BASIC PRINCIPLES OF NUCLEAR MAGNETIC RESONANCE (NMR) SPECTROSCOPY

NMR spectroscopy deals with those nuclei which behave as tiny magnets.

Which nuclei do behave as tiny magnets?

Those nuclei which possess mechanical spin or angular momentum would behave as tiny magnets, since such a nucleus is associated with a +ve charge, and if it spins around its axis it would generate a magnetic field whose axis is coincident with the axis of its spin. The total angular momentum depends on the nuclear spin or spin number I which may have values $0, \frac{1}{2}, 1, 3/2, 5/2, 2, \ldots$ (depending on the particular nucleus). The numerical value of the spin number I is related to the mass number and atomic No. as follows:

Type	Mass No.	Atomic No.	Spin No(I)	Examples
1.	odd	even or odd	$\frac{1}{2}, 3/2, 5/2$	i) $^1H_1, ^{13}C_6, ^{15}N_7, ^{19}F_9, ^{29}Si_{14}, ^{31}P_{15}, ^{107}Ag_{47}, ^{119}Sn_{50}, ^{199}Hg_{80}$ (all have $I = \frac{1}{2}$) (ii) $^{35}Cl_{17}, ^{37}Cl_{17}, ^{11}B_5$ $(I = 3/2)$ (iii) $^{17}O_8, ^{127}I_{53}$ $(I = 5/2)$
2.	Even	odd	$1, 2, 3, \ldots$	$^2H_1, ^{14}N_7$ (both have $I=1$) $^{10}B_5$ $(I = 3)$

Nuclei of types 1 and 2 having $I \neq 0$ come under the perview of NMR spectroscopy.

| 3. | Even | even | 0 | $^{12}C_6, ^{16}O_8$ $(I=0)$ |

[In these nuclei individual pairs of protons and neutrons have opposed spins and so the net spin of these nuclei as a whole is zero]

Nuclei of types 3 having $I = 0$ cannot be studied by NMR spectroscopy.

Thus, only nuclei having $I \neq 0$ can be studied by NMR spectroscopy.

o ^1H, natural abundance ^{13}C, ^{15}N, ^{19}F, ^{31}P (all having $I = \frac{1}{2}$) NMR quite extensively studied. ^2H and ^{14}N NMR are also studied quite frequently.

o In recent years ^{29}Si, ^{107}Ag, ^{119}Sn and ^{199}Hg NMR are being studied.

Why is it necessary for a nucleus to behave as a tiny magnet to be studied by this spectroscopy?

This is because when such a tiny nuclear magnet is placed in a uniform external magnetic field, it takes up any one of the possible orientations given by the number $\underline{2I+1}$ (where I is the spin number of the nucleus), each orientation being characterised by a definite energy level. This provides a situation where it is possible to induce nuclear transition from a lower to a higher energy orientation by the absorption of energy of appropriate frequency and corresponding to this absorption of energy one gets a signal.

Thus, for hydrogen (or any other nucleus) having $7=\frac{1}{2}$, the number of such possible orientations that the nuclear magnet can assume when placed in a uniform magnetic field $= 2 \times \frac{1}{2} + 1 = 2$. One is a lower energy and the other is a higher energy orientation as shown below:

Higher energy orientation

$\Delta E = h \nu$

Lower energy orientation

↑ Ho
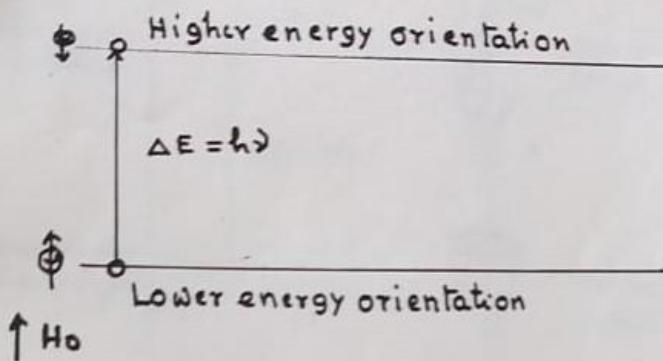
It is now possible to induce a transition of the nucleus from the lower energy state to the higher energy state by absorption of energy of appropriate frequency and corresponding to this absorption of energy ($\Delta E = h \nu$) one gets an NMR signal for the nucleus.

What is the nature of the frequency of energy that is necessary to induce such a nuclear transition and how is it related to the strength of the applied mag. field Ho?

This is given by the following relation:

$$\Delta E = h\nu = \frac{\mu \beta_N Ho}{9} \qquad \text{or} \qquad \nu = \frac{\mu \beta_N Ho}{h 9}$$

$$\text{or} \quad \nu = \frac{\mu \beta_N \times 2\pi}{h 9} \times \frac{Ho}{2\pi}$$

$$= \gamma \frac{Ho}{2\pi}$$

where γ is a constant for a particular nucleus and is called the gyromagnetic ratio of the nucleus. The value of γ is different for diff. nuclei

μ = nuclear mag. moment
β_N = constant called Bohr's magneton
Ho = strength of the applied mag. field
h = Planck's constant
9 = spin No. of the nucleus

Thus for a particular nucleus $\nu \propto Ho$

For a mag. field strength of $7.1 T$ (Ho), $\nu = 300 MHz/sec$ i.e. the frequency of energy necessary to induce such nuclear transition falls in the radiofrequency region. A radiofrequency oscillator having capacity matching with the applied mag. field may serve as the source of energy.

Represention of nuclear transition in the resonance condition

higher energy orientation

$\Delta E = h\nu$

Precessing nuclear magnet opposed to Ho

lower energy orientation

Precessing nuclear magnet aligned to Ho

Ho
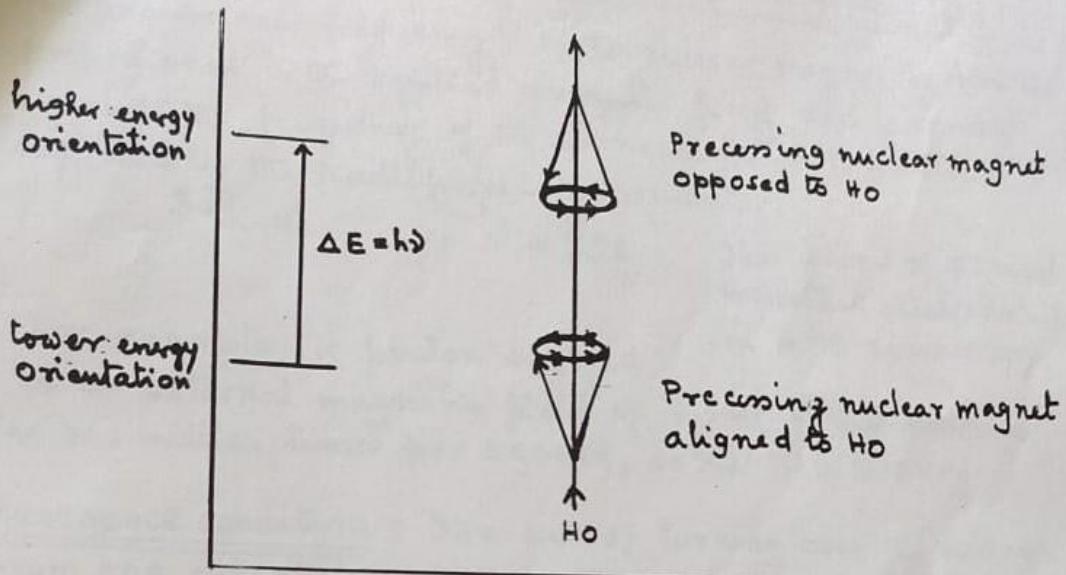
What is the necessary condition that ensures net absorption of energy by the nuclear magnet?

The necessary condition that ensures net absorption of energy by the nuclear magnet is the maintenance of small but finite excess of nuclei always at the lower energy state.

How is this maintained?

The Theory of electromagnetic radiation indicates that the probability of an upward transition by absorption of energy from the magnetic field is exactly equal to the probability of a downward transition by a process stimulated by the field. Further, the Theory shows that a spontaneous transition from a higher energy state to the lower energy state is negligible in the radiofrequency region. Thus, if two possible spin states in a collection of nuclei were populated exactly equally, the probability of an upward transition (absorption) would exactly equal to that of a downward transition (emission) and there would be no observable nuclear resonance effect.

When does a nucleus absorb energy of frequency ν in a mag. field H_0?

The nucleus aborbs energy of frequency ν in a mag. field H_0 only when the resonance condtion is achieved.

What is meant by resonance condition?

In the foregoing simplified model of nuclear transition the precessional motion of the spinning nuclear magnet has not been specified. Unless the nuclear magnet is oriented exactly parallel or antiparallel with H_0 There will be a certain force by the external field to so orient it. But because the nucleus is spinning, the effect is that its rotational axis draws out a circle $\perp$ to the applied mag. field. This motion of the nucleus is called precession. The nucleus thus has a precessional frequency. The common example of this type of gyroscopic motion is a common top which precesses when spun with an initial axis of rotation diff. from earth's gravitational field.
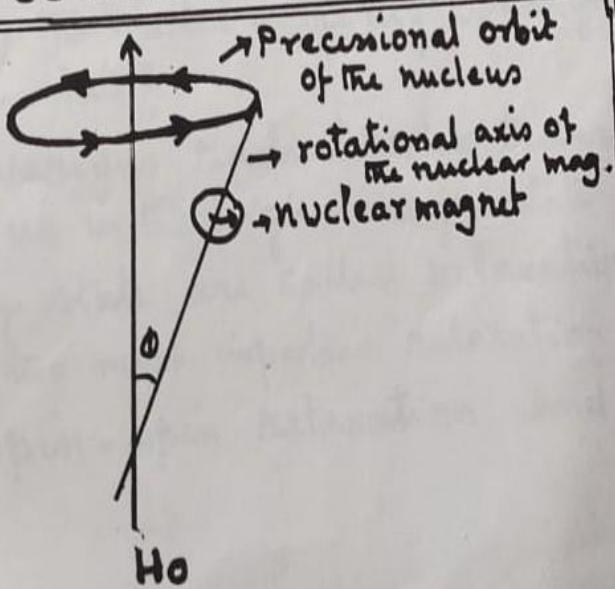
Precessional orbit of the nucleus

rotational axis of the nuclear mag.

nuclear magnet

θ

H_0

Under ordinary condition in a magnetic field, however, there is a very slight excess of nuclei in the lower energy state; they take up a Boltzmann distribution — the Boltzmann factor is about 0.001%. It is this very small but finite excess of nuclei in a lower energy state that gives rise to net absorption of energy in the radiofrequency region.

How is this maintained even after the nuclear transition from the lower energy state to the higher energy state in the light of the second postulate of the theory of electromagnetic radiation?

As the collection of nuclei continually absorbs radiofrequency radiation, the excess of nuclei originally present in the lower energy state may diminish; accordingly the intensity of the absorption signal may diminish and may, under certain circumstances, vanish entirely. Such a phenomenon is known as <u>saturation</u>; the population of nuclei in the two spin states becomes equal.
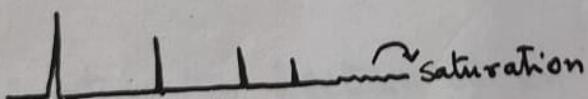
saturation

But under normal condition saturation does not take place. Therefore, there must be some processes which are responsible for the return of the nuclei from the upper state to the lower state to maintain the original excess of nuclei in the lower energy state.

Resonance frequency and chemical shift

Absolute resonance frequency is difficult to measure with an accuracy of ~ ±1cps

However, relative proton resonance frequencies can be readily determined with an accuracy of ±1cps

The separation of resonance frequencies of nuclei in different structural environments from that of an arbitrarily chosen standard is termed the **chemical shift** or relative resonance frequency

The resonance frequency of the protons of TMS (tetramethyl silane : Me_4Si) used as an internal standard is arbitrarily taken as zero, and the chemical shift of a proton of an org. compound is given by the separation of its signal from that of the TMS signal.

proton signal
of a compd.   TMS

chemical shift
$\Delta\nu$ in Hz

0
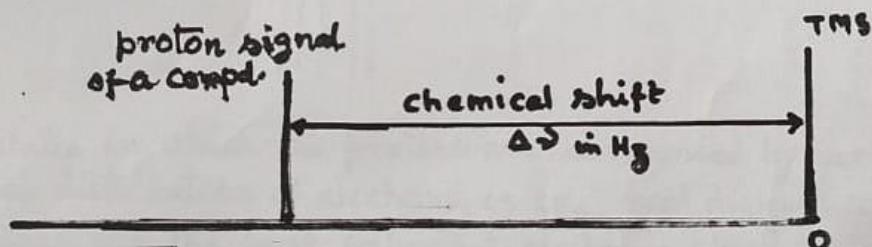
Units of chemical shift : (i) cps or Hz

(ii) δ (ppm : parts per million)

$$\delta = \frac{\Delta\nu \times 10^6}{\text{Oscillator frequency (Hz)}} = \frac{\Delta\nu \text{ in Hz}}{\text{Oscillator frequency (MHz)}}$$

(iii) $\gamma = 10 - \delta$

Chemical shift expressed in Hz is directly proportional to the strength of the applied mag. field H_0 which is again related to the oscillator frequency But when expressed in δ (or γ) it is independent of the oscillator frequency or the instrument used.

Reason for the different chemical shifts of different types of protons

The shielding that a proton experiences is a combination of at least three types of electronic circulations causing a change in the effective magnetic field (diff. from applied mag. field Ho):

(i) Circulation of the pair of electrons with which the proton is bonded to other nuclei producing a local <u>diamagnetic effect</u>

spinning nucleus

$[Heff = Ho - \sigma Ho]$

→ Induced diamagnetic field at the proton

→ circulation (diamag.) of the bonded electrons

C — H

Ho
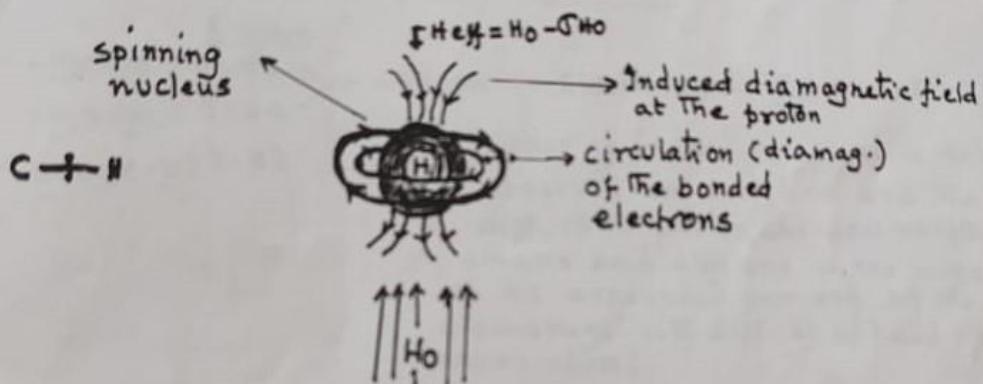
For molecules in which the protons are surrounded by very nearly spherical distribution of electrons, e.g. CH_4, local diamag. circulations of electrons are the most important electronic circulations contributing to shielding. Such local diamagnetic shielding always reduces the apparent mag. field at the proton and is a source of positive shielding. The degree of such shielding is clearly dependent on the electron density around the proton. Higher the electron density at the proton, higher the field and consequently lower the δ value at which the proton absorbs.

Thus, if local diamag. effect is the only source of shielding, it is in line with the inductive effects of the attached atoms or groups. More electronegative substituents would cause greater

correlation of shieding characteristics and electronegativity in simple saturated molecules

	δ value
CH_4 :	0.23
$CH_3 I$:	2.16
$CH_3 Br$:	2.68
$CH_3 Cl$:	3.05
$CH_3 F$:	4.26

	δ value
CH_4 :	0.23
$Ph CH_3$:	2.34
$Ph_2 CH_2$:	3.92
$Ph_3 CH$:	5.63
$Ph_2 \overset{\oplus}{CH}$:	9.70

	δ value
$-C-CH_3$:	~ 0.9
$-N-CH_3$:	~ 2.2
$-O-CH_3$:	~ 3.5

(ii) Biamagnetic and paramagnetic effects caused by electronic circulations in the neighbouring groups

	δ value
CH_3-CH_3 :	0.96
$CH_2=CH_2$:	5.84
$H-C\equiv C-H$:	2.88

→ 4.88 ppm

Electronegativity : $sp\,c > sp^2 c > sp^3 c$

Order of inductive effect is not observed in acetylene and the diff. of the proton chemical shifts of ethane and ethylene is too large to be accounted for only by the electronegativity diff. of sp^3 and sp^2 carbon atoms.
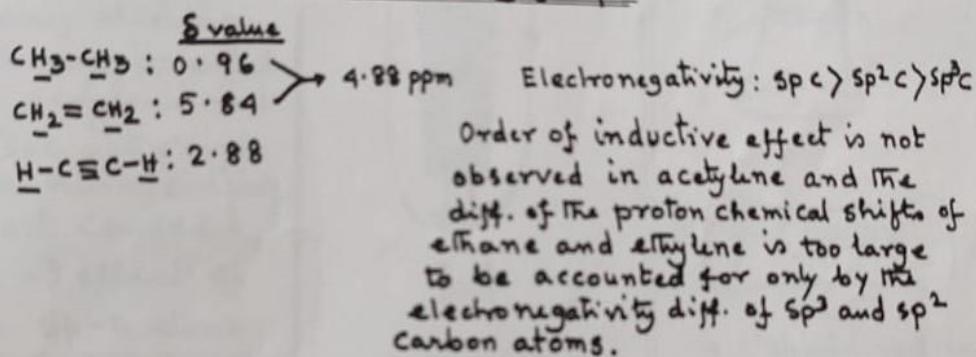
### Explanation for the upfield shift of the acetylenic protons

In linear molecule like acetylene an important contribution to the total shielding a proton experiences is the result of a paramagnetic effect causing a paramagnetic shielding which arises from electronic circulations within molecules, when it is specifically oriented with respect to the applied mag. field. Such is the case with acetylene molecule when it is oriented $\perp$ to the applied field; The induced field is paramagnetic at the carbon but diamag. at the proton.

→ induced paramag. field
$H_{eff} = H_0 + \sigma H_0$

→ resultant diamag field
$H_{eff} = H_0 - \sigma H_0$
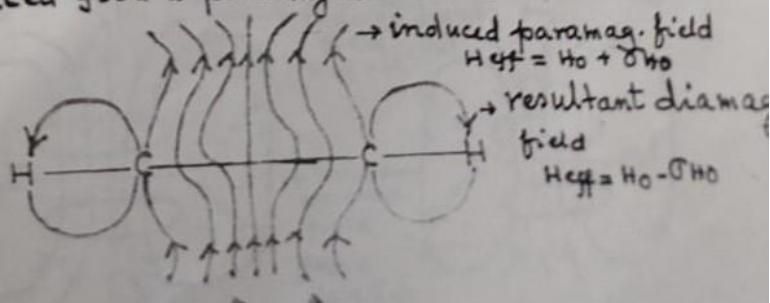
In addition to the paramagnetic effect that results in the diamagnetic shielding of the proton, There is a diamagnetic anisotropic effect, when the linear acetylene molecule is oriented parallel to The applied mag. field. Electronic circulations within the cylindrical π-electron cloud induce a diamagnetic shielding at the acetylenic proton.

> The paramag. & diamag. shielding are more important in acetylene and these outweigh the deshielding effect caused by the -$\mathcal{I}$ effect of the Sp-C atoms

Qualitative representation of the shielding and de-shielding zone of $C=x$ & $C\equiv x$

+ : shielding zone
− : Deshielding zone
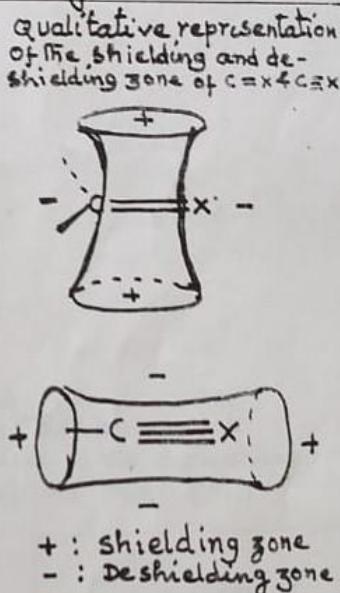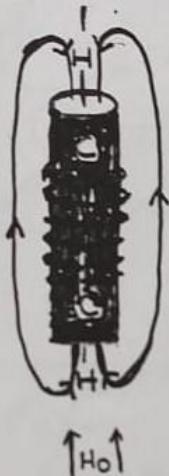
Explanation for the downfield shift of olefinic protons and in general all protons of the type $_H \! \! >\!\!C = x$ ($x = CH_2, O, $ etc)

The external mag. field causes a diamag. circulation of the π-electrons, which, in turn, produces an induced diamag. field in between The double-bonded atoms and a resultant paramag. field in the region of the olefinic and aldehydic protons causing a deshielding of these protons.

induced diamag. field
$H_{eff} = H_0 + \sigma H_0$

→ resulta paramag. field
$H_{eff} = H_0 + \sigma H_0$

> Diamag. anisotropic effect of The $c=c$ and $>\!c=0$ are The more important factors Than the -$\mathcal{I}$ effect of The $Sp^2 C$ and $c=0$
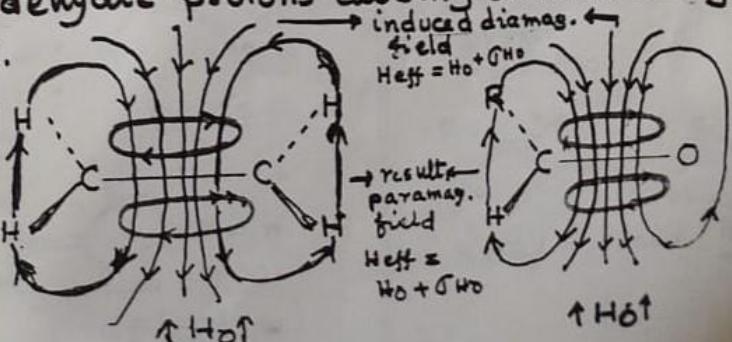
Some common examples of shielding and deshielding
by the diamagnetic anisotropic effect of $C=C$ & $C=O$

Me δ 0·99

δ 1·01

δ 1·17

Pinane

Me δ 1·63

δ 0·85

δ 1·27

α-pinene

CH_2 → δ 0·72
→ more close
to the symmetry
axis of $C=C$

δ 1·23

β-pinene

δ 9·86

δ 7·72

H δ 7·72

δ 7·40

$\Delta\delta$ 0·32 ppm

δ 7·15

δ 2·35
Me

δ 7·86

δ 3·82

δ 7·86

δ 7·15

δ 2·15
$CH_3 - C = O$
H
δ 9·68

H → more deshielded

H
β
H —
normal   α

— deshielded
(because these protons fall
more close to the deshielding
zone of the $C=O$ gr.)

more deshielded

Me
$C \equiv CH - CH_2OH$
R
phytol
R = $Me_2CH(CH_2)_3 - CH - (CH_2)_3 CH(CH_2)$

Me
EtO
H δ 6·86
Me
Me normal
γ

Me
EtO
CH_3
Y
H
δ 5·98
normal

R   H
CH₂OH
Me
↓ MnO_2

R   CH₂OH
H
Me
↓ MnO_2

δ 7·34
H
OMe
H
MeO
O
δ 7·34

trans-trans

δ 7·87
H   H
MeO
OMe
H   O
H δ 7·87

cis-cis

H   H
H
OMe
H O
MeO
→ δ 8·20

cis-trans

R   H
Me   O
Natural
phytol
δ 2·09
Phytenal
(ii) AgOH
(iii) CH_2N_2

R   O   H
H
δ 1·90   Me
Phytenal
i) AgOH
ii) CH_2N_2

R   H
Me   O
OMe
δ 2·15
Methyl phytenoate

R   O   OH
δ 1·79 Me
Methyl
phytenoate

(iii) Interatomic ring currents : Diamagnetic anisotropic effect exhibited by aromatic compounds

paramagnetic anisotropic effect by antiaromatic compounds

Determination of aromaticity & antiaromaticity

All aromatic compounds contain closed loop of π-electrons above & below the planar σ-skeleton. When they are placed in a uniform external mag. field acting $\perp$ to the plane of the aromatic ring, the π-electrons are set into motion and a ring current is generated. This, in turn, produces an induced diamagnetic field inside the aromatic ring and a resultant paramag. field outside the ring. The induced diamag. field is strongest at the centre of the ring and the resultant paramag. field is maximum in the region of the aromatic protons. Thus, all aromatic compounds exhibit diamagnetic anisotropic effect which is manifested by the low field resonance of aromatic protons (δ 6.5 - 8.5) and the high field resonance of any proton falling inside the ring.


Induced diamag. field
$H_{eff} = H_0 - \sigma H_0$
ring current

Resultant paramag. field
$H_{eff} \subset H_0 + \sigma H_0$

+ : Shielding zone
− : Deshielding zone

$\uparrow H_0 \uparrow$
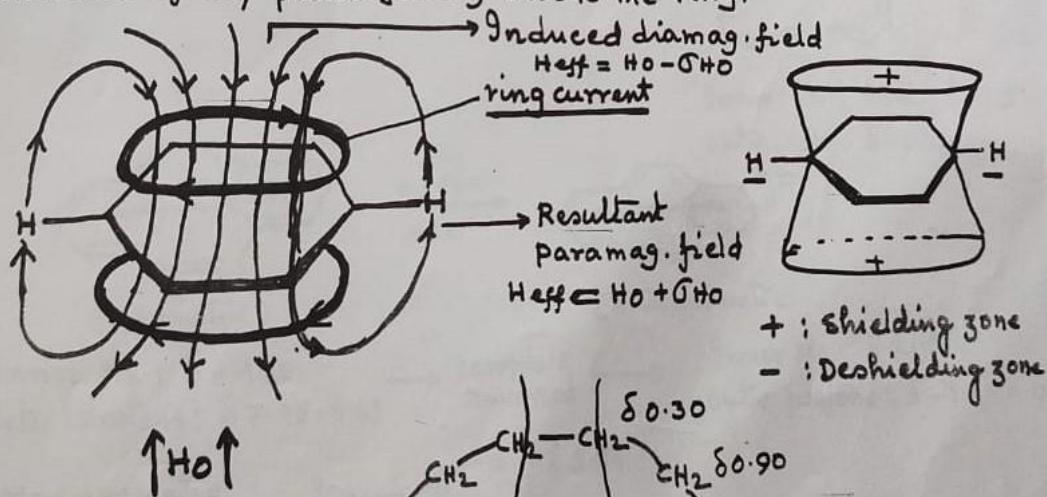
Thus ^1H NMR spectroscopy provides an elegant method for qualitative measurement of

$\delta 0.30$
$CH_2 - CH_2$
$CH_2 \, \delta 0.90$
$CH_2 \, \delta 1.30$
$CH_2 \, \delta 2.50$
$\# \sim \delta 7.2$
$\delta 3.81$

[1.8] paracyclophane
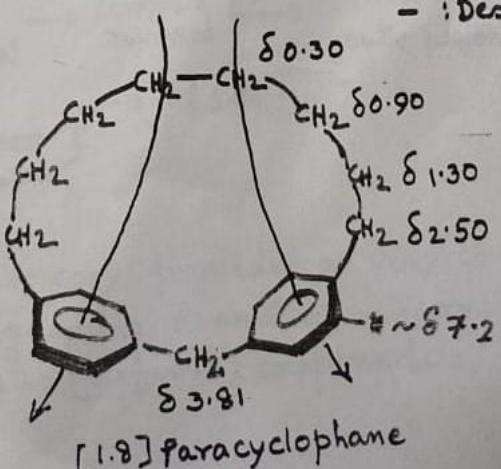
some nonbenzenoid aromatic compounds
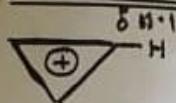
cyclopropenium cation   cyclopenta-dienide anion   Tropylium cation
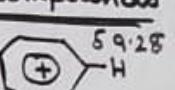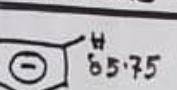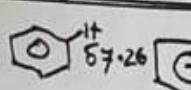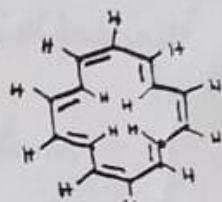
[14] annulene

Inner 4H : δ 0.0

Outer 10H : δ 7.60
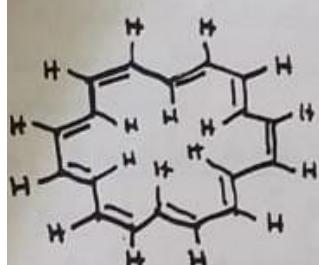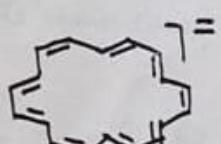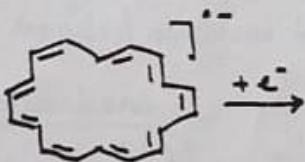
[18] annulene
(Aromatic)

Inner 6H : δ -2.0

Outer 12H : δ 8.94

$\xrightarrow{\text{K/THF, low temp. + e}^-}$ $\xrightarrow{+ e^-}$

Complete reversal of the proton chemical shifts $\longrightarrow$

Antiaromatic

$\downarrow\uparrow$

Inner 6H : δ 28.1 & 29.5
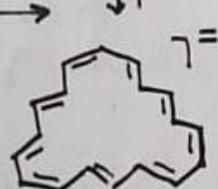
Outer 12H : δ -1.30

$\xrightarrow{\text{K/THF} \ +2e}$

(Aromatic)

Inner Me : δ -4.25
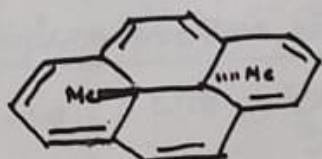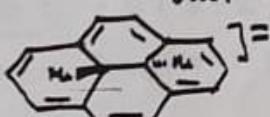
Outer protons: δ 7.95-8.67

$\longrightarrow$ complete reversal $\longrightarrow$

(Antiaromatic

Inner Me : δ 21.0

Outer protons: δ -3.2 - 4.0

Nonaromatic :   H ~ δ 5.84

Thus ^{1}H NMR spectroscopy provides a very convenient method for distinguishing aromatic, antiaromatic and non aromatic (olefinic) compounds

A GENERAL SURVEY OF THE CHEMICAL SHIFTS
## OF THE MORE COMMON TYPES OF PROTONS

The different types of protons may be divided into two broad types:

Type 1: Protons attached to carbon atoms

Type 2: Protons attached to atoms other than carbon atom.

Type 1: i) Aliphatic protons — In the absence of any other deshielding effect the aliphatic protons usually appear at the highest field. Local diamagnetic circulation of the bonded electrons is the main cause of shielding.

(a) Acyclic saturated hydrocarbons

H_3C-C- : $\sim \delta\ 0.90$ $-CH_2-$: $\sim \delta\ 1.25$ $-CH-$: $\sim \delta\ 1.50$
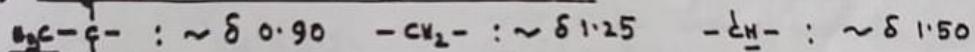
(b) Methylene protons of cycloalkanes : Chemical shifts vary with the size of the ring.

Cyclopropane : $\sim \delta\ 0.2 - 0.5$ Cyclobutane : $\sim \delta\ 1.97$

Cyclopentane : $\sim \delta\ 1.51$ Cyclohexane : $\sim \delta\ 1.43$ Cycloheptane and higher homologues : $\sim \delta\ 1.53$
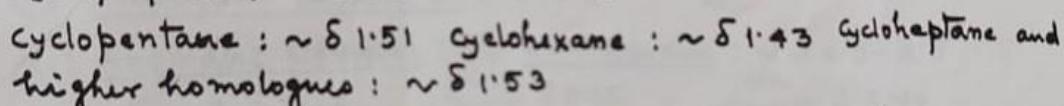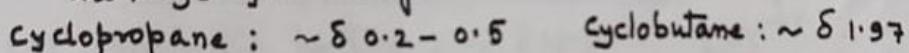
(ii) Methylene protons of an epoxide (oxirane): $\sim \delta\ 2.30$

cf. $- CH_2-O-$: $\sim \delta\ 3.60$
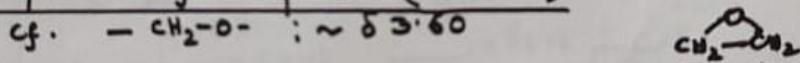
(iii) Methylene protons attached to $X=O$: $\sim \delta\ 1.9 - 2.2$

CH_3CHO : $\delta\ 2.15$ $\underset{CH_3}{\overset{CH_3}{>}}C=O$: $\delta\ 2.09$ Exception: $\sim \delta\ 2.60$

$- CH_2-C=O$ $\Big|$ slightly more deshielded $CH_3-\overset{O}{\underset{}{C}}-R$
$- CH-C=O$ ↓ $R = H$, alkyl, OH, OR', NH_2 etc.
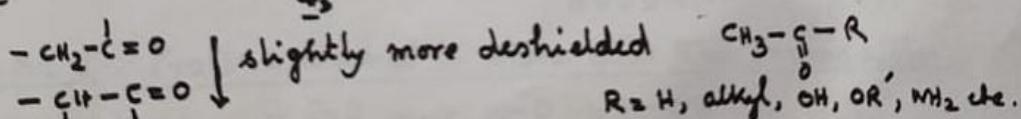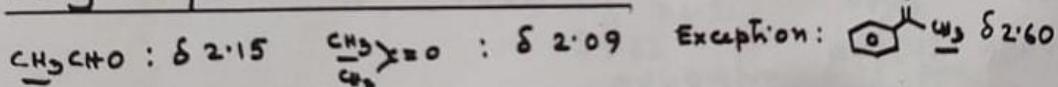
(iv) Methyls attached to $C=C$: $\delta\ 1.6 - 1.8$
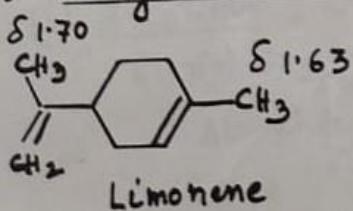
$\delta\ 1.70$ CH₃ ... $\delta\ 1.63$ —CH₃   In case of extended conjugation such methyl signals are shifted downfield to $\sim \delta\ 1.8 - 2.1$

Limonene

$H_3C-CH=CH-CH=CH-\overset{O}{\underset{}{C}}-$
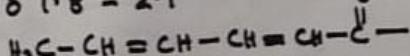
(v) Methyl attached to aromatic rings: $\sim \delta\ 2.34$

$-CH_3 \rightarrow \delta\ 2.34$
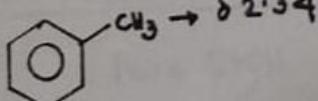
) Methyl attached to O & N

Aliphatic   aromatic

-OMe ~δ3.50   ~δ3.70 - 4.0   Methyl esters.

-N-Me ~δ2.2   ~δ3.0   ~δ3.65 - 3.75 (R-C(=O)-OMe)

(vii) CH₂ and CH attached to OH and OAc

R-CH₂-OH $\xrightarrow{Ac_2O/Py}$ R-CH₂-OAc   ΔS = 0.5 ppm
~δ3.60   ~δ4.10

R₂CH-OH $\xrightarrow{Ac_2O/Py}$ R₂CH-OAc   ΔS = 1.1 ppm
~δ3.90   ~δ5.0
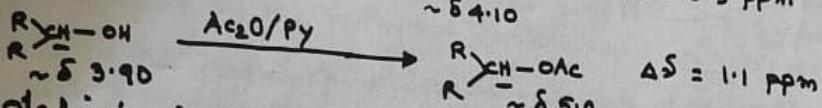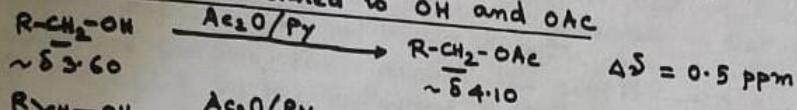
(viii) olefinic protons : ~δ 4.6 - 6.4

Me ... CH₂ δ4.63 ... H δ5.32
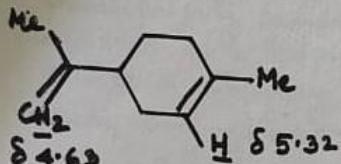
In case of extended conjugated olefins, the olefinic proton signals merge with those of aromatic protons (~δ6.5-8.9)

(ix) Acetylenic protons : ~δ 2.5 - 3.0
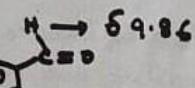
(x) Aldehydic protons : ~δ10.0   H→δ9.86 (O=CH)
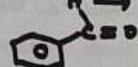
(xi) Aromatic protons : (a) Carbocyclic : ~δ 6.5-8.5

H δ7.26   H δ5.95 (MeO, OMe)   H δ9.47 (NO₂, NO₂)

(b) Hetrocyclic :

H δ7.56   H δ7.18   H δ8.56

δ6.29   δ7.12
H δ6.12   H   H
δ6.52   δ7.34   δ7.22
δ7.53   Δδ=1.05   Δδ=0.20
Δν=0.4 ppm   ppm   ppm.

Type 2 : Protons attached to atoms other than carbon atoms

X—H + D₂O → X—D + H-O-D

(X = O, N, S, etc)   ~δ 4.7
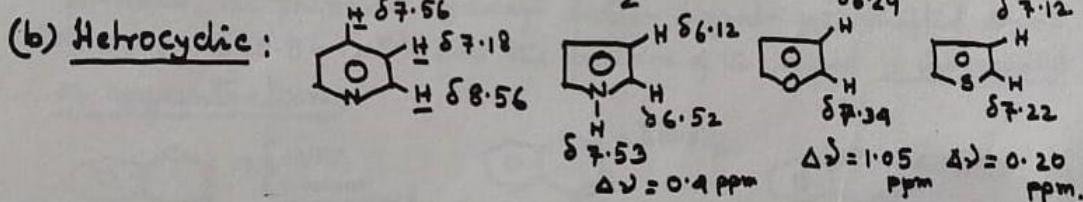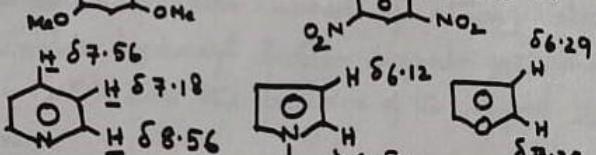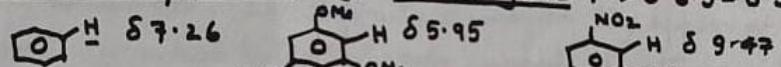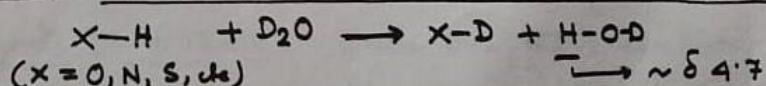
(i) Alcohols : ~δ 4.0 - 5.5 (with moderately conc. solution.

δ1.17(t) CH₃-CH₂-OH δ5.28(br.s) shifted upfield on dilution
        δ3.68,q   due to decreased intermol. H-bond.

At infinite dilution → ~δ 0.5

δ5.28 δ3.68 δ1.17 TMS
OH   CH₂   2-CH₃

CH₂   CH₃   TMS
OH
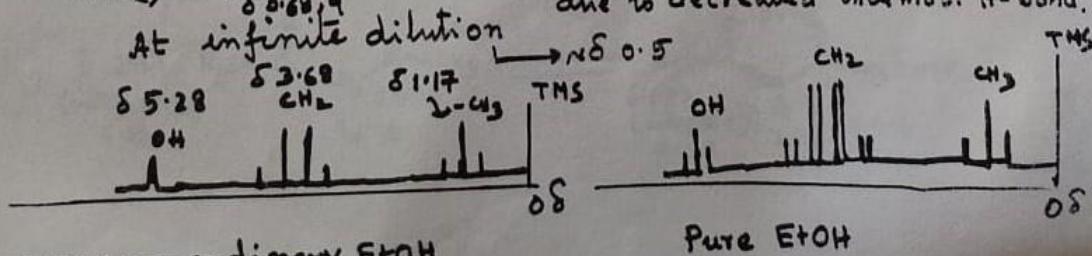
Pure EtOH

The appearance of the hydroxyl proton as a broad singlet in ordinary ethanol containing traces of acidic or basic impurities is due to <u>rapid chemical exchange</u>. Due to rapid chemical exchange a particular hydroxyl proton, within the NMR time scale, is not attached to a particular ethanol molecule, but is attached to a number of different ethanol molecules so that a hydroxyl proton experiences an average of the spin orientations of the methylene protons. As a result, the signal for the hydroxyl proton is not split by the methylene protons and <u>vice versa</u>.

But if the spectra of the alcohols are run in solvents like d_6-DMSO which is capable of forming strong H-bonding with the hydroxyl protons, the chemical exchange is retarded and the expected multiplicity results. Thus in d_6-DMSO, a primary hydroxyl proton appears as a triplet, a secondary hydroxyl proton gives a doublet, while a tertiary hydroxyl proton appears as a singlet.

$$R-CH_2-O-H\cdots O=S\diagdown^{Me}_{Me}.$$
triplet

$$R\diagdown_{R'}{}^{}CH-O-H\cdots O=S\diagdown^{Me}_{Me}$$
doublet

$$R\diagdown_{R'}{}^{R''}C-O-H\cdots O=S\diagdown^{Me}_{Me}$$
singlet
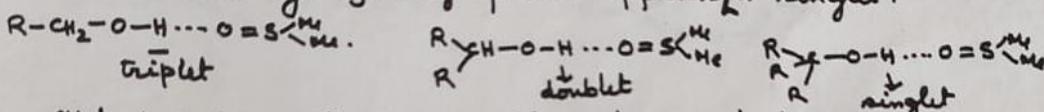
This technique offers a rapid and convenient method for distinguishing between primary, secondary and tertiary alcohols.

(ii) <u>Phenols</u>: ~δ 6.0-7.7 (in moderate concn.; shifted upfield on dilution; at infinite dilution they appear at ~δ 4-5.

In some <u>o</u>-substituted phenols capable of strong intramolecular H-bond, the phenolic hydroxyl proton signals are shifted down-field (~δ 10.5 - 12.5) and the position of the signal is <u>independent of concentration</u>.

Me δ 2.46   → δ 12.05. (remains unchanged on dilution)

→ δ 10.58   OMe

→ δ 10.95
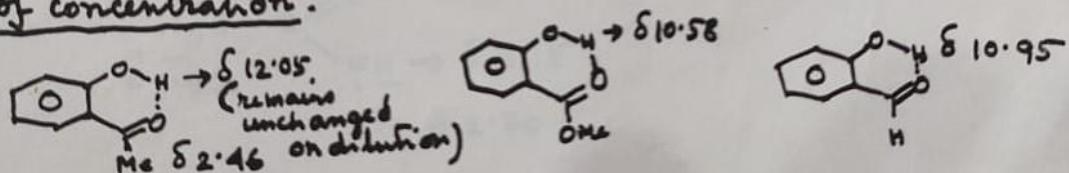
i) <u>Enols</u>: ~δ 15-16. Enols owe their existence to strong intramolecular H-bonding. The enolic hydrogen appears at a very downfield position and the position of the signal remains unchanged on change of concentration.

δ 2.14 $H_3C-\overset{O}{\overset{\|}{C}}-CH_2$ δ 3·37 δ 2·14 $-CH_3$
0·16   16%

→ δ 14.92
H_3C- δ 1·97 (integral = 9)
δ 1·97 $-CH_3$ δ 1·97 δ 5·5   84%
0·94

Electron-coupled spin-spin interaction

CH_3COCH_3 :

CH_3CHO :

$ClCH_2CHO$: -CHO

Cl_2CHCHO -CHO

Cl_3CCHO -CHO
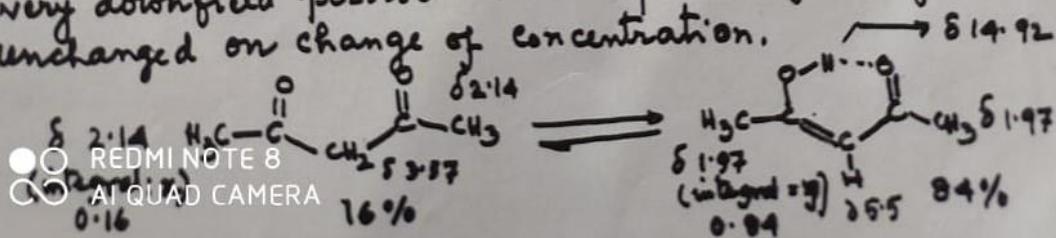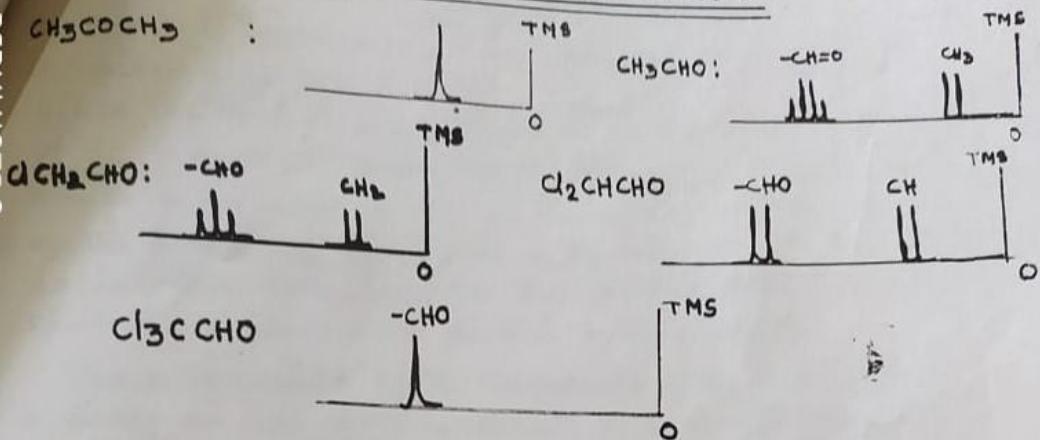
Explanation for the multiplicity of the signal of a proton or protons by an adjacent nonequivalent proton or a group of protons

i) **Multiplicity of the signal of proton(s) by an adjacent non-equivalent proton :**

The local mag. fields created by the instantaneous spin arrangements of H_A ...... results in the split signal of H_X

unperturbed signal signal of H_X in absence of H_A

$\downarrow \quad H = H_0 - H'$ ----------

$\uparrow \quad H = H_0 + H'$ --------- → intensity ratio 1:1

splitting of the H_X signal arising from electron-coupled spin-spin interaction with H_A

Let us consider the splitting of the H_X signal by H_A. The spin states of H_A may be either parallel (↑) or antiparallel (↓) with the external magnetic field. Accordingly, there will be two local fields $H = H_0 + H'$ and $H = H_0 - H'$. The magnetic effects of the two spin arrangements of H_A is transmitted through the bonded electrons to H_X. Thus proton H_A can either increase the net mag. field of H_X (when the spin of H_A is aligned) or decrease it (when the spin of H_A is opposed).

in fact, it does both. Thus the two spin orientations of H_A create two different magnetic fields around H_X. Therefore H_X comes to resonance, not once, but twice, and so H_X gives rise to a doublet.

Since the probability of (each of the two spin arrangements existence of of H_A) is equal, it follows that the intensities of the two transitions will be in the ratio of 1:1 i.e. the intensities of the components of the doublet of H_X will be in the ratio of 1:1. The same explanation holds true for the splitting of the H_A signal which also appears as a doublet in the ratio of 1:1.

The separation of the components of the doublet of H_X is same as that of the components of the doublet of H_A. This separation or spacings is called coupling constant or J.

ii) Multiplicity of the signal of a proton or protons by two adjacent protons :

The local fields created by the instantaneous spin arrangements of the H_A protons - - - - - results in the split signal of H_X

unperturbed signal of H_X in absence of H_A

splitting of the H_X signal arising from electron-coupled spin-spin interaction with H_A

$\downarrow\downarrow$ $\quad H = H_0 + 2H'$ - - - - - - - -

$\downarrow\uparrow$ $\quad H = H_0 - H' + H' = H_0$ ⎫ equiv.

$\uparrow\downarrow$ $\quad H = H_0 + H' - H' = H_0$ ⎭

$\uparrow\uparrow$ $\quad H = H_0 + 2H'$ - - - - - →

Intensity ratio. 1:2:1

$\uparrow\uparrow$ $\uparrow\downarrow$ $\downarrow\downarrow$

$\downarrow\uparrow$

spin arrangements of two H_A

$\uparrow H_0$ $\quad H_A \overset{C}{\diagdown} H_A$ $\qquad\qquad\qquad \overset{C-}{H_X}$
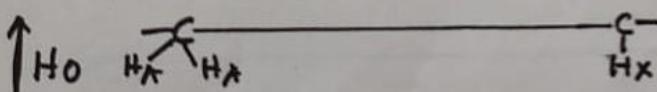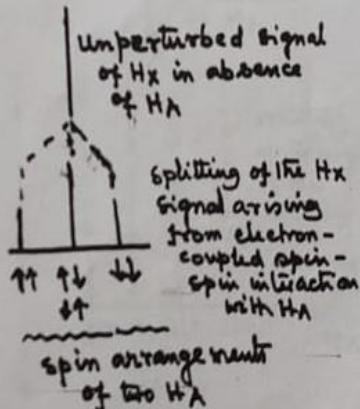
The resonance position of H_X depends on its total magnetic environment, part of which is due to the nearby H_A protons which are themselves magnetic. In the external mag. field, there can be four possible instantaneous spin orientations of the two H_A protons w.r.t the external field : (i) both parallel, (ii) one parallel, one antiparallel, (iii) one antiparallel and one parallel, and (iv) both antiparallel. The spin arrangements (ii) and (iii) are equivalent ...... same local mag. fields. Thus the two H_A protons

would produce three different magnetic fields, the effect of which are transmitted through the bond electrons to H_x. Thus the spin orientations of the two H_A protons would create three different magnetic fields around H_x. As a result H_x comes to resonance, not once, but thrice to give a triplet. Since the probability of the existence of each of the spin arrangement of the H_A protons is equal and taking into account that (ii) and (iii) are equivalent, it follows that the intensities of the three transitions will be $1:2:1$.

iii) **Multiplicity of the signal of a proton or a group of protons by three adjacent protons**

The local fields created   results | unperturbed
by the instantaneous spin   in the | signal of H_x
arrangements of the H_A protons ...   split signal   in absence
                                   of H_x of H_A

(viii) $\downarrow\downarrow\downarrow$ $H = H_0 - 3H'$

(vii) $\uparrow\downarrow\downarrow$ $H = H_0 + H' - 2H' = H_0 - H'$

(vi) $\downarrow\uparrow\downarrow$ $H = H_0 - H' + H' - H' = H_0 - H'$

(v) $\downarrow\downarrow\uparrow$ $H = H_0 - 2H' + H' = H_0 - H'$

(iv) $\uparrow\uparrow\downarrow$ $H = H_0 + 2H' - H' = H_0 + H'$

(iii) $\uparrow\downarrow\uparrow$ $H = H_0 + H' - H' + H' = H_0 + H'$

(ii) $\downarrow\uparrow\uparrow$ $H = H_0 - H' + 2H' = H_0 + H'$

(i) $\uparrow\uparrow\uparrow$ $H = H_0 + 3H'$

splitting of the sig. of H_x arising from spin-spin coupling with H_A

$\uparrow\uparrow\uparrow$ $\uparrow\uparrow\downarrow$ $\downarrow\uparrow\uparrow$ $\downarrow\downarrow\uparrow$
$\uparrow\downarrow\uparrow$ $\downarrow\uparrow\downarrow$
$\downarrow\uparrow\uparrow$ $\uparrow\downarrow\downarrow$

spin arrangements of the H_A protons

H_A —————————————— H_x

$\uparrow$ H_x H_A
H_0
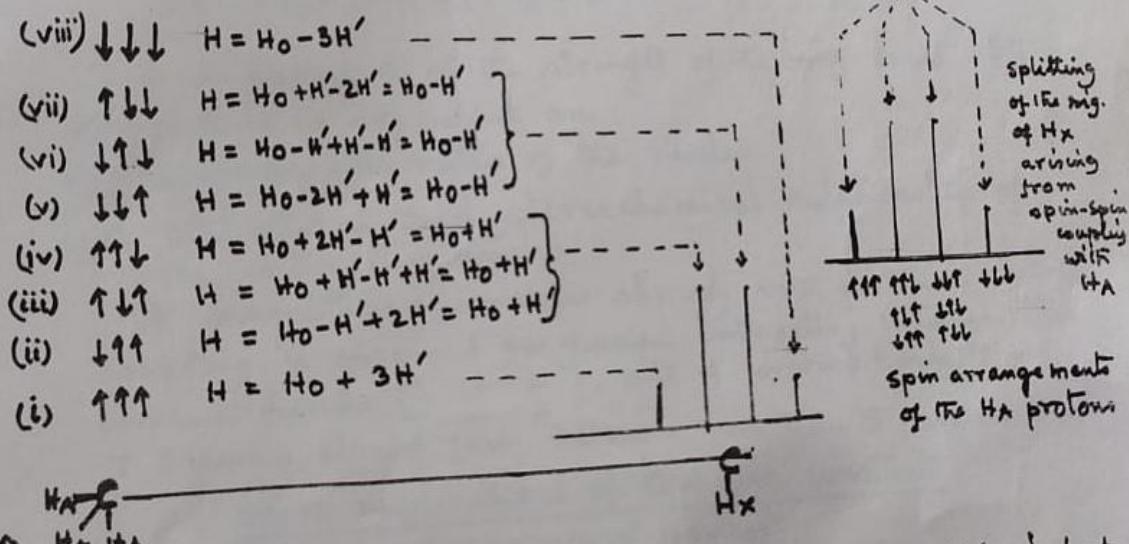
In the external mag. field there can be eight possible instantaneous spin arrangements of the three H_A protons (i – viii) and the local mag. fields created these spin orientations are shown above. The spin arrangements (ii) & (iv) are equivalent and produce the same local mag. fields. So also are the spin arrangements v – vii, each producing the same local mag. fields. Thus there are four different local mag. fields created by the eight spin arrangements of the three H_A protons. These local mag. fields are transm

Coupling Constant (J)

In cases where the chemical shift between two groups of nuclei involved in electron coupled spin-spin. interactions is large compared with the multiplet spacings, the separations of the adjacent components in a multiplet will be equal to each other and to the separation of the components in the multiplet arising from the second group involved in the mutual splitting. This separation which is a direct measure of the effectiveness of the electron-coupled spin-spin interaction is known as coupling constant (J)
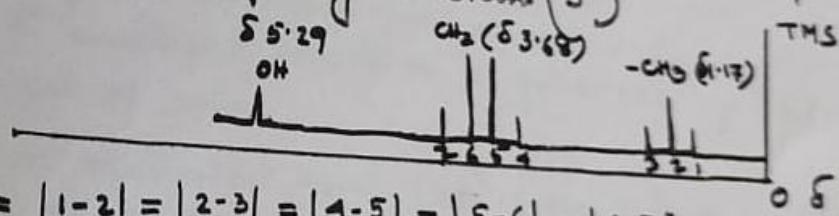
$$J = |1-2| = |2-3| = |4-5| = |5-6| = |6-7| = 7.1 \, Hz$$

J is independent of the strength of the mag. field. Its magnitude is dependent on :

(i) Gyromagnetic ratio of the nuclei

(ii) Structural and stereochemical relationship of the interacting nuclei

Its magnitude decreases sharply with distance. Maximum coupling is observed for nuclei interacting through three covalent bonds [$\overset{|}{\underset{H}{C}} - \overset{|}{\underset{H}{C}}$]. With 4 covalent bonds, J is ~1Hz. J becomes almost zero between more than 5 covalent bonds.