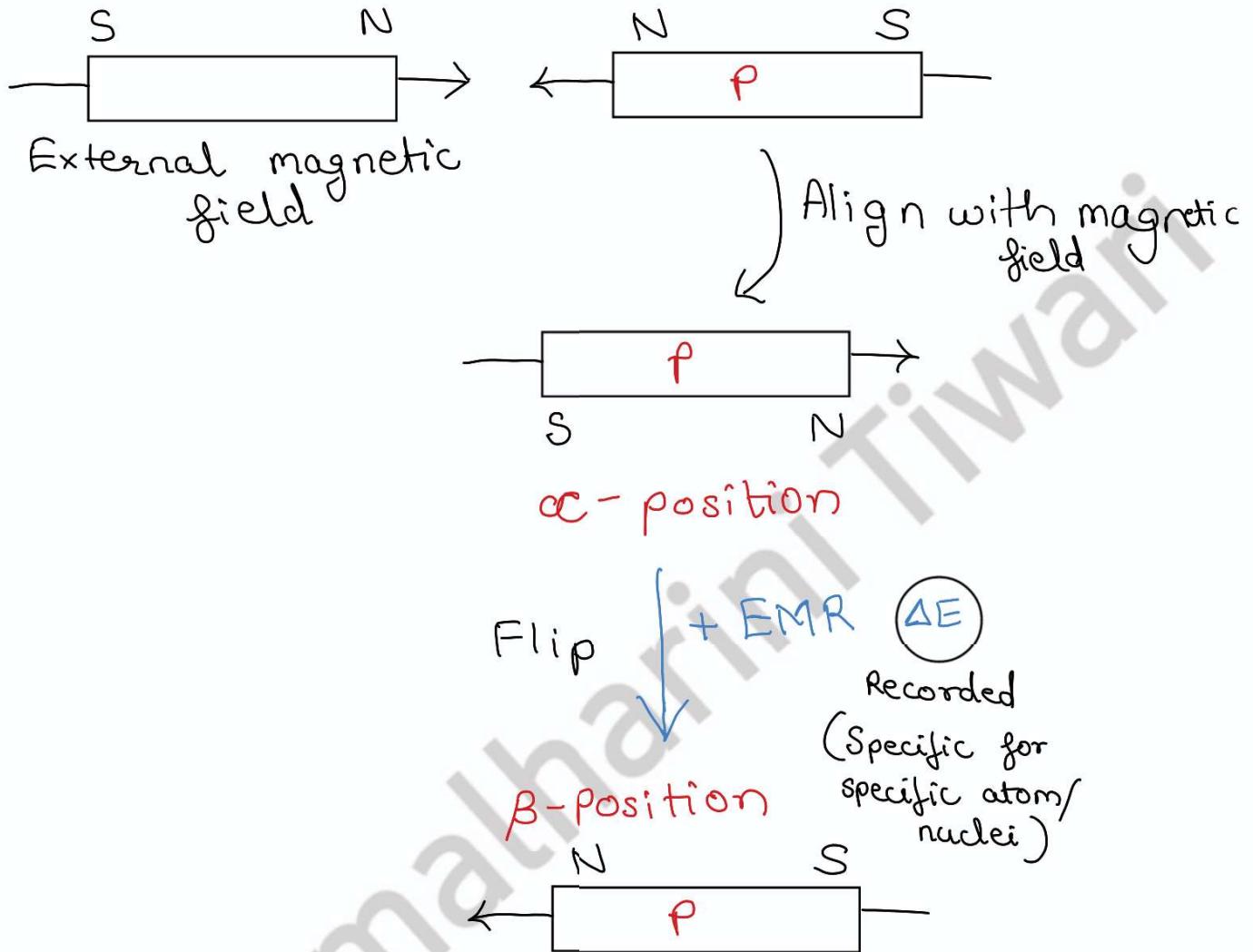
1H , $^{13}C_6$, $^{14}N_7$,
 $^{17}O_8$, $^{19}F_9$, $^{31}P_{15}$,
 $^{35}Cl_{17}$

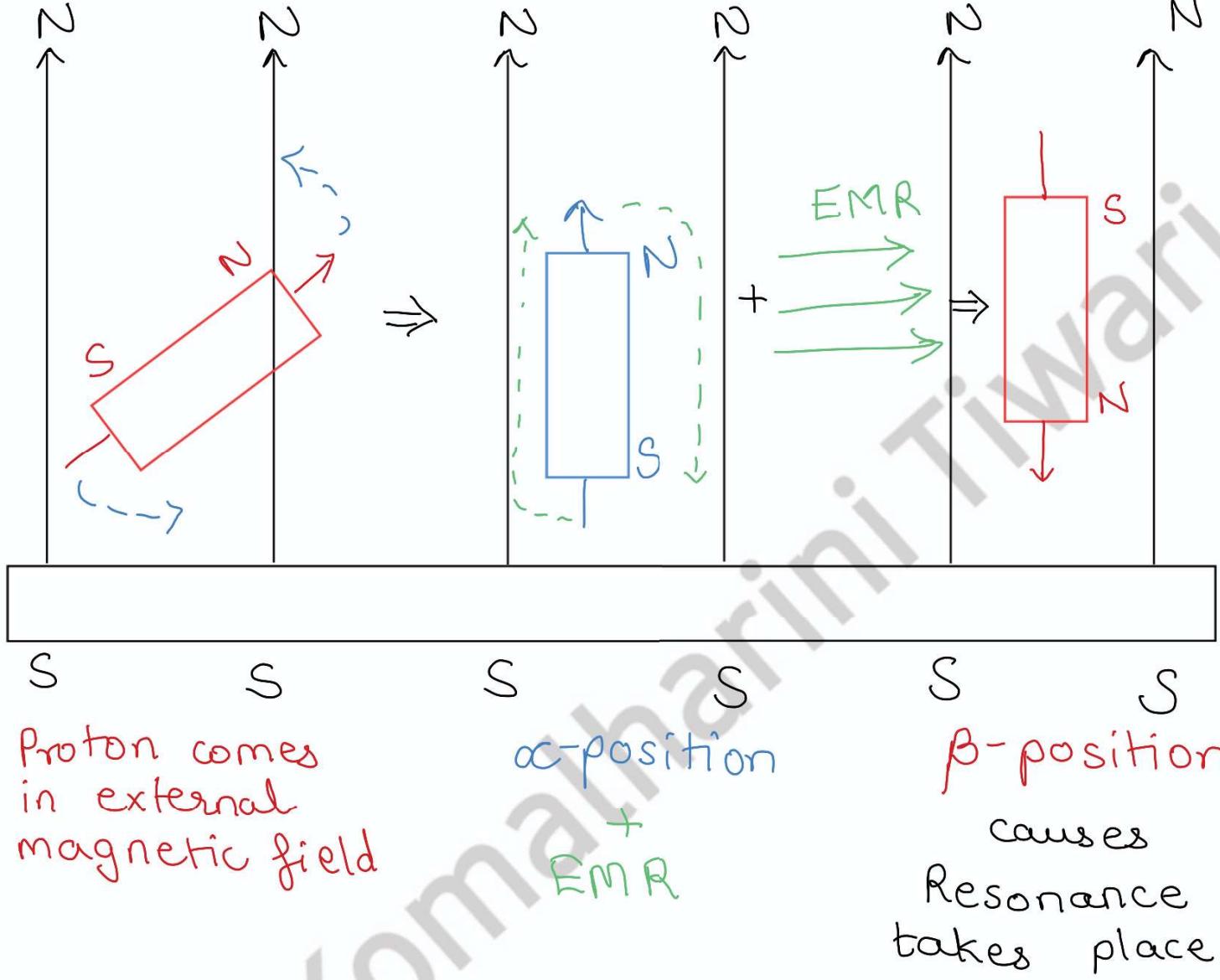
NMR Inactive atoms

$^{12}C_6$, $^{16}O_8$

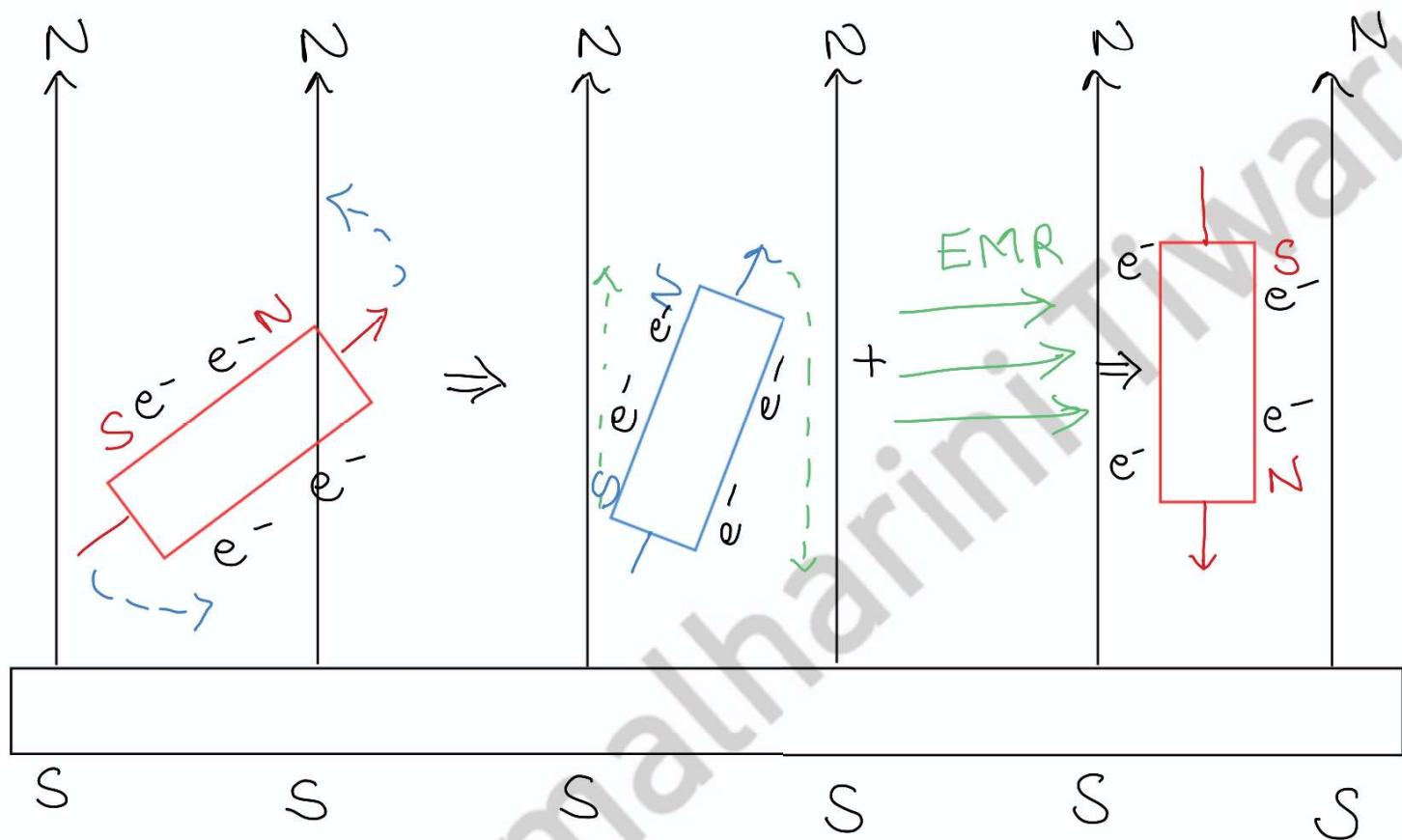


1H atom acts as a magnet





Shielding: $\text{CH}_3 - \text{CH}_3$ (Equal shielding)

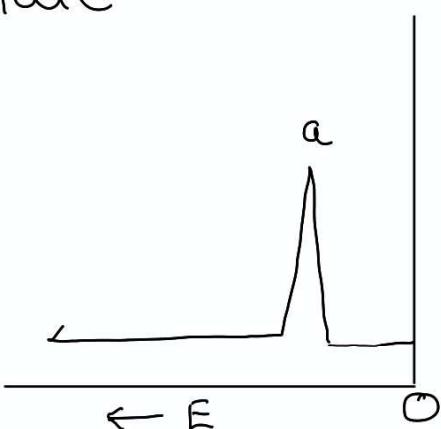


Proton comes
in external
magnetic field

Not completely in
 α -position
+
EMR

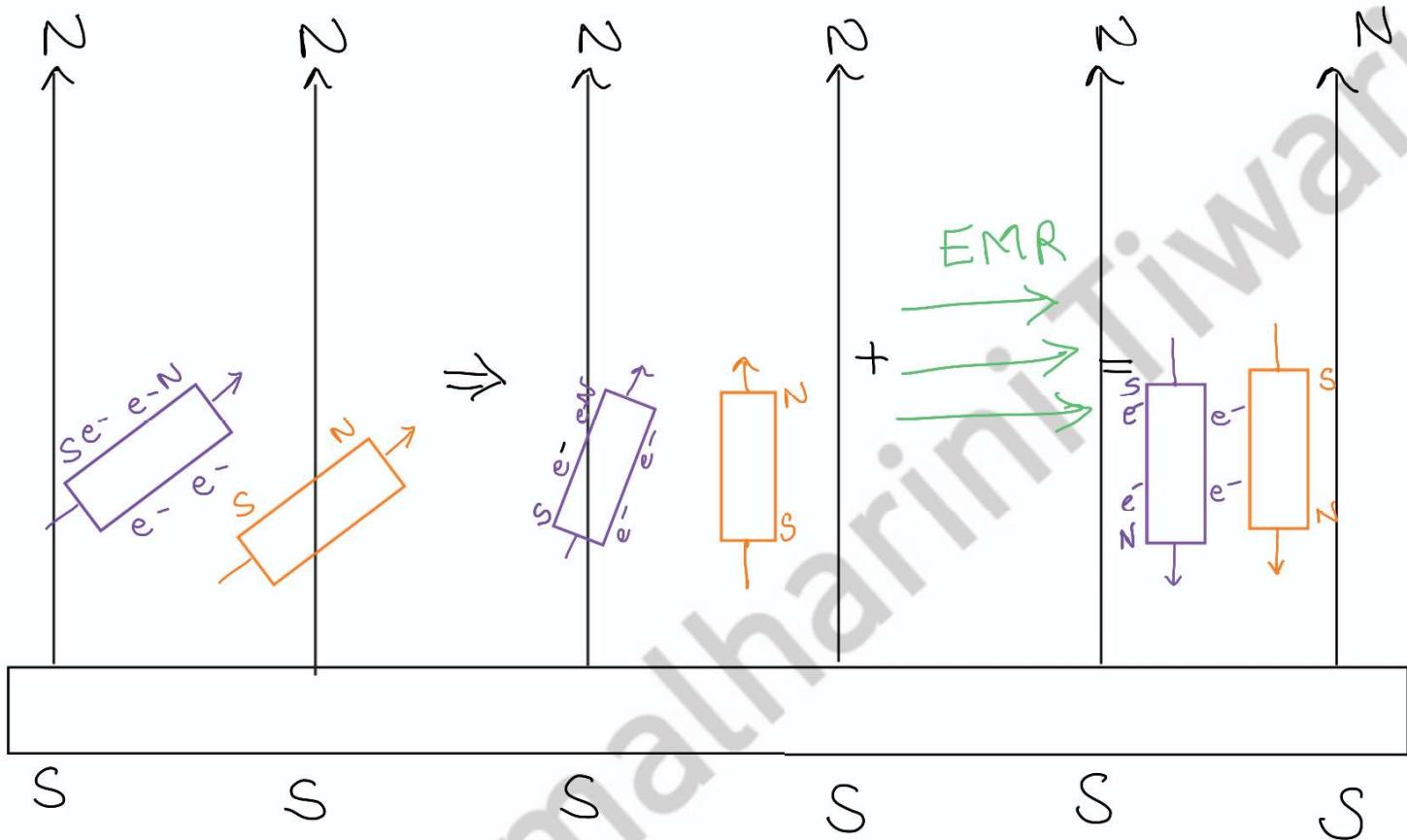
β -position
causes
Resonance
takes place

Lesser energy absorbed
 \therefore Lower energy state



Deshielding: $\text{CH}_3 - \text{CH}_2 - \text{Br}$ (Desheilding)

Electronegativity of Br is local effect
It will carry its effect only till (b) & deshield it



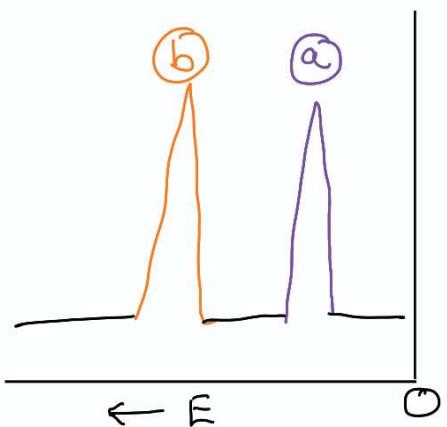
High shielding
Deshielding

Not completely in α -position

In α -position

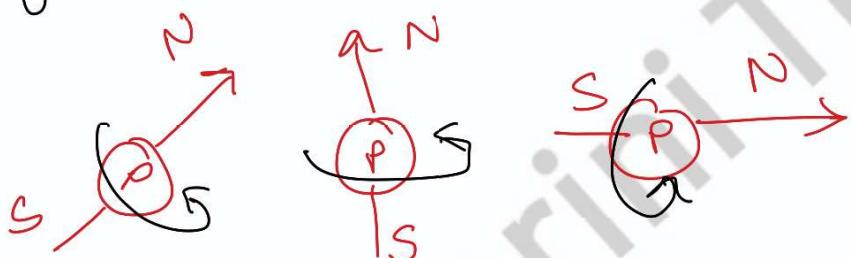
+
EMR

- (a) flips first as it requires less energy because of shielding
- (b) flips next. Absorbs more energy than (a)



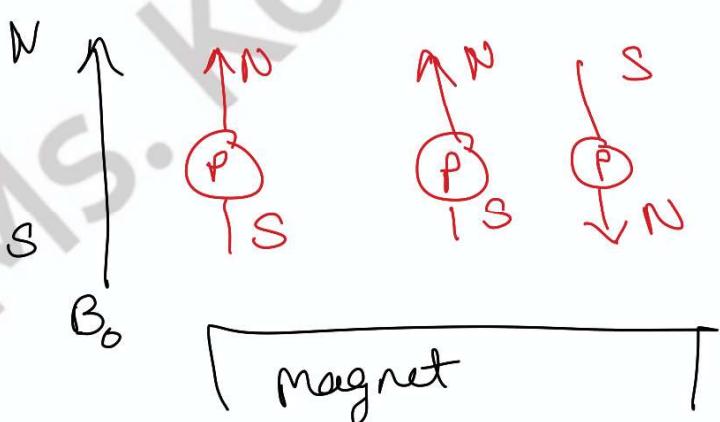
Principle:
 Proton spins around its axis. Aligns to external magnetic field. EMR is absorbed, it goes to the higher energy level & oppose to the external magnetic field.

1) Spinning nucleus



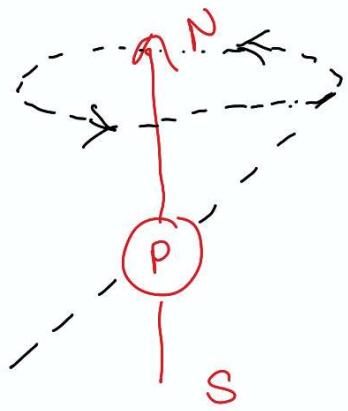
2) Effect of external magnetic field

- Proton is aligned $\vec{\omega}$ magnetic field (low energy level & parallel)
- Proton opposes the (high energy level & anti parallel)



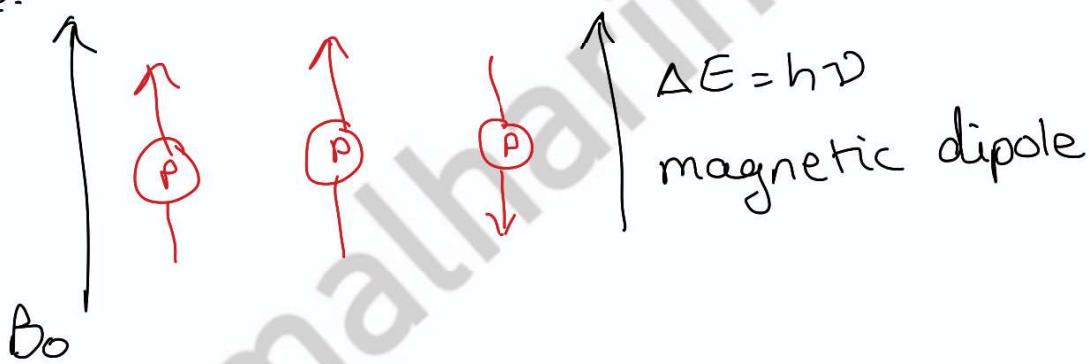
3) Precessional Motion:

Proton will be showing precessional motion due to interaction of spin & gravitational force of earth \rightarrow Gyroscopic motion.



Energy of orientation of magnetic dipole is given by $h\nu$

\Rightarrow Some protons are aligned & some are opposed to external magnetic field. This causes magnetic dipole.

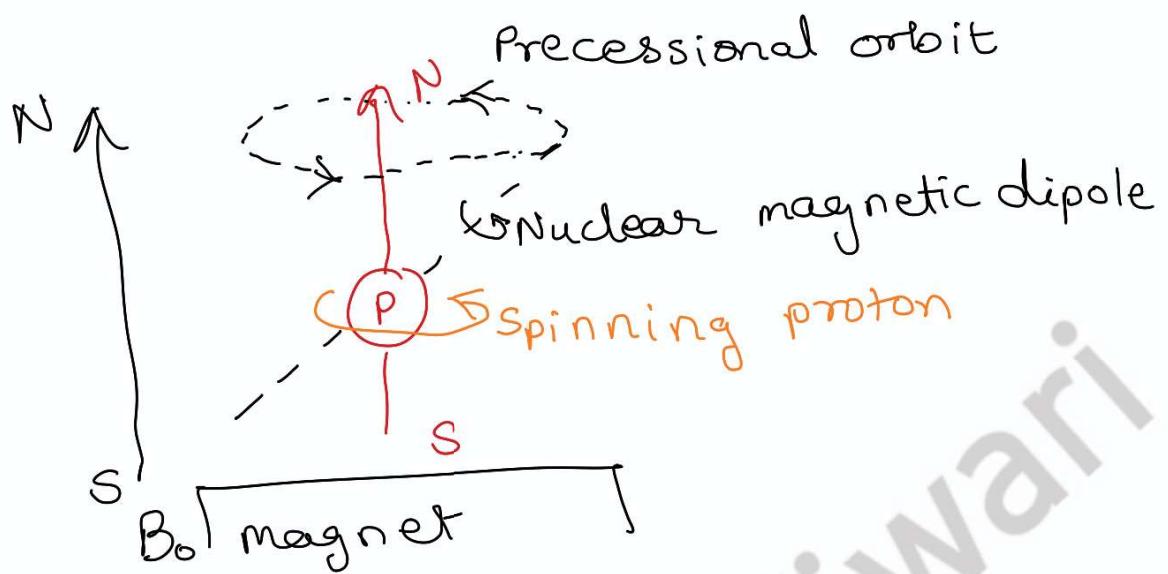


protons aligned \neq # protons opposed
This is when magnetic dipole will occur

↳ Precessional frequency:

- ↳ Spinning frequency remains constant
- ↳ Precessional frequency is directly proportional to external magnetic field.

$$\gamma \propto B_0$$



5.) Energy Transition:

If proton's precessional frequency is exactly same as EMR frequency, only then it will absorb the electromagnetic radiation (radio frequency) & resonance will take place \Rightarrow NMR.

When proton goes from low energy level to higher energy level because of absorption of EMR
 \Rightarrow Resonance.

Angular Precessional velocity

$$\omega = \gamma B_0 \quad \begin{aligned} \gamma &\rightarrow \text{Gyromagnetic ratio} \\ &\text{---(I)} \end{aligned}$$

$$B_0 \rightarrow \text{External magnetic field.}$$

Larmour equation for NMR:

$$\nu = \frac{\gamma B_0}{2\pi} \quad \nu \rightarrow \text{Precessional frequency}$$

$$\gamma B_0 = 2\pi\nu \quad \text{---(II)}$$

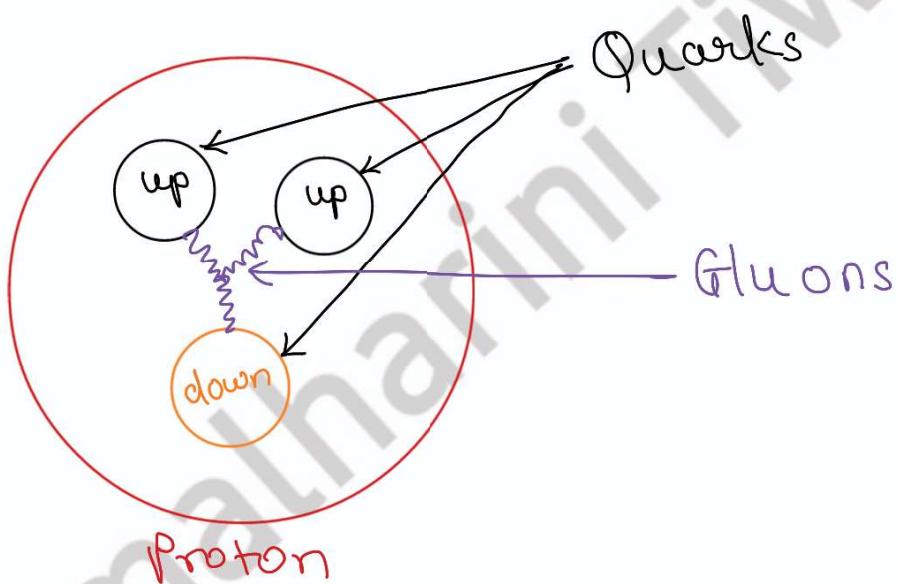
$$\omega = 2\pi\nu \quad \text{---(III)}$$

$$\gamma = \frac{2\pi\mu}{hI} \quad \begin{aligned} \mu &\rightarrow \text{Magnetic moment of} \\ &\text{proton} \\ h &\rightarrow \text{Planck's constant} \\ I &\rightarrow \text{Spin quantum no.} \end{aligned}$$

Spin quantum Number

$I=0$ NMR inactive

$I>0$ NMR active



Electric charge in Quarks:

$$\text{Upward} = \left(+\frac{2e}{3} \right)$$

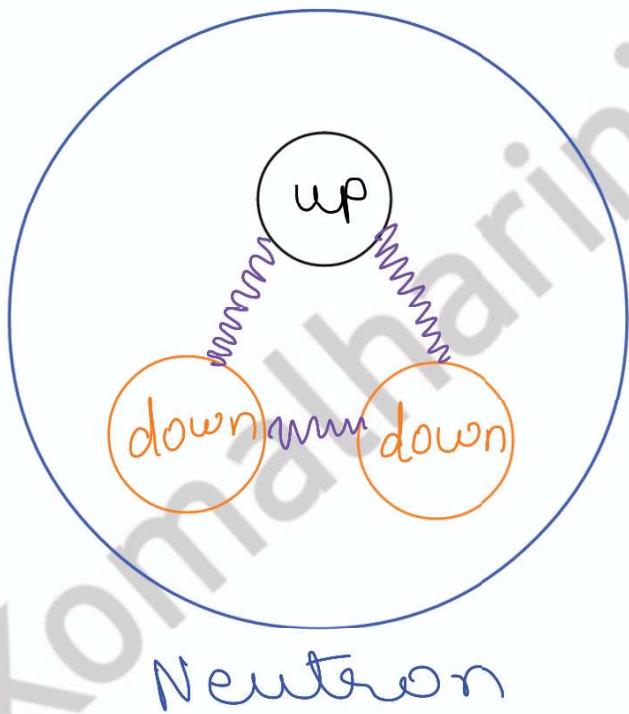
$$\text{Downward} = \left(-\frac{e}{3} \right)$$

\therefore 2 upward quarks are present, electric charge in a proton is :

$$2 \times \left(+\frac{2e}{3} \right) \left(-\frac{e}{3} \right) = +1e$$

\therefore Protons are positively charged.

Neutron:

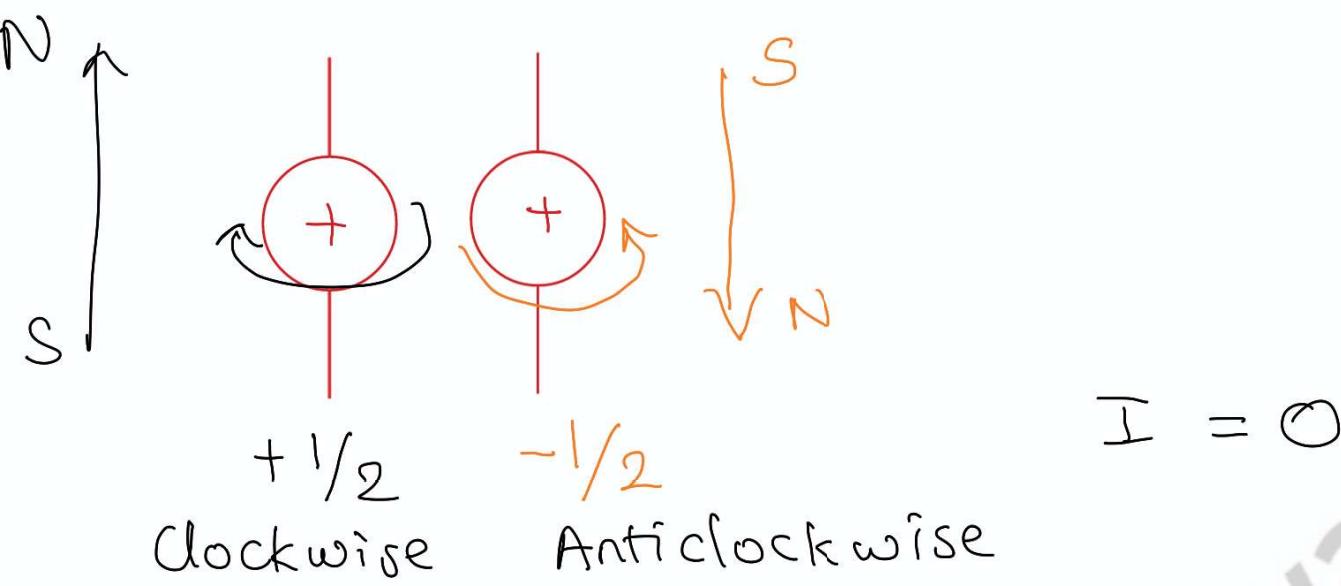


∴ 2 downward quarks are present in a neutron, the electric charge of a neutron is

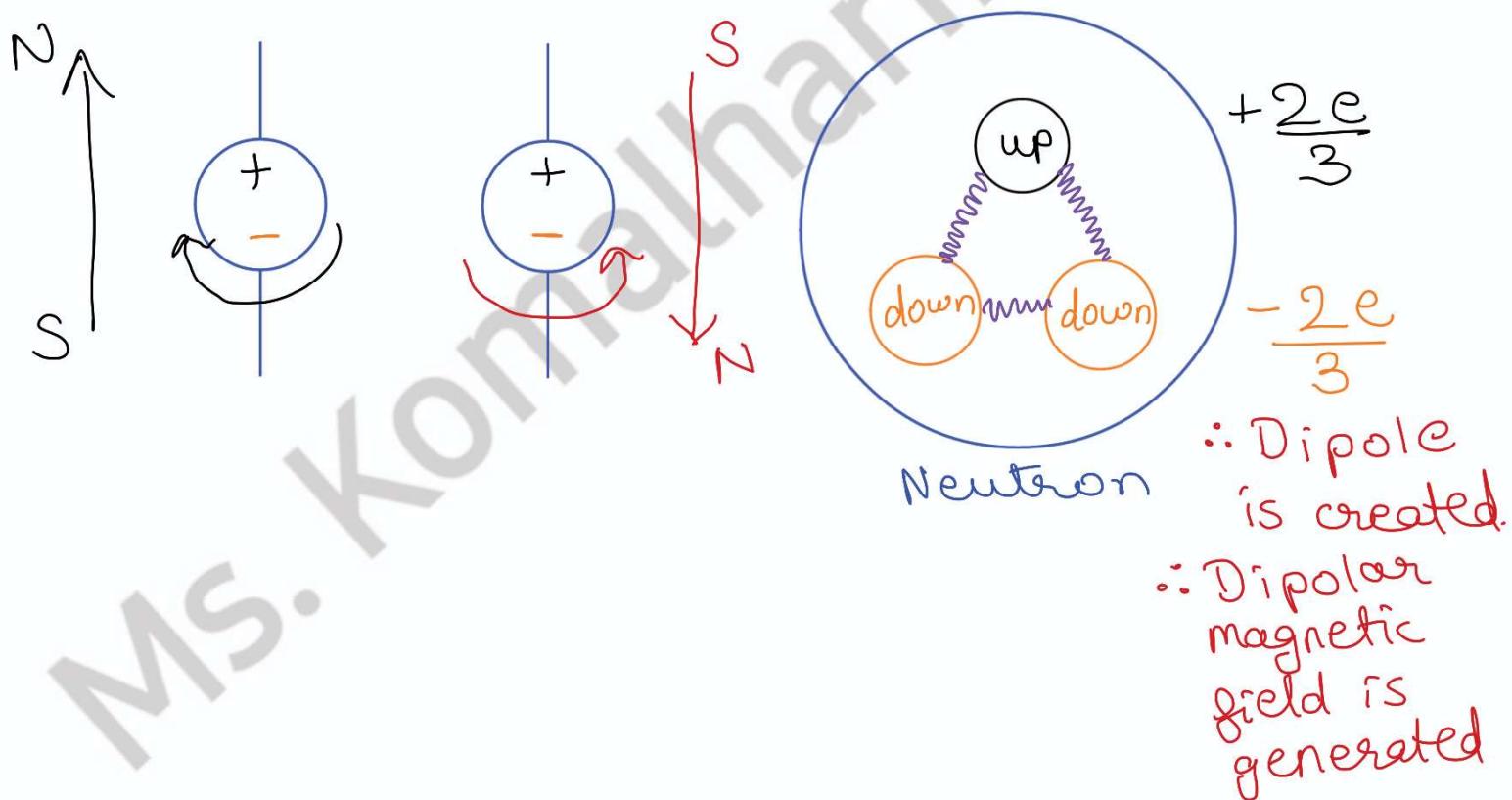
$$+\frac{2e}{3} - \frac{e}{3} - \frac{e}{3} = 0$$

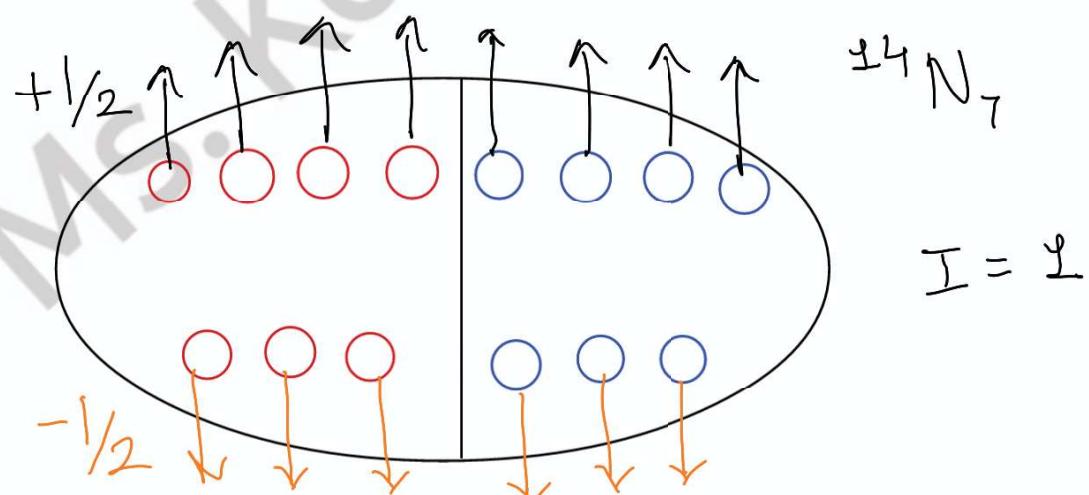
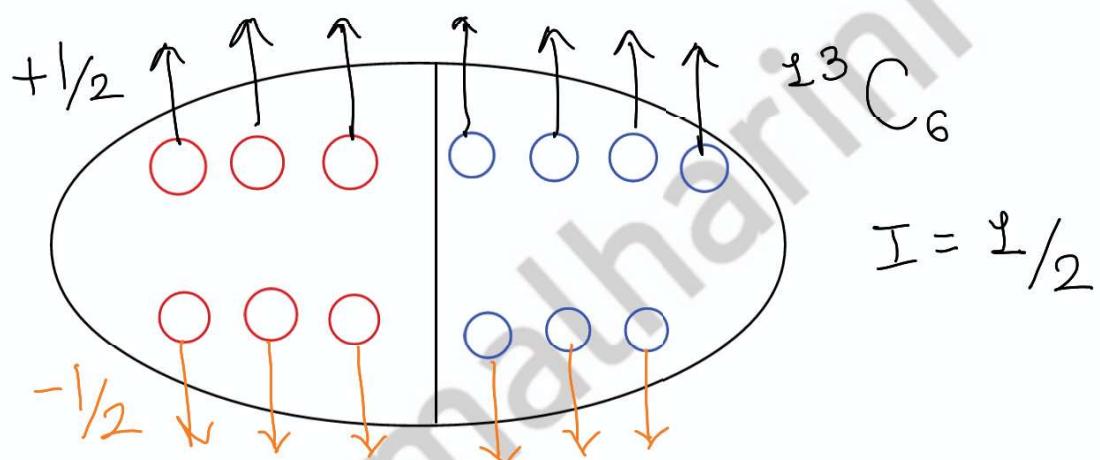
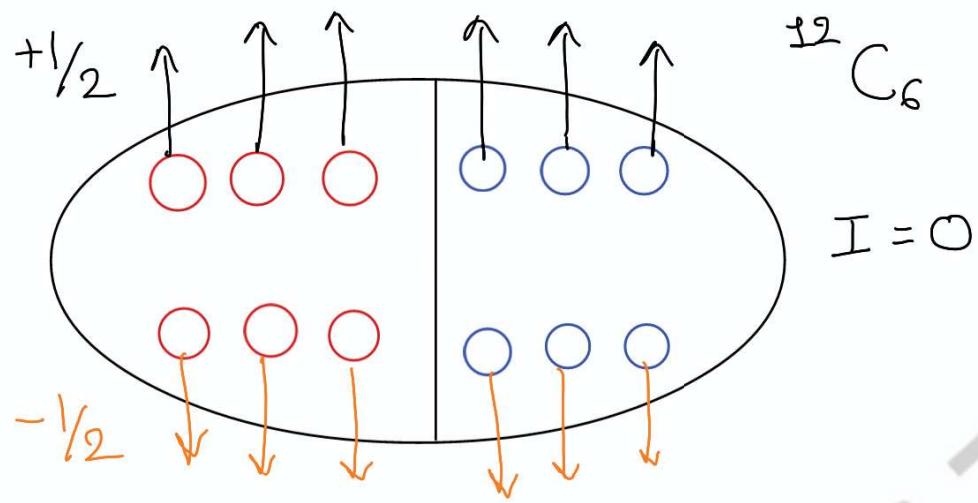
∴ No charge is present in the neutron.

Spins of proton & Neutron:
 ↳ able to create magnetic field.



If no. of proton is odd the $I > 0 \therefore$
 1st proton will always go with $+ \frac{1}{2}$
 as it is at low energy level





$${}^1H_1 \Rightarrow \text{Proton} = 1 \quad \therefore I = \pm 1/2 \\ \text{Neutron} = 0$$

INSTRUMENTATION:

1. Sample Holder

2. Magnet

Relationship b/w B_0 & ν

Larmour Equation:

$$\nu = \left(\frac{r}{2\pi} \right) B_0$$

$$r = 267.53 \text{ radians/T}$$

for ($\pm H$)

Magnetic field

1.41 T or 14100 G

2.35 T or 23500 G

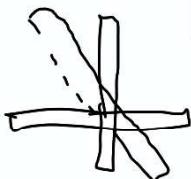
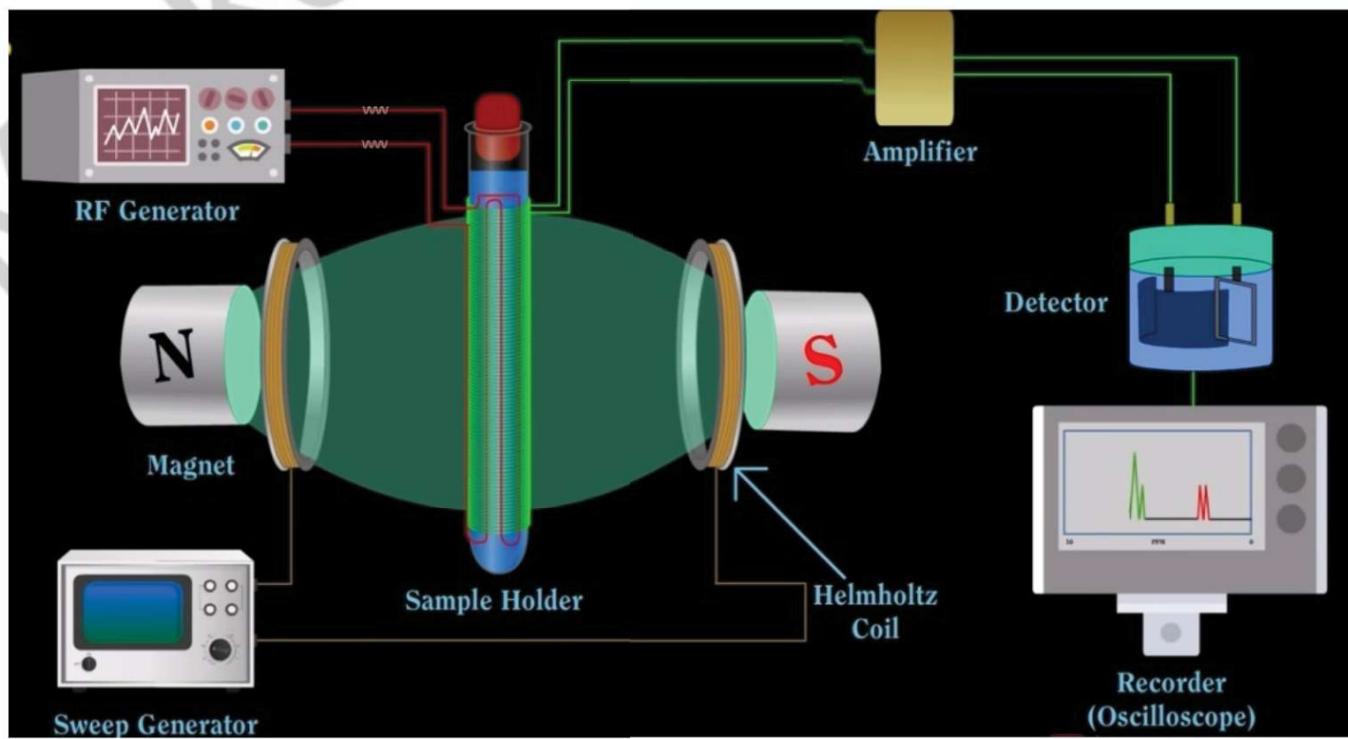
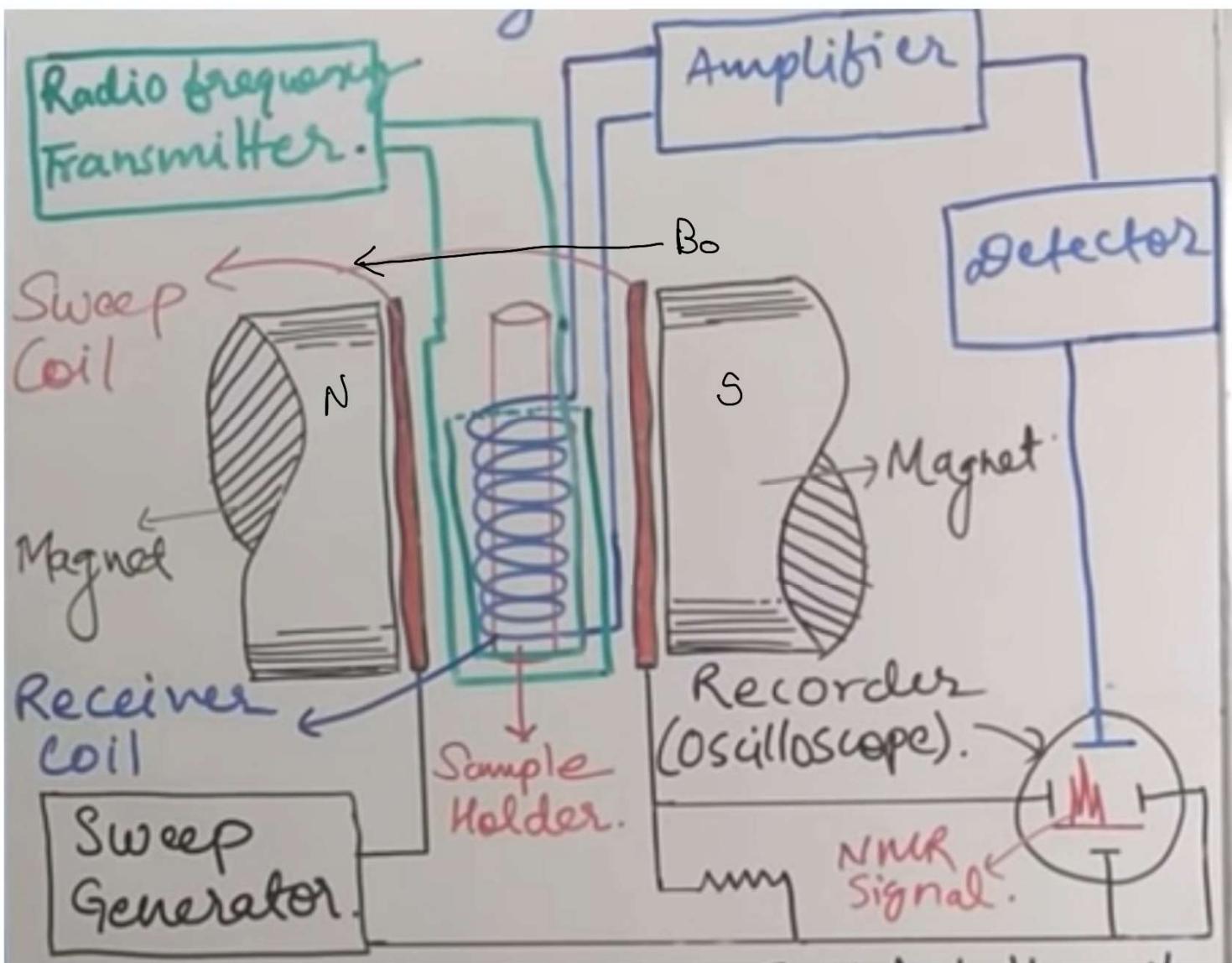
4.70 T or 47000 G

Frequency

$$\nu = \frac{267.53}{2 \times 3.14} \times 1.41 = 60 \text{ MHz}$$

$$\nu = \frac{267.53}{2 \times 3.14} \times 2.35 = 100 \text{ MHz}$$

$$\nu = \frac{267.53}{2 \times 3.14} \times 4.7 = 200 \text{ MHz}$$

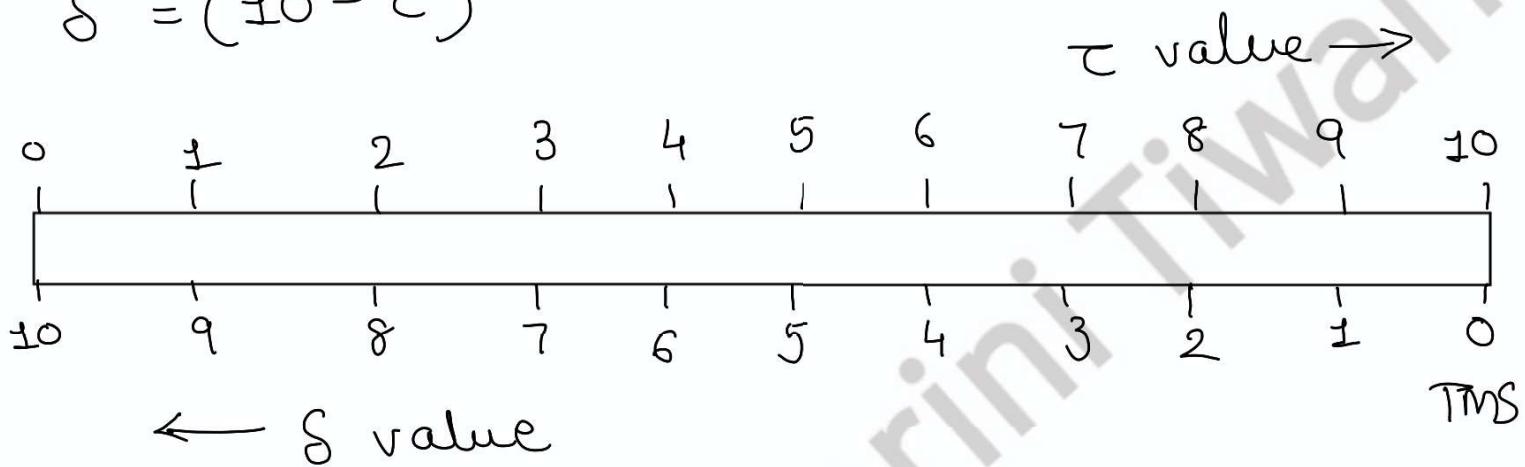


CHEMICAL SHIFT SCALE

Chemical Shift value is denoted by δ or τ

$$\tau = (10 - \delta) \quad \text{unit = ppm}$$

$$\delta = (10 - \tau)$$



← Deshielding

← Downfield

← High frequency

← High Chemical
Shift value

Shielding →

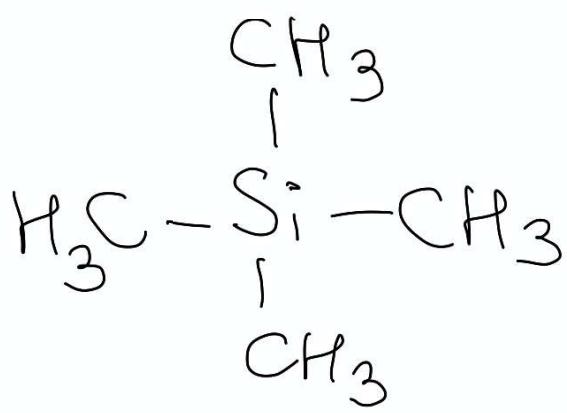
Upfield →

Low frequency →

Low Chemical →
shift value

TMS ⇒

(Tetra methyl
Silane)



- TMS is added to the sample.
- Since silicon is less electronegative than carbon, TMS protons are highly shielded. Signal defined as zero.
- Organic protons absorb downfield (to the left) of the TMS signal.

Formula :

$$\delta = \frac{\nu_{\text{sample}} - \nu_{\text{TMS}}}{\text{Operating frequency (MHz)}}$$

ν_{sample} → Resonant frequency of sample
(Sample will absorb at that frequency)

ν_{TMS} → Resonant frequency of TMS
(TMS will absorb at that frequency)

Unit of δ : $\frac{\text{Hz}}{\text{MHz}} = \frac{\cancel{\text{Hz}}}{\cancel{\text{Hz}} \times 10^6}$

$$= 10^{-6} \times 10^6 \text{ ppm}$$

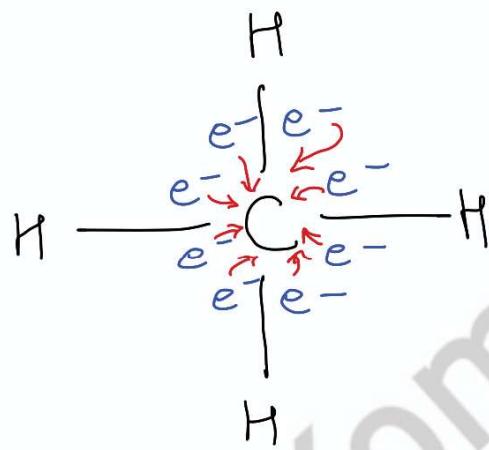
$$= \text{ppm}$$

Factors affecting Chemical Shift:

i) Inductive effect

← Electronegativity

CH_3F	CH_3Cl	CH_3Br	CH_3I	CH_4
δ value 4.26	3.05	2.68	2.16	0.23



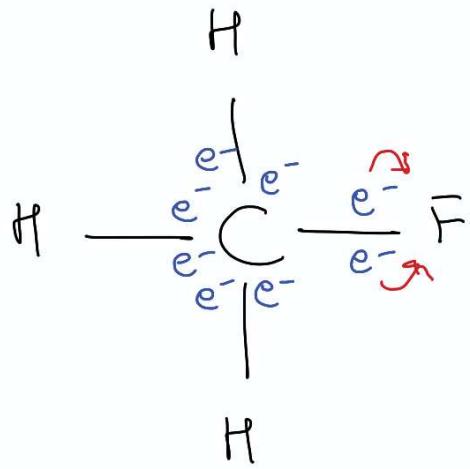
Electronegativity (in Pauling's scale)

$$\text{H} = 2.2, \text{C} = 2.55, \text{F} = 4.0$$

(Hypothetical Example)

Length of C-H bond = 1.09 \AA

Distance between H & e⁻ will be 0.6 \AA
& " " " C & e⁻ will be 0.49 \AA
due to higher electronegativity of C-atom



(Hypothetical Example)

Length of C-H bond = 1.09 \AA°

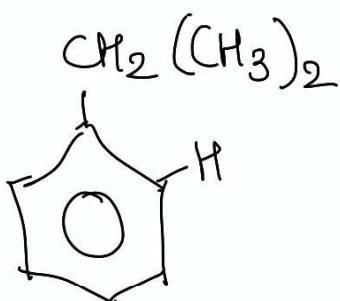
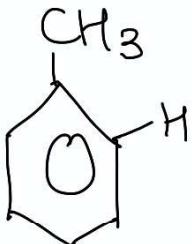
Distance between H & e⁻ will be 0.6 \AA°
 & " " C & e⁻ will be 0.49 \AA°
 due to higher electronegativity of C-atom

Length of C-F bond = 1.1 \AA°

Distance between C & e⁻ will be 0.8 \AA°
 & " " F & e⁻ will be 0.3 \AA°
 due to higher electronegativity of F-atom

2) Vander Waal's Deshielding (Steric effect):

In overcrowded molecules it is possible that some protons may occupy sterically hindered position.



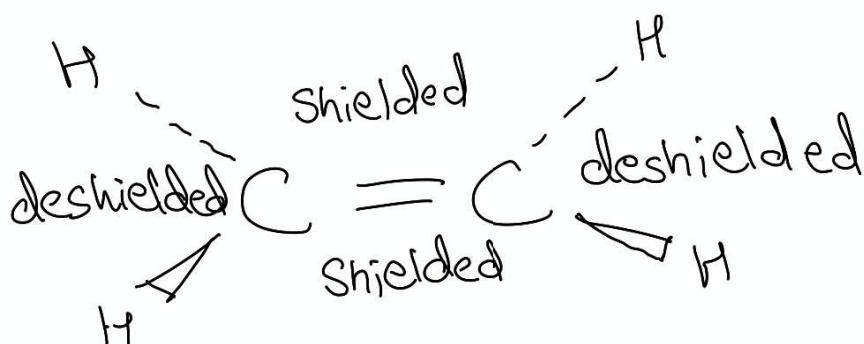
e^- -cloud of bulky group will repel the e^- -cloud of proton due to electrostatic repulsion.

Deshielding \uparrow ses the δ value.

3) Anisotropic effect:

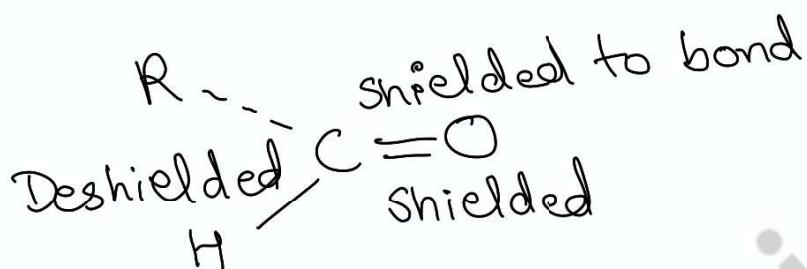
↳ Chemical bonds of the molecules are also high e^- density regions & sets magnetic field.

↳ These fields are stronger in one direction than the others & are known as anisotropic



Shielded \Rightarrow Upfield $\Rightarrow \downarrow \delta$

Deshielded \Rightarrow Downfield $\Rightarrow \uparrow \delta$

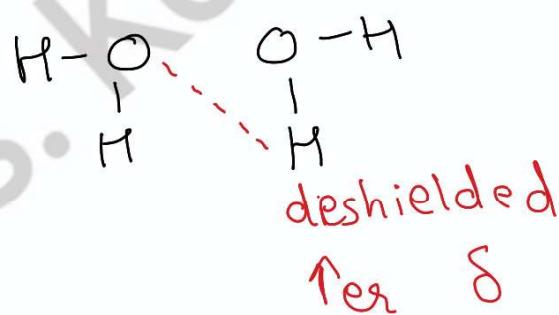


4) H-bonding:

\hookrightarrow H-atom goes for H-bonding.

\hookrightarrow Electronegative atoms take the e⁻ cloud from H-atoms & deshields it.

$\hookrightarrow \delta$ will \uparrow se



5) Hybridization of C-atom attached w/ H-atom
Hybridized C affects the e⁻ density of H-atoms

sp	1:1	High δ	↑ Deshielding of H
sp^2	1:2	Lower δ	
sp^3	1:3	Lowest δ	

- ↳ When proportion of s is 1/e_r
- ↳ Bonding e⁻ will be more closer to carbon
- ↳ e⁻ are away from H-atom
- ↳ Deshielding happens (↑ e_r S)

NUMERICALS:

1) Calculate Chemical shift in ppm (δ) for a proton that has resonance at 150 Hz downfield from TMS on NMR spectrophotometer that operates at 60 MHz

Formulae:

$$\delta = \frac{\nu_{\text{sample}} - \nu_{\text{TMS}}}{\text{Operating frequency (in MHz)}}$$

$$\delta = \frac{\Delta\nu}{\text{Operating } \nu (\text{MHz})}$$

$$= \frac{150 \text{ Hz} \times 10^6 \text{ ppm}}{60 \text{ MHz}}$$

$$= \frac{150 \cancel{\text{Hz}}}{60 \times \cancel{10^6 \text{ Hz}}} \times \cancel{10^6 \text{ ppm}}$$

$$\delta = 2.5 \text{ PPM}$$

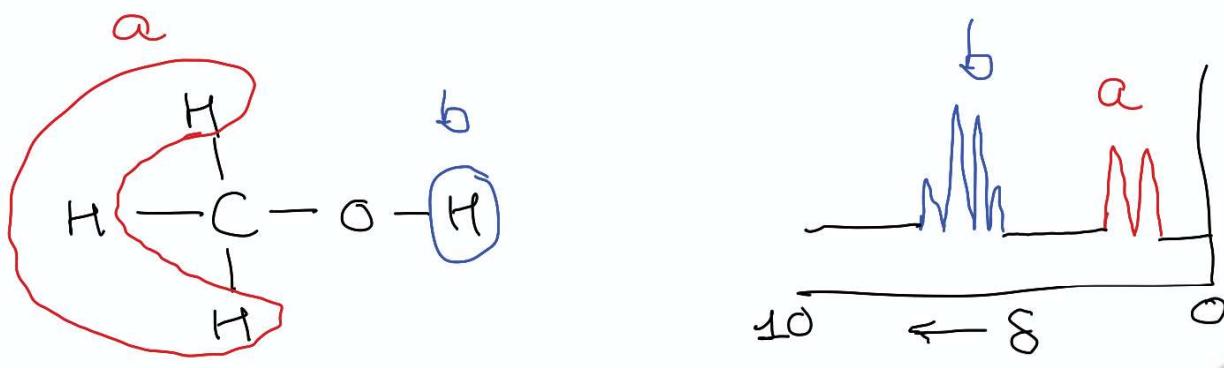
2.7 If observed shift from TMS is 300Hz
& operating ν is 100 MHz.
Calculate δ

$$\boxed{\delta = \frac{\Delta\nu}{\text{operating } \nu}}$$

$$= \frac{300 \text{ Hz}}{100 \text{ Hz}} \times 10^6 \text{ PPM}$$
$$= \frac{300 \cancel{\text{Hz}}}{100 \times 10^6 \cancel{\text{Hz}}} \times 10^6 \text{ PPM}$$
$$= 3 \text{ PPM}$$

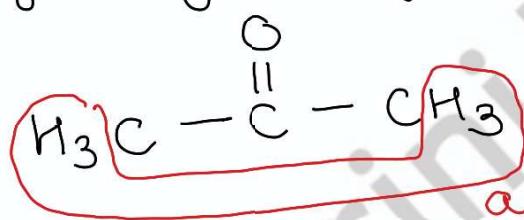
NUMBER OF SIGNALS:

- ↳ Each signal represents a set of equivalent protons.
- ↳ Magnetically equivalent proton are chemically equivalent
 - ↳ give single signal in NMR .



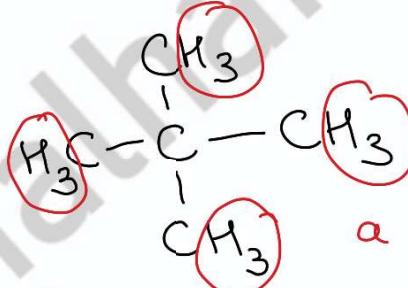
Molecules giving single signal :-

1.) Acetone

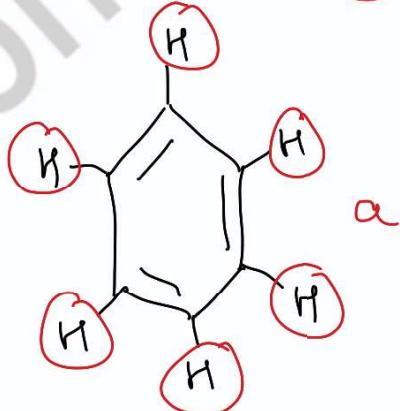


^1H NMR signal

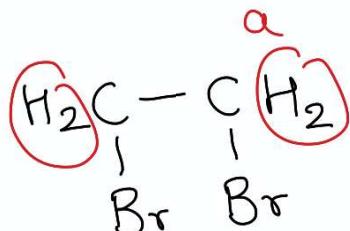
2.) Tetramethyl methane



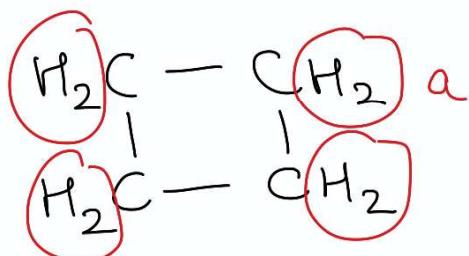
3.) Benzene



4.) 1,2-Dibromoethane

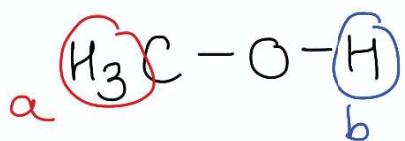


5.) Cyclobutane



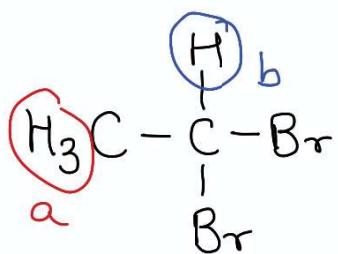
Molecules giving double NMR signal :-

1) Methanol

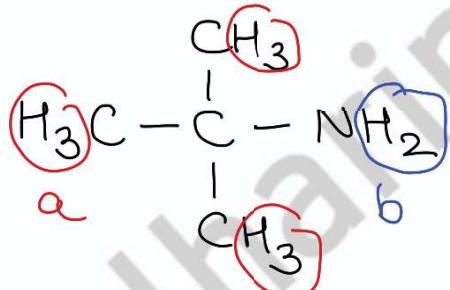


2 NMR signals

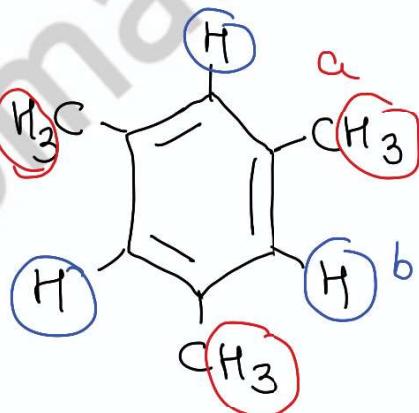
2) 1,1-Dibromoethane



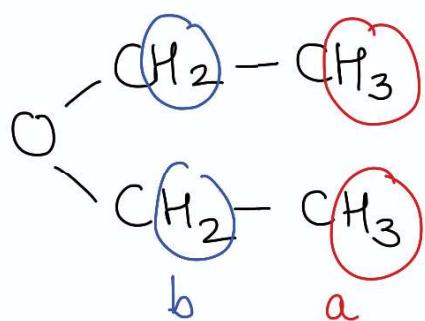
3) Tert-Butyl amine



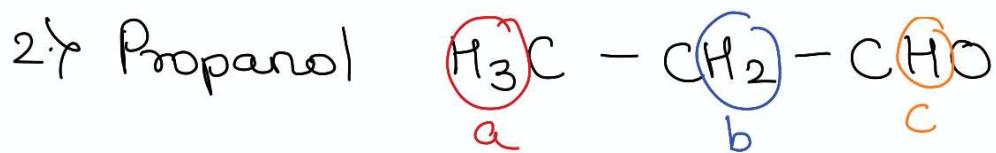
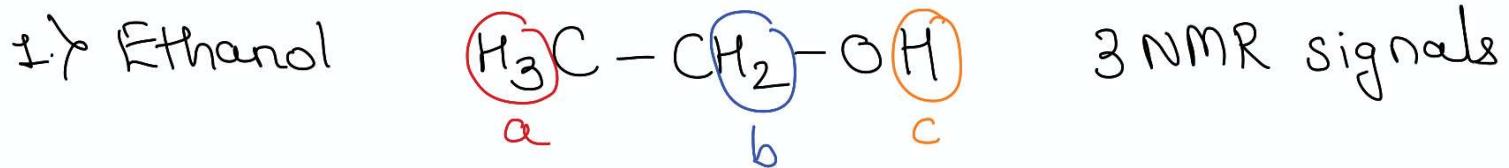
4) Mesitylene



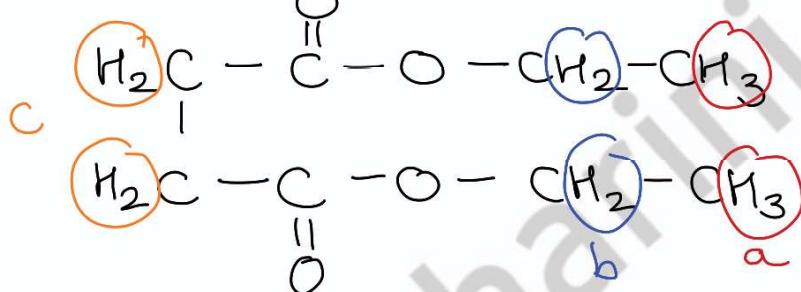
5) Diethyl ether



Molecules giving three NMR signals:

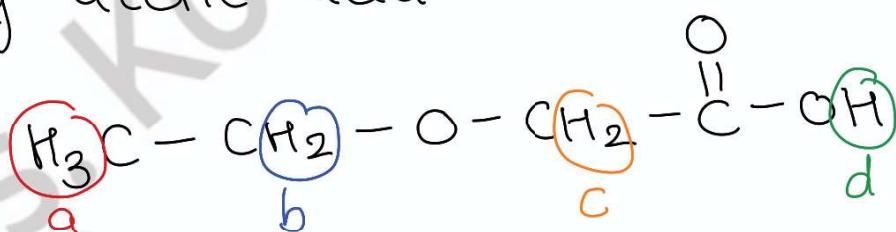


3) Diethyl succinate



Molecules giving four NMR signals:

1) Ethoxy acetic acid



∴ C is attached with carboxy (-COOH) group which is more electronegative than methyl (-CH₃) group (to which b is attached)

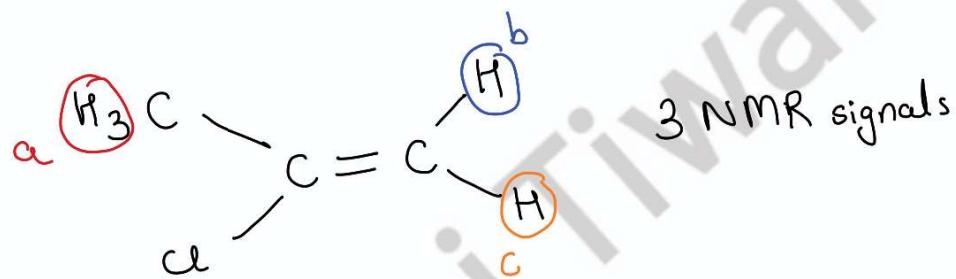
∴ 4 NMR signals will be produced

Stereoisomers related signals:

- ↳ Chemically equivalent protons must be stereo-chemically equivalent to get a single NMR signal.
- ↳ If not, then they will produce more than one signal.

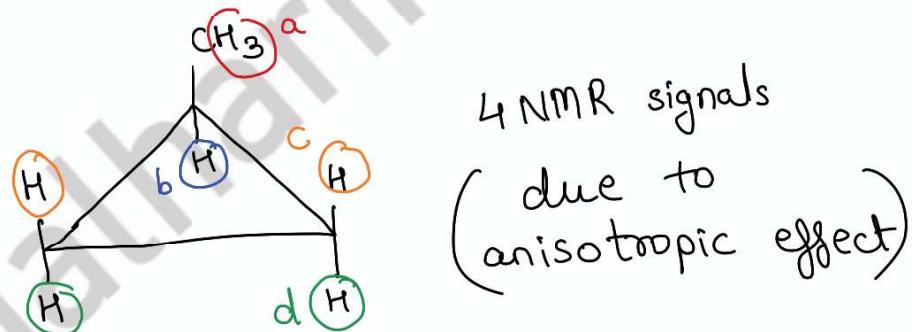
Example:

1) 2-Chloropropene



3 NMR signals

2) Methyl Cyclopropane



4 NMR signals

(due to
(anisotropic effect))

SPLITTING OF NMR SIGNALS:

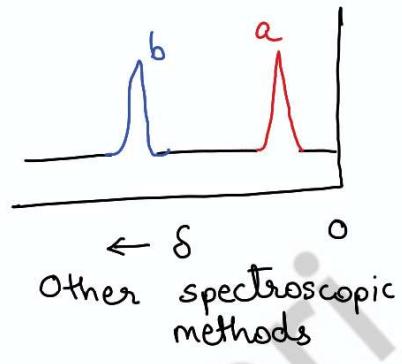
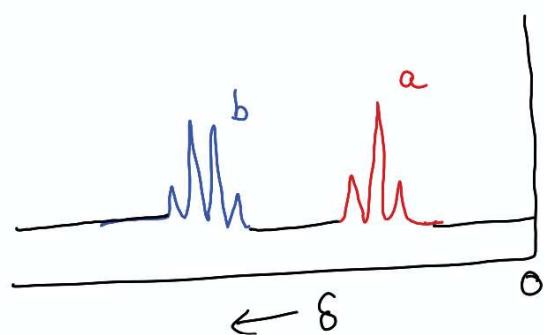
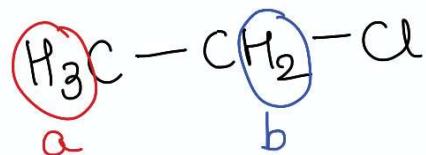
- ↳ Each Signal represents one kind or one set of proton(s) in a molecule.
- ↳ In some molecules, singlet of signal will not be observed.

Multiplet signals

- Doublet
- Triplet
- Quartet
- ... → etc.

Example:

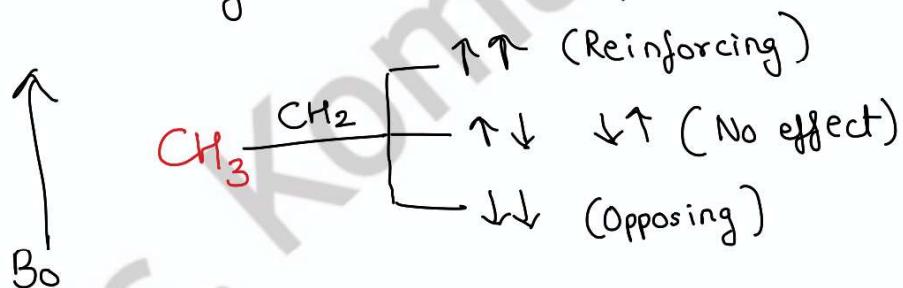
→ Ethyl Chloride



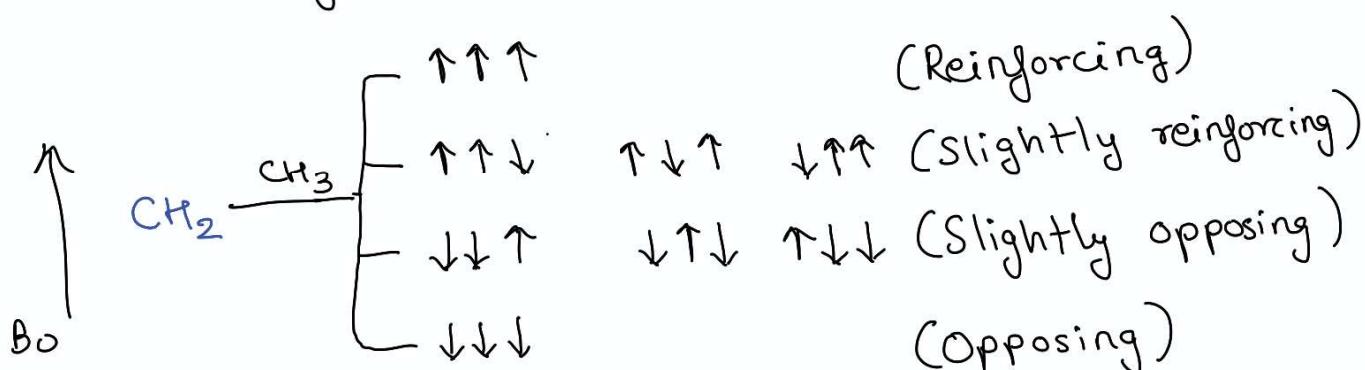
NMR spectroscopy will show splitting

Mechanism of splitting :-

Interaction between the spins of neighbouring magnetic nuclei in a molecule may cause the splitting of the signal in NMR spectrum.



In CH_3 , neighbouring $-\text{CH}_2-$ gives 2 protons which can show 3 possible alignments wrt B_0
∴ The signal will split into 3.

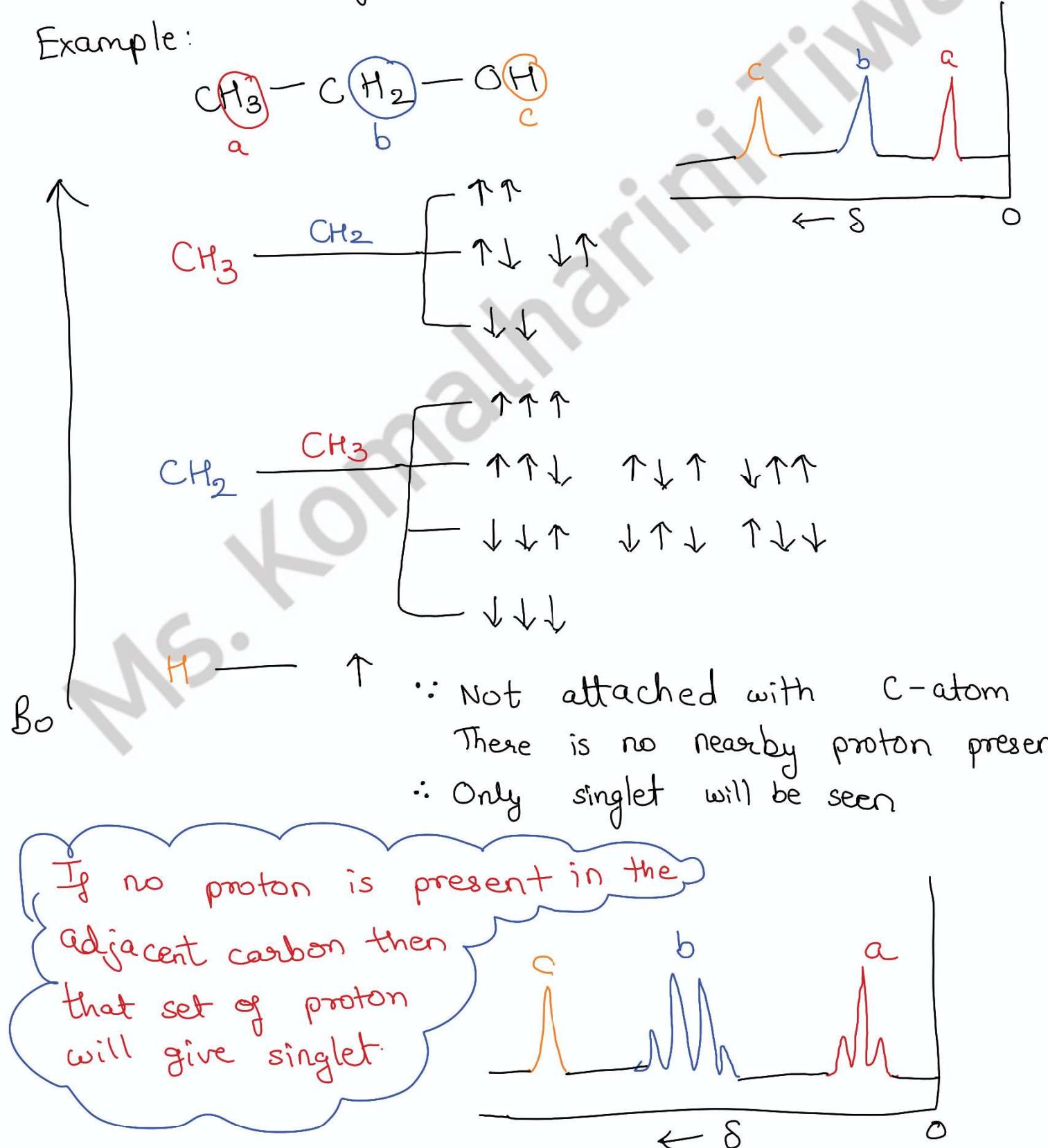


∴ signal will split into 4

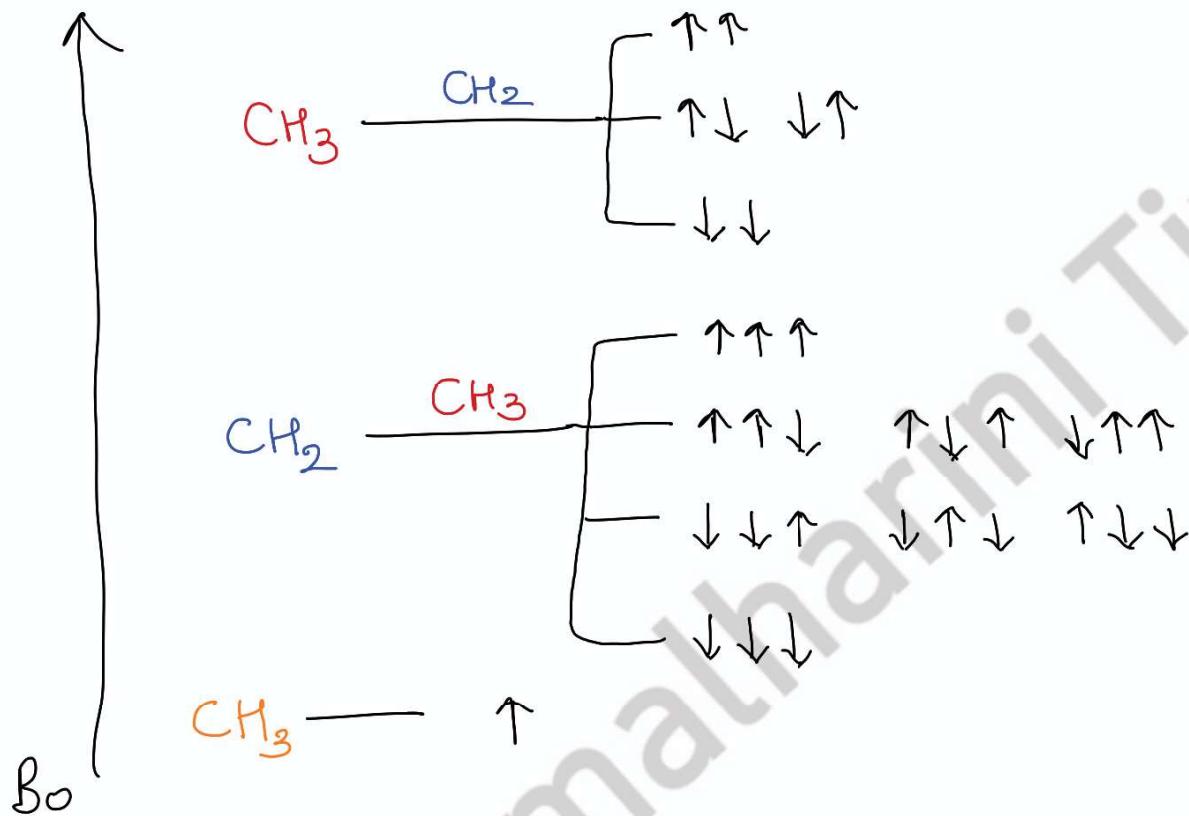
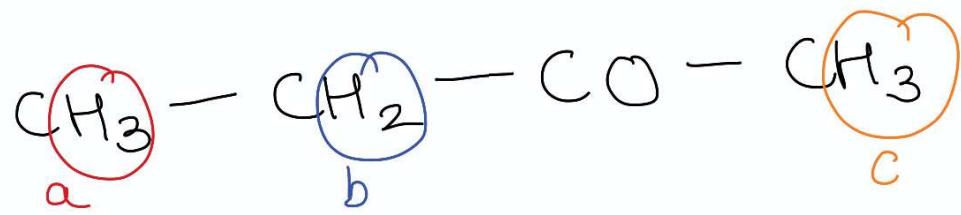
SPIN- SPIN COUPLING :-

- ↳ Minimum 2 sets of protons are essential.
- ↳ The spins of 2 protons are coupled
- ↳ Due to spin-spin coupling between nearby protons, splitting of signal will be observed.

Example:



2- Butanone



\therefore No proton is present in the adjacent carbon

\therefore Only singlet will be seen

PEAK INTENSITIES OF VARIOUS MULTIPLETS:-

Peak area Ratio & Signals

1 Singlet

1 : 1 Doublet

1 : 2 : 1 Triplet

1 : 3 : 3 : 1 Quartet

1 : 4 : 6 : 4 : 1 Quintet

1 : 5 : 10 : 10 : 5 : 1 Sextet

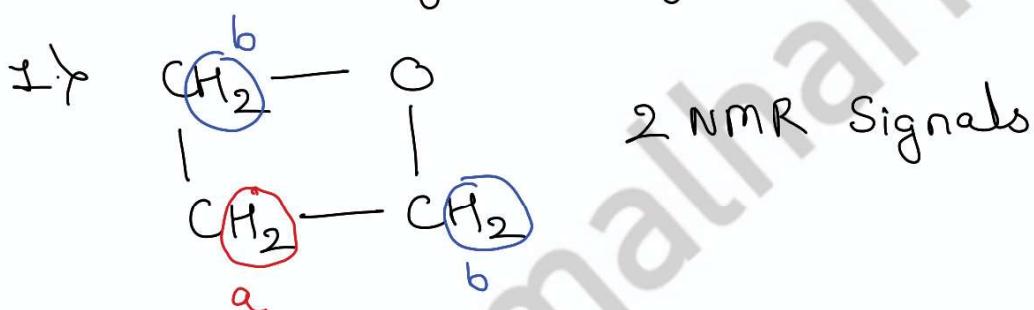
1 : 6 : 15 : 20 : 15 : 6 : 1 Septet

Pascal's Triangle
(Ratio of the area of peaks in multiplets)

Relative Peak Intensities of Symmetric Multiplets

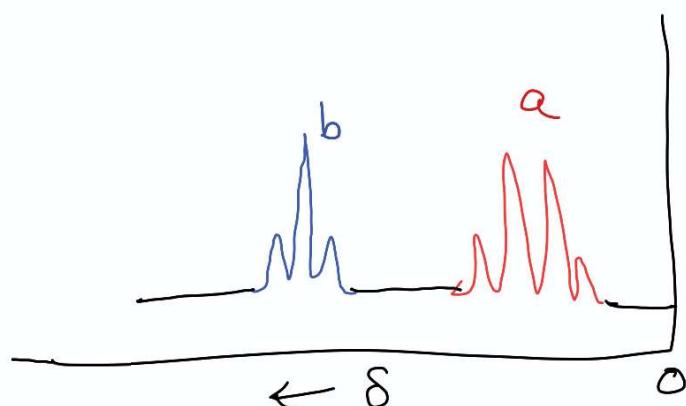
Number of Equivalent Protons Causing Splitting	Number of Peaks (multiplicity)	Area Ratios (Pascal's triangle)
0	1 (singlet)	1
1	2(doublet)	1 1
2	3 (triplet)	1 2 1
3	4 (quartet)	1 3 3 1
4	5 (quintet)	1 4 6 4 1
5	6 (sextet)	1 5 10 10 5 1
6	7 (septet)	1 6 15 20 15 6 1

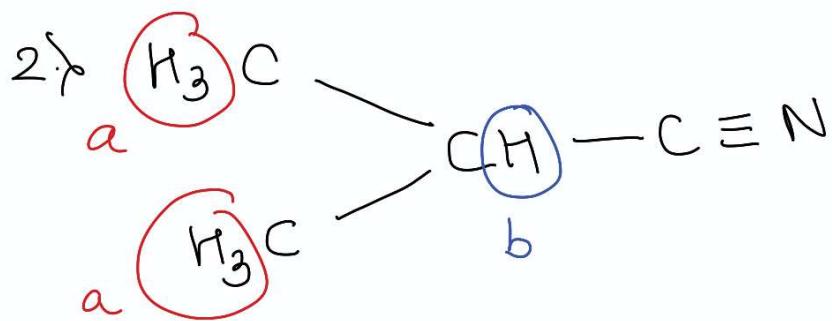
Calculation of no. of signals with Splitting:-



(a) \Rightarrow 4 adjacent protons are present \Rightarrow Quintet signal (upfield)

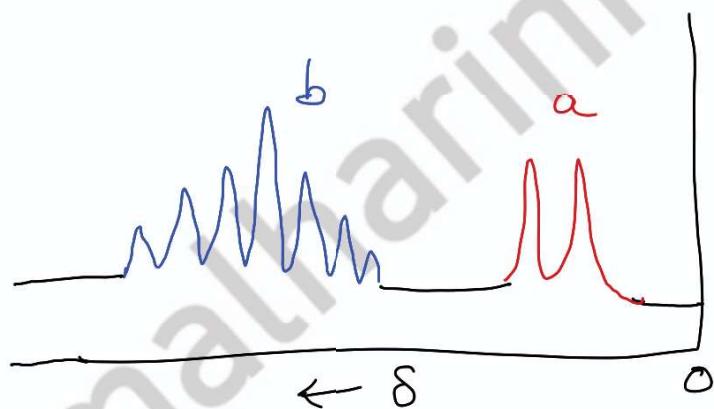
(b) \Rightarrow 2 adjacent protons are present \Rightarrow Triplet signal
 $(\because \text{O-atom is electronegative, the signal will be downfield.})$



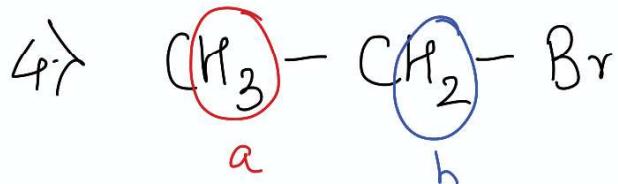
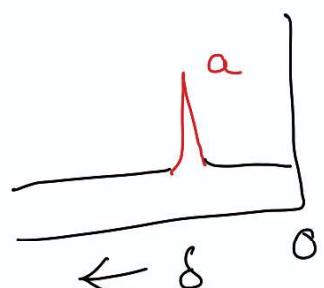
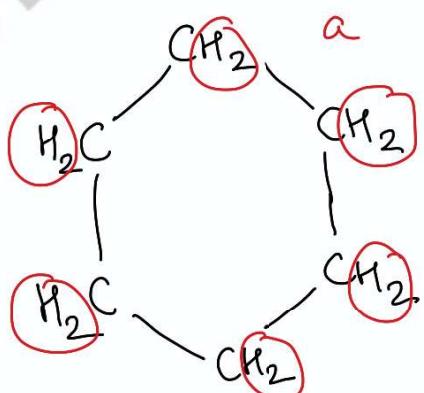


(a) \Rightarrow 1 adjacent proton \Rightarrow Doublet \Rightarrow Upfield

(b) \Rightarrow 6 adjacent proton \Rightarrow Septet \Rightarrow Downfield

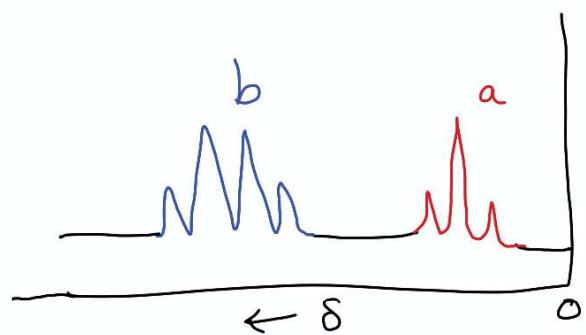


3.) Cyclohexane

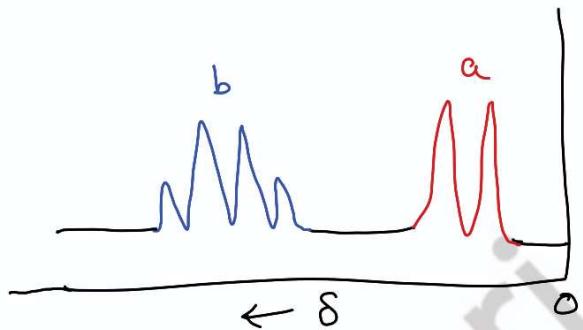
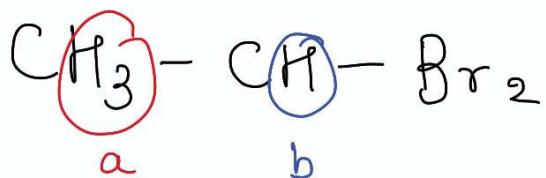


a \Rightarrow Triplet \Rightarrow Upfield

b \Rightarrow Quartet \Rightarrow Downfield



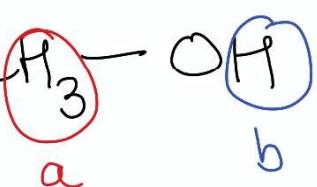
5)



$a \Rightarrow$ Doublet \Rightarrow Upfield

$b \Rightarrow$ Quartet \Rightarrow Downfield

6)



$a \Rightarrow \because$ no adjacent proton \therefore Singlet \Rightarrow Upfield

$b \Rightarrow$ Singlet \Rightarrow Downfield

