

* NMR active & inactive nuclei

- All atomic nuclei possess nuclear spin which is represented by 'I'. which may be having a integral or half-integral values. ($1, 2, 3, \frac{1}{2}, \frac{3}{2}, \frac{5}{2}$)
- commonly study nucleus - Proton ($\frac{1}{2}$)
- Determine only by experimentally.
- The proton & neutron each has a spin of ($\frac{1}{2}$)

* Rules :-

- (i) If the mass no. is odd, the nuclear spin is half integral.

for e.g. ^1H , ^{15}N , ^{31}P ($I = \frac{1}{2}$)

$$^{11}\text{B} = \frac{3}{2}$$

- (ii) If mass no. and atomic no. both are even then spin is zero, in that case, $I = 0$

e.g. $^{12}\text{C} = 0$ $^{16}\text{O} = 0$ {inactive}

- (iii) If mass no. is even atomic no. is odd then spin having a integral values.

e.g. $^{14}_7\text{N} = (I = 1)$

$$^{10}_5\text{B} = (I = 3)$$

- When a magnetic nucleus is placed in a uniform magnetic field. The magnetic dipole, associated with the magnetic moment, assumes only a discrete set of orientation.

magnetic nucleus assume, any one of the $(2I+1)$ orientation, which respect to the direction of any applied magnetic field as a result of quantization of spin. The observable component (m_I) of the spin along the dirⁿ of the applied magnetic field is given by,

$$m_I = I-1, I-2, 0, -I-1, -I \quad \text{for integrals spin.}$$

and

$$m_I = I, I-1, I-2, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}, \quad \text{for half-integral spin.}$$

- A nucleus with spin has associated with it a magnetic dipole moment. (magnetic moment), which is represented by (μ) and it is proportional to the angular momentum, whose magnitude is given by

$$\boxed{\vec{\mu} = g_N \cdot \mu_N \cdot \vec{I}}$$

g_N = nuclear g-factor

μ_N = nuclear magneton and its value is given by

$$\left\{ \frac{eh}{4\pi mp} \right\}$$

$$\left\{ \mu_N = 5.05 \times 10^{-27} \text{ J/Tesla} \right\}$$

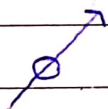
$\vec{I}$ = angular momentum $\left\{ \vec{I} = \sqrt{I(I+1)} \frac{h}{2\pi} \right\}$

also,

$\left\{ \vec{I} = \sqrt{I(I+1)} \frac{h}{2\pi} = \sqrt{I^2} \approx I \right\}$

- Since the magnetic moment $\vec{\mu}$ and the angular momentum can be parallel and anti-parallel vectors g_N can be +ve or -ve values.
- g_N can be obtained accurately only from experiment and it is different for different nuclei.
- $g_N = \text{electron } (2.0023)$

* NMR of a 'bare' nucleus :-



The energy of interaction of a nuclear magnetic moment with an external magnetic field (B_z) applied in the z-direction is given by.

$\{ E = -\vec{\mu} \cdot \vec{B}_z \}$

$E = -g_N \mu_N \vec{I} \cdot \vec{B}_z$

$\{ I = m_I = +\frac{1}{2} \text{ or } -\frac{1}{2} \}$

if $m_I = \frac{1}{2}$, $E_{(\frac{1}{2})} = -\frac{g_N \mu_N B_z}{2}$

NR	
21	1
2	1
	0
	0
	0
	0
	0
2	
0	

IPAIGN
aluru
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ai

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cricket chief Richard Gould insisting he can "adapt and evolve" the

and England managing director of men's cricket Rob Key will all

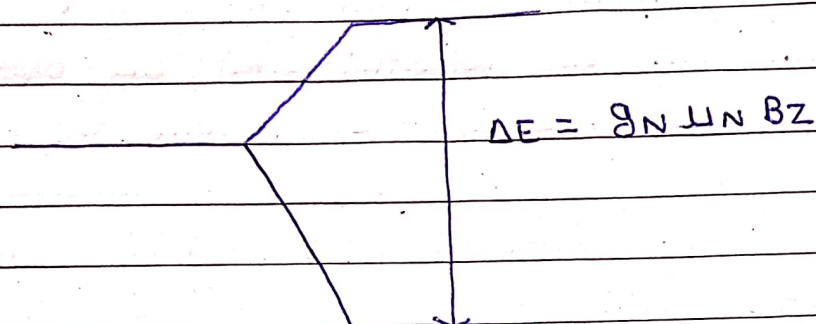
Player (men): Prince Deep Singh, Manmeet Singh, Anmol Ekka, Arshdeep Singh; Upcoming

Monday. "If it w safe coun do that

$$m_I = -\frac{1}{2}, \quad E_{(-\frac{1}{2})} = \frac{g_N \mu_N B_z}{2}$$

$$\Delta E = E_{(-\frac{1}{2})} - E_{(\frac{1}{2})} = \frac{g_N \mu_N B_z}{2} + \frac{g_N \mu_N B_z}{2}$$

$$\Delta E = g_N \mu_N B_z$$



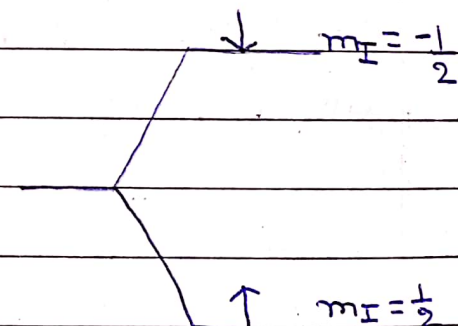
- In order to induce the transition b/w two energy level b/w $E_{(-\frac{1}{2})}$ & $E_{(\frac{1}{2})}$, the nuclear spin flips from the upward direction to the downward dirⁿ by the application of oscillating radiofrequency, perpendicular to the direction of the external magnetic field, i.e.,

$$\Delta E = g_N \cdot \mu_N B_z$$

or,

$$\Delta E = h\nu$$

$$\therefore [h\nu = g_N \cdot \mu_N \cdot B_z]$$



Q. (^1H) calculate the NMR frequency in MHz of the proton in a magnetic field of $[1.4 \text{ Tesla}]$.

$$g_N = 5.585 \text{ and } \mu_N = 5.05 \times 10^{-27} \text{ J/Tesla}$$

Soln,

$$h\nu = g_N \cdot \mu_N \cdot B_z$$

$$\nu = \frac{g_N \cdot \mu_N \cdot B_z}{h} = \frac{5.585 \times 5.05 \times 10^{-27} \times 1.4}{6.626 \times 10^{-34}}$$

$$= \frac{39.485 \times 10^{-27}}{6.626 \times 10^{-34}} \text{ MHz (Same) (Hz)}$$

Now, For ^{13}C , $g_N = 1.404$

$$\nu = \frac{1.404 \times 5.05 \times 10^{-27} \times 1.4}{6.626 \times 10^{-34}} = \frac{9.92 \times 10^{-27}}{6.626 \times 10^{-34}}$$

$$= 1.497 \times 10^7 \text{ MHz (Hz)}$$

• ^{19}F & ^1H same g_N values.

• classically, the phenomena of magnetic resonance can be understood by 'Larmor precession' (British mathematician)

a nucleus having a magnetic moment μ behaves as a bar magnet which spin on its axis in the presence of the magnetic field B_z . The interaction of μ , i.e., with B_z produces a 'torque'. This torque causes magnetic moment μ to precess about B_z . This phenomena is called 'Larmor precession' and the

angular frequency of precession as referred to as Larmor frequency represented by ' ω '. unit is (radians/sec) and it is given by

$$[\omega = \gamma B_z]$$

γ (gyromagnetic ratio)

defined as the ratio of nuclear magnetic moment and the nuclear spin angular momentum.

$$\left\{ \gamma = \frac{\mu}{\frac{I h}{2\pi}} \right\}$$

Q. An spectrometer operating at 1 Tesla. The NMR frequency of ^{19}F is 40.06 MHz. calculate the gyromagnetic ratio of ^{19}F .

Given, $B_0 = 1 \text{ Tesla}$

$$\nu = 40.06 \text{ MHz} = 40.06 \times 10^6 \text{ Hz}$$

$$\therefore [\omega = \gamma B_0]$$

$$\therefore \omega = 2\pi\nu$$

$$\gamma = \frac{\omega}{B_0} = \frac{2\pi\nu}{B_0} = \frac{2 \times 3.14 \times 40.06 \times 10^6 \text{ Hz}}{1}$$

$$= 2.5157 \times 10^8 \text{ T}^{-1} \text{ s}^{-1}$$

$$= 2.5157 \times 10^8 \text{ T}^{-1} \text{ s}^{-1}$$

Q. The magnetic moment of ^3P is equal to $1.1305 \mu_N$. calculate its gyromagnetic ratio and g-factor. Given, $(\mu_N = 5.05 \times 10^{-27} \text{ J T}^{-1})$ & $\left\{ I = 3/2 = \frac{1}{2} \right\}$

$$\therefore \gamma = \frac{\mu}{I \times \frac{h}{2\pi}} = \frac{1.1305 \times 5.05 \times 10^{-27}}{\frac{1}{2} \times \frac{6.626 \times 10^{-34}}{2 \times 3.14}}$$

$$= \frac{5.7090 \times 10^{-27}}{0.5 \times 10^{-34}}$$

$$= 11.418 \times 10^7$$

$$= 1.1 \times 10^8 \text{ T}^{-1} \text{ s}^{-1}$$

actually $(1.08 \times 10^8 \text{ T}^{-1} \text{ s}^{-1})$

Now,

$$\left\{ \mu = g_N \mu_N I \right\}$$

$$1.1305 \mu_N = g_N \cdot \mu_N \cdot I$$

$$g_N = \frac{1.1305}{I}$$

$$= 1.1305 \times 2 = 2.261 \text{ Ans.}$$

Q. write solvents used in NMR Spectroscopy?

- (i) CDCl_3 (ii) Deuterated DMSO (iii) Deuterated Acetone
(iv) Deuterated water (v) Deuterated chloroform.

* Bare nucleus :-

which nucleus have no any electron around nucleus.

* chemical shift :-

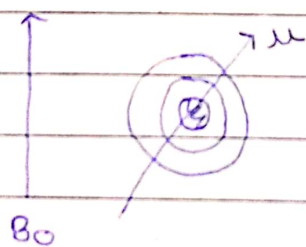
The difference between the magnitude of the magnetic field at which free nuclei and molecular nuclei resonate is called "chemical shift".

The most frequently employed reference compound is tetramethyl silane (TMS). The local magnetic field.

$$B_{\text{local}} = B_0 (1 - \sigma)$$

where σ is a dimensionless quantity

σ = screening constant & shielding constant



- For two nuclei A & B in a molecule, the local field are given by.

$$B_A = B_0 (1 - \sigma_A)$$

$$B_B = B_0 (1 - \sigma_B)$$

$$\begin{aligned}
 \nu_B - \nu_A &= \nu_0 - \nu_0 \sigma_B - \nu_0 + \nu_0 \sigma_A \\
 &= \nu_0 (\sigma_A - \sigma_B) \\
 &= \nu_0 \delta_{AB}
 \end{aligned}$$

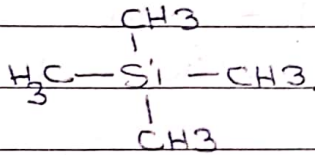
δ_{AB} or δ is the chemical shift of nucleus A w.r.t to nucleus B.

$$\delta = \frac{\nu_B - \nu_A}{\nu_0} \quad \text{or} \quad \left\{ \frac{\nu_{\text{sample}} - \nu_{\text{reference}}}{\nu_0} \right\}$$

$$\text{or, } \left\{ \frac{(\nu_{\text{sample}} - \nu_{\text{reference}}) \times 10^6 \text{ ppm}}{\nu_0} \right\}$$

$\nu_0 \rightarrow$ Frequency of instruments.

Q. Why TMS is selected?



Ans 12 - Hydrogen but all have same "Hydrogen".
 and also TMS have low boiling point,
 So easy to remove.

Q. Why all records in ppm? Not in Frequency (Hz)?

Ans because frequency is changed on other - other instruments (60 Hz, 400 MHz, 300 MHz) of some compounds.

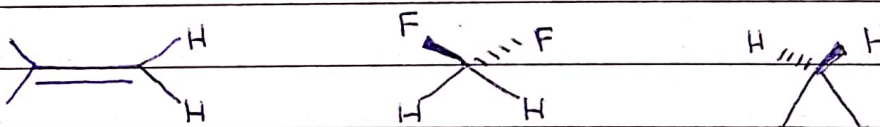
* characteristic of a ^1H NMR spectrum

- NMR spectrum contain a lot of structural information
- Number of signals
- Signal location (chemical shift)
- Signal intensity (area under the signal)
- Signal shape (splitting pattern)

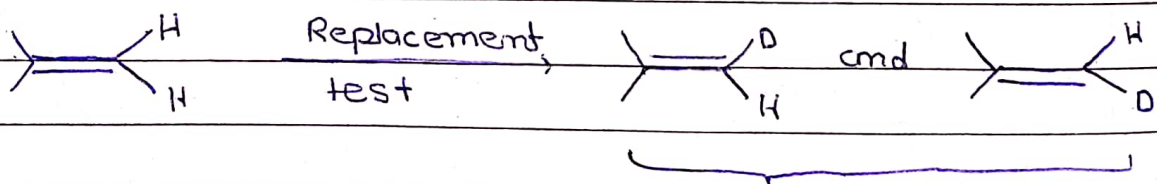
* Number of signals

- The no. of signal in ^1H NMR spectrum indicates the no. of different kinds of protons in a compound
- Identical protons are chemically equivalent. such proton fall into the category of being either homotopic or enantiotopic

Homotopic protons: If the molecule has an axis of rotational symmetry that allows one proton to be rotated onto the other without changing the molecule.

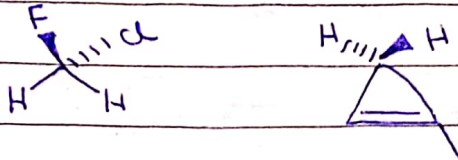


- Another test for homotopic protons is to replace the protons one at a time with another atom:

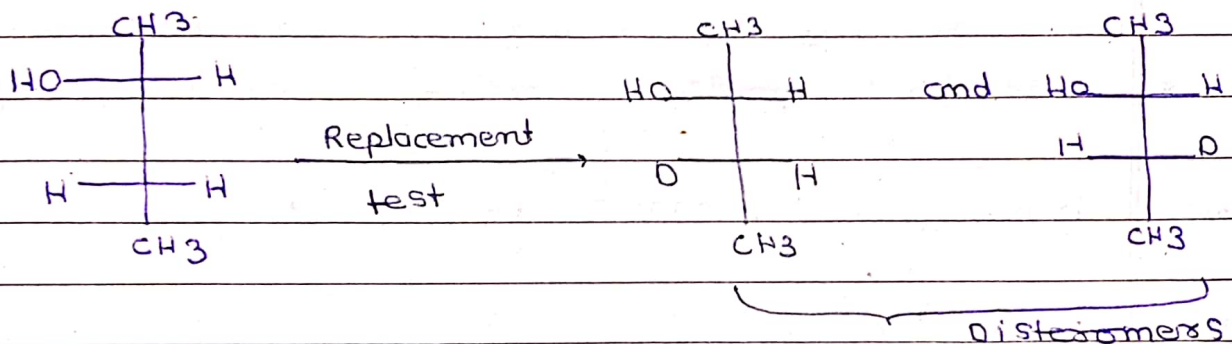


Same compound

- If the resulting compounds are identical, then the protons that you replaced are homotopic.
- Enantiotopic protons: If the molecule has a plane of reflection that makes one proton the mirror image of the other.

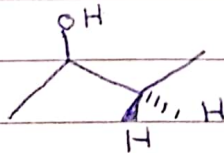


- If the resulting compounds are enantiomers, then the protons that you replaced are enantiotopic.



- These protons are called diastereotopic and not chemically equivalent.

- If the protons are neither homotopic & enantiotopic then not chemically equivalent.

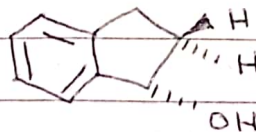


e.g.-



two protons

chemically equivalent



not chemically equivalent

- In cyclohexane, there are two types of protons here, but only one signal is observed in the $^1\text{H NMR}$.

$$\delta = \frac{\text{observed shift from TMS in hertz}}{\text{operating frequency of the instrument in hertz}}$$

- The shift relative to TMS (δ) is a dimensionless no. because Hz units cancel out.
- Units for δ are often given as ppm, which simply indicates that signals are reported as a fraction of operating frequency of the spectrometer.
- Most ^1H signals appear between 0-10 ppm.

Note:- 14092 gauss = 1.4092 Tesla

Q. In a given organic compound 2 kinds of protons exhibit signal at 50 Hz at 200 Hz using a 60 MHz instruments. what will be their related position using 90 MHz Spectrometer also convert the position of signal into δ value?

Soln:-
$$\left[\delta = \frac{\Delta \nu \times 10^6}{\nu_0} \right]$$

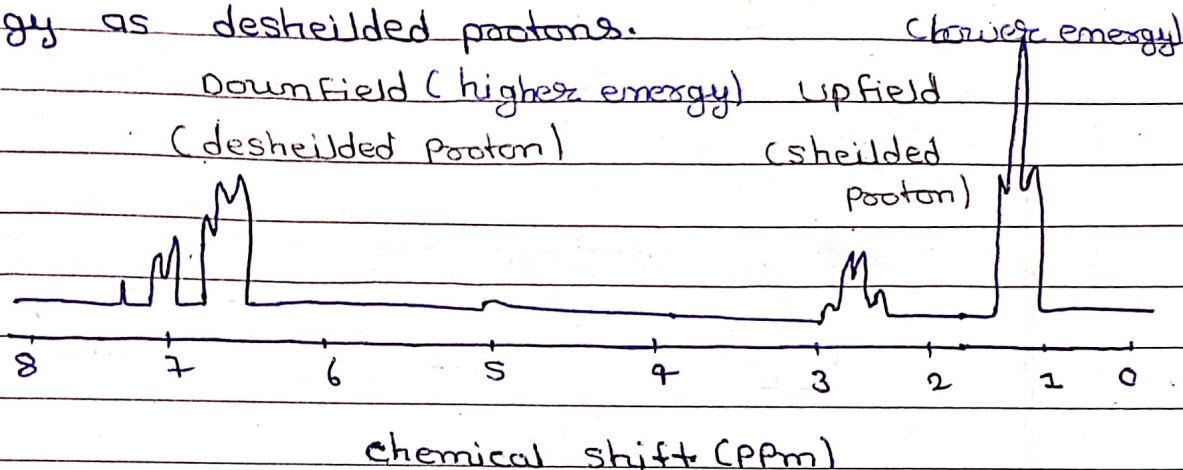
$$\delta = \frac{50 \times 10^6}{60 \times 10^6} = 0.8$$

$$\text{or, } \delta = \frac{75 \times 10^6}{90 \times 10^6} = 0.8$$

$$\delta = \frac{200 \times 10^6}{60 \times 10^6} = \frac{10}{3} = 3.3$$

$$\text{or, } \frac{300 \times 10^6}{90 \times 10^6} = 3.3$$

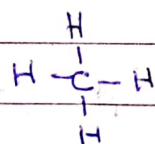
- early NMR analyzed samples at a constant energy over a range of magnetic field strength.
- low field strength = downfield
- high field strength = upfield
- shielded proton required a stronger external magnetic field to be excited at the same energy as deshielded protons.



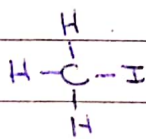
- current NMRs analyze samples at a constant field strength over a range of energies.
- Shielded protons have a smaller magnetic field acting on them, so they have smaller energy gap and absorb lower energy gaps, radio waves.

⇒ Alkane protons generally give signals around 1-2 ppm

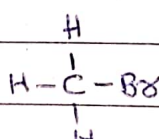
- Protons can be shifted downfield when nearby electronegative atoms causes deshielding



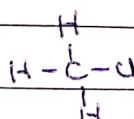
1.0 ppm



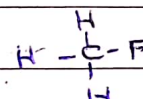
2.2 ppm



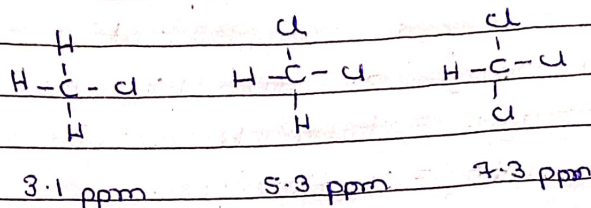
2.7 ppm



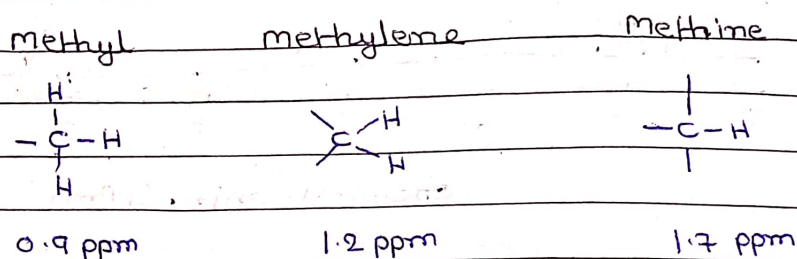
3.1 ppm



4.3 ppm



- To predict chemical shifts, start with the standard ppm for the type of proton (methyl, methylene, methine)



9-10 ppm → Aldehydes, $-\text{C}(=\text{O})-\text{H}$

10-12 ppm → $-\text{C}(=\text{O})-\text{O}-\text{H}$

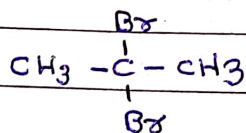
7-8 ppm → Aromatic substituent

5-6 ppm → olefinic peaks ($\text{C}=\text{C}$)

3-4 ppm → $\left. \begin{array}{l} \text{O}-\text{H} \\ \text{N}-\text{H} \end{array} \right\}$ protons

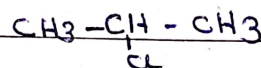
1-2 ppm → Aliphatic protons.

Q. 2,2-dibromopropane



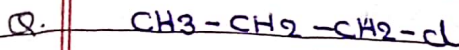
Signal = 1

Q. Isopropyl chloride



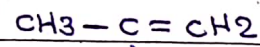
Signal = 2





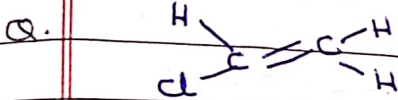
Q. 2-bromo propene

Signal = 3

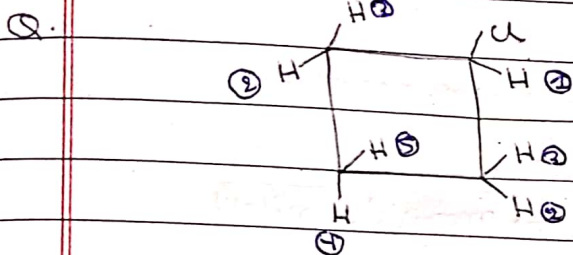


Br

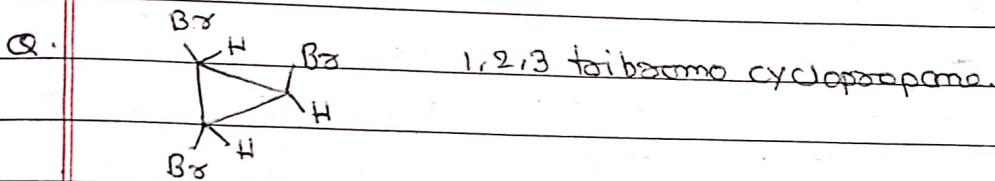
Signal = 2



Signal = 3

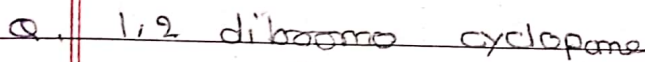


Signal = 5

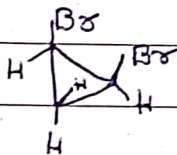


1,2,3 tribromo cyclopropane.

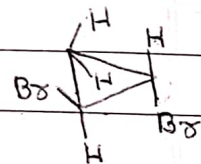
Signal = 1



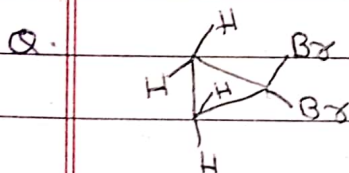
Q. trans



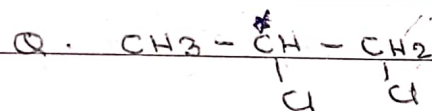
Signal = 3



Signal = 2



Signal = 1



Signal = 4



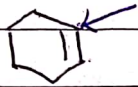
Signal = 3

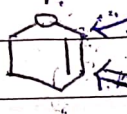
Q. CH_3OH , CH_3NH_2 and $\text{CH}_3\text{-CH}_3$ arrange increasing order downfield shift (desheilding)

$\text{CH}_3\text{OH} > \text{CH}_3\text{NH}_2 > \text{CH}_3\text{CH}_3$
 $\swarrow$
 more electronegative

Q. $\text{H}_3\text{C}-\overset{\text{O}}{\parallel}-\text{CH}_2-\text{CH}_3$
 Signal = 3

Q. $\text{H}_3\text{C}-\text{O}-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_3$
 Signal = 3

Q. (8.5-8.7)


or  more downfield

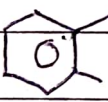
Q.  ①
 ②

which one is more downfield.
 ② more desheilded than ①

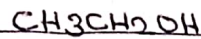
Q.  H (8.7-8.7)

Q.  CH_3 (8.1-6.8)

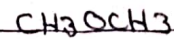
Q. $\text{H}-\text{C}\equiv\text{C}-\text{H}$
 (8.2-9)

Q.  CH_3 (8.2-8.2)
 H (8.7-8.7)

Q. How can use to NMR technique to distinguish to two compound.



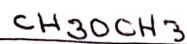
VLS



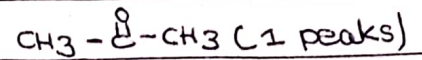
Peaks = 3

Peaks = 1

Now,



VLS



Peak = 1

Peak = 1

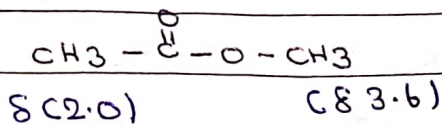
downfield shift

less chemical

more

shift.

Q.

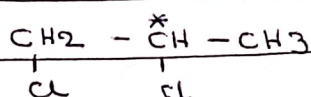
 δ (2.0) δ (3.6)

Peaks = 2

- The protons of RMgX (Grignard reagent) are usually observed around δ 0.5 ppm. While those of organo lithium compounds (nBuLi) are observed around (δ -1.2). The proton of organomercury, organocadmium compound give peaks around δ +1 ppm. Since these organometallic compounds have substantial covalent character. The shift of H-bonded proton is depends on the concⁿ. In concⁿ solution these protons are deshielded by H-bonding and they absorb at lower field. When the alcohol or amine is diluted with the non-H-bonding solvents, its bonding becomes less important and resonances are observed at slightly shielded region or higher field region.

Q. 1,2 dichloro propane.

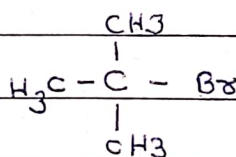
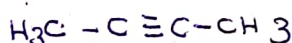
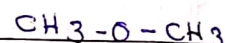
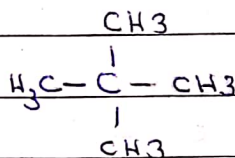
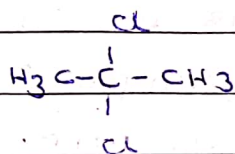
Note:- chiral carbon adjacent two Hydrogen count diastereotopic hydrogen. count



Signal = 4

Q. Draw the structure of the compound with each of the following molecular formula that will show only one peak in NMR Spectra.

(i) $\text{C}_3\text{H}_6\text{Cl}_2$ (ii) C_5H_{12} (iii) $\text{C}_2\text{H}_6\text{O}$ (iv) C_4H_6 (v) $\text{C}_4\text{H}_9\text{Br}$



* Anisotropic effect :-

The downfield shift of proton attached to (C=C), aldehydic & Aromatic protons can be explained, by considering the magnetic field induced by the action of applied on π -electron.

- The magnetic field induced by π -electrons are directional i.e., unsymmetrical. and therefore, they are known as Anisotropic effect.

Since the π -electron are more polarizable than Sigma-electrons. They are more free to move on response to a magnetic field. on application of magnetic field to a compound with the π -electrons, will move in a circulate path. The movement of π -electrons around a benzene ring is called Ring currents. This induced electron motion results an induced magnetic field.

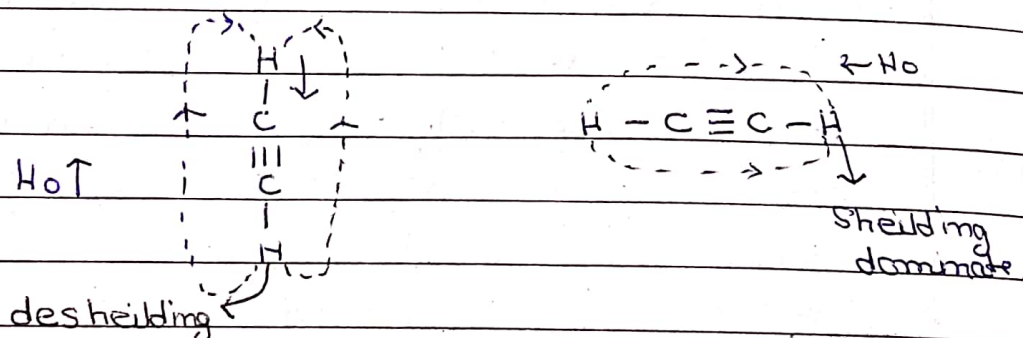
Aromatic rings displaced from strong Magnetic Anisotropy above and below the ring. There is a strong shielding region. while in the plane of the ring. There is a strong deshielding region. consequently protons and groups attached to the ring are in the plane and are strongly deshielded. Aromatic proton generally give peak at around δ 7.0 ppm and Benzylic methyl group at around δ 2.4 ppm.

Just like in benzene both in an alkene and an aldehyde, the induced magnetic field, because of the π -electrons causes deshielding in the region where the protons are located.

Unlike the alkenes and aldehydic protons, which appear downfield the alkyne ($\equiv$)-proton on the other hand appear at high field. circulation of electrons around

The triple bond occurs in a way, so that the proton (alkyne) experiences a diamagnetic shielding effect.

The alkyne molecule is linear when the excess of the alkyne group lies parallel to the direction of the applied magnetic field. The cylindrical sheath of π -electrons to induce to circulate around the axis. The electronic motion induces a small local field which opposes the applied field at the acetylenic protons. Thus a higher applied field is required to bring this proton into resonance, and this induced field is causing effective shielding of the alkyne protons.



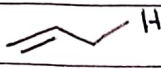
- When one considers the molecule aligned perpendicular to the applied magnetic field. The acetylenic proton is deshielded as in the case of alkenes. This deshielding component however, is smaller when compared to the shielding as described above.

TYPE of Proton chemical shift (δ)

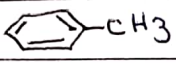
Methyl $R-CH_3$ ~ 0.9

Methylene $>CH_2$ ~ 1.2

Methine $-CH$ ~ 1.7

Allylic  ~ 2

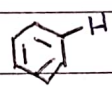
Alkynyl $R \equiv H$ ~ 2.5

Aromatic Aryl  ~ 2.5

Alkyl Halide $R-\overset{\overset{H}{|}}{\underset{\underset{R}{|}}{C}}-X$ $2-4$

Alcohol $R-O-H$ $2-5$

Vinyllic  $4.5-6.5$

Aryl  $6.5-8$

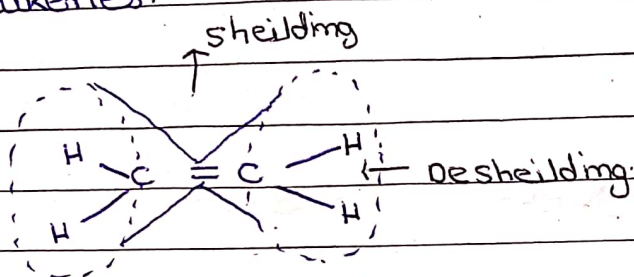
Aldehyde $R-\overset{\overset{O}{||}}{C}-H$ ~ 10

Carboxylic $R-\overset{\overset{O}{||}}{C}-O-H$ ~ 12

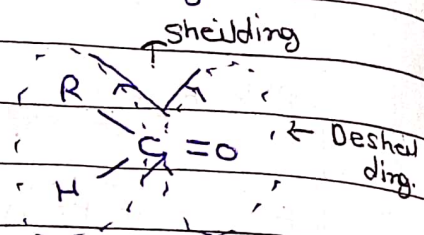
acid $\begin{array}{c} O \\ \\ -C-H \\ \\ O \\ \\ -C-OH \end{array}$		$\sum=C-H$ vinylic	$\begin{array}{c} Z \\ \\ -C-H \\ \end{array}$ $Z = O, N, \text{halo gen}$	$\begin{array}{c} O \\ \\ C-C-C-H \\ \end{array}$ allylic	Saturated $\begin{array}{c} C-C-H \\ \end{array}$		
12	9.0	8.0	6.5	4.5	2.5	1.5	0
δ (ppm)							

- carbonyl, olefinic, Aromatic always give "Desheilding".
- Desheilding $\rightarrow$ e^- cloud ka durt hama.
- Alkynes gives both but in horizontal sheilding effect dominate.

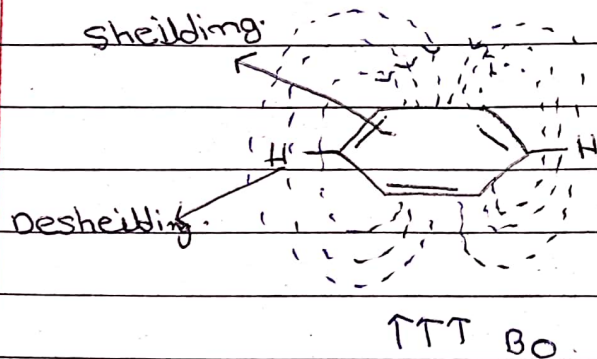
$\Rightarrow$ alkenes.



carbonyl.

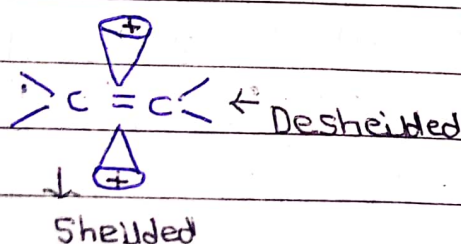


$\Rightarrow$ Benzene

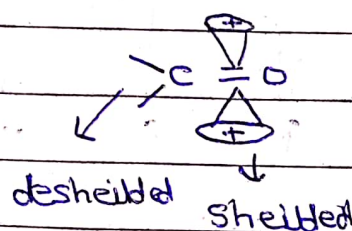


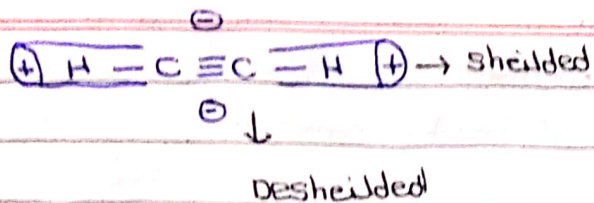
- Protons attached to the ring have high δ values.

* Shielding and deshielding cones.



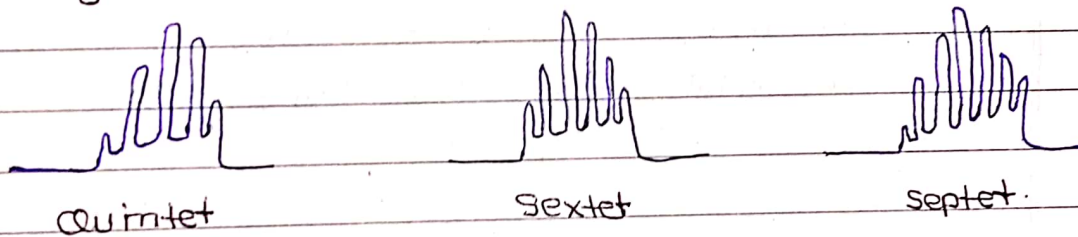
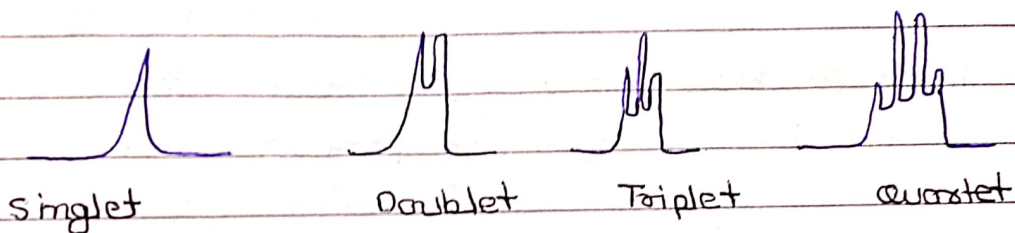
or





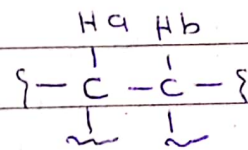
Q. what is anisotropy effect and comes?

* Multiplicity (splitting pattern): The no. of peaks in a given signal.

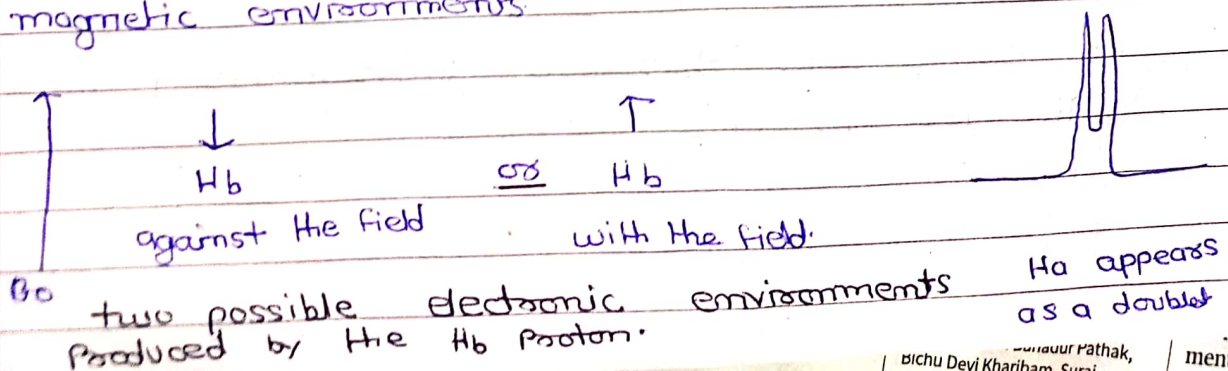


• Multiplicity results from effects that protons have on each other.

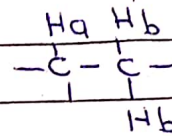
• consider protons H_a and H_b



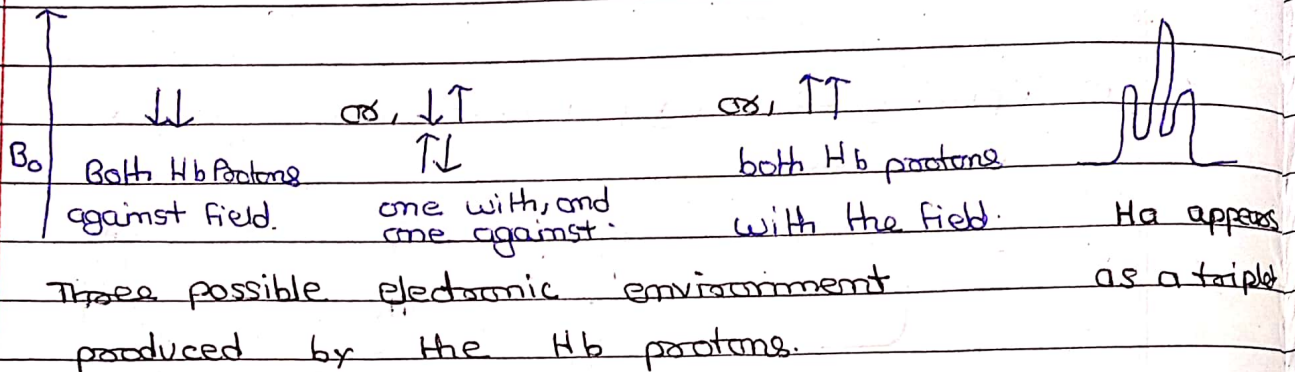
• Since protons align with or against the external magnetic field, so there will be two different magnetic environments.



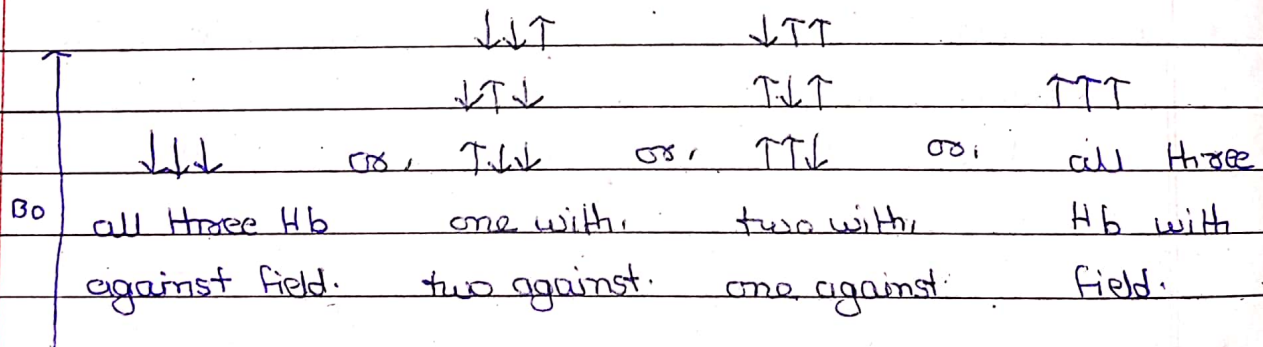
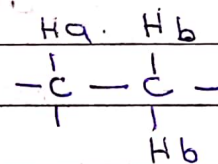
- consider an example where there are two protons on the adjacent carbon.



- Here, there are three possible environments for H_a .



- Now, consider a scenario where H_a is split by three neighboring H_b atoms.



H_a appears as a quartet.

Four possible electronic environments produced by the H_b protons.

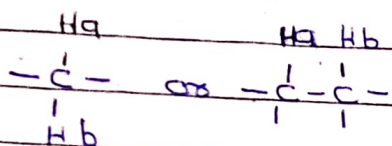
- Peaks are often split into multiple peaks due to magnetic interactions b/w nonequivalent protons on adjacent carbons. The process is called spin-spin splitting.
- The splitting is into one more peak than the no. of H's on the adjacent carbon(s). This is the "n+1" rule.
- The relative intensities are in proportion of a binomial distribution given by pascal triangle.
- The set of peaks is a multiplet (2 = doublet, 3 = triplet, 4 = quartet)...

* Relative Peak intensities of symmetric multiplets

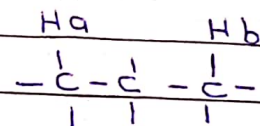
No. of equivalent protons causing splitting	No. of Peaks (Intensity)	Area Ratio (Pascal's triangle)
0	1 (Singlet)	1
1	2 (doublet)	1 1
2	3 (triplet)	1 2 1
3	4 (quartet)	1 3 3 1
4	5 (quintet)	1 4 6 4 1
5	6 (sextet)	1 5 10 10 5 1
6	7 (septet)	1 6 15 20 15 6 1

* Three conditions for splittings.

1. Equivalent protons can not split one another because they resonate together.
2. To split each other protons must be within a 2 or 3 bond distance.



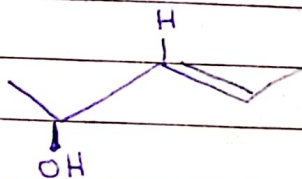
Geminal vicinal
splitting observed.



To far apart
splitting is generally
not observed.

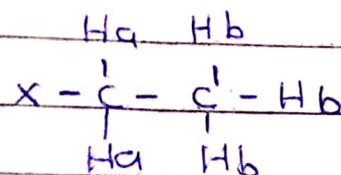
3. The $n+1$ rule only applies to protons that are all equivalent.

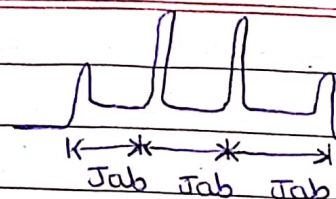
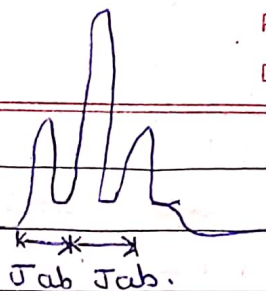
- The splitting pattern observed for the proton shown below will be more complex than a simple triplet.



- complex splitting will be discussed later in this section.

- The degree to which a neighbouring proton will couple to its neighbour is called a coupling constant, or J value.
- The J value is the distance between peaks of a splitting pattern measured in units of Hz.
- Protons splitting each other will have the same coupling constant.
- $J_{ab} = J_{ba}$



Signal for H_a Signal for H_b

- Higher field strength instruments will give better resolution b/w peaks.
- complex splitting results when a proton has two different kinds of neighbouring protons.
- In the molecule shown, H_b is split into a quartet by H_a and into a triplet by H_c .

- If J_{ab} is much greater than J_{bc} then the signal will appear as a quartet of triplets.

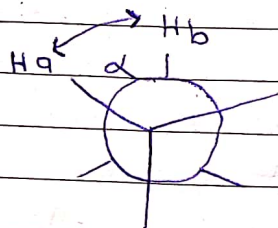


- If J_{bc} is much greater than J_{ab} , the signal will appear as a triplet of quartets.
- If J_{bc} is similar to J_{ab} , then several lines may overlap, and the signal is called a multiplet.

* Coupling constant (J) :-

- Distance b/w the peaks of multiplet measured in Hz (usually 0-18) called coupling constant.
- J is a quantitative measure of the magnetic interaction of nuclei whose spins are coupled.
- Not dependent on strength of the external field.
- Gives info on type of H.

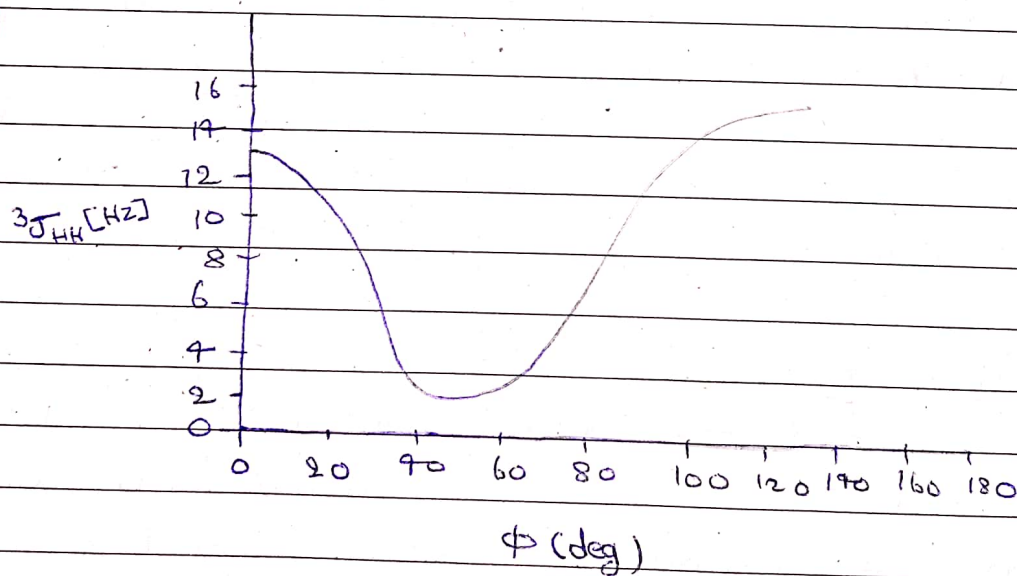
- multiplets with the same coupling constants may come from adjacent groups of protons that split each other.
- An important factor is vicinal coupling is the angle α b/w the C-H sigma bonds and whether or not it is fixed.
- coupling is a maximum when α is 0° and 180° , it is minimum when α is 90° .



- The general form of the Karplus relationship is:

$$^3J(\phi) = A \cos^2(\phi) + B \cos(\phi) + C$$

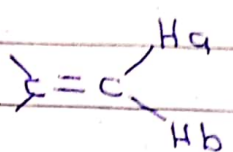
where the coefficients (A, B and C) are parameterized for particular molecule types, atoms and substitution.



- Protons on carbon-carbon double bonds often give characteristic splitting patterns.
- A disubstituted double bond can have two geminal

protons, two cis protons, or two trans protons.

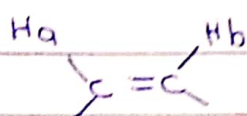
- When these protons are different, each proton splits the NMR signal of the other so that each proton appears as a doublet.
- The magnitude of the coupling constant J for these doublets depends on the arrangements of hydrogen atoms.



geminal H's

J_{geminal}

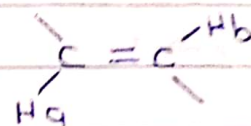
0-3 Hz



cis H's

J_{cis}

5-10 Hz



trans H's

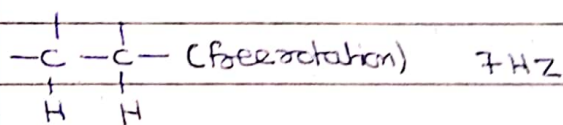
J_{trans}

11-18 Hz



characteristic coupling constant for these types of disubstituted alkenes:

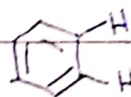
Approx. J



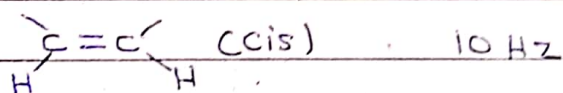
(free rotation)

7 Hz

Approx. J



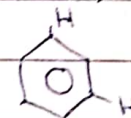
8 Hz



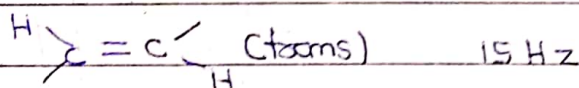
(cis)

10 Hz

(ortho)



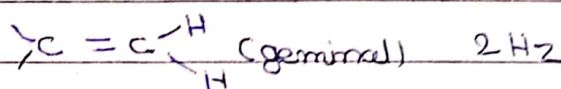
2 Hz



(trans)

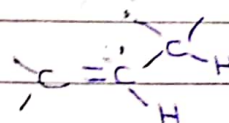
15 Hz

(meta)



(geminal)

2 Hz

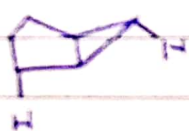


6 Hz

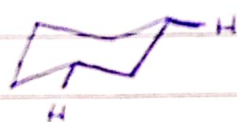
(allylic)

Long Range coupling :-

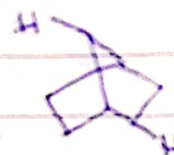
- Couplings between atoms 4 or more bonds away from one another collectively are denoted long-range coupling.
- tend to be small and not generally observable
- In some cases, when the atoms form a "W" four-bond ($^4J_{HH}$) coupling) are large enough to be observed.



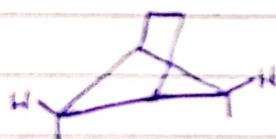
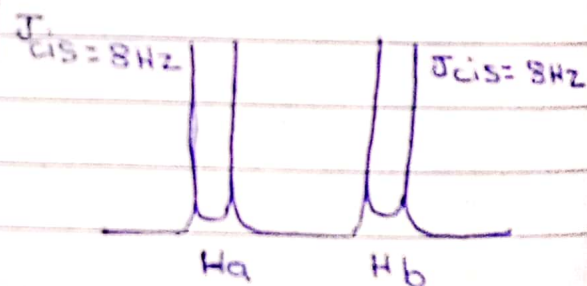
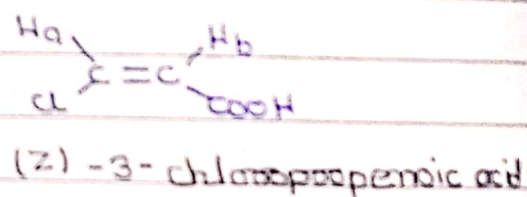
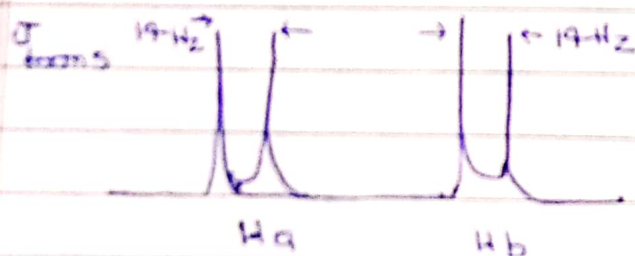
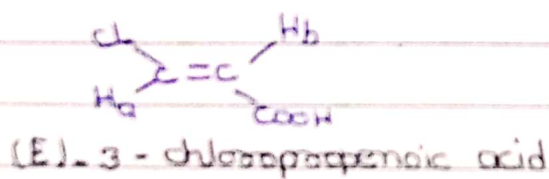
+0.9



+1.1



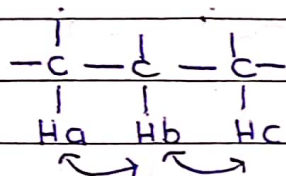
+3 to +4

 $J_{AB} = 7 \text{ Hz}$ 

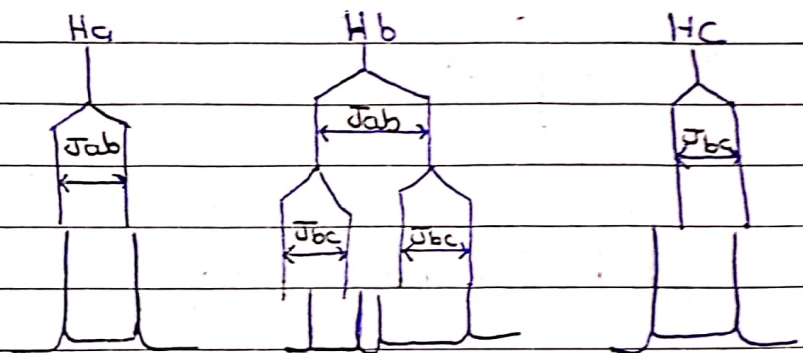
- Although both (E)- and (Z)-3-chloropropenoic acid show two doublets in their ^1H NMR spectra. For their alkenyl protons, $J_{trans} > J_{cis}$.

* complex splitting pattern: Non-equivalent coupling.

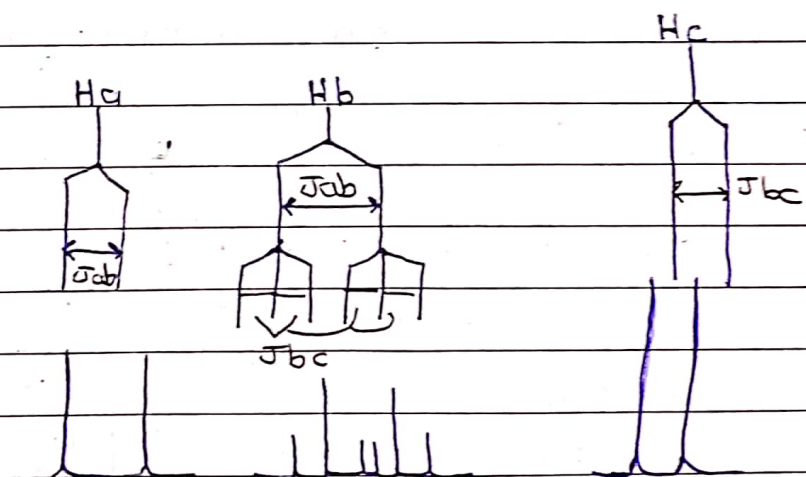
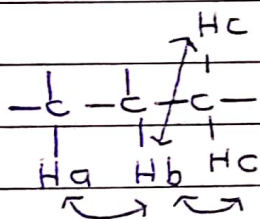
- complex splittings arise when a set of H atoms couples to more than one set of non-equivalent H atoms.
- A tree diagram shows that when H_b is adjacent to nonequivalent H_a on one side and H_c on the other, the resulting coupling gives rise to a doublet of doublets. ($J_{ab} > J_{bc}$).



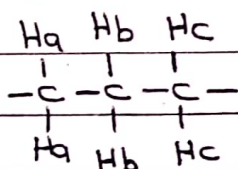
spin-spin coupling.



- If H_c is a set of two equivalent H, then the observed splitting is a doublet of triplets.

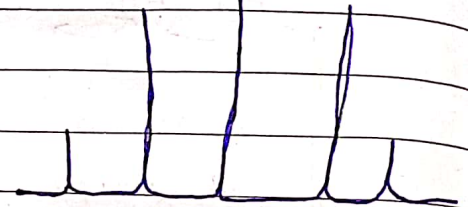
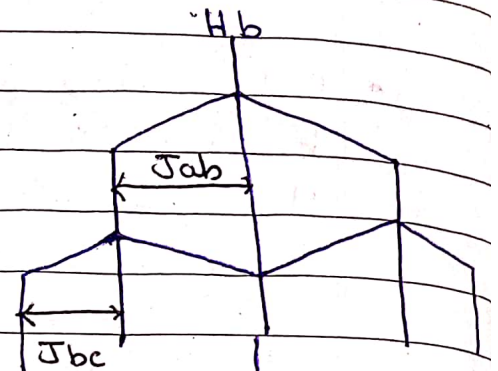
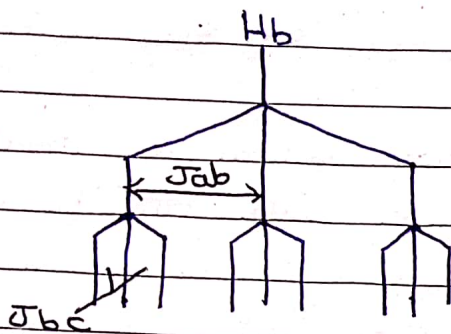


*.

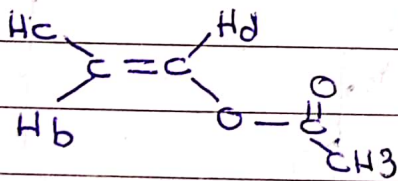


J_{ab} and J_{bc} are not equal.

J_{ab} and J_{bc} are equal



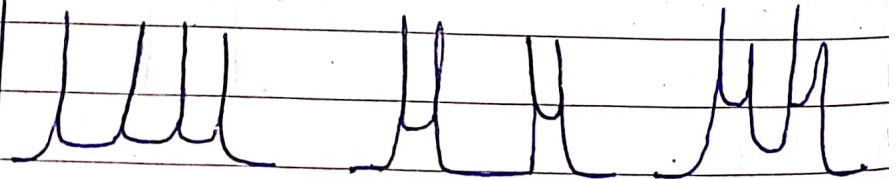
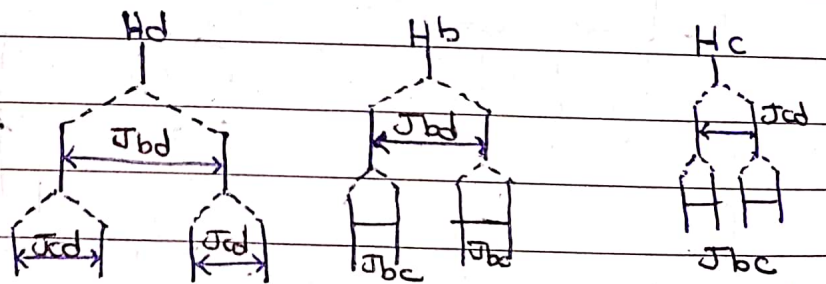
Spilling diagram for the alkenyl protons in vinyl acetate are shown below. Note that each pattern is different in appearance because the magnitude of the coupling constants forming them is different.



$J_{bc} = 1.2 \text{ Hz}$ (geminal)

$J_{cd} = 6.5 \text{ Hz}$ (cis)

$J_{bd} = 14 \text{ Hz}$ (trans)



Doublet of

H_b

H_c

Doublets

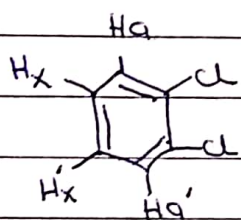
due to H_d

* The analysis of NMR patterns is assisted by general labelling method for spin systems - Pople Notations.

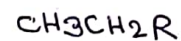
- each set of chemically equivalent protons is designated a letter from alphabet.
- Nuclei are labelled AX or AMX if their chemical shift differences are large compared coupling b/w them ($\tau_{AX} \gg 8J_{AX}$), sets are weakly coupled two - AX, three AMX.
- Small chemical shift difference represented by AB ($\tau_{AB} < 8J_{AB}$), strongly coupled sets.
- can also have mixed system: ABX, one strongly and one weakly coupled.

⇒ First-order spin systems:

AX (two doublets), A_2X (doublet, triplets), A_2X_2 (two triplets), A_3X_2 (triplet, quartet)



A_2X system



A_3X_2 system



AB system

$[AX]_2$



A_2

A3 system :-

Three equivalent nuclei always shows a singlet in NMR spectra. CH_3I , $\text{CH}_3\text{COOCH}_3$

AX_2 , A_2X system :-

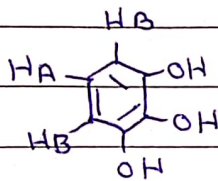
In this system, two magnetically equivalent protons are coupled to the third proton which has chemical shift. e.g. - $\text{Cl}_2\text{CHCH}_2\text{Cl}$, $\text{Cl}_2\text{CHCHdCHd}_2$.

AB_2 , A_2B system :-

two magnetically equivalent protons are coupled to third proton which has comparable chemical shift value.

e.g. - 2,5-dichloronitrobenzene,

2,6-dichloropyridine, pyrogallol etc



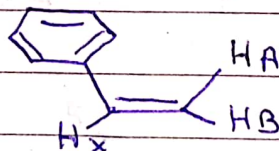
AB_2 system.

* AMX system :-

e.g. - Vinyl system ($\text{CH}_2=\text{CHY}$)

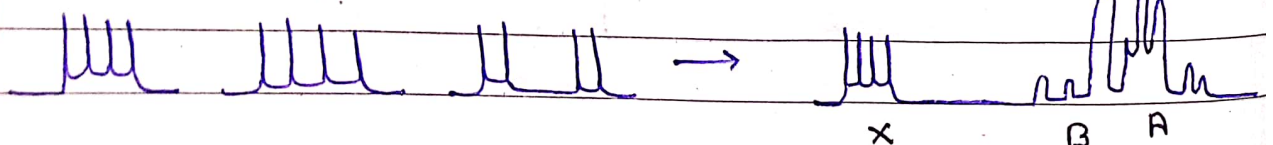
* ABX system :- e.g. - p-chlorostyrene and styrene.

e.g. -



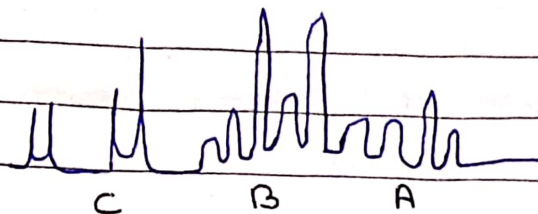
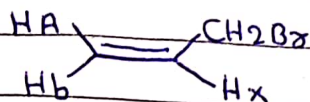
AMX

ABX



ABC System :-

e.g. - allyl bromide

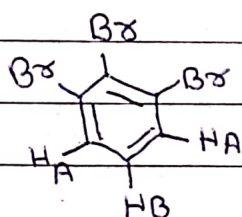


ABC

*. Magnetic equivalent protons

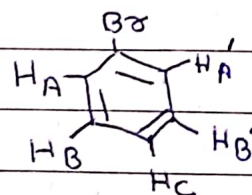
- Protons which have same chemical shift as well as have the same coupling constants with the same partner nuclei in the molecule.
- homotopic or enantiotopic protons are chemically equivalent but may or may not be magnetically equivalent.
- all magnetically equivalent protons are chemically equivalent but vice-versa not true.

tribromo benzene



- HA & HB are chemically and magnetically equivalent

bromo-benzene



- HA & HA' chemical shift will same but magnetically equivalent not.

Simple NMR

Complex NMR

(i) (n+1) Rule follow

These rules not

(ii) first-order spectra

follow.

(iii) chemical shift value should

be 5 to 7 times greater than J value

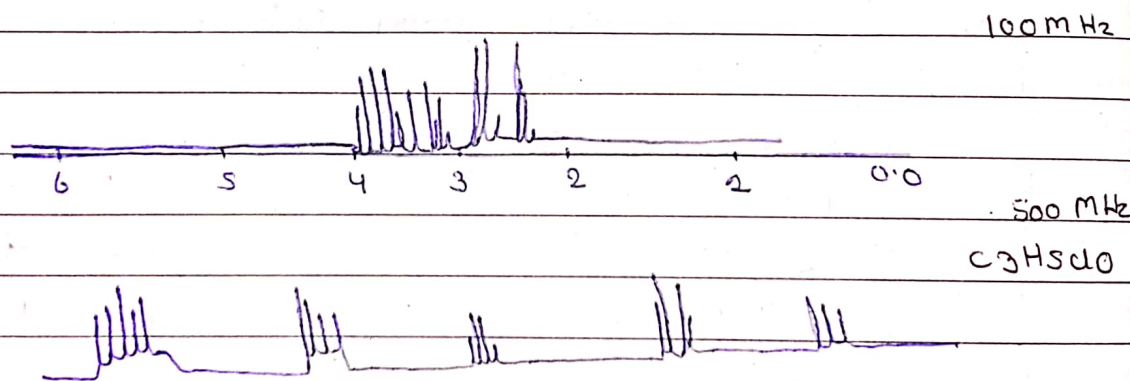
Q. What do you understand by spin-spin splitting?

* Simplification of second order spectra.

The complete NMR spectrum becomes difficult when signals overlap and hence useful information is buried due to complexity.

1. High Field strength

chemical shift measured in hertz and directly proportion to the applied magnetic field, whereas coupling constant remains the same. The value of $\Delta\nu/J$ will increase which further gives more separation b/w individual multiplets, overlapped at lower field strength C_3H_5ClO in $CDCl_3$ solution.



2. Solvent effects

- chemical shifts depends on the solvent used to record NMR spectra. The interaction b/w the solvent molecules and the solute molecule may shift the resonance position of a proton.
- If the solvent is non-polar such as hydrocarbon there will only be weak interaction b/w solvent and solute molecule and hence the chemical shift.

of the proton in a molecule will remain same or very minute will occur.

- If the solvent is polar in nature such as acetone, chloroform, DMSO, strong dipole interaction b/w solvent & solute molecules.
- Because of these interactions, the observed chemical shift will shift to a greater extent with respect that taken in non-polar solvent.
- Thus, we can use these solvent shift effect to resolve the complex spectra to some extent. By adding a small of deuterated benzene or pyridine to the NMR samples, can cause a dramatic difference in appearance of NMR spectrum.

3. Deuterium Exchange Reactions.

- Deuterium exchange is the most elementary and very useful technique for assigning the proton of OH, NH₂, SH etc. groups which are exchangeable with deuterium. Due to the above reactions, the peak due to alcoholic hydrogen will disappear and a signal due to HOD proton will appear in the spectrum.

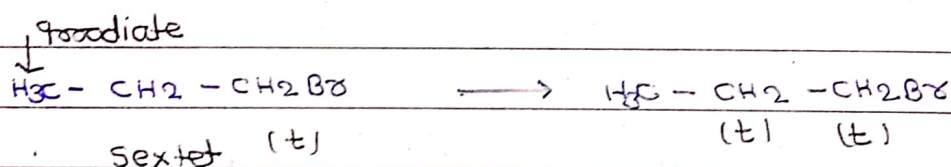
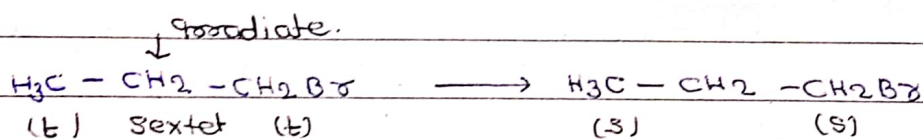
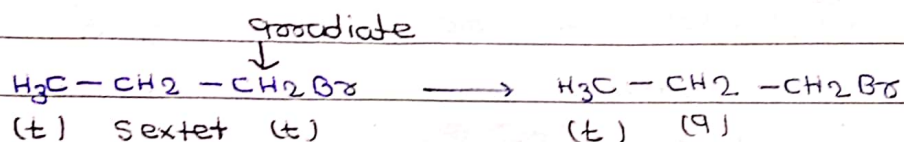


- The deuterium is not detected in the ¹H NMR as it absorbs at different field strength and hence there will not be any coupling due to proton which has been exchanged with deuterium.

4. Spin - Spin Decoupling

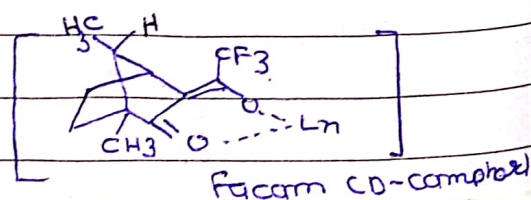
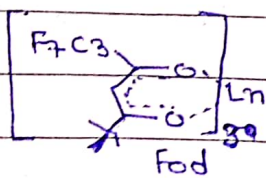
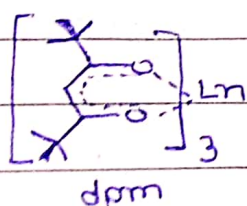
The spin-spin decoupling technique is used to simplify of the NMR spectra.

- In spin decoupling, a second strong radiofrequency is applied while the spectrum is scanned in usual fashion. This radiofrequency can be set to irradiate a particular group of equivalent hydrogen in the molecule. Irradiation with high energy radio waves causes rapid transition among their nuclear spin states. Thus the neighbouring protons cannot see different spin states of irradiated protons and consequently any spin-spin interaction are effectively removed, and the NMR spectrum is simplified.

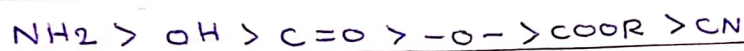


5. Use of Lanthanide shift Reagents.

- The Lanthanide shift reagents are β -diketonate complexes of rare-earth metals (Lanthanides).
- The commonly used Lanthanide shift reagents are Tris (1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane 4,6-dionato) europium, $\text{Eu}(\text{fod})_3$.
Tris-(C-dipivaloylmethanato) europium, $\text{Eu}(\text{dpm})_3$.



- The lanthanide shift reagent are Lewis acids, which attach themselves to the sites which have lone pairs such as amines, hydroxyl, aldehydes, ketones, thiols.
- The amount of shift in resonance position depends on the lanthanide metal ion, proton under investigation and concn of the shift reagent in the solution.
- more in the availability of the lone pairs, greater is the complexation.
- The strength of the complex formation is in the following order, provided the complexation site of the molecule is not sterically hindered.



- The strength of the effect of the chiral shift reagent depends on:
- most chiral shift reagent are very expensive.
- The maxm downfield and upfield shift is provided by europium and praseodymium tris- β -diketone complexes.
- The magnetic field associated with the metal ion which is paramagnetic causes marked changes in the observed shifts of the protons in the substrate. hence called shift reagents.

Paramagnetic materials:

- They cause line broadening by shortening relaxation times. They also cause a shift in signals.
- Co and Ni cause severe line broadening thus cannot be used.
- Lanthanide ions are found to cause shifts without line broadening.

medium-pacer
Arundhati Reddy won the
ICC Player of the Month
(women)



2023 season.
The nominations were
announced on Monday.
The nominees:

Women
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sion to p

6. Nuclear Overhauser Effect (NOE) :-

- The NOE effect was first introduced by Overhauser in 1953.
- The effect is a change in the intensity of a signal due to a particular proton on double irradiation of nearby protons within the molecule. In this case less intense radiation is used than the spin-spin decoupling or double irradiation.
- An increase of few percent in the intensity of absorption is observed b/w protons which are in close proximity. It is generally observed over very short distances, 2-4 Å.
- NOE and spin-spin coupling are two different concepts. NOE is the interaction of the nuclei through space and the no. of intervening bonds b/w the concerned protons has no significance whereas spin-spin coupling takes place via the bonds separating the nuclei.
- NOE is associated with dipolar relaxation mechanism. A spin excited nucleus may undergo spin relaxation via the transfer of its spin energy to the nuclei in close proximity. The efficiency of this process is directly related to the distance b/w the two nuclei.
- Thus NOE may be useful in studying the stereochemical relationship b/w molecules.

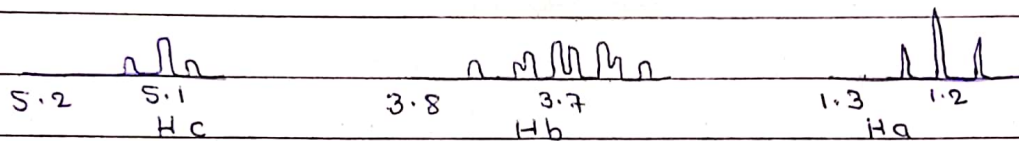
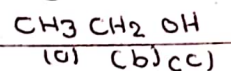
* Exchangeable protons

Protons are on electronegative atoms rapidly exchange b/w molecules in the presence of trace amounts of acid or base. Thus, the CH₂

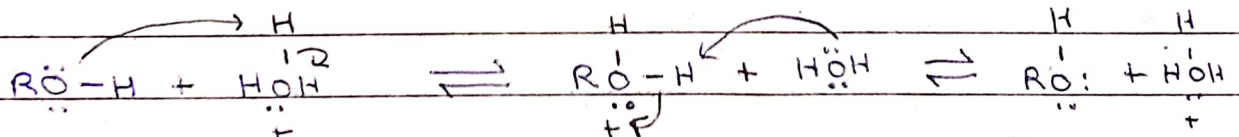
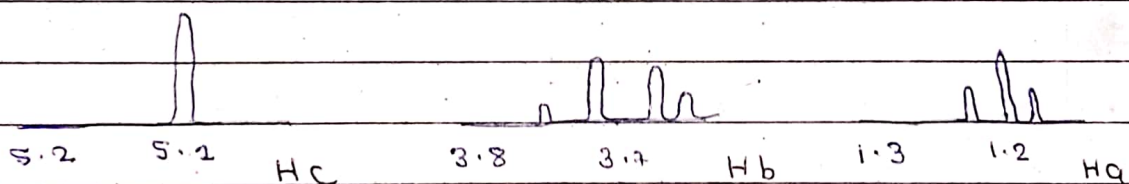
group of ethanol never "feels" the presence of the OH proton, because the OH proton is rapidly moving from one molecule to another.

- Rate of exchange of these protons is rapidly moving from made slow by:
- Removal of trace quantities of acid and base.
- Recording the spectrum at low temp. which retards the exchange.
- Dissolving the sample in highly polar solvents like DMSO, exchange is slowed due to strong solvation.

Ultra pure samples of ethanol show splitting



Ethanol containing a very small amount of HCl



amp

Q. what the different way to simplify the different spectra?

Q. what are shift reagent? State an example.

Q. Lanthanide why?

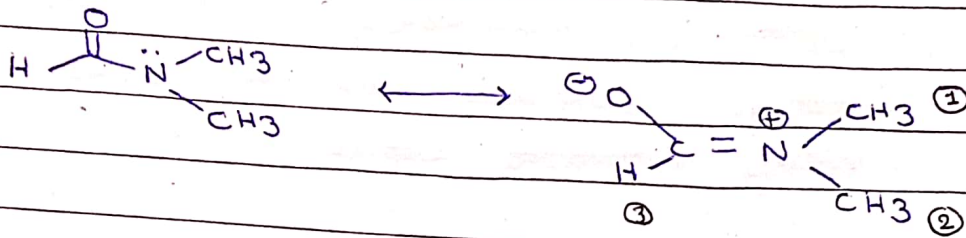
only other metal give peak broad
but Lanthanide there is no peak broad only
peak shift.

Q. $(CH_3)_2C=CHCH_2CH_2C(CH_3)=CHCHO$ two form

E & Z The C_3 methyl group of one isomer
on irradiation. it produces the enhancement of
20% due to hydrogen at C_2 in one isomer.
Predict the structure of isomers of that give
peak shift.

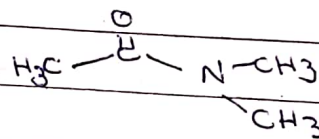
In cyclohexane axial & equatorial have same peak.
because there are ring flipping
if flipping is removed then give two peaks
in cyclohexane system.

Q. Predict the spectra of DMF (Dimethyl formamide)



- Three peaks obtained because of the partial double bond character due to carbon & nitrogen bond.
- If 165°C recorded then double bond character is removed & observed only two peaks in NMR spectra. rotation of double bond is allowed.

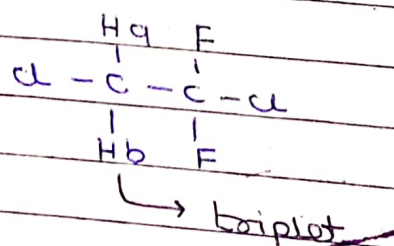
Q. Dimethyl acetamide



* Fluorine (NMR) :-

^{19}F ($I = \frac{1}{2}$) is the naturally occurring isotope of Fluorine 100% abundance and I value of ($\frac{1}{2}$).

The splitting of proton signal caused by spin-spin coupling b/w protons ^{19}F is observed.

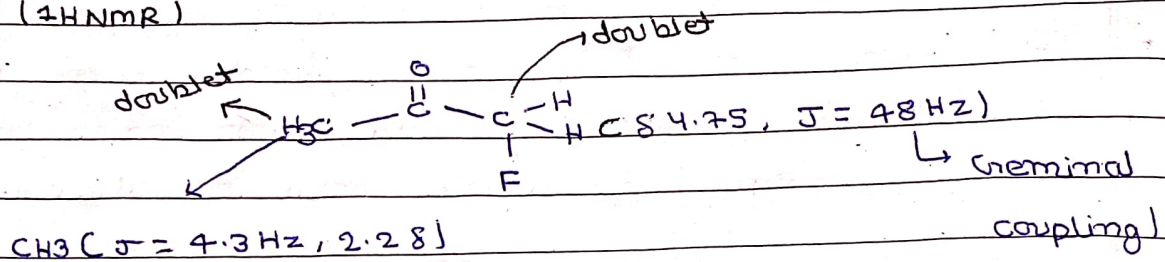


coupling constant
 $J = 12\text{ Hz}$

- coupling b/w ^1H & ^{19}F is strong
- Geminal coupling ranges from 42-80 Hz and Vicinal coupling 1.2-30 Hz
- The coupling constant for HF covers a comparatively larger range.

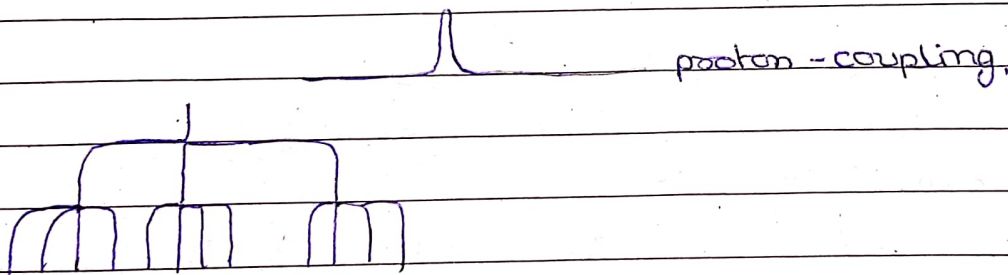
e.g. - fluoroacetone

(^1H -NMR)



^{19}F -NMR

① Proton-decouple

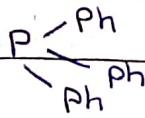


*. ^{31}P -NMR :-

^{31}P -nucleus is a natural abundance of 100% and ($I = \frac{1}{2}$). The coupling constants are large with P-H-coupling around 200-700 Hz and phosphorus-carbon-hydrogen value co's to 20 Hz and are observable through at least four bonds.

e.g. -

triphenyl phosphine.



1 peak observed for the phosphorus.

* ^{29}Si - NMR :-

^{29}Si has a natural abundance of 4.70% and ($I = \frac{1}{2}$). The value of coupling constant is around 6 Hz

$$J_{\text{Si-C-H}} = 6 \text{ Hz}$$

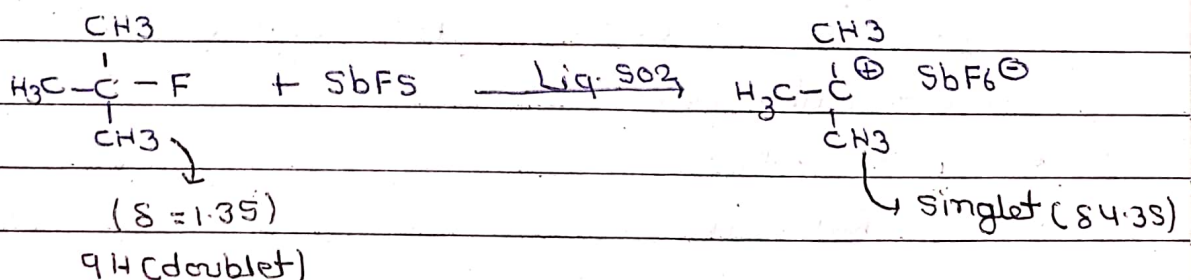
* NMR - spectrum of carbocation (study of carbocation Colah (scientist)).

In liq. SO_2 alkyl fluorides (RF) reacts with Lewis acid antimony pentafluoride to give solutions of carbocations.

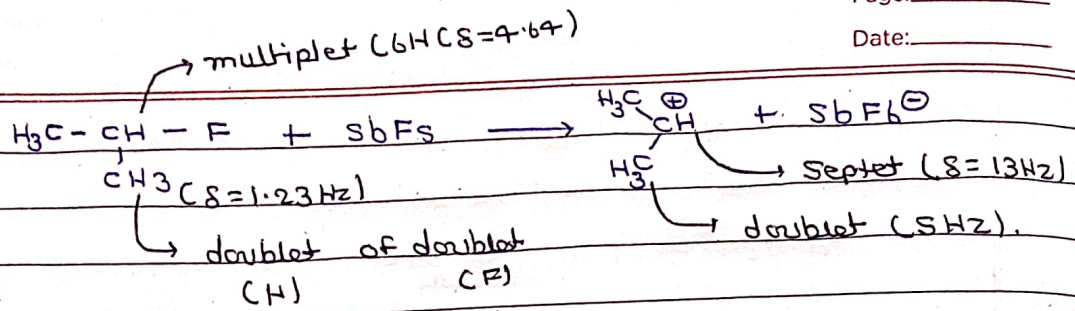


(Lewis acid)

e.g. tert-butyl fluorides



e.g. isopropyl fluoride.



Assignment.

Q. Write a short notes on MRI?

Introduction & Definition

MRI is a non-invasive, non-ionizing imaging modality that uses strong magnetic field and radio frequency pulses to create high-resolution images of soft tissues.

Basic physics.

1. Alignment: protons normally spin randomly. When placed in external magnetic field.
2. Precession: Protons rotates around the B_0 axis.
Larmor frequency.

$$\omega = \gamma B_0$$

3. Relaxation: When the RF pulses is turned off, protons returns to equilibrium, emitting an electrical signal.
 - T_1 Relaxation
 - T_2 Relaxation

Instrumentation.

- Main magnet: Provides the static field (801 - 1 Tesla)
- Gradient coils: Responsible for spatial encoding
- RF coils: Act as transmitters and receiver.
- Shimming: Process to ensure the magnetic field is perfectly uniform.

Contrast agents

- GdCl₃ used to enhance T₁ images, it highlights areas of increased vascularity or blood brain barrier breakdown.

Advantages :-

No ionizing radiation; superior soft-tissue contrast; multi-planar imaging.

Disadvantages :-

Expensive, Long scan times, Loud noise, metal safety hazards.

Assignment

Q.1. Predict the structure of given compound on the basis of ^1H -spectrum ($\text{C}_6\text{H}_{10}\text{O}_2$)

- ① (a) δ 6.95 (dq; $J = 16\text{Hz}$, 6.8Hz , for 1H)
- ② (b) δ 5.81 (dq; $J = 16\text{Hz}$, 1.7Hz , for 1H)
- ③ (c) δ 4.13 (q; $J = 7\text{Hz}$, 2H)
- ④ (d) δ 1.88 (dd; $J = 6.8\text{Hz}$, 1.7Hz for 1H)
- ⑤ (e) δ 1.24 (triplet, $J = 7\text{Hz}$ for 3H)

Ans. Degree of unsaturation = $\frac{C(\text{no. of carbon}) + 1 - H(\text{no. of H})}{2}$

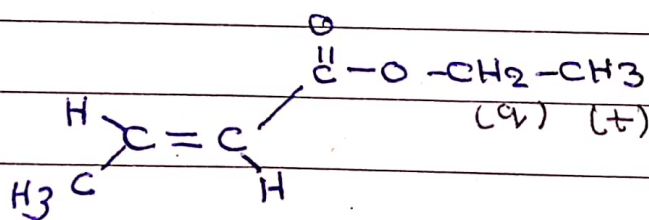
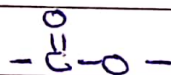
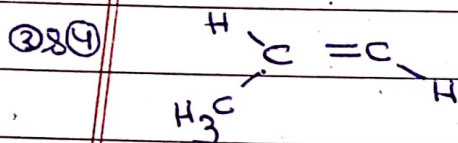
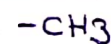
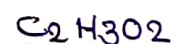
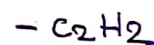
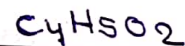
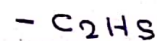
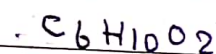
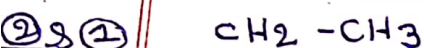
$$= \frac{C + 1 - H}{2}$$

$$= \frac{6 + 1 - 10}{2}$$

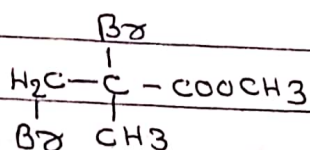
$$= 7 - 5$$

$$= 2$$

means two ($=$) or ($\equiv$) bonds.



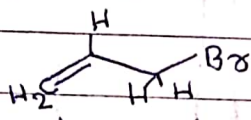
Q.2 Predict the no. of signals splitting chemical shift position of



No. of signal = 3 Ans

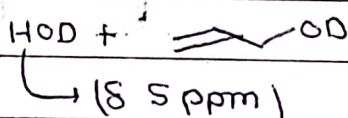
Q.1 Predict the spectrum of allyl bromide. A pure sample of allyl bromide became impure on storage. The impurity ($\text{C}_3\text{H}_6\text{O}$) on deuterium exchange shows the disappearance of one signal and appearance of new signal at $\delta 5 \text{ ppm}$. Assign a structure to this impurity.

Ans.



total 3 peaks observed.

impurity $\rightarrow$ $\text{CH}_2=\text{CH}-\text{CH}_2\text{OH}$ (allyl alcohol)



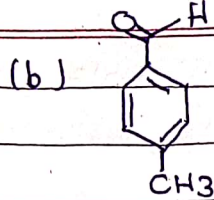
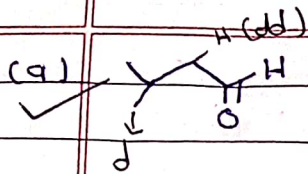
Q.2 Match the following $^1\text{H NMR}$ spectra with one of the following substance.

9.72 (t, $J = 2.1 \text{ Hz}$, 1H)

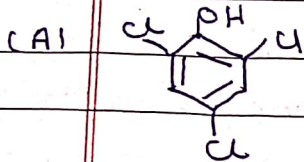
2.36 (dd, $J = 7.1, 2.1 \text{ Hz}$, 2H)

2.21 (m, 1H)

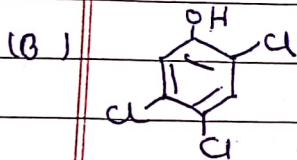
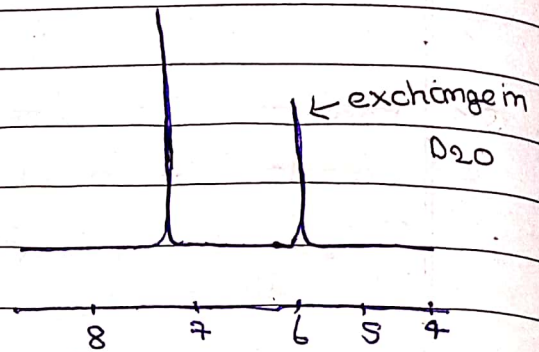
0.98 (d, $J = 6.7 \text{ Hz}$, 6H)



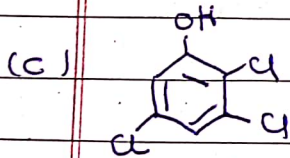
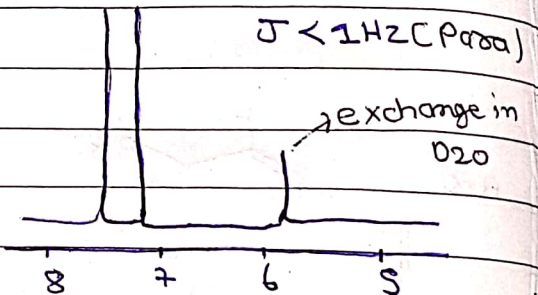
Q.3 match the following compound with the spectrum given:



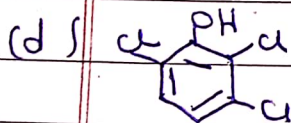
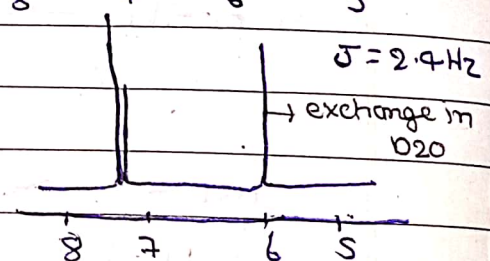
→ only 2 peaks



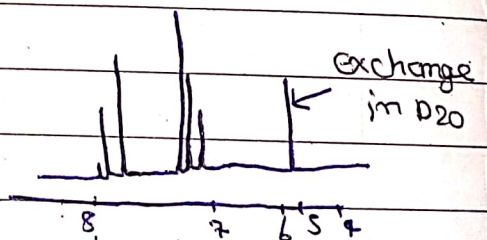
→ Three signals.
(Para position)



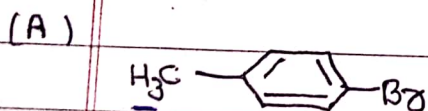
→ Three signals.
(meta 2.4 Hz)



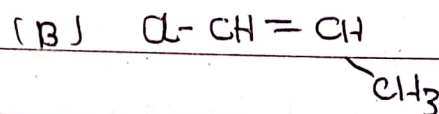
→ Three signals.
($J = 9 \text{ Hz}$)
(ortho position)



Q.4 Name the following compounds in terms of spin systems:



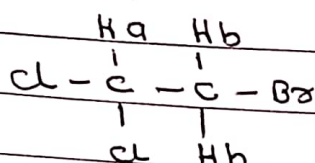
AA'BB'



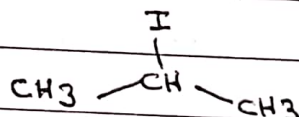
ABX₃

(c) $\text{CH}_3\text{-CH}_2\text{-Br}$ R_3X_2

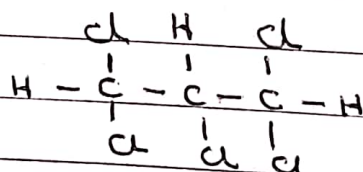
Q.1. Work out the spin system and splitting pattern for molecule?



Q.2 Explain the pattern & intensities of the isopropyl group in isopropyl iodide.

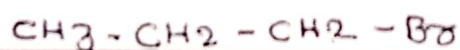


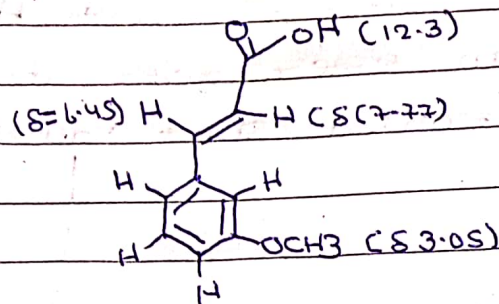
Q.3. What spectrum would you expect for the following molecule.



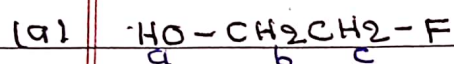
Q.4 what arrangements of protons would give two triplets of equal area.

Q.5. Predict the appearance of the NMR spectrum of propyl bromide.





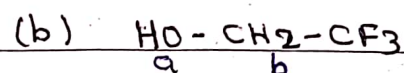
Q.2. Predict the ^1H spectra of the following compounds:-



$\text{H}_\text{a} \rightarrow$ triplet

$\text{H}_\text{b} \rightarrow$ doublet of triplet

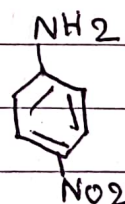
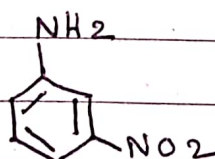
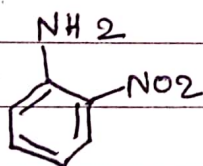
$\text{H}_\text{c} \rightarrow$ triplet
doublet of



$\text{H}_\text{b} \rightarrow$ quartet

$\text{H}_\text{a} \rightarrow$ triplet.

Q.3. How will you differentiate b/w the following compounds on the basis of ^1H NMR:



1. o - Nitroaniline (Ortho-isomer)

- Aromatic protons (4H): all non-equivalent
- pattern: complex multiplets
- Reason: 1,2-disubstitution $\rightarrow$ no symmetry
- NH_2 protons: broad singlet ($\sim 4-6$ ppm)

2. meta - nitroaniline (meta-isomer)

- Aromatic protons (4H): all non-equivalents
- Pattern: 4 different signals
- Shows doublet, triplet, singlet combinations
- NH_2 : broad singlet

3. p - Nitroaniline (Para-isomer)

- Aromatic protons (4H): two sets of equivalent
- pattern: two doublets, protons
 $\rightarrow$ (AA' BB' system)
- Integration: $2\text{H} + 2\text{H}$
- NH_2 : broad singlet.

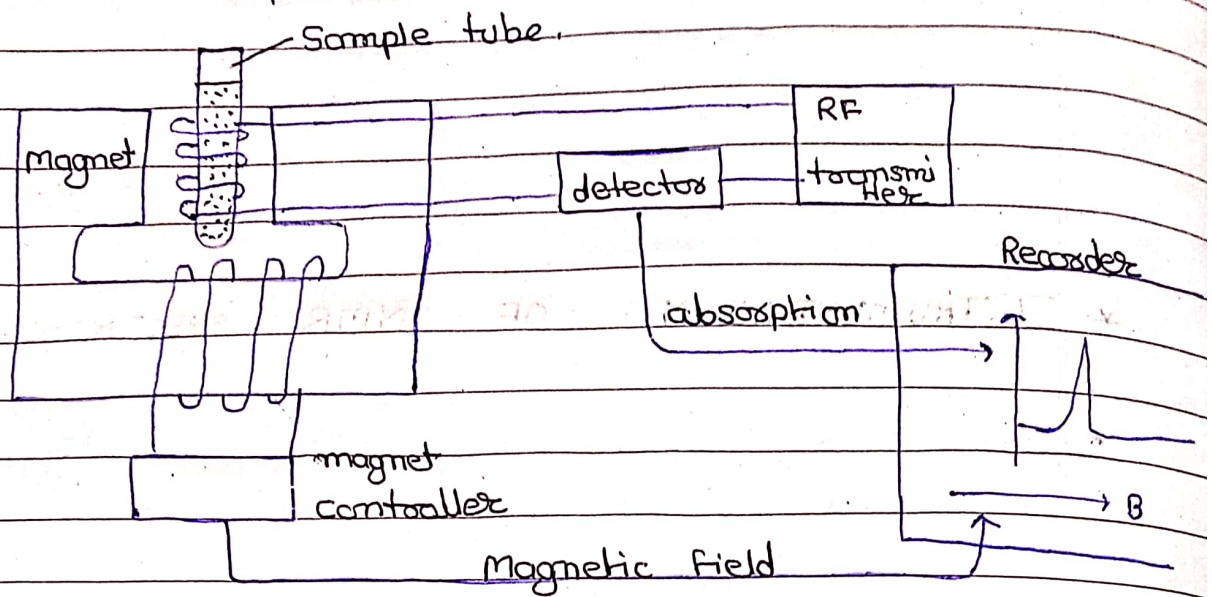
* INSTRUMENTATION OF NMR SPECTROSCOPY

- The NMR spectrophotometer consists of following components.

- A Magnet
- Sample and sample holder
- Radiofrequency generator
- Detector
- Recorder

- In NMR spectrophotometer, the sample is dissolved in CDCl_3 and placed in magnetic field. Then radiofrequency generator irradiates the sample with short pulse of radiation causing resonance. When nuclei fall back to their low energy state, detector measures the energy released and spectrum is recorded. The superconducting magnet in modern NMR spectrometers have coils that are cooled in liquid helium and conduct electricity with no resistance.

- A line diagram of NMR spectrophotometer along with its components are as follows:



Magnet :-

A strong magnet provides stable and homogeneous field. The magnet size is 15 inches in diameter and capable of producing strong fields up to 23,500 gauss for 100 MHz.

Sample and Sample holder :-

A 1-30 mg sample is used in the form of dilute solution ($2-10\%$) and solvent doesn't contain hydrogen of its own ions. The sample holder is glass tube about 5 mm in diameter and 15-20 cm in length.

Radiofrequency oscillator :-

The RF oscillator is installed perpendicular to magnetic field and transmit radio waves of some mixed

frequency such as 60, 100, 220, 300 MHz. a sweep generator is installed to supply dc current to sec. magnet.

RF detector or Receiver :-

It is installed perpendicular to both magnetic field and the oscillator coil and is tuned to the same frequency as transmitter. When precession frequency is match with RF the nuclei induces (emf) in detector coil and this signal is amplified and sent to recorder.

Recorder :-

The Recorder gives a spectrum as a plot of strength resonance signal on y axis & strength of magnetic field on x axis. The strength of Resonance signal is directly proportional to number of nuclei resonating at that particular field strength.

* Working of instrument

- sample placed in long cylindrical glass tube especially made for NMR
- Dissolved the sample in proton free solvent like $CDCl_3$ or CCl_4 and add small amount of TMS as internal reference
- placed the sample in gap b/w two magnetic poles where coil is attached to a specific RF generator.

- The coil supply EMR energy and to change spin orientation of proton.
- The detector coil detects radiofrequency signal when resonance occurs.
- TMS is shown at a peak value of $\delta = 0$ ppm.

* Solvents

- The solvents used for dissolving sample should have following properties:
 - Should not contain proton,
 - Inexpensive
 - Low boiling point and non-polar in nature.
- Generally deuterated chloroform CDCl_3 is used as solvents.
- If sample is soluble in polar solvent, then deuterium oxide (D_2O), DMSO, CDCl_4 , CS_2 , CF_3 , COOH are used as solvent.