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NMR SPECTROSCOPY

- Magnetic nuclei expose to magnetic field absorb light radiation at unique combination of field strength & frequency of irradiated radiations the phenomenon is called nuclear magnetic resonance.

- Hydrogen nucleus consist single proton only so it is magnetic, so like any other magnetic nuclei proton absorb radio frequency light radiation this phenomenon is called proton magnetic resonance (PMR).

- PMR spectroscopy based on the net absorption of energy in the radio frequency range by hydrogen nuclei expose to strong magnetic field.

- Hydrogen nuclei due to their spin generate magnetic moment along their spin axis in the absence of applied field the magnetic moment vector oriented in all possible direction but when the protons are placed in uniform applied field, the magnetic moment vector align in only one of two orientation with respect to direction of applied magnetic field.

(2)

*) Magnetic & non-magnetic nuclei -
 - On the bases of resultant spin of nucleon present in nucleus, the nuclei are assign a nuclear spin quantum number (I), depending upon I value we have following two types of nuclei.

I] Magnetic nuclei:-
 They are nuclei of atom whose spin quantum number is greater than zero. ($I > 0$) depending upon their mass no. & atomic no. the value of I can be integral or half integral. This nuclei are act like bar magnets and align in the applied magnetic field.

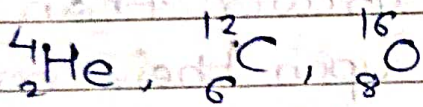
Atomic No	Mass No	I value	Examples.
Odd	Odd	$1/2, 3/2, 5/2$	${}^1_1\text{H}, {}^{19}_9\text{F}, {}^{31}_{15}\text{P}$
Even	Odd	$1/2, 3/2, 5/2, 7/2$	${}^{13}_6\text{C}, {}^{17}_8\text{O}, {}^{31}_{16}\text{S}$
Odd	Even	$1, 2, 3, \dots$	${}^{10}_5\text{B}, {}^{30}_{15}\text{P}$

- The phenomenon of nuclear magnetic resonance is shown by magnetic nuclei only.

II] Non-magnetic nuclei -

- They are nuclei of atom whose spin quantum number is zero ($I=0$).
- These nuclei do not align in applied magnetic field so they do not show nuclear magnetic resonance phenomenon.
- All nuclei having even atomic number and even mass number have I -value equal to zero, so they are non-magnetic.

e.g.,



★ Shielding & deshielding -

- An electron has both charge & spin. So under the influence of external applied field electrons circulate & generate their own magnetic field called induced magnetic field.

- The induced field generated by circulation of electron may oppose or reinforce the external applied field around proton.

- When induced field opposes the external field ($\uparrow\downarrow$) the proton experiences a field which is slightly less than applied field strength so they are said to be protected or shielded.

- This phenomenon of partially protecting proton from applied field by induced field

called shielding or diamagnetic shielding.

- When induced field reinforces the external (M) field the proton experience a field which slightly greater than applied field so they said to be deprotected or deshielded.

★ Chemical Shift -

★ Van der waal deshielding -

- In an overcrowded molecule, proton occupying hindered position bear slightly higher δ value because the electron clouds of bulky group tends to repel electrons clouds of surround proton.

Hydroxyl proton signal remain unsplit

★ Chemical Shift -

- The difference in peak or resonance position of proton w.r.t orbital standard is called chemical shift.

- The difference in peak of proton is due to electron density around the proton as compare with electron density around the proton of standard chooser.

- Chemical shift signifies the exact position of resonance signals of different types of proton. From orbitally choosen standard.

- Proton which are identically electronic environment have same chemical shift are called equivalent proton.

- Proton which one in different electronic environment have diff. chemical shift are called non-equivalent proton.

★ Characteristics δ value of different types of proton -

Types of proton

δ ppm

(A) Methyl ($-CH_3$) proton.

- | | | |
|-------|---------------------------------------|-----|
| (i) | $CH_3 - R$ | 0.9 |
| (ii) | $CH_3 - C = C$ | 1.6 |
| (iii) | $CH_3 - \underset{O}{\parallel} - OR$ | 2.0 |

(IV)	$\text{CH}_3-\overset{\text{N}}{\underset{ }{\text{C}}}-\text{R}$	2.3
(V)	$\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{Ar}$	2.6
(VI)	$\text{CH}_3-\text{N}-\text{Ar}$	3.0
(VII)	$\text{CH}_3-\text{O}-\text{R}$	3.3
(VIII)	$\text{CH}_3-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}$	3.7
(IX)	$\text{CH}_3-\text{O}-\text{Ar}$	3.8

(B) Methylene (-CH₂) proton.

(i)	$\text{C}-\text{CH}_2-\text{C}$	1.4
(ii)	$\text{C}=\text{CH}_2-\text{COOR}$	2.2
(iii)	$\text{C}-\text{CH}_2-\text{C}\equiv\text{C}-$	2.5
(iv)	$\text{C}-\text{CH}_2-\text{OH}$	3.6
(v)	$\text{C}-\text{CH}_2-\text{N}$	2.5
(vi)	$\text{C}-\text{CH}_2-\text{I}$	3.2
(vii)	$\text{C}-\text{CH}_2-\text{Br}$	3.5
(viii)	$\text{C}-\text{CH}_2-\text{Cl}$	3.6
(ix)	$\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}$	2.1
(x)	CH_3-S	2.1
(xi)	CH_3-Ar	2.3

(C) Methylenic (-CH) proton -

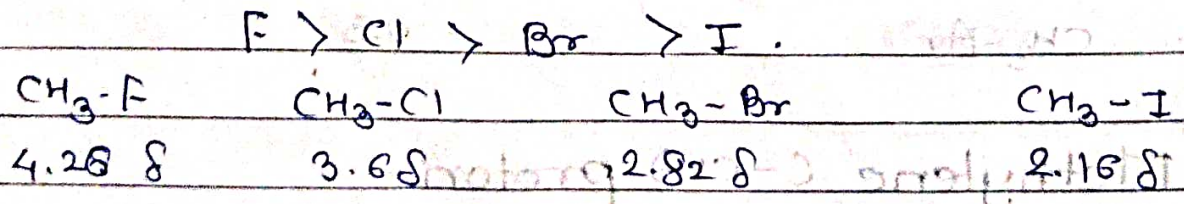
(1)	$\text{C}-\text{CH}-\text{Ar}$	2.7
(2)	$\text{C}-\text{CH}-\text{C}$	1.5
(3)	$\text{C}-\text{CH}-\text{OH}$	3.9
(4)	$-\text{C}-\text{CH}-\text{O}-\text{COR}$	4.8

Other proton.		
(i)	H-Ar	7.0
(ii)	R-C(=O)-H	9.7
(iii)	R-C(=O)-O-H	11.0
(iv)	R-O-H	5.0
(v)	>N-H	1.0
(vi)	-C≡C-H	2.5
(vii)	>C=C-H	5.5

* Factors affecting chemical shift (δ -values) -
 - The factors which affect shielding or deshielding affect the δ -values.

(i) Electronegativity & Inductive effect -
 - Presence of electron withdrawing atom or group, deshield the proton & push the δ value to the higher side (down field shift).

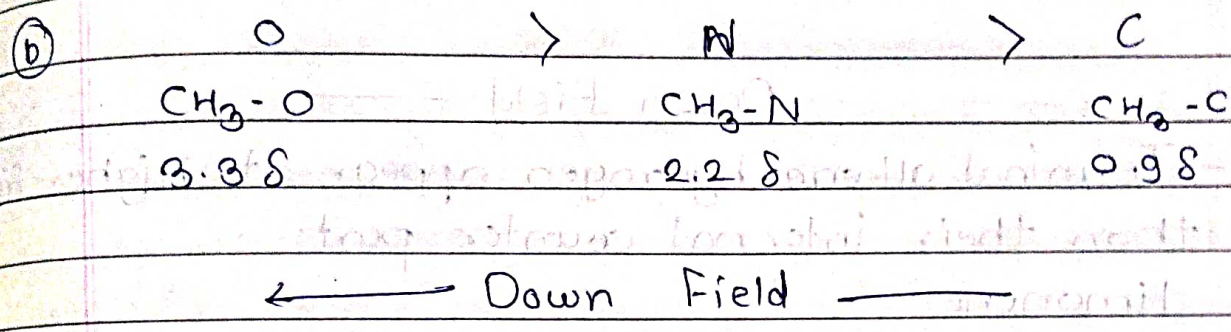
@ eg., The order of electronegativity of Halogen & its effect of δ -value is as under



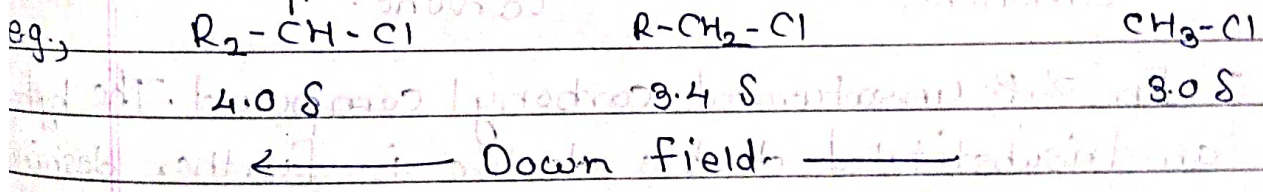
← Down Field (deshielding) →

- Deshielding of proton increases from right to

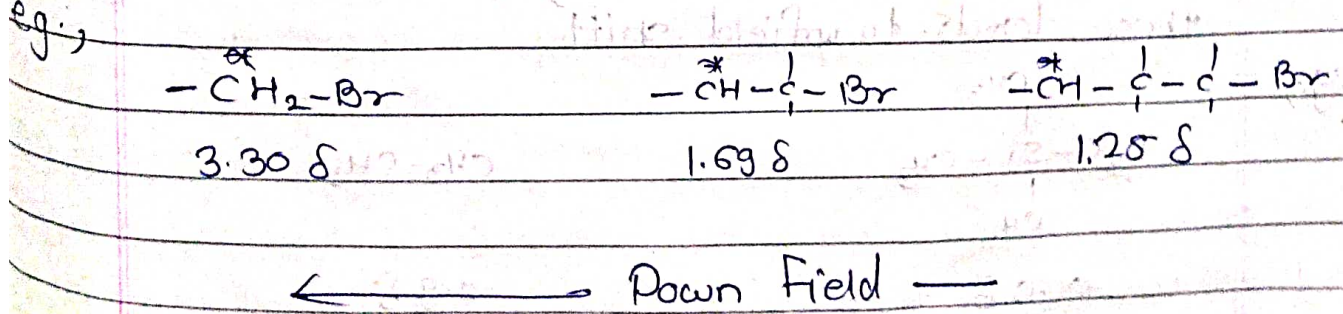
left i.e., shielding increases from left to right.
 - similar effect observe in following cases.
 - The order of electronegativity is under O, N, C.



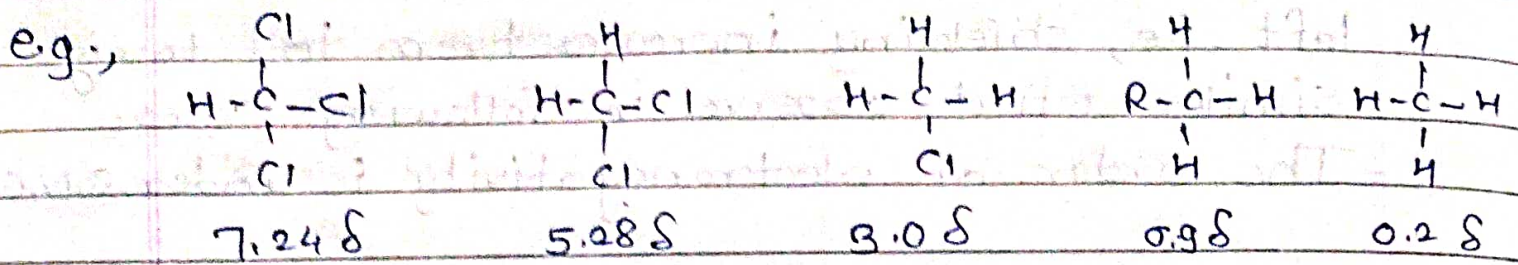
(c) The more no. of halogen atoms on the carbon more the magnetic shielding so smaller the δ_p values:



(d) As electron withdrawing group is remove away from concerned proton, lesser the deshielding & lower the δ value.



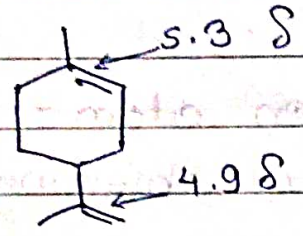
(e) The increasing the no. of electron with-drawing group attach to carbon increases deshielding increasing δ -value.



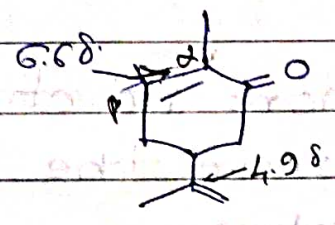
← Down Field →

- Terminal alkene hydrogen appear at higher field than their internal counter part

e.g. limonene.



Limonene

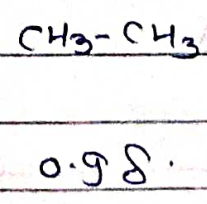
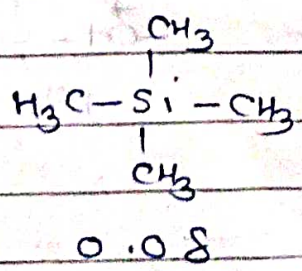


Carvone.

- In α,β -unsaturated carbonyl compound. The hydrogen on trisubstituted double bond is further deshielded to show higher δ -value. e.g., Carvone.

- Electropositive atom or electronegative group in the vicinity of proton increases e^- density around the proton causing proton shielding these leads to upfield shift.

e.g.:



Shielding

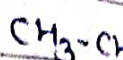
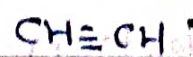
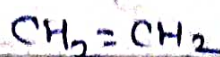
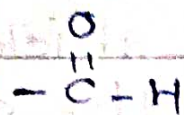
upfield ←

* Anisotropic Effect -

The π -electrons of molecule under the influence of applied field circulate & generate magnetic field. However a field generated by π -electron is unsymmetric & does not operate equally in space that is it may bear paramagnetic effect causing a upfield shift in certain direction & diamagnetic effect causing downfield shift in other direction.

eg-

Consider the δ value of series of compound



$\sim 9.7 \delta$

$\sim 7.3 \delta$

5.8δ

2.9δ

0.9δ

← Anisotropic deshielding →

I] Aldehydic Proton.

- Aldehydic proton is deshielded due to electronegative nature of oxygen.

- The induced field generated by circulating π electron of -C=O reinforce the applied field around the aldehydic proton. so the δ values increases to $\sim 9.7 \delta$ which is down field.

II] Benzene —

- The induced field reinforce the applied field around the proton so aromatic protons are deshielded hence show higher δ value.

III] Alkene —

- The applied field & induced field have same direction at vinyl proton producing paramagnetic deshielding this causes downfield shift resulting higher δ value.

IV] Alkyne —

- The π electrons in alkynes are most free to circulate around the symmetry axis of triple bond. Electron circulation around the triple bond occur in such way that proton experiences a diamagnetic shielding effect. This cause proton absorb the up field.

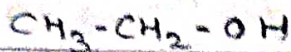
* Peak Area (Integration): —

- Each peak in NMR spectra at low resolution correspond to set of equivalent proton.
- The area recorded under the peak is in proportion to the intensity of signal generated which depends on number of proton absorbing at that instance of time.
- So, it follows that area under the peak is in proportion to the no. of proton in that environment.
- Electronic integrator fitted in an instrument measures the area & record the integrals.
- The height of integral is in the proportion to the area under the peak.
- The peak area recorded can give actual number of proton of each type or give only a relative ratio of proton of each type depends on nature of compound.

e.g. - Ethanol -

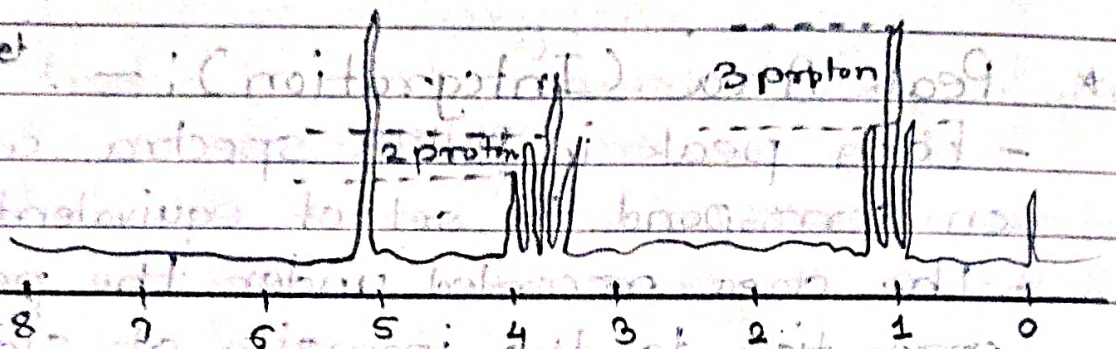
- The peak area or integral ratio of different proton in ethanol is 1:2:3.

- It gives actual no. of different kinds of proton.



- 1) 3 - triplet
- 2) 4 - quartet
- 3) 1 - singlet

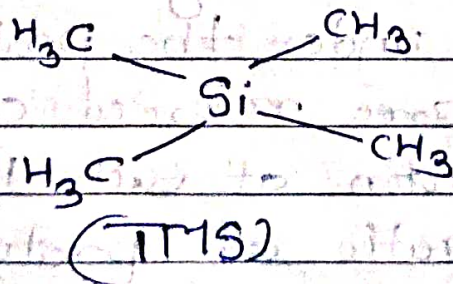
1:2:3



★ Merits of TMS as a PMR reference compound

- The universally accepted reference for proton in non-aqueous solvent is tetramethyl silane. (TMS)

- The field at which proton of TMS absorb is taken as a reference field.



Advantages of TMS

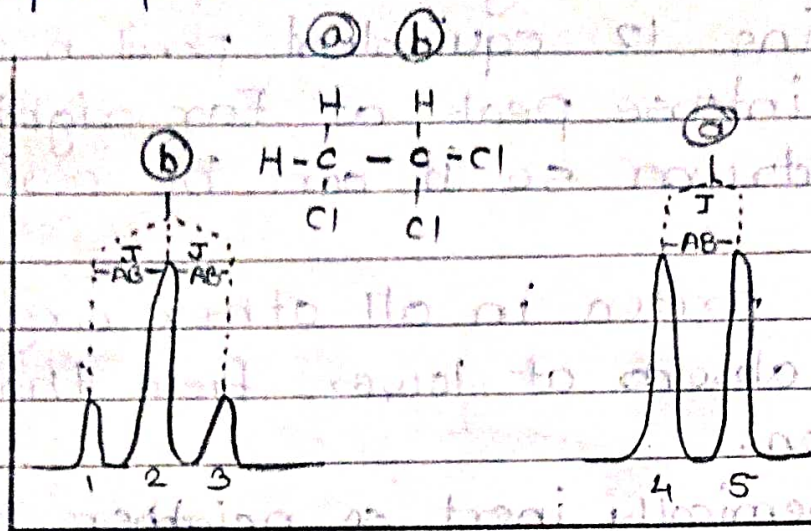
- 1) Silicon is less electronegative so methyl proton or TMS are strongly shielded than the most other organic compound.
- 2) It contains 12 equivalent proton so give a sharp intense peak at far right of PMR spectrum so it can be easily recognised.
- 3) Generally proton in all other organic compound absorb at lower field than the TMS proton.
- 4) It is chemically inert so neither react nor forms intermolecular association with sample hence it can be used safely as an internal standard.
- 5) It is miscible with almost all organic compound & soluble in some organic solvent.
- 6) It is volatile liquid. B.P. = 299 K = 26°C. So it can be removed easily & recovered the sample after analysis.

* Coupling Constant :-

- The distance between the centre of two adjacent or successive peak in a multiplet is usually constant & is called coupling constant; denoted by J .
- It is expressed in units of cycles/sec. or Hz.

- It's value vary from 0 to 20.

- The value of J depends upon number of covalent bond through which proton interact and also upon structural relationship between couple proton.



Types of coupling constant -

- The distance between the centre of two adjacent or successive peak in a multiplet is usually constant & is called coupling constant.

- The different types of coupling are as under -

① one bond coupling (1J) -

- This type of coupling occurs between two spin active nuclei join by single bond.

eg - $^{13}\text{C}-\text{H}$

- The bonding electron in the single bond are assume to avoid each other so that one electron is near to left nucleus & other

electron is near right nucleus.

- According to Pauli's principle the electron pair in the same orbital has opposite spin therefore dirac model predict that, when both the nuclei have opposite spin i.e., the most stable condition.

- So, when two nuclei prefer opposite spin the coupling constant J is positive.

- When the nuclei have parallel or same spin coupling constant J is negative.

② Two bond coupling (2J) -

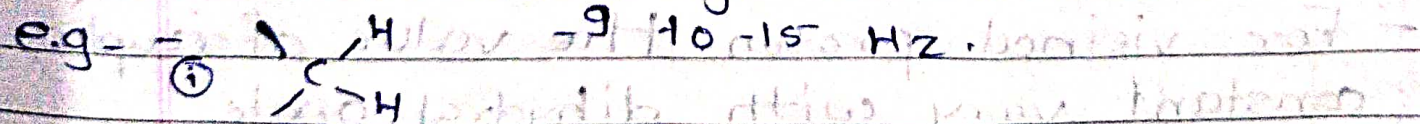
- This type of coupling are common in NMR.

- This are sometime called geminal coupling because the two nuclei that interact are attach to the same centre atom.

- Two bond coupling constant are represented as (2J).

- They occur in carbon compound when two spin active atom are attach to the same carbon atom.

- Two bond coupling constant are typically smaller in magnitude than one bond coupling.



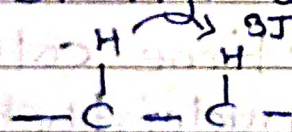
- The value of 2J depends upon bond angle

in case of geminal proton of saturated compound. If these protons are in different environment then the coupling is usually strong.

- When bond angle is 105° , J is nearly -25 Hz .
- When bond angle increases to 109° , J becomes -12 Hz and becomes zero when bond angle is 125° .

③ Three bond coupling (3J) - (Vicinal)

- In a hydrocarbon the spin of hydrogen nucleus in one C-H bond is coupled to the spin of hydrogens of adjacent carbon.



- These $\text{H}-\text{C}-\text{C}-\text{H}$ also called vicinal coupling because hydrogens are on neighbouring carbon.
- These coupling produces spin-spin coupling pattern that follow $n+1$ rule in a synthetic simple aromatic hydrocarbon chain.
- For vicinal proton the value of coupling constant vary with dihedral angle.
- Coupling constant have maximum value when dihedral angle is 0° or 180° .
- The value of J is slightly negative.

when dihedral angle is 90° .

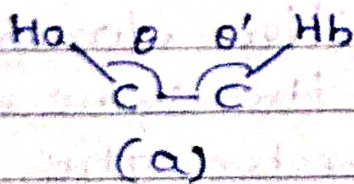
.) Factors affecting vicinal coupling -

1. Dihedral angle -

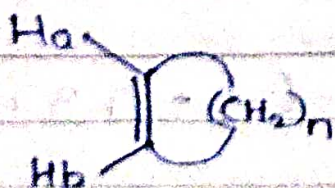
- When two adjacent C-H bond are perpendicular there is minimum overlap of orbitals so there is no spin interaction.
- The result is non-transmission of nuclear spin information & coupling constant is equal to zero.
- Where as two bonds are parallel (0°) or antiparallel (180°) the coupling constant has maximum J value.

e. Valence angle -

- The value of J decreases as a valence angle increases in case of 'a'



The effect is noticeable in olefinic proton in cyclic alkenes as the ring size changes the coupling constant changes as,



n	Jab Hz
1	0.5 - 2.0
2	2.5 - 4.0
3	5.1 - 7.0
4	8.8 - 10.5

- 3] Bond length -
- The value of coupling constant are depend on whether the coupling nuclei on adjacent carbon are joined by single or double bond.
 - Aromatic 'C-C' bonds have length between normal single & double bond length hence ortho coupling constant are nearly 8 Hz slightly lower than cis-olefinic coupling constant in cyclohexane 8.8 - 10.5

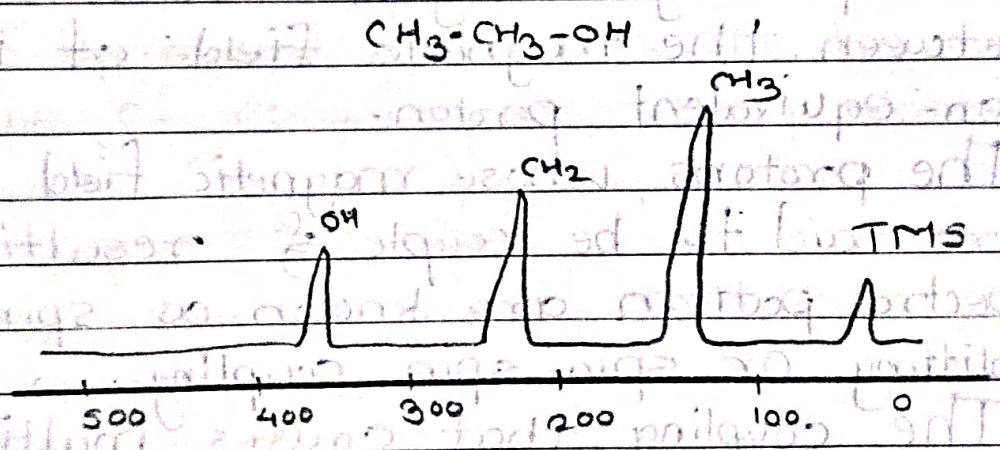
- 4] Presence of electronegative & electropositive substituents -
- When electronegative elements are directly attach to the same carbon atom as vicinally couple proton, the coupling constant is reduced.
 - Where as electropositive elements are directly attached to the same carbon atom as vicinally couple proton, the coupling constant is rises.
 - For freely rotating chains the effect is small.

e.g -



* Spin-spin coupling (splitting of signal $n+1$ rule) :-

- Imp - The PMR spectrum of many compound at low & high resolution differ largely. at low resolution the absorption peak is broad, favour in number & then correspond to different types of proton.
- But at high resolution some of all the signals may split into several narrow peak or signal corresponding to the same set of equivalent proton and show multiplicity.

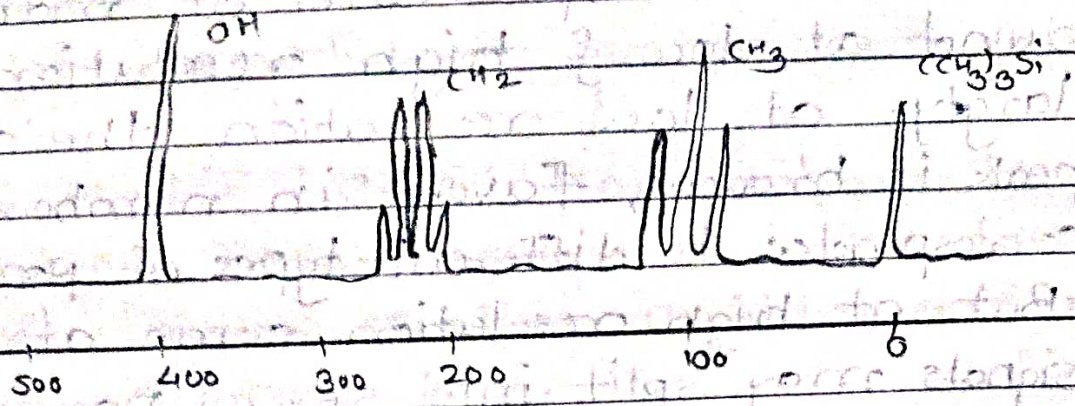


Low resolution of PMR spectrum of ethanol

- At low resolution PMR spectra of ethanol shows three signal having the relative area 3:2:1.
- They respectively represent three methyl proton, two methylene proton & one hydroxyl proton.
- Under high resolution the methyl & methylene

group signal are split, but hydroxyl proton remain unsplit.

3:2:1

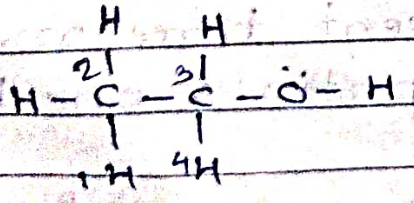


High resolution PMR spectra of Ethanol:

- The splitting of signal is caused by interaction between the magnetic field of neighbouring non-equivalent protons.
- The protons whose magnetic field interact are said to be coupled & resulting PMR spectral pattern are known as spin-spin splitting or spin-spin coupling.
- The coupling that causes multiplicity can be of three (3) types -

① Vicinal Coupling :-

When two coupled non-equivalent protons are separated by three bonds, so it is also known as 1:3 coupling.

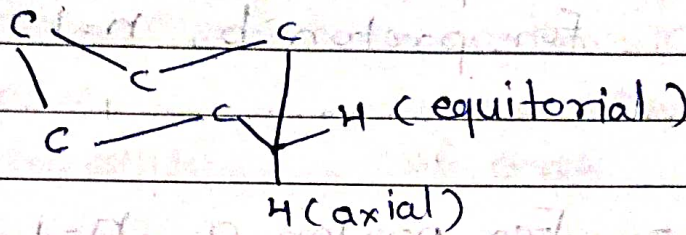


Example of methyl & methylene protons of ethanol.

(a)

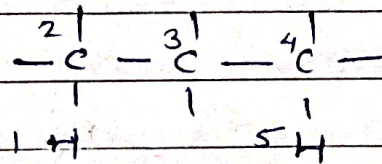
② Geminal Coupling -

- The two couple non-equivalent protons are separated by two bonds so it is also known as 1:3 coupling.
- e.g., axial & equatorial cyclohexane are coupled.



③ Long-range Coupling -

- The two couple non-equivalent protons are separated by four bonds however this type of coupling is rarely observed.

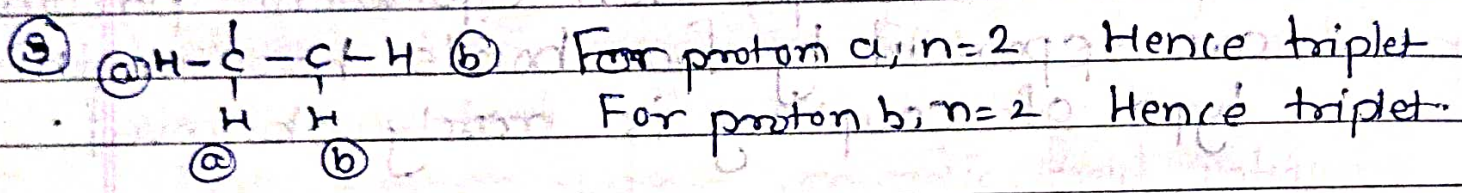
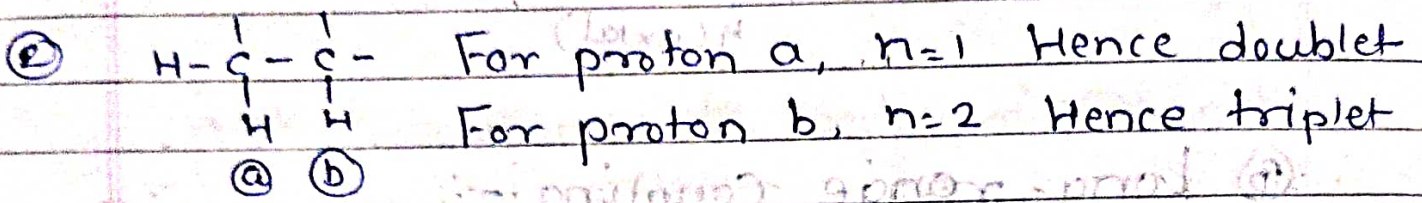
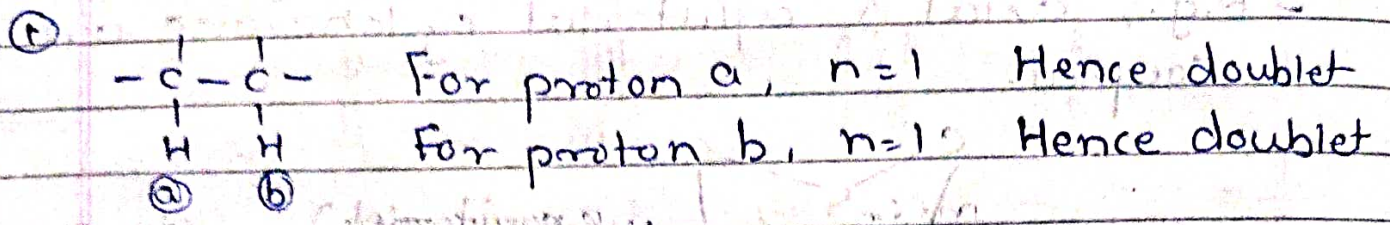


* Rule governing splitting of signals -

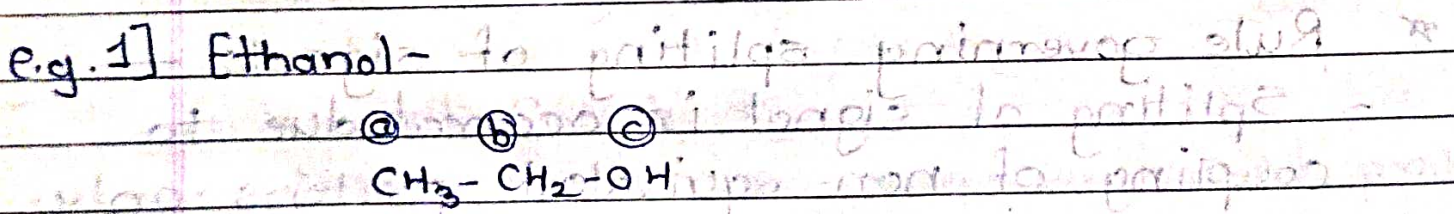
- Splitting of signal is occurred due to coupling of non-equivalent protons only.
- Means the total number of split signals (N) of peak is equal to one number more than the number of non-equivalent protons (n) on adjacent carbon this is called n+1 rule.
- That is, $N = n + 1$

When $N=2$, splitting of signal as doublet
 $N=3$, splitting of signal as triplet
 $N=4$, signal is quartet.

e.g. →



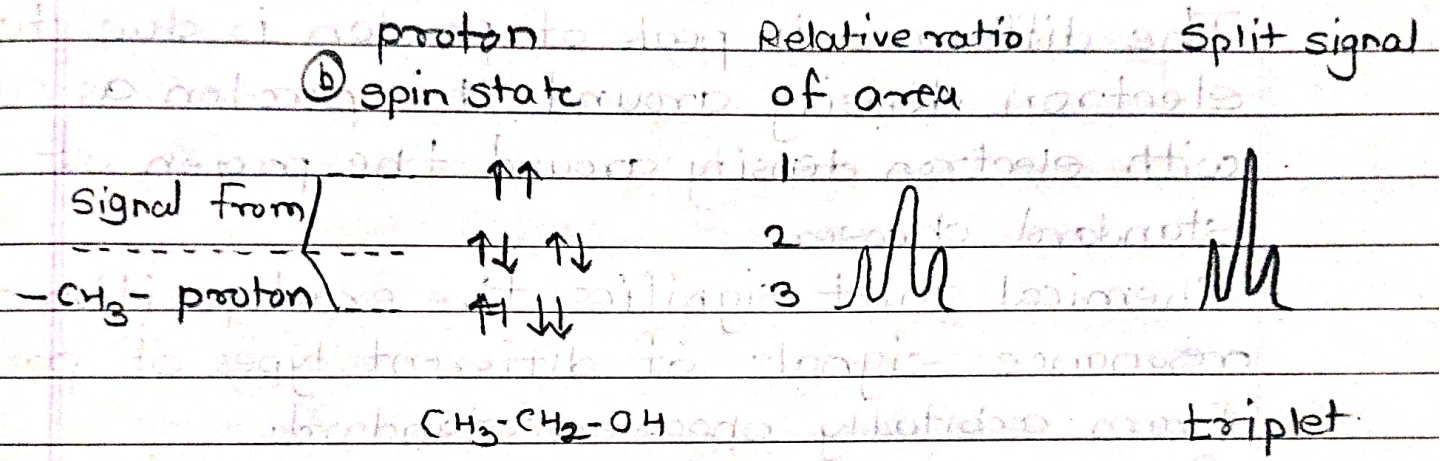
Q. Why does



- Protons \textcircled{a} & \textcircled{b} are non-equivalent & are in adjacent position so they vicinal 1:4 coupling.
- Because of this, magnetic field felt by proton \textcircled{a} increase or decrease depends on

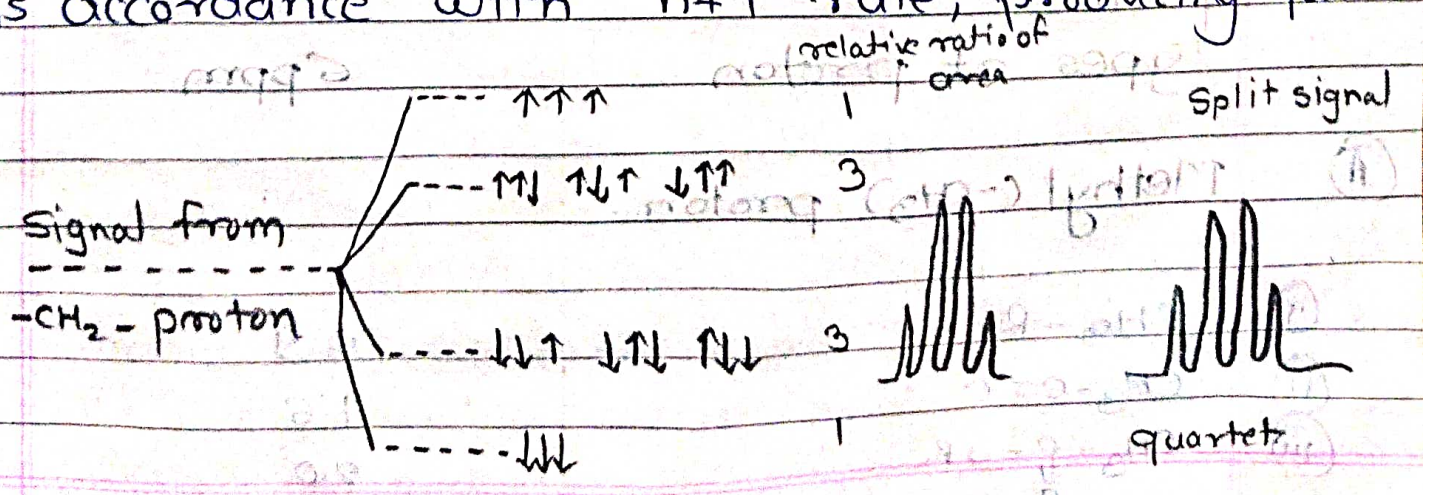
spin state of proton (b).

- Methyl signal is split into triplet with respect to proton (a), proton (b) can take up three possible orientation.
- The situation can be schematically represented as below, hence a triplet results.
- This is in accordance with $n+1$ rule.



- The two orientation in the middle are identical, so, the observed signal is two times smaller than outer signal.

- Methylene signal split into quartet. With respect to proton (b), proton (a) can take up four possible orientations. This is accordance with $n+1$ rule, producing quartet



✓ Chemically equivalent but magnetically non-equivalent.

→ ① The Chemical & magnetic equivalence plays important role in determining the number of peaks in NMR spectroscopy.

- Protons in organic compound may have different environment either by linkage or by orientation resulting in non-equivalence.

② - All nuclei which are magnetically equivalent will give sig single NMR signal. Similarly nuclei which are magnetically non-equivalent will produce different NMR signals.

③ - If two protons are magnetically equivalent they will be ^{also} chemically equivalent but as a reverse the protons are chemically equivalent then they may not always magnetically equivalent. Sometimes they may be - chemically equivalent but magnetically non-equivalent.

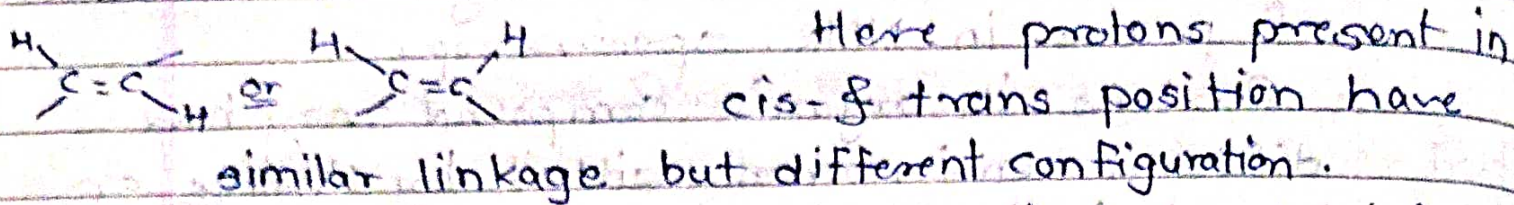
④ Chemical equivalence means similar chemical environment when nuclei are attached by similar linkage then they are called chemically equivalent.

e.g. - Methane

$\text{H}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\text{H}$ In methane, protons has spin quantum number $I = \frac{1}{2}$ & therefore can give NMR

signal. Here all protons attached to carbon in similar way & hence chemically equivalent.

Magnetic equivalent — When nuclei are attached in or arranged in similar way in space they are called as a magnetic equivalent.

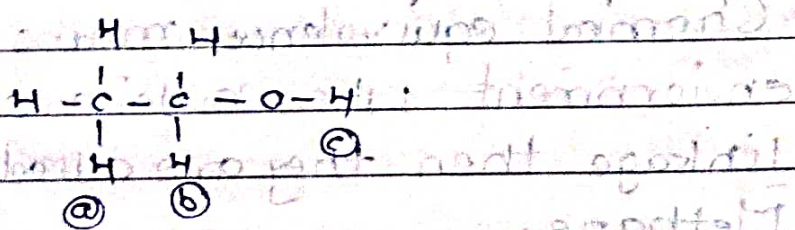
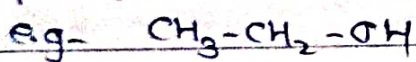


Cis-protons are same side of double bond & trans-protons are opposite side of double bond.

Hence these protons are chemically equivalent but magnetically non-equivalent.

Q. Explain the effect of purity on PMR spectrum of ethanol —

→ The pure sample of ethyl alcohol or ethanol shows three peaks this indicates three types of protons present in ethyl alcohol.

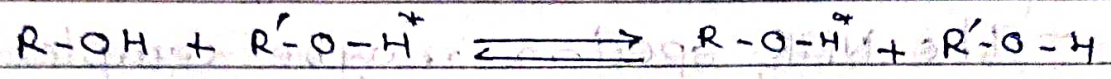


- The $-\text{CH}_3$ group shows triplet due to coupling by $-\text{CH}_2$ group & shows triplet at δ value 1.3 ppm.

- The $\text{O}-\text{H}$ also shows triplet due to coupling by $-\text{CH}_2$ group.

The most interesting peak of CH_2 which gives eight peaks. This is because the CH_2 peak is split into quartet by CH_3 group.

- Each line split into two by the -OH proton.
- There are two different types of coupling constant involves (8 Hz & 6 Hz) appear at $\delta = 3.7$ ppm.
- In case of impure ethanol the -OH coupling is not observed.
- The acidic proton of ethanol that is the hydrogen attached to the oxygen keeps on exchanging. This exchange is so rapid



$\delta \Delta t \cdot \Delta \nu = \frac{1}{2} \pi$, Here Δt is time needed to resolve accurately the multiplicity in the CH₂ & OH group brought about by their coupling & $\Delta \nu$ is their coupling constant.

The coupling constant is only observed when Δt is very long.

- In case of impure alcohol the CH₃ gives triplet due to CH₂ group & CH₂ gives quartet due to coupling with CH₃.
- While a singlet at $\delta = 5.2$ ppm due to OH group. The OH does not stay for enough time for to be splitted by CH₂ group.

Q. What are the factors that increase complexity of PMR. Give the techniques to resolve them.

→ The complete analysis of compound is frequently made difficult when signals overlap & useful information in result get burnt due to

Complexity of spectrum. In a spectrum several signals may overlap of closely related methylene groups in a molecule. In such situation methylene signals may appear between δ 1-2 ppm.

- Another cause of complexity is where a coupling constant is comparable with the chemical shift difference between coupled proton.

- The NMR spectra maybe complex with following complicating factors.

- ① Overlap
- ② Exchange
- ③ Hydrogen bonding
- ④ Solvent effect

① Overlap — The complete analysis of compound is difficult when signals are overlap in a spectrum of compound several signals may overlap of closely related methylene group in a molecule. in such situation methylene signals may appear between δ 1-2 ppm.

② Exchange — Complication in the spectrum also arises when two or more species are present & both carries same protons at which may exchange with each other if the rate of exchange is slow then the peak of each type of identical proton will be seen at

as usual position. If the rate of exchange is increases then the peaks of each types of identical proton will seen at unusual position.

⑥ Hydrogen bonding — If the structure of simple molecule have strong hydrogen bonding then the proton involve will have chemical shift much lower field.

④ Solvent Effect — The present of solvent also affect the NMR spectrum. The affect cannot be eliminated. Standard solvents include acetone, benzene usually has little effect on PMR spectrum.

* Techniques to Resolve —

2-10-23 Active hydrogen atom hydroxyl & amine groups maybe remove by shaking the solution.

— Double resonance is another important technique which assist the sorting out spectra.

— Use of shift reagent provides useful technique of spreading out ^1H -NMR absorption pattern. Which normally overlap without increasing the strength of applied magnetic field.

— High field strength chemical shift in Hz is directly proportional to the applied field but the chemical shift value is independent of field strength.

- The magnitude of coupling constant (J) is independent on the strength of applied field. But their appearance in spectrum change as magnetic field change.

- Spin decoupling :- Coupling between neighboring nuclei give coupling pattern that is splitting pattern & their analysis is useful for structure determination. However these patterns are so complex that simplification of spectra is desirable & spin decoupling provide one such technique.

- Deuterium labelling & exchange :- Deuterium molecule is used in this technique due to it's easily introduce into the molecule. The presence of deuterium in the molecule is not detected in $^1\text{H-NMR}$ spectra.

✓ Lanthanide Shift reagent :-

- The PMR spectra of some compound are more overlapping of proton signal due to virtual coupling takes place. a complete spectrum can be resolved by using shift reagent.

- The shift reagent is used because the chemical shift of several groups of protons are all very similar which show their proton resonance in the same area of the spectrum & also peak overlap so extensively that individual peak & splitting

can't be detected.

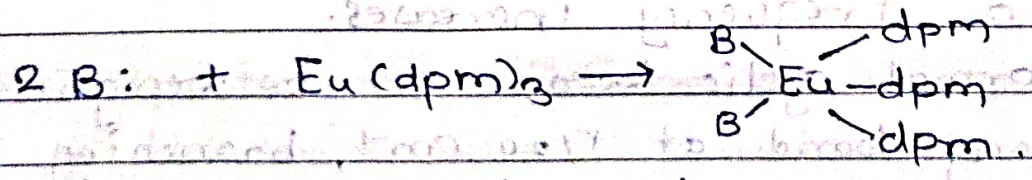
- Chemical shift reagents are organic complexes of paramagnetic rare earth metals from the lanthanide series.

- In the lanthanide series, Europium is probably a most commonly used metal.

- Two of its widely used complexes are $\text{Eu}(\text{dpm})_3$ & $\text{Eu}(\text{fod})_3$. When such a metal complex is added to the compound whose spectrum is being determined there is a profound shift in the ~~proton~~ various groups of protons. ~~the~~ direction of shift ^{up} or down field depends on which metal is used.

- Complex of Europium, ~~Er~~ Erbium, Thulium shift resonance to the lower field. While complex of Cerium generally shift resonance to the higher field.

- These lanthanide complexes interact with relatively basic pair of electron (unshared pair) which can co-ordinate with Eu^{+3} [Eu^{+3}]



Ex - The spectra of or 1-Hexanal

→ In absence of shift reagent is added to the spectrum shows only the triplet of terminal methyl group.

- The triplet of methylene group is resolved