Unit - 1

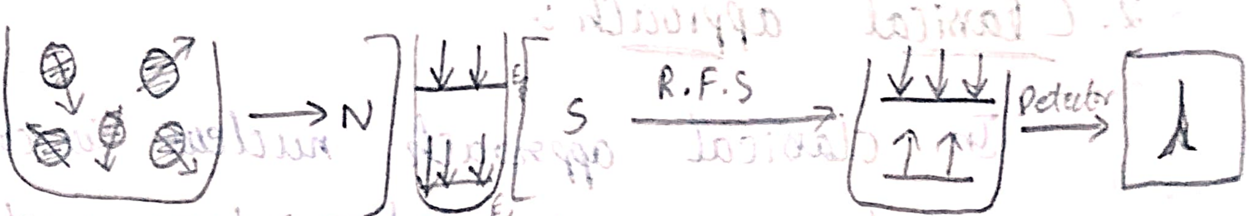
10M

NMR Principle :

NMR Principle is explained by two methods.

1. Quantum approach
2. Classical approach

Quantum approach :



In the absence of external magnetic field all the protons present in random orientations. whenever the sample is present in external magnetic field the disorder is dissappear.

Little ~~less~~ exess no. of protons present in lower energy level that is E_α.

Little less no. of protons present on the higher energy level that is E_β.

The matching of radio frequancy radiation and energy difference between the nuclear energy level is nothing but resonance.

Under the resonance condition E_α nuclei taken energy from radio frequancy source and exited to the E_β level.

How much energy is gained by E_α nuclei is detected by detector.

The obsorbed energy is converted into signal.

Spin flipping :-

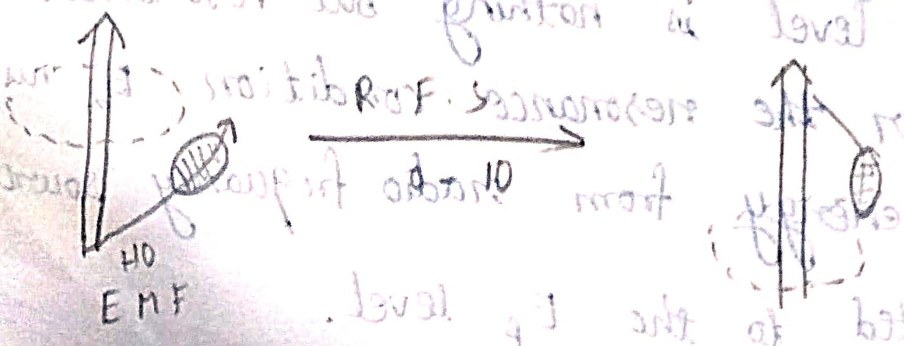
Inverse (or) oppose in spin orientation is called flipping.

2. Classical approach :-

In classical approach nucleus is considered as nacked one (or) isolated (or) bare nucleus. That means Nucleus considered as without revolution of electron.

Precession :- The rotation of a spinning particle with respect to outer force is called Precission.

The rotation of a spinning particle about the direction of external magnetic field taking by an eliptical path discovered by Joseph Larmur.



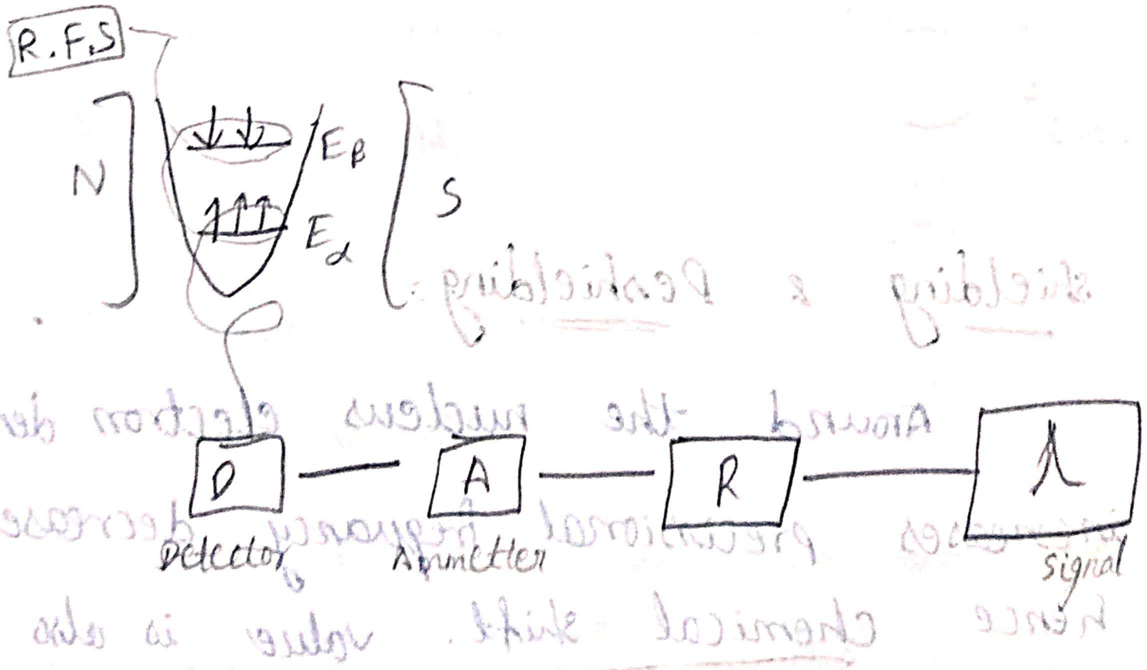
* Precissional Frequancy :-

No. of rotations formed by the nucleus in a unit time is called precissional frequancy. when nucleus is present in external magnetic field the rotation is about the direction of E.M.F hence the motion is called precissional motion. and the frequancy is called precissional frequancy ×

it is observed by Joseph Larmer hence it is called as Larmer precissional frequancy ν_1

under resonance condition precissional frequancy is matched with radio frequancy spin flipping is takes place.

NMR Block diagram :-



Factors effecting precissional Frequency :-

1. E.M.F ↑ α P.F ↑

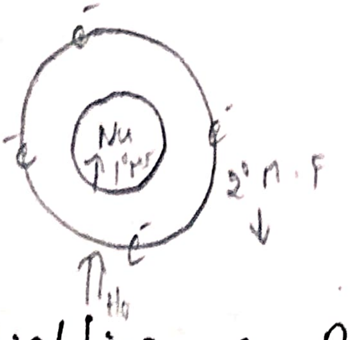
1.4 T = 60 MHZ

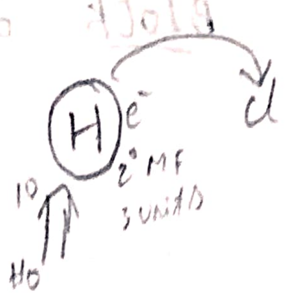
2.3 T = 100 MHZ

4.7 T = 200 MHZ
7.5 T = 300 MHZ
9.3 T = 400 MHZ
14.7 T = 600 MHZ.

2. **Electron Density :-**

whenever electron around the nucleus electron cloud increases precissional frequency decreases.



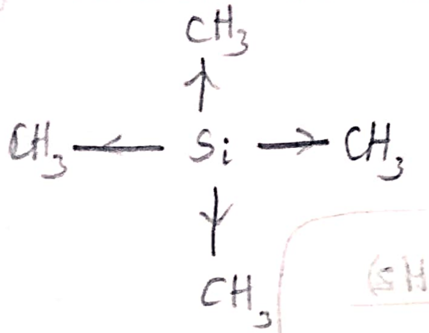


shielding & Deshielding :-

Around the nucleus electron density increases precissional frequancy decreases hence chemical shift. value is also decrease. This process is called shielding (upfield). where as electron density decreases around the nucleus precisional frequancy increases. Hence chemical shift valeie also increases. This process is called deshielding. (downfield).

(TMS) Tetra Methyl Silane :-

TMS is used as reference standard.



$$CH_3 \leftarrow Si(CH_3)_3$$

It is highly volatile compound.

In the ~~sam~~ 12 protons are in same environment

Here silicon is electropositive element.

These are highly shielded protons.

Hence the chemical shift value of EMF is very low comparitive all other organic compound.

5M Chemical shift :-

Shift of the signal from our reference standard. (or) Difference b/w the precisional frequancy of sample protons & reference proton.

Before chemical shift is expressed in frequancy units.

whenever we increase the strength of the magnetic field change is developed in frequancy units. so it is difficult to remember that values.

chemical shift is independent of the operating frequancy.

Now overcome this problem we introduce δ-scale (τ-scale)

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

$$\delta = 10 - \tau$$

$$\boxed{\delta = \frac{\nu_{sample} - \nu_{reference}\ (Hz)}{\text{operating frequancy}\ (MHz)}}$$

Chemical shift values of different functional Group :-

i Alkanes

CH_3 0.9 δ

CH_2 1.2 δ

CH 1.5 δ

Ex:- $CH_3 - CH_2 - CH_3$

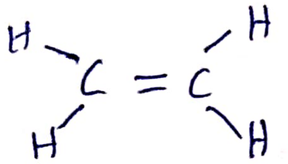
$\delta_A = 0.9$ PPM

$\delta_B = 1.2$ PPM

Alkenes

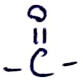
4.5 to 6.5δ

5.5δ



W.D.G

$C=C$, $C\equiv C$, ,



$-\overset{O}{\overset{\|}{C}}-$,

$CH_3-CH=CH_2$

(2 to 3) 5.5δ

Alkynes

$H-C\equiv C-H$ Anisotropic effect

(2 to 3)

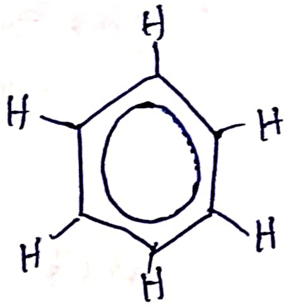
$CH_3-C\equiv CH$

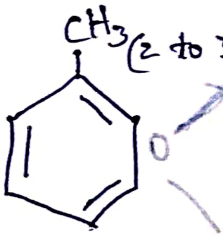
2.3δ ~~(2 to 3)~~ 2.5δ

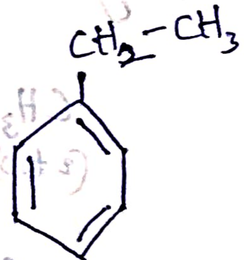
Benzene

6.5 to 8.5δ

7.2δ

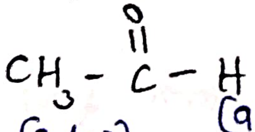






Carbonyl compounds :-

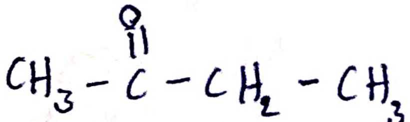
Aldehyde



$CH_3-\overset{O}{\overset{\|}{C}}-H$

(2 to 3) (9 to 10)

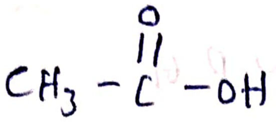
Ketone



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

(2 to 3)

Acid

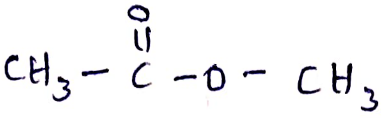


$CH_3-C(=O)-OH$

(2 to 3) (10-12)

Ester

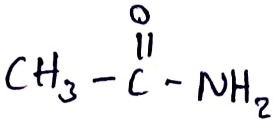
attached to oxygen (3-



$CH_3-C(=O)-O-CH_3$

2.4δ 3.6δ

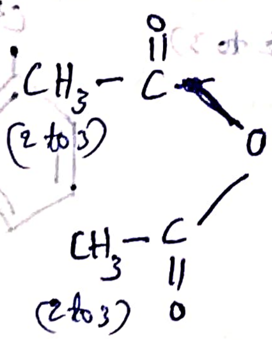
Amide



$CH_3-C(=O)-NH_2$

2.4δ 6.7δ

Anhydride



Alcohol

CH_3-O-H

>3.5δ <3.5δ

CH_3-CH_2-OH

1.1δ >3.5 <3.5

Amines

$CH_3 - NH_2$

(2 to 3) (1 to 5)

↓

3

Ether

$\underset{A}{CH_3} - O - \underset{B}{CH_2} - \underset{C}{CH_3}$

3.4 δ   3.7 δ   1.2 δ

Alkyl halides

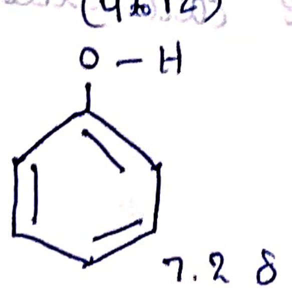
$CH_3 - F$ (4.2 δ)

$CH_3 - Cl$ (3.3 δ)

$CH_3 - Br$ (2.7 δ)

$CH_3 - I$ (2.1 δ)

Phenol



Ethyl Bromobide

$\underset{A}{CH_3} - \underset{B}{CH_2} - Br$

1.1 δ   2.7 δ

5M Multiplicity rule (or) spin-spin coupling :

Each line will be splitt up into no. of lines is explained by multiplicity rule.

$$M = (n+1)$$

Here,

n = no. of neighbouring non-equavalent protons.

1 - Proton	2 - H	3 - H
↑	↑↑	↑↑↑
↓	↓↓	↓↓↓
2 lines	↑↓, ↓↑	↑↓↓, ↓↑↓, ↓↓↑
doublet	3 lines	↑↑↓, ↑↓↑, ↓↑↑
	triplet	4 lines
		quartet

spin orientation

Signal height :

signal height can be calculated by using Pascal's triangle.

Pascal triangle

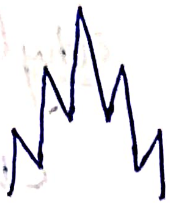
1 singlet

1 1 doublet

1 2 1 triplet

1 3 3 1 Quartet

1 4 6 4 1 Quintet



1 5 10 10 5 1 ~~per~~ sextet :

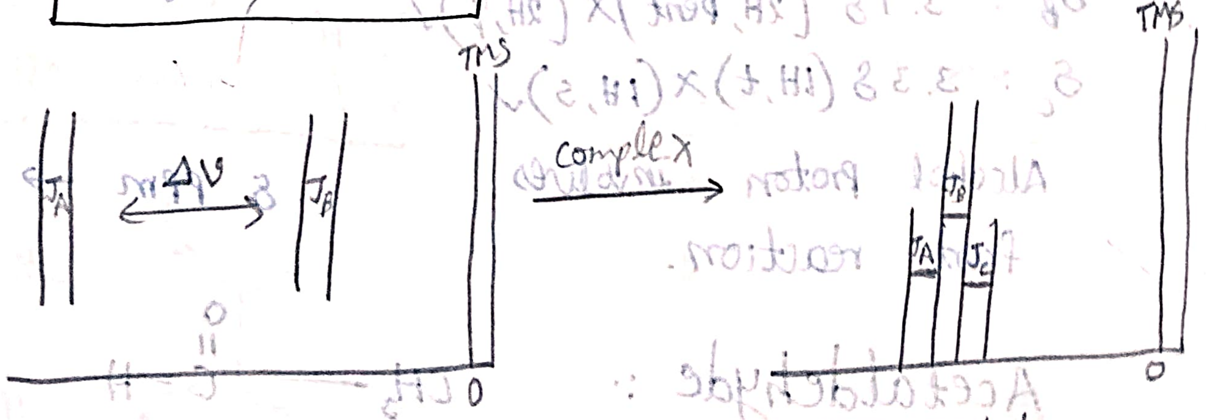
5M

Coupling constant (J) :-

Distance b/w two lines in a single multiplet is called coupling constant.

It is used to distinguish two doublets from a quartet.

$\boxed{J_{value} = 0 - 20 \text{ Hz}}$



simple spectra
doublet

Quartet

$J_A \neq J_B \neq J_C$

$J_A = J_B = J_C$ } Normal spectra of quartet

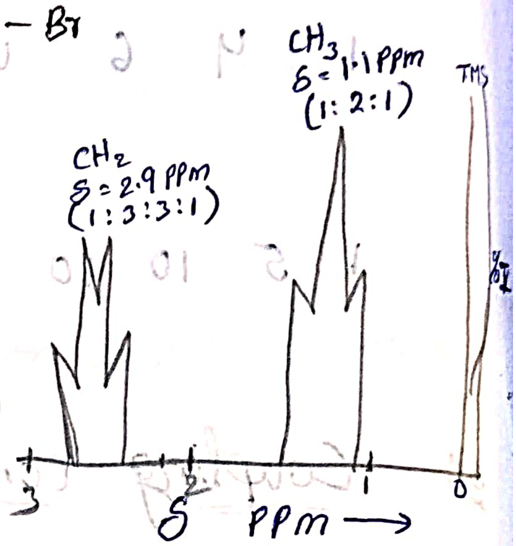
Applications of NMR :-

Ethyl Bromide :- CH_3-CH_2-Br

$CH_3 - CH_2 - Br$
A B

δ_A : 1.1 ppm, (3H, t)

δ_B : 2.9 ppm (2H, q)



Ethanol :- $CH_3 - CH_2 - OH$

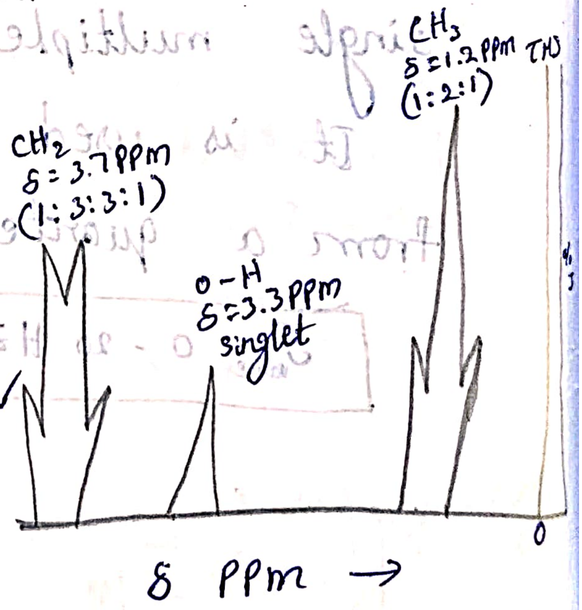
$CH_3 - CH_2 - OH$
A B C

δ_A : 1.2 δ (3H, t)

δ_B : 3.7 δ (2H, pent) × (2H, q) ✓

δ_C : 3.3 δ (1H, t) × (1H, s) ✓

Alcohol proton involves fast reaction.

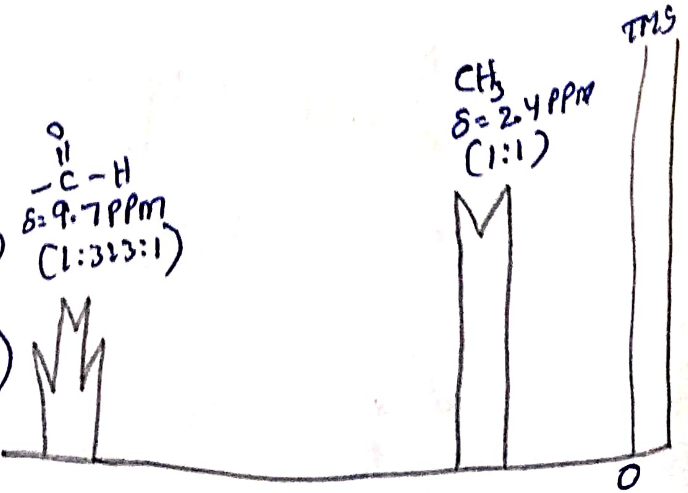


Acetaldehyde :- $CH_3 — \overset{O}{\overset{||}{C}} - H$

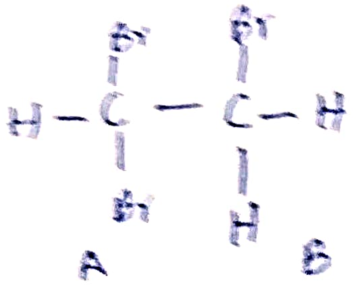
$CH_3 - \overset{O}{\overset{||}{C}} - H$
A B

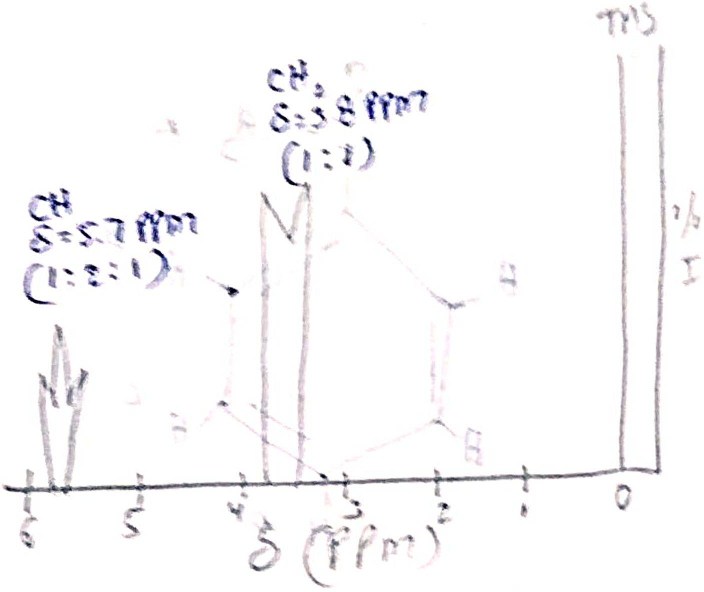
δ_A : 2.4 ppm (3H, d)

δ_B : 9.5 ppm (1H, q)



1,1,2-tri bromo ethane

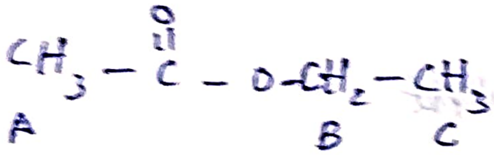




δ_A : 5.7 ppm (1H, t)

δ_B : 3.8 ppm (3H, d)

Ethyl Acetate

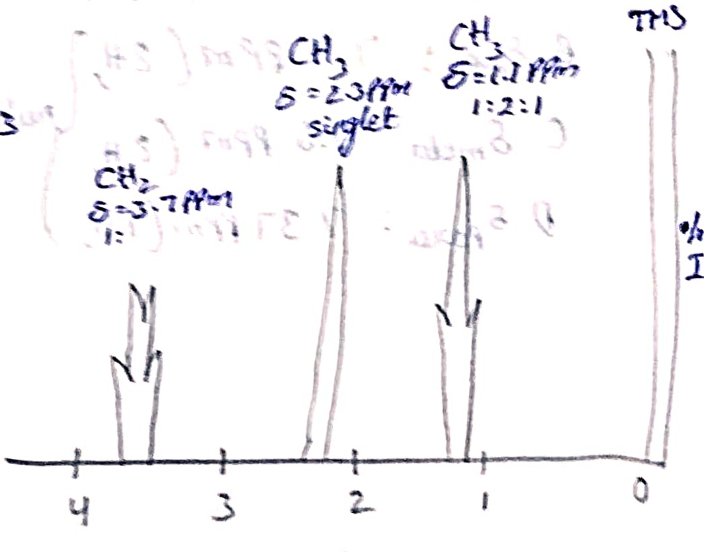


$CH_3-\overset{\overset{O}{\|}}{C}-O-CH_2-CH_3$

δ_A : 2.3 ppm (3H, s)

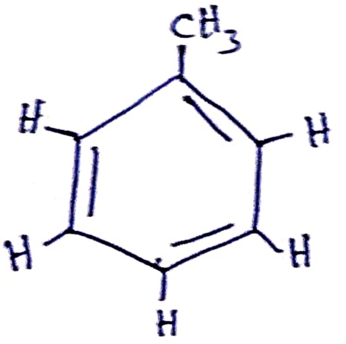
δ_B : 3.7 ppm (2H, q)

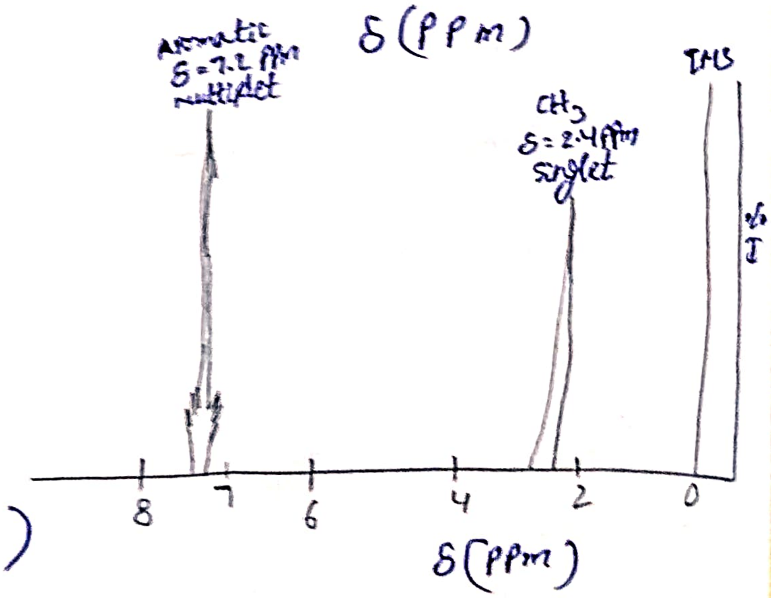
δ_C : 1.1 ppm (3H, t)



δ (ppm)

Toulene

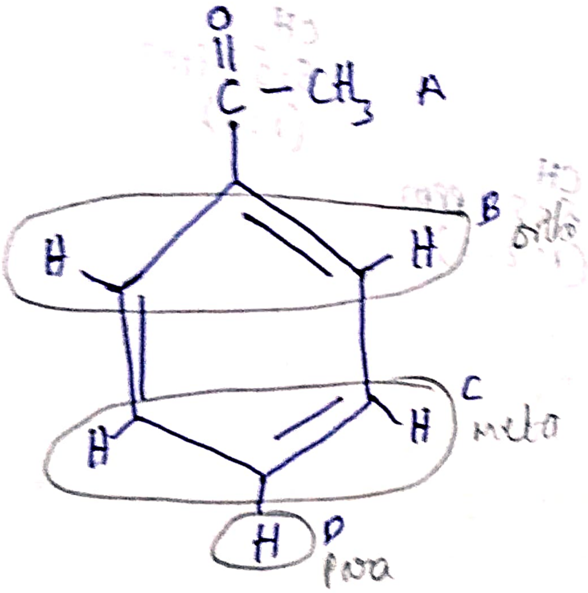


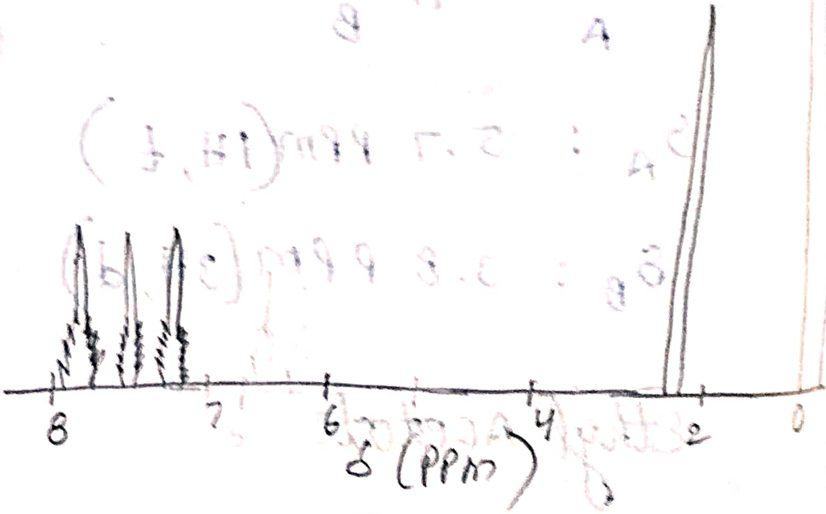


δ_{CH_3} : 2.4 ppm (3H, s)

$\delta_{Aromatic}$: (7-7.2) ppm (5H, multiplet or singlet)

Acetophenone :-





A δ_{CH_3} : 2.4 PPm (3H, S)

B δ_{ortho} : 7.9 PPm (2H,

C δ_{meta} : 7.6 PPm (2H, } multiplet

D δ_{para} : 7.37 PPm (1H,)