NMR Spectroscopy

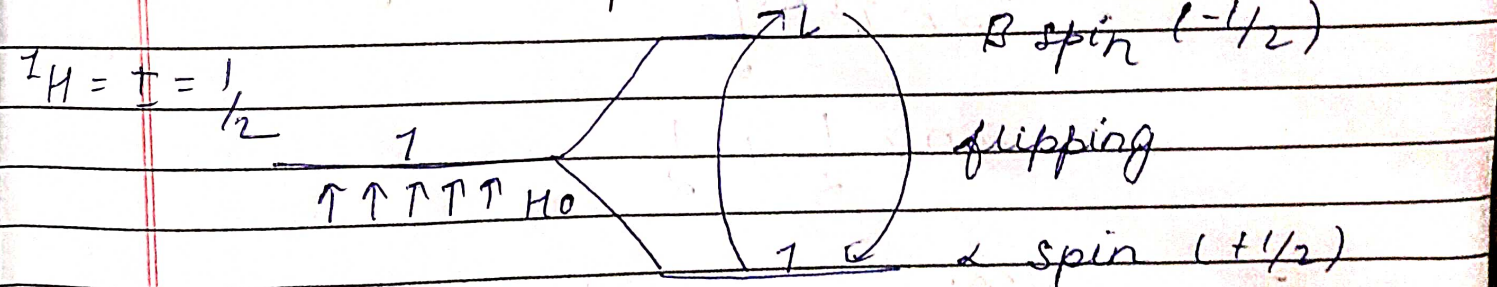
NMR - Nuclear Magnetic Resonance

NMR active species : Those species which have odd no. of proton or neutron or the nuclear spin quantum no. (I) is not equal to 0.

$I \neq$ zero

^{12}C	=	6 + 6	= inactive
^{13}C	=	6 + 7	= active
^{1}H	=	1	= active

Basic Principle



→ In this technique organic, inorganic, polymer, steroids, terpenoids and other compound put in a high external magnetic field.

→ When compound has $I \neq 0$ value that time compound will be NMR active.

→ In this process proton or neutron converts into the α spin to β spin or β spin to α spin process.

This process is called resonance or flipping and this type of phenomenon is called nuclear magnetic resonance and this type of spectroscopy is called NMR spectroscopy.

No. of Signals

No. of signal = Type of proton = Type of chemical environment

Types of Signal / Spin-Spin coupling

TOS = Type of proton on adjacent 'C'

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

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

Type of 'P' = $\boxed{n+1}$

n = no. of proton on adjaunt C atom

1. Singlet
2. doublet
3. Triplet
4. Quadrate

⇒ $CH_3 - CH_2 - Br$

Examples:

1. CH_3-CH_2-OH (a) (b) (c)
   No. of signals = 3
   Types of signal = 3
   (t) (q) (s)

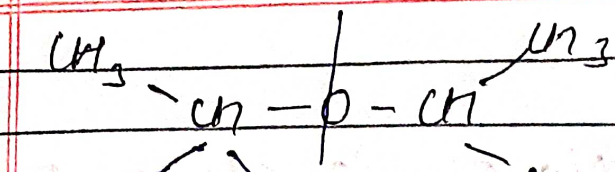
   for (a) = n+1 = 2+1 = 3 (t)
   (b) = n+1 = 3+1 = 4 (q)
   (c) = n+1 = 0+1 = 1 (s)

2. $CH_3-CH_2-\underset{\underset{F}{|}}{\underset{|}{C}}-CH_2-CH_3$
   (a) (b) $\underset{|}{C}$

   No. of signal = 2
   Type of signal = (a) = n+1 = 3 (t)
   (b) = n+1 = 4 (q)

3. $CH_3-CH(CH_2-Br)-CH_2$
   No. of signals = 3
   CH_3: 1+1 = 2 (doublet)
   CH: 8+1 = 9 (multiplet)
   CH_2: 1+1 = 2 (doublet)

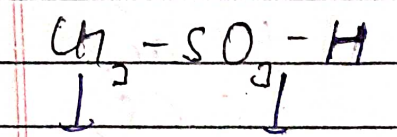
4. $CH_3-CH_2-O-CH_2-CH_3$
   N.O.S = 2
   CH_3: 2+1 = 3 (triplet)
   CH_2: 3+1 = 4 (quartet)

5. 

NOS = 2

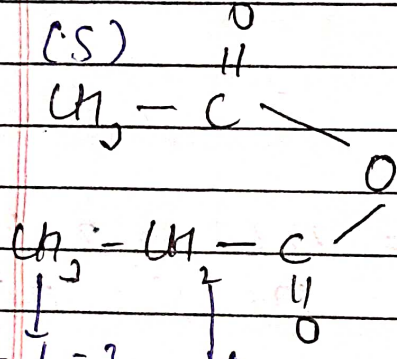
1+1 = 2 (doublet)

6+1 = 7 (septate)

6. 

NOS = 2

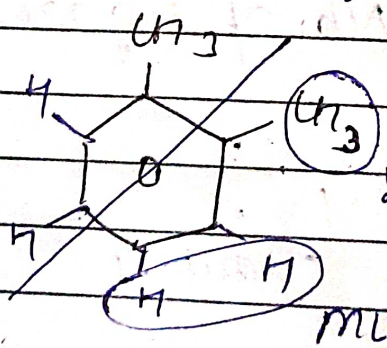
(singlet) (singlet)

7. (S) 

N.O.S = 3

2+1 = 3 (triplet)

3+1 = 4 (quartet)

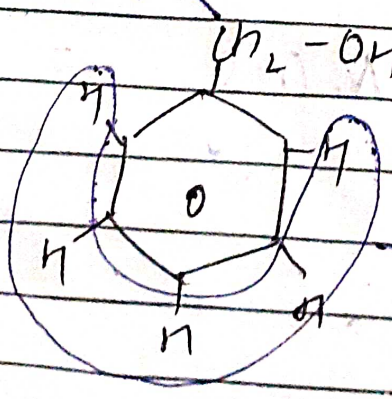
8. 

NOS = 2

singlet

multiplet

singlet

9. 

NOS = 3

→ multiplet

(singlet)

10. $CH_3-\underset{\underset{H}{|}}{\overset{OH}{\overset{|}{C}}}-\underset{\underset{H}{|}}{\overset{H}{\overset{|}{C}}}-CH_3$

$n+1=2$ (doublet)

$5+1=6$ (sextet)

$n+1=3$ (triplet)

$4+1=5$ (Pentate)

11. $\underset{(a)}{CH_3}-\underset{(b)}{CH_2}-\underset{(c)}{CH_2}-\underset{(d)}{CH_2}-\underset{(e)}{OH}$

$2+1=3$ (triplet)

$4+1=5$ (pentet)

$2+1=3$ (triplet)

singlet

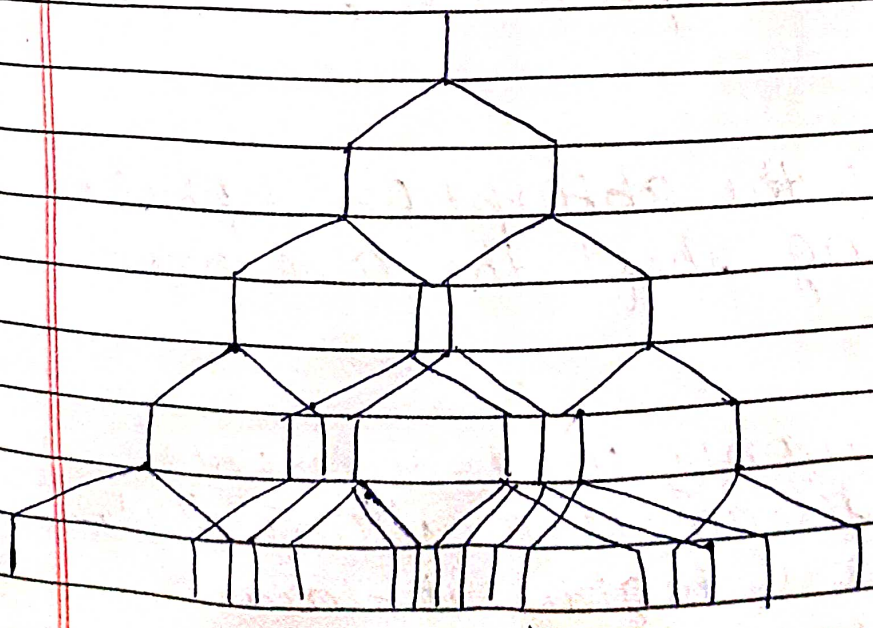
$5+1=6$ (sextet)

12. $\underset{(a)}{CH_3}-\underset{(b)}{CH_2}-\underset{(c)}{CH}-Cl$ NOS - 4

$2+1=3$ (triplet) $4+1=5$ (multiplet) $CH_3 \rightarrow 1+1=2$ (doublet)

Intensity of Signals

⇒ It is described by Pascal Triangle Method



1 Singlet

1 : 1 Doublet

1 : 2 : 1 Triplet

1 : 3 : 3 : 1 Quadrate

1 : 4 : 6 : 4 : 1 quintate

Chemical Shift (Position of Signal)

→ The position of signals in the spectrum helps us to know the nature of the proton viz. aliphatic, aromatic, acetylenic & vinylic.

→ When a molecule is placed in a magnetic field, its e⁻ are caused to circulate and thus they produce secondary magnetic field i.e induced magnetic field

→ Rotation of e's about the proton itself generates a field in such a way that at the proton, it opposes the applied field. This proton is said to be shielded.

→ If the induced field opposes the applied field, the proton is said to be shielded.

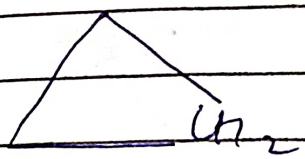
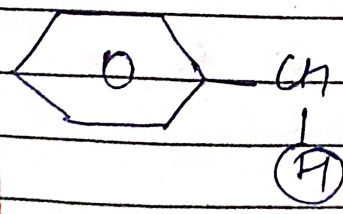
→ If the induced field reinforces the applied field, the proton has a higher field strength, the proton is said to be deshielded.

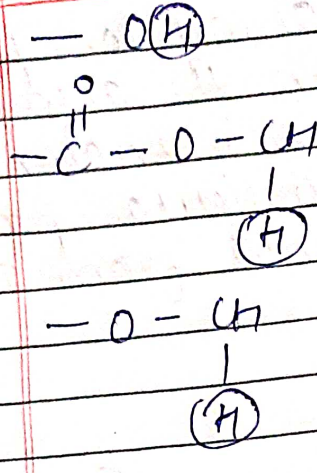
→ Shielding shift the absorption upfield and deshielding shift the absorption downfield.

→ The most commonly used reference compound is tetramethyl silane $(CH_3)_4Si$. All the 12 H's are highly shielded, so they appear in upfield.

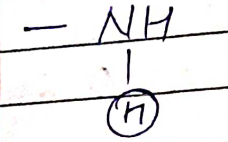
→ Thus the difference in the absorption position of a particular proton from the absorption position of a reference proton is known as the chemical shift of the particular proton.
→ The shifting of specific signal from TMS known as chemical shift.

Values :

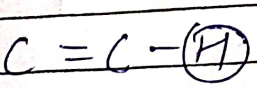
		δ
1.		0.2
2.	$1^{\circ}-CH(H)$	1
3.	$2^{\circ}-CH(H)$	1.2
4.	$3^{\circ}-CH(H)$	1.5
5.	$C=C-C(=O)-H$	1.7
6.	$CH_3-C(=O)-CH_2(H)$	2.1
7.		3
8.	$C\equiv C-H$	3

9. 

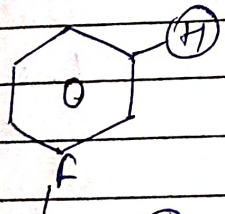
3.5 - 4.5

10. 

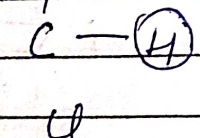
1 - 5

11. 

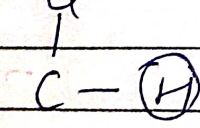
6

12. 

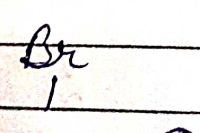
6 - 8

13. 

4

14. 

3.5

15. 

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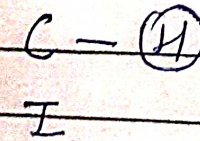
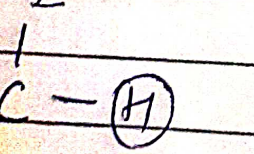
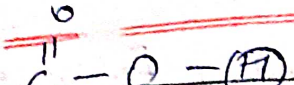
16. 

2.8

17. 

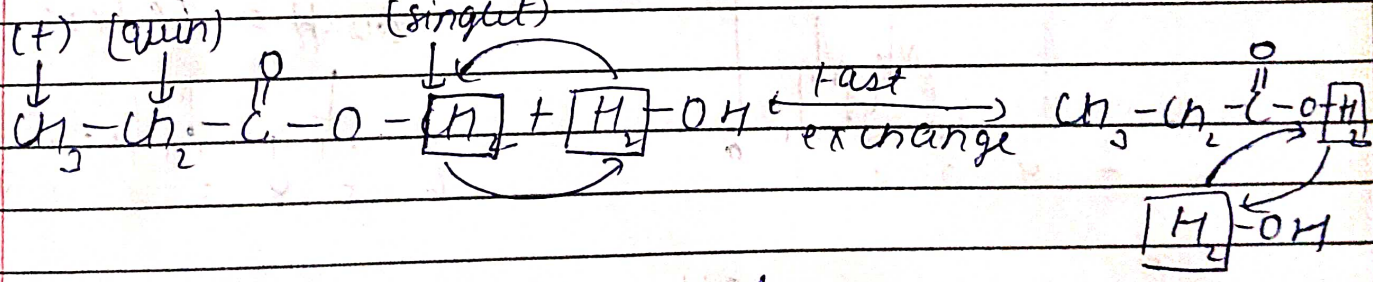
9 - 10

18.  11-12

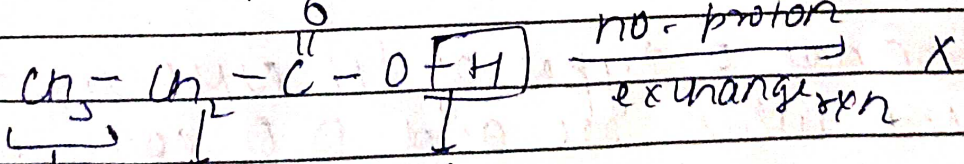
19.  7-8.

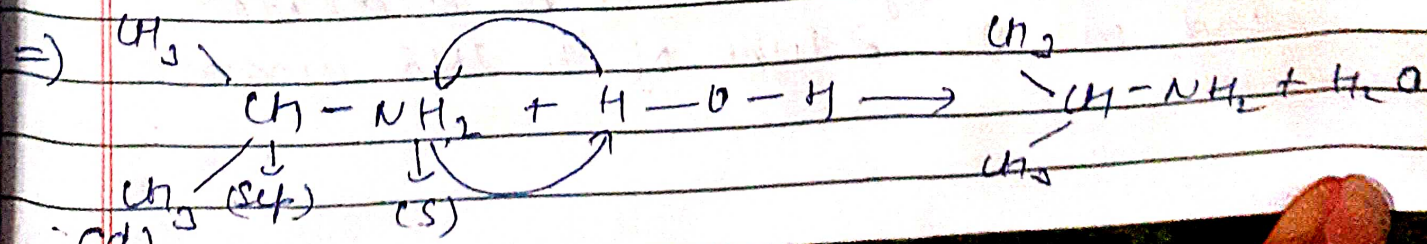
Proton Exchange Reaction

→ In a proton exchange rxn when minimum amount of solvent or water present in a compound then proton of functional group exchange with a proton of solvent. This exchange will bi very fast due to this proton of functional group will not couple with nearst proton and functional group proton give singlet signal.



In ultrapure compound



(d) 

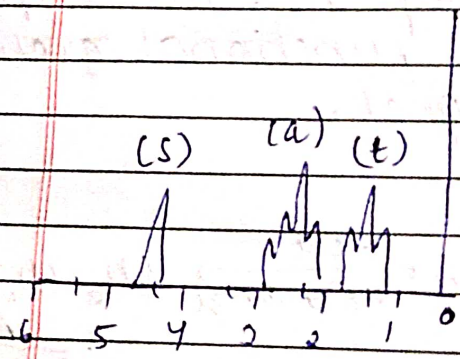
Deuterium Exchange Rxn / Effect of Deuterium

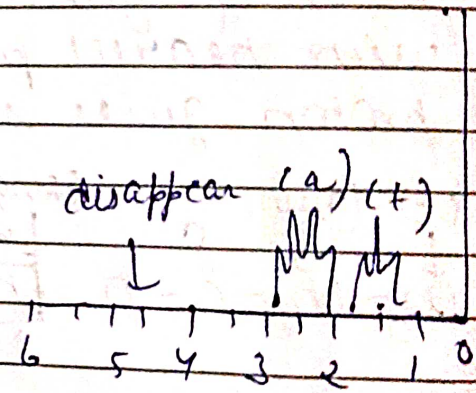
→ In a deuterium exchange method deuterium atom exchange with a proton of functional group due to this deuterium exchange no. of ^1H NMR signal will be decrease due to presence of deuterium in a product.

(1) $CH_3-CH_2-OH + D-OD \longrightarrow CH_3-CH_2-OD + H-OD$

(t) (quad) (s) — 3 Type of proton

(t) (q) — 2 Type of proton





Example => ethanol

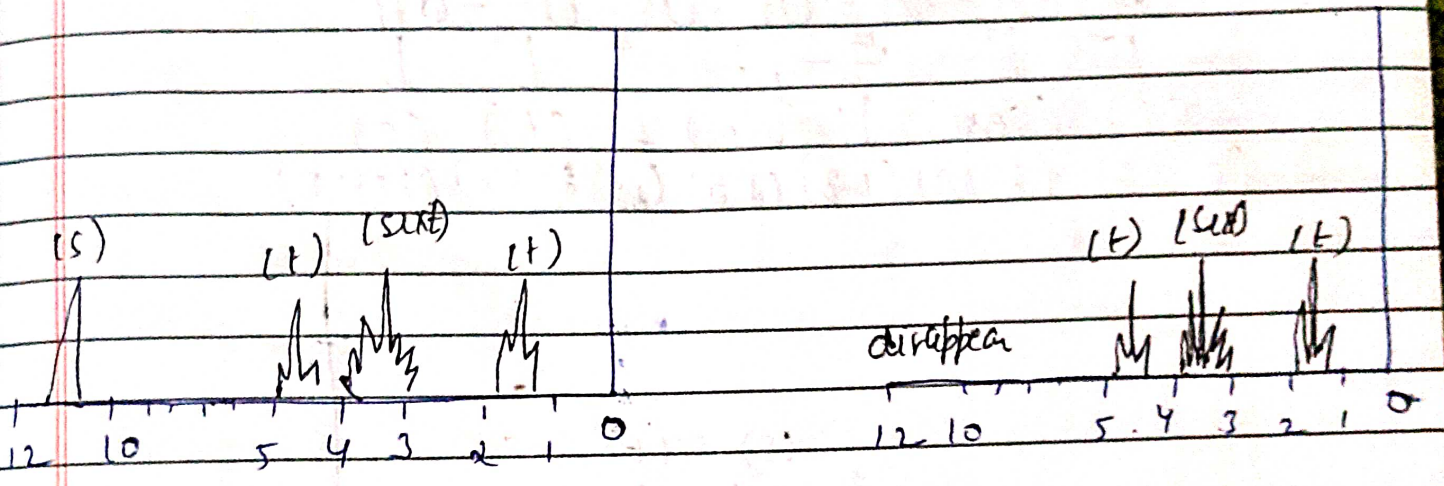
In ethanol 3 types of ^1H NMR signal is present when we add D_2O solvent this OH group convert into in OD group and no. of signal will be decreased and we get 2 types of ^1H NMR signals.

(2) $CH_3-CH_2-CH-\overset{O}{\overset{\|}{C}}-O-H + D_2O \longrightarrow CH_3-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-O-D$

(a) (b) (c) (d)

(t) (sext) (t) (s)

$\delta = 1.7$ $\delta = 3.5$ $\delta = 4.5$ $\delta = 11.50$



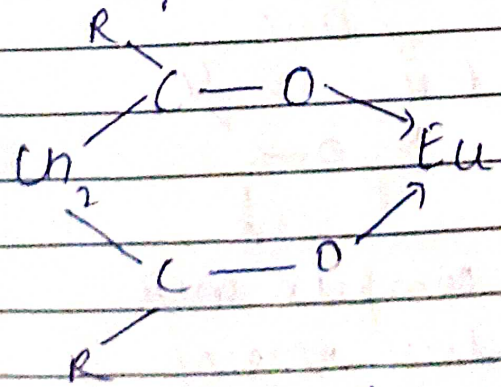
Contact Shift Reagent

→ Contact shift reagent is diketo Europium (III) compound.

→ It is very useful reagent for separation of close PMR signal.

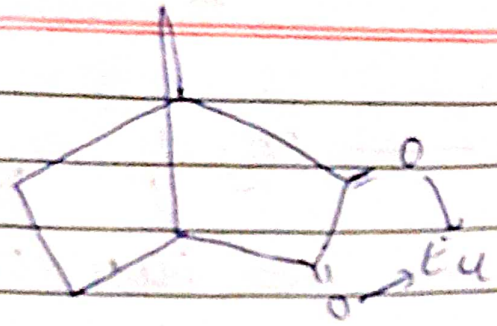
Example:

1.



diketo Eu (III) complex

2.

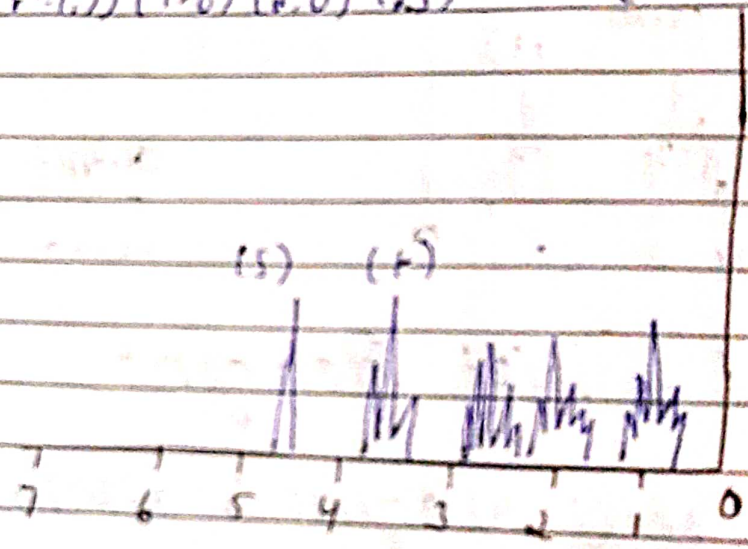


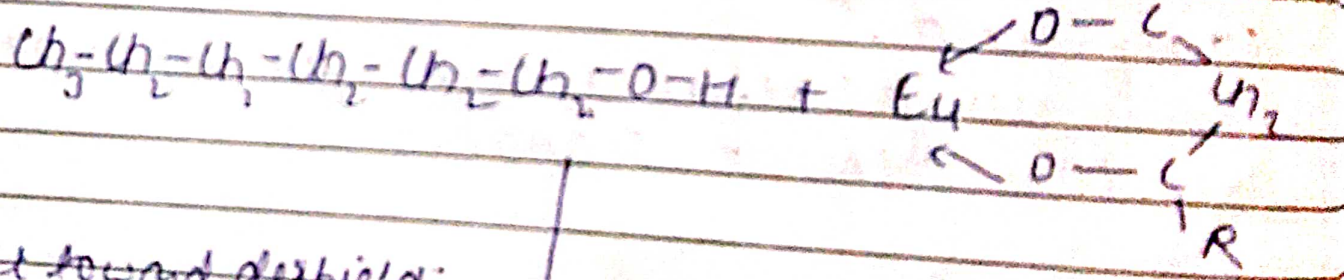
diketo Eu (III) compl

$CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-OH$

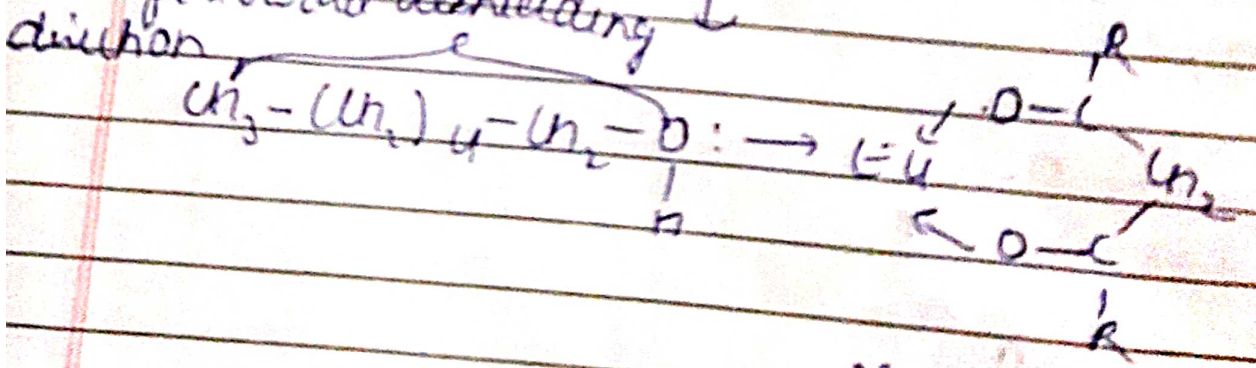
(t) (sext) (quin) (t) (s)

(δ = 1.2) (δ = 1.7) (1.8) (2.0) (4.5) δ = 3.5) (δ = 4.5)





shift toward deshielding direction



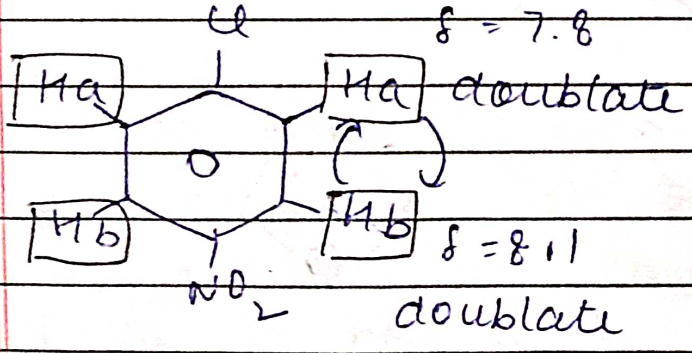
complex with shift reagent

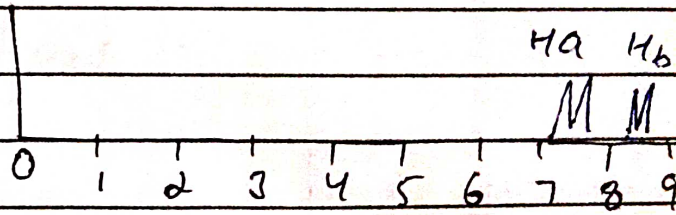
→ In 1-hexanol compound 7 types of ^1H NMR signal but in a NMR group $CH_3-CH_2-CH_2-CH_2-CH_3$ group give overlap ^1H NMR signal this all signals are highly shielded signal it show δ value b/w 2.5 — 1.2 ppm.

→ When we add shift reagent in this compound then lone pair of oxygen form coordination bond with (Eu) due to this bond all the NMR signals of 1 hexanol shift towards higher δ value and $CH_3-CH_2-CH_2-CH_2-CH_3$ group will be spread out in a ^1H NMR spectroscopy and we get separate signal of every proton.

Complex Spin-Spin Interaction b/w 2, 3, 4 and 5 Nuclei

(i) Spin-spin Interaction b/w 2 Nuclei ⇒ A-B Spectra :





In a para nitro chloro Benzene two type of Hydrogen are present Ha & Hb.

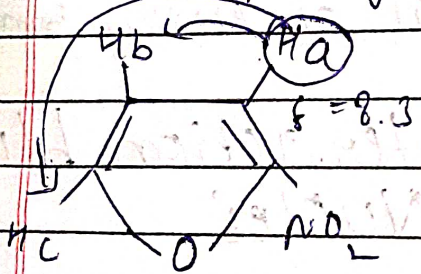
In this molecule plane of symmetry is present due to this Ha & Hb protons are chemically equivalent and Ha, Hb protons are also chemically equivalent.

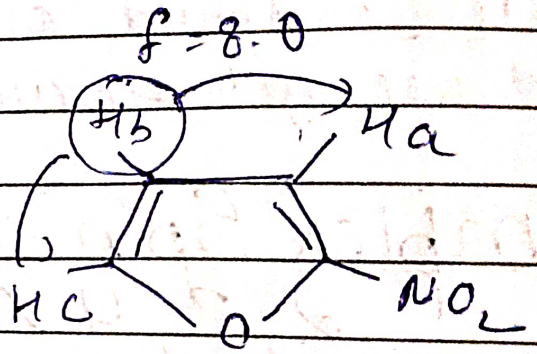
This type of spectra is called AB Nuclei spectra.

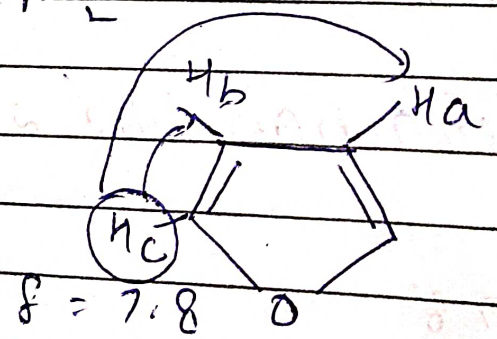
(iii) 3 Nuclei spectra => ABC Type

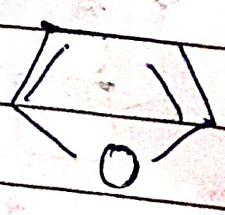
In this type of system we have 3 different type of proton H_a, H_b & H_c

This type of aromatic molecule shows long range coupling as well as vicinal coupling.



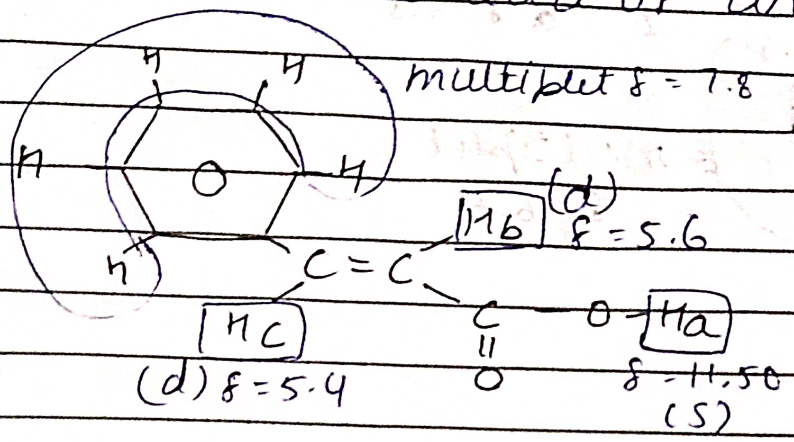


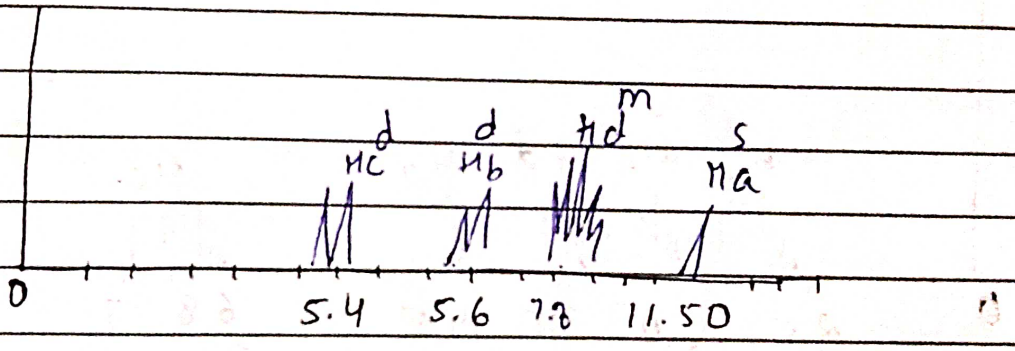




(iii) 4 Nuclei Spectra or ABCD Spectra ⇒
In this type of spectra 4 different types of proton are present in a molecule it shows 4 different signal.

Ex : Cinamic acid or cinamic aldehyde.



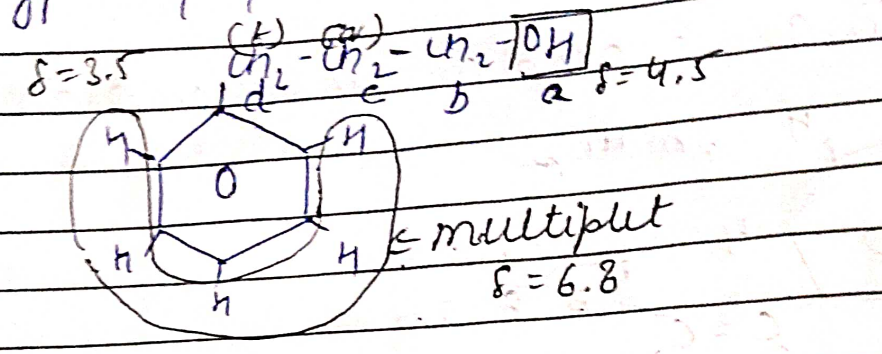


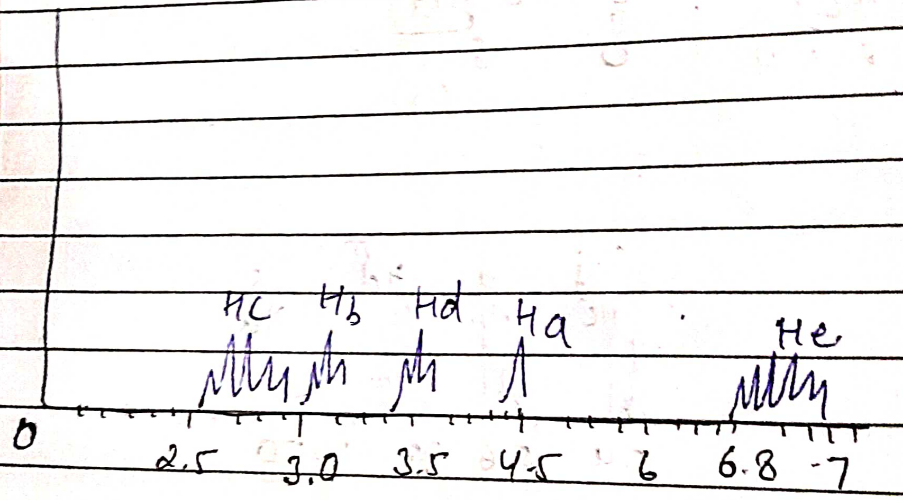
In a cinamic acid 4 type of protons are present given singlet value δ = 11.50
Hb proton given doublet value due to presence of vicinal hydrogen at δ = 5.6

Hc proton also give doublet signal at 5.4
All the proton also given of benzene are accidently equivalent it show multiplate value on δ = 7.8.

(iv) 5 Nuclii Spectra =>

In this type of molecule different types of proton are present.





→ 3 phenyl propanol give 5 type of ^{1}HNMR signal. In this molecule proton of benzene are exidentally equivalent and it give multiplate δ = 6.8 at δ = 6.8

→ Hd proton give triplet due to vicinal hydrogen coupling at δ = 3.5.

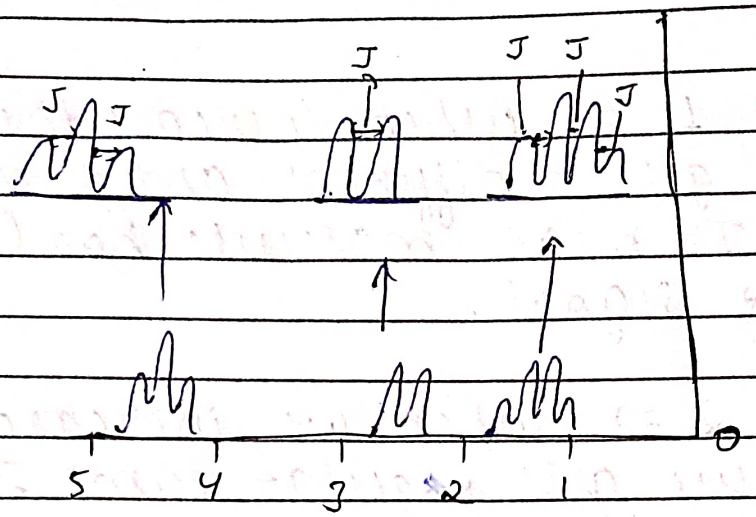
→ Hc proton give quintate signal δ = 2.5.

→ H_b proton give also triplet signal δ = 3.0

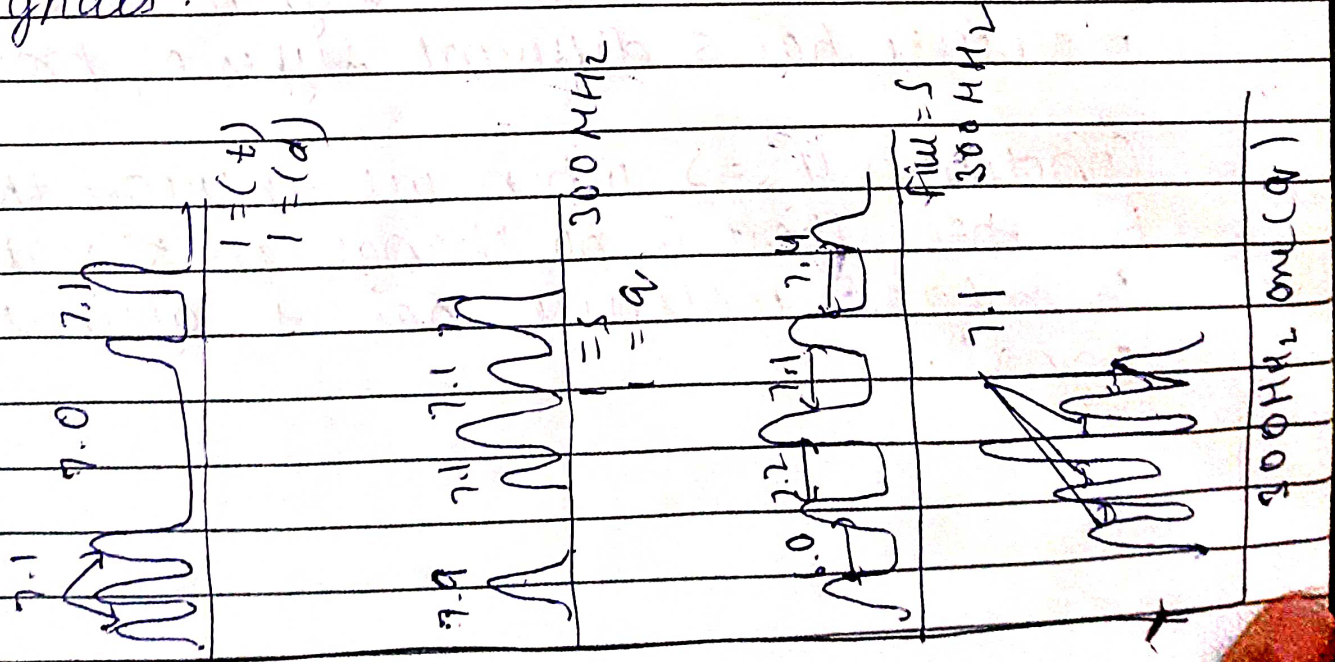
→ Hydrogen of OH give slight at 4.5

Coupling Constant (J)

→ The distance between 2 NMR signal is called coupling constant. Signals should be present in a regular form.



When we increase magnetic magnetic field in ^{1}HNMR spectra. Then J value not change it means molecule have similar signals. Or when J value changes it means different type of proton and it give different type of signals.



In above ex. we get quintent value at 100 MHz magnetic field on the J value are same (J = 7.1). when we increase M.f. then we get diff types of signals at different type of J value.

Condition 1 => when increase the M.F then we get 1 different and 3 similar J value. It means molecule has (1 = trip and NMR signal.

Condition 2 => when we increase the M.F then we gets regular same J value and or 1 - different value it means molecule has 1 = qu. values.
2 = Sin.

Condition 3 => when we increase the M.f then we get 4 different J value it means molecules has 5 - signals and molecule has 5 different types of proton.

Condition 4 => when we increase the M.F then there is no change in J value it means molecule has 1 - quintet signal.

CH_3-CH_2-Br

(t) (q)

$\delta = 2.0$ $\delta = 3.5$

$J = 7.5$ cps $J = 7.5$ cps

1 Bromo ethane CH_3-CH_2 are attached directly with other the group show an $J = 7.5$ cps.

$CH_3-CH_2-O-CH_3$

(t) (q) (s)

$\delta = 1.3$ $\delta = 3.1$ $\delta = 3.5$

$J = 7.5$ cps $J = 7.5$ cps $J = 7.2$ cps

In a methoxy ethane we have a 2 types of proton and 2 types of J value it means (CH) containing group are directly attached with each other

Karplase Equation

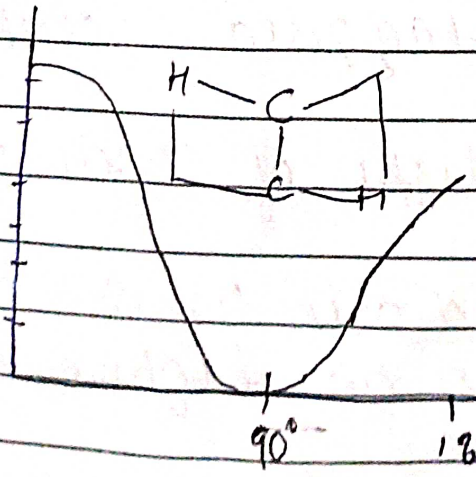
→ Karplase eq gives idea about bond angle between 2 regular hydrogen.

→ It shows different J value for different bond angle.

→ Acc. to Karplus eq. $\theta = 60°, 90°, 180°$ ha different J. value.

→ when $\theta = 180°$ or zero = J value high

$\theta = 90°$ = lower J value



→ The relationship between dihedral angle Φ & vicinal coupling constant J is given by Karplus eq.

→ When we draw graph b/w bond angle and J vicinal coupling we get U-shape graph.

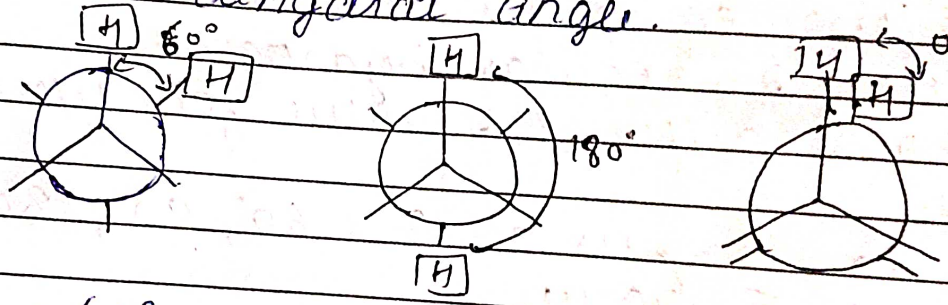
→ Formula of calculation of J

$J_{vic} = 10 \cos^2\theta \quad [0 < \theta < 90^\circ]$

$J_{vic} = 16 \cos^2\theta \quad [90^\circ < \theta < 180^\circ]$

→ Value of coupling constant J with various dihydral angle.

eg.



$\theta = 60^\circ$ [J = 3.5] gauche

$\theta = 180^\circ$ [J = 13-15] anti staggered

$\theta = 0^\circ$ [J = 5-7] eclipsed

→ In an alkane 3 types of condition can present.

→ Anti staggered Hydrogen or 180° angle dihydral. Hydrogen has highest J value 13-15 Hz.

→ When dihydral angle will be 60° then J value be 3-5 Hz.

Ex. Coupling constant value of cis and trans compound.
When trans alkene is present then value of J will be 11-19 Hz and cis alkene show. J value will b/w 5-8 Hz

trans
J = 11-19

cis
J = 5-8.

Nuclear Overhauser Effect

→ NO enhancement is the technique by which the intensity of NMR signals can be enhanced significantly by saturation (irradiation) of some of the nearby nuclei within the molecule.
→ The NOE effect is only noticeable over short distance, generally 0.2 to 0.4nm.
→ NOE tells whether the two protons are in close proximity within the molecule or not.
→ An important consequence of this effect is that the line intensity observed in the normal spectrum may not be the same as in the decoupled spectrum.