

NMR Spectroscopy:

NMR spectroscopy is abbreviated as Nuclear magnetic resonance spectroscopy and also known as PMR - proton magnetic resonance.

" Nuclear magnetic resonance spectroscopy is the study of molecules by recording the interaction of radio frequency (RF) electro magnetic radiations (2KHz - 300MHz) with the nuclei of molecules placed in a strong magnetic field.

principle of NMR:

✓ we know that electrons have spin. In a similar manner the nuclei of atoms also have spin. Because the nuclei spin, they have spin angular momentum, given by

$$\sqrt{I(I+1)} \frac{h}{2\pi} 2\pi$$

where "I" is the spin quantum number of the nucleus. It may have value of $0, \frac{1}{2}, 1, \frac{3}{2}, 2, \dots$ depending on the particular nucleus. The numerical

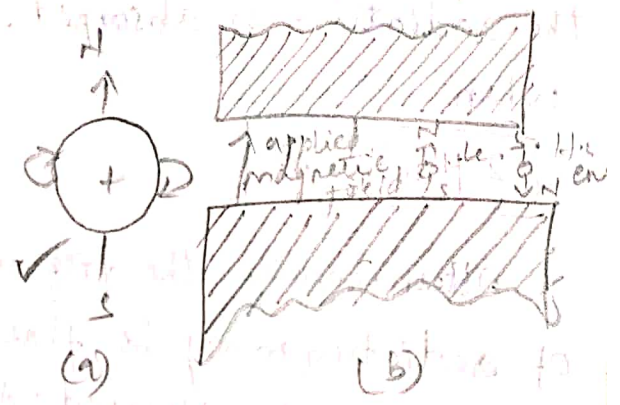
Value of the nuclear spin quantum number I is related to the mass number of and the atomic number as given in table.

mass number	Atomic number	spin Quantum	Example
odd	even or odd	$\frac{1}{2}, \frac{3}{2}, \frac{5}{2}$	$^1H, ^{13}C, ^{19}F, ^{31}P$ etc
Even	Even	0	$^{12}C, ^{16}O, ^{32}S$ etc
Even	odd	1, 2, 3	^{14}N etc

✓ The nuclei with $I=0$ are non-magnetic. Hence $^{12}C, ^{16}O$ etc. cannot be observed by NMR spectroscopy. 1H Nucleus has $I = \frac{1}{2}$ and hence can be studied.

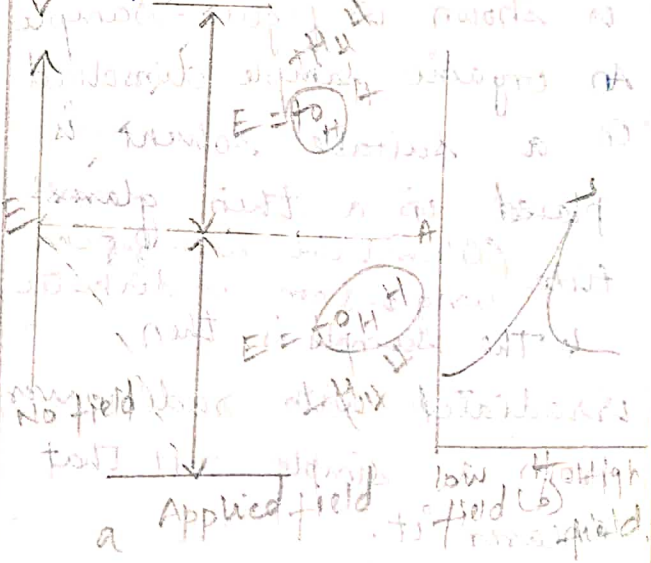
Most of these Nuclear magnetic Resonance studies have been done with the hydrogen nucleus for which I is equal to $\frac{1}{2}$. If a proton is placed in an external magnetic field its magnetic moment can be aligned against the external field. This

alignment is low stable



If H is the external field strength the magnetic moment of the protons is μ_H . Then the energy of the protons is given by $\mu_H H$. The energy required to proton (flip) a proton from the lower stable level to the higher unstable level given by $2\mu_H H$.

$E =$ Energy $M =$ magnetic field strength
 $A =$ Absorption of radiation $S =$ Signal.



NMR Spectrum
 Now if a fixed magnetic field is applied on the sample and the frequency:

of the radiation is varied the radiation is absorbed. when

$$2\pi H = h\nu$$

Alternatively the frequency of radiation may be fixed and H may be varied. At some value of the field strength, the energy required to flip the proton matches the energy of the radiation absorption occurs and signal is observed. Such a spectrum is called NMR spectrum.

NMR Spectrometer:

Instrumentation:

* A simplified schematic diagram of NMR Spectrometer is shown in figure. Sample An organic sample dissolved in a suitable solvent is placed in a thin glass tube (Glass tube with 0.5 cm length, 3 mm in diameter). * The sample is then irradiated with radiowaves from a simple coil that encases it.

* The radio frequency is held constant at say, 60 MHz

Magnet: Homogenous magnetic field at 60-100 MHz

Radio frequency generator:

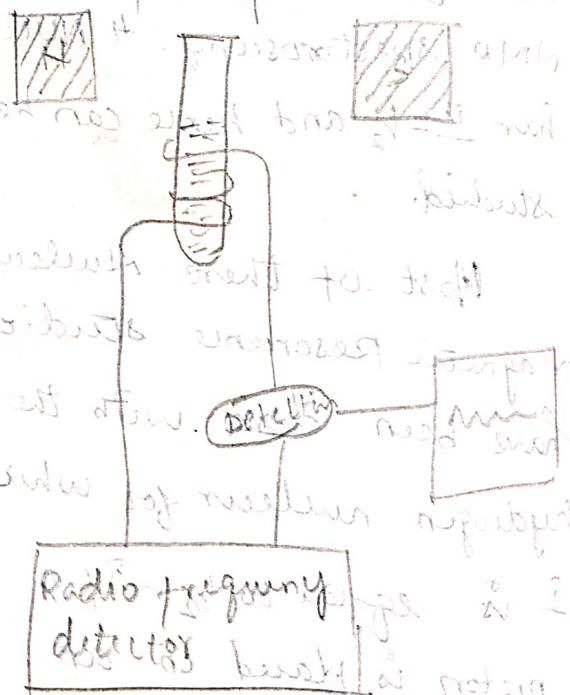
At certain values of the magnetic field absorption of RF energy occurs. (4-100 MHz)

Detectors:

Sensitive detector monitors the absorption of energy which is recorded peak on the graph.

Recorder:

The spectra can be plotted at low resonance A-modern NMR Spectrometer also records automatically the areas under each peak.



NMR Spectra are displayed in charts which show the magnetic field strength against energy absorption.

In order to define the exact position of the absorptions due to the protons in the given - organic compound.

tetramethyl silane (TMS) $\text{Si}(\text{CH}_3)_4$ is used as the standard. A small amount of it is mixed with the sample and the spectrum recorded. TMS contains 12 equivalent protons and shows a single absorption peak at field strength say B . Any other proton in the sample will show a single absorption at a

different field strength B' . The relative change of field strength $\frac{B' - B}{B}$ is characteristic of the proton concerned and is expressed as parts per million (ppm).

This is known as the chemical shift (δ) for this particular proton.

$$\delta = \frac{B' - B}{B} \times 10^6$$

NMR charts are calibrated in delta units

which reads the absorption position directly, the value for δ TMS being zero. Chemical shifts are also expressed in tau (τ) units with

$$\tau = 10 - \delta$$

Chemical shift:

(The difference b/w the magnitudes of the magnetic field at which free nuclei and molecular nuclei resonance is called chemical shift.)

(For measuring chemical shift it is not possible to use a free nucleus as a reference.) Instead chemists use those compounds which give a signal of sharp resonance line as a reference for chemical shift as follows

(The separation in the position of the spectral signal of hydrogen atoms in different chemical environment from a standard is known as the chemical shift δ . Chemical shift is defined as

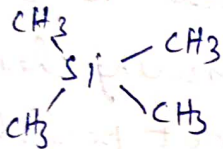
$$\delta = \frac{H_{\text{sample}} - H_{\text{reference}}}{H_{\text{reference}}} \times 10^6$$

The reference chosen is usually tetramethylsilane (TMS) $(\text{CH}_3)_4\text{Si}$, 10^6 is introduced because the absorption takes place at fields that differ by the order milligauss. Chemical shift is also represented by τ (tau) where

$$\tau = 10 - \delta$$

Importance of TMS:

* It has 12 equivalent protons since all the protons.



are having the same environments. This gives a single intense peak in its NMR spectrum.

* It has a lower boiling point (27°C) so it can be easily recovered after the spectrum is recorded.

* It is chemically inert so it will not react with substance under study.

* The methyl groups in TMS are highly shielded by their electrons from the external magnetic field. So TMS shows NMR signals at a very high magnetic

field strength compared to other protons.

Significance:

Chemical shifts indicate the type of environment that a particular proton has. The following table gives the chemical shift for hydrogen in different environments.

Type of hydrogen	δ (ppm)
<u>methyl hydrogen</u>	
$(\text{CH}_3)_4\text{Si}$	0.00
$\text{CH}_3\text{CH}_2\text{CH}_3$	0.80
$\text{CH}_3\text{CH}_2\text{Cl}$	1.40
CH_3Cl	3.05
<u>methylene hydrogen</u>	
Cyclopropane	0.30
$\text{CH}_2\text{CH}_2\text{CH}_3$	1.25
Cyclohexane	1.50
$\text{CH}_2\text{CH}_2\text{OH}$	3.60

Aromatic proton:

in benzene	7.27
in toluene	7.10
in naphthalene	7.23

Thus we find that different protons in different environments exhibit different chemical shifts so we get different NMR signals. Thus chemical

shift help us in interpreting the NMR spectra.

Thus the positions of the NMR signals by us what kind of proton they are viz a primary, secondary, tertiary benzylic, vinylic acetylenic adjacent to halogen ortho these atoms or groups and to on.

Factor affecting chemical shift

Chemical shift is affected by environment we have seen. that chemical shift is direct consequence of magnetic shielding. Also we have seen that shielding arises from the circulation of electrons induced by the applied magnetic field opposes the external magnetic field then it is known as diamagnetic shielding. As a result of the effective magnetic field experienced by the proton is less than the applied field this effect is known as local diamagnetic shielding. Its magnitude depends on the electron density in the

vicinity on the proton. The electron density of C-H bond depends on the nature of the group attached to the carbon. If an electronegative atom or an electron withdrawing group is attached to the carbon, which is having a proton, occurrence to the density of the electron cloud around the proton decreases, such a proton is said to be deshielded. so it feels a greater effect of the applied field. This produces greater downward chemical shift i.e.

large δ values.

Eg.

Compound	δ
CH ₄	0.40
CH ₃ I	2.16
CH ₃ Br	2.68
CH ₃ Cl	3.05
CH ₃ F	4.26

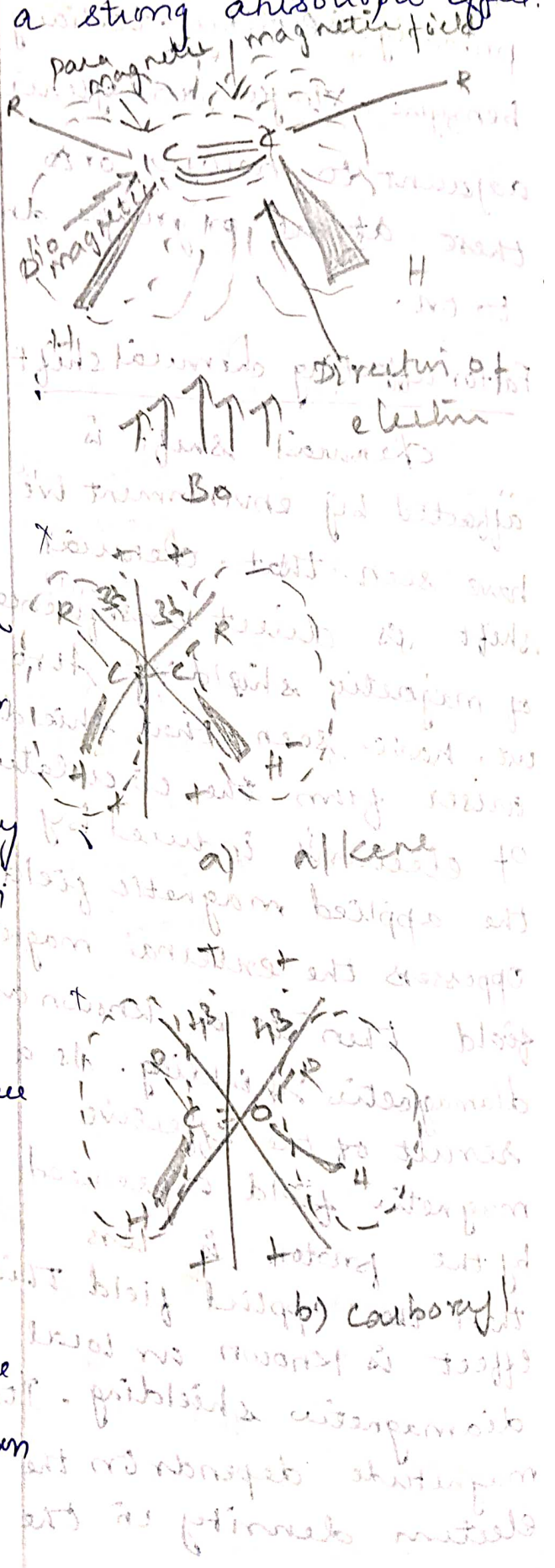
Similarly successive substitution of electronegative group increases δ value sharply.

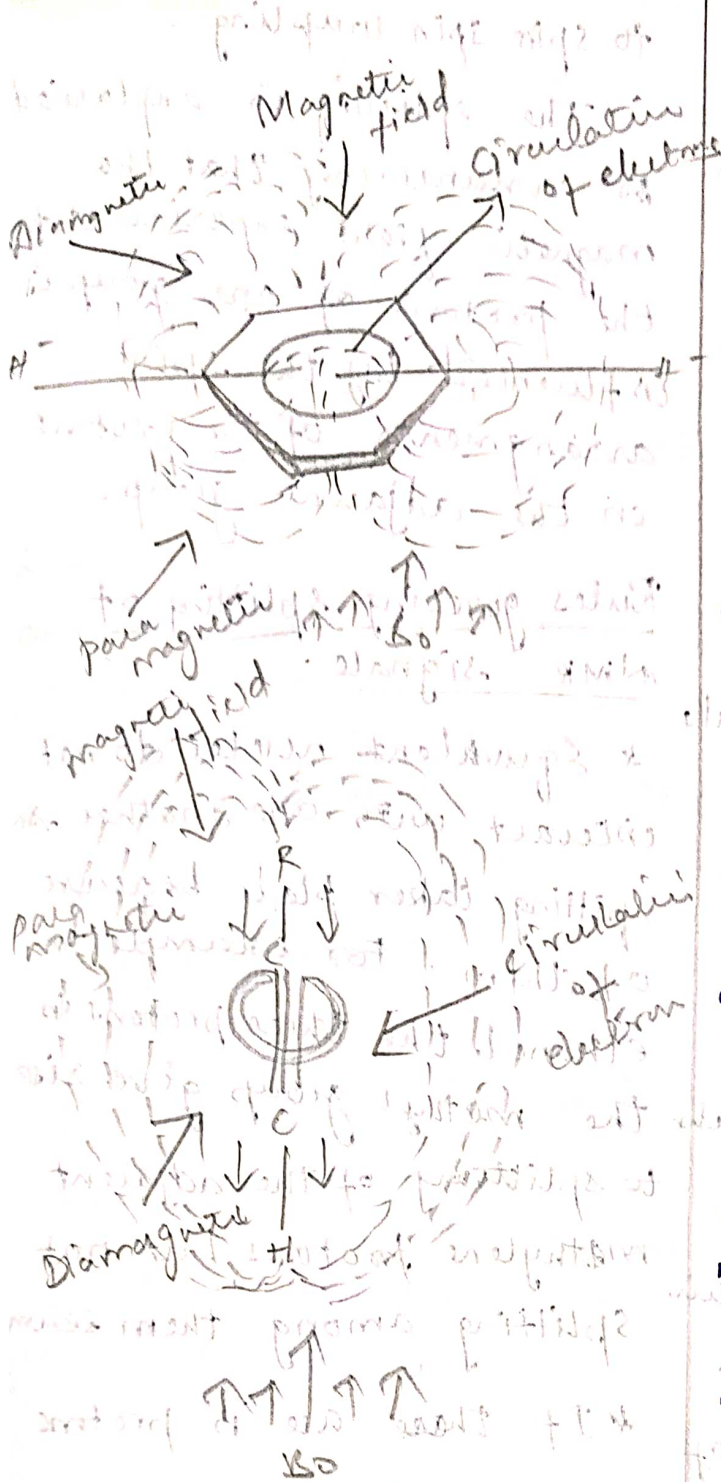
Compound	δ
CH ₂ Cl \rightarrow chloroform	3.05
CHCl ₂	5.30
CCl ₃	7.30

There is another type of diamagnetic shielding. It is called anisotropic diamagnetic shielding. This type of shielding we come across in the case of protons in the vicinity of a π -electron cloud. Eg: alkanes, alkenes, aromatic rings, aldehydes etc. protons having such an environment may be shielding or deshielded depending upon their location with respect to the magnetic lines of force of the secondary magnetic field generated by the circulation of π -electrons. The induced circulation of π -electrons and the resultant secondary magnetic field depends upon the orientation of the molecule with respect to the external field. Figure shows shielding (+) and deshielding zones in the neighbourhood of single, double and triple bonds.

In $C=C$ and $C=O$ bonds the deshielding

zone extends along the bond direction. Even $C-C$ bonds show some deshielding in this direction. Aromatic rings exhibit such a strong anisotropic effect.





from the relative position we can get the details, information about the molecular structure & its Number of signals:

In a given molecule proton with same environment absorb at the applied field strength. A set of protons with the same environment are said to be equivalent protons with different environments above at different applied field strength. The number of signal in an NMR spectrum tells us how many sets of equivalent protons are there in a molecule.

Ex: $\text{CH}_3\text{-CH}_3$ ethane
 a b
 1-NMR signal.

$\text{CH}_3\text{-CH}_2\text{-Cl}$ - Ethyl chloride
 a b
 2-NMR signal

$\text{CH}_3\text{-CHCl-CH}_3$ - Isopropyl Chloride
 a b c
 2-NMR signals.

$\text{CH}_3\text{CH}_2\text{-CH}_2\text{Cl}$ n-propyl chloride
 a b c
 3-NMR signals.

* At a given radio frequency all protons a molecule may give NMR signals at different applied field strengths. It is the applied strength that is measured. It is plotted against the absorptain. we get a spectrum with many absorptain peaks.

Peak area and proton-

proton counting:

The area under an NMR signal is directly proportional to the number of protons giving rise in the signals.

E.g: $\text{CH}_3\text{-OH}$ $\text{CH}_3\text{-CH}_2\text{-OH}$
a b a b c
3 : 1 1 : 2 : 3
2 NMR signal 3 NMR signals

$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{OH}$
a b c d
3 : 2 : 2 : 1
4 NMR signals.

Area under NMR signals

are found by integration using electronic integration from the ratio of areas we can get the number of equivalent protons present.

Spin-spin coupling:

splitting of signals:

with high resolution NMR spectrometers. The NMR signals for a set of equivalent protons are found to split into several signals. The splitting of NMR signals is caused due

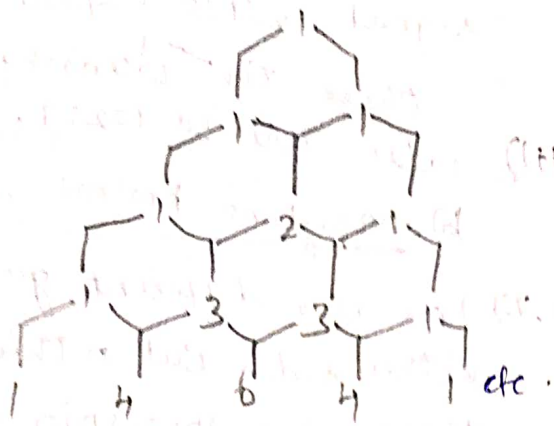
to spin-spin coupling.

The splitting is explained as assuming that the magnetic field experienced by the protons of one group is influenced by the spin arrangements of the protons in the adjacent group.

Rules governing splitting of NMR signals:

* Equivalent nuclei do not interact with one another. So splitting takes place because of them. For example in ethanol the three protons in the methyl group give rise to splitting of the adjacent methylene protons but not splitting among themselves.

* If there are 'n' protons in the adjacent carbon atom then multiplicity is given by $(n+1)$. The multiplicity of NMR signal by adjacent methylene group protons is equal $2+1=3$. Similarly the multiplicity caused by methyl group protons is $3+1=4$.



If the protons of atoms B and are affected by protons on atoms A and C that are not equivalent the multiplicity of B is equal to $(n_A + 1)(n_C + 1)$ where n_A and n_C are the number of equivalent protons on A and C respectively.

The relative intensities of triplet caused by methylene protons will be given by the coefficient of the terms of $(x+1)^2$

$$\text{i.e. } x^2 + 2x + 1 \text{ (i.e. } 1:2:1)$$

similarly for methyl protons $(x+1)^3$

$$x^3 + 3x^2 + 3x + 1 = 1:3:3:1$$

In general the relative intensity of the multiplets is given by the coefficients of the terms of $(x+1)^n$ where n is the number of neighbouring protons

i.e. The intensities of

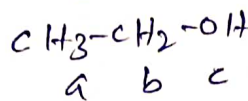
these lines will be given by the $(n+1)^{\text{th}}$ line of Pascal's triangle

COUPLING CONSTANT:

The distance b/w peaks in a multiplet is called the coupling constant $\cdot J$. This gives a measure of the effectiveness of the spin-spin coupling.

NMR Spectrum of Simple organic compounds

1. Ethanol (pure):



No. of equivalent sets of protons = 3

No. of groups of peak = 3

splitting:

a) methyl protons:

They have an adjacent methylene group with two equivalent protons. So the methyl NMR signal will be split into three the intensity ratio will be 1:2:1.

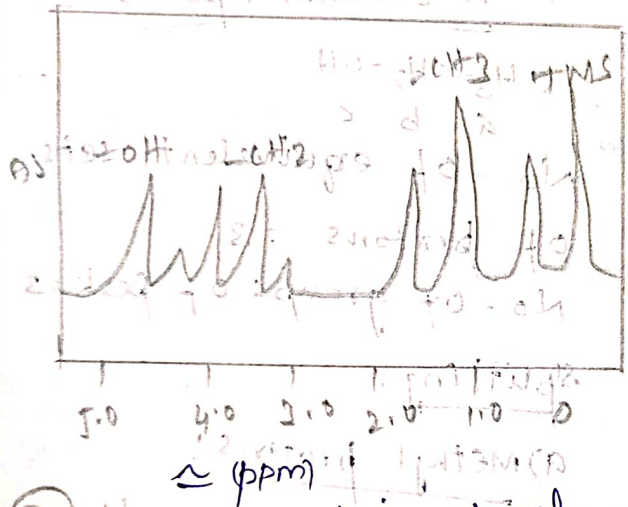
b) Methylene protons:

They have two different groups on either sides.

So according to rule 3 given above, the methylene NMR signal will split into eight $[n(n+1)(n+1) = (3+1)(1+1) = 4 \times 2 = 8]$. The area ratio will be $1:7:21:35:35:21:7:1$.

c) Hydroxyl proton

It has an adjacent methylene group with two equivalent protons. The OH NMR signal will be split into the area ratio will be $1:2:1$.



A8 = Absorption signal.

B. Acidified ethanol (impure)
 No. of equivalent sets of protons = 3.
 No. of group of peaks = 3

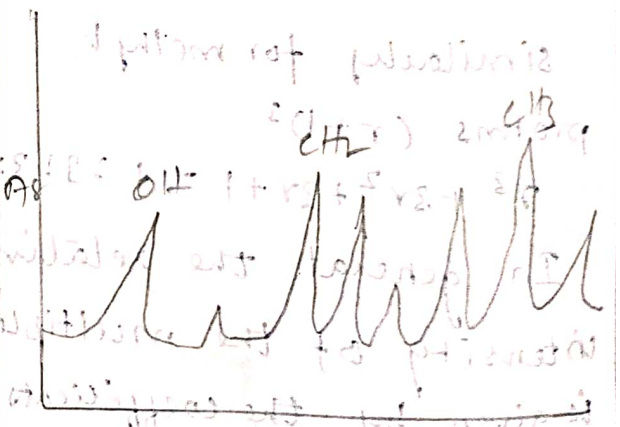
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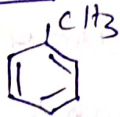
have two different groups on either side. But in this case there is no spin-spin interaction b/w OH protons and CH2 protons. (This is because the H⁺ in of the acid induces the exchange of protons b/w OH protons and acid protons) so (the life time of an OH proton in any given environment becomes too short to permit the observation of the effect of the OH protons on CH2 protons (so only CH3 protons interact with CH2 protons). (so the peak will be split into four. The intensity ratio will be $1:3:3:1$).



A8 = Absorption signal.

c) Hydroxyl protons: If bar on adjacent CH_2 group. we have already seen that there will be no spin-spin interaction b/w the two so there will be only one peak.

2. Toluene:

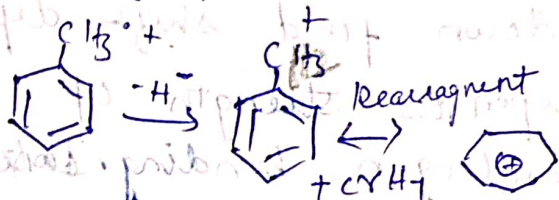


No. of equivalent sets of protons = 2
 No. of groups of peaks = 2

splitting:

As the various protons are separated by more than two bonds they don't interact so no splitting takes place.

Consider the mass spectrum of toluene two strong peaks at m/e 91 and at m/e 65 are formed. The peak at m/e 91 is due to the formation of tolylium cation (stable) which loses a molecule of acetylene (C_2H_2 26 mass units) to give C_5H_7^+ (m/e 65)



Toluene

Benzyl cation

$m/e = 91$

C_6H_5^+
(m_1)

Suppose the transition C_7H_7 (91) to C_5H_7 (65) occurs in the second field free region. Then a metastable peak is formed. The position of the broad metastable peak is determined as

$$m^* = \frac{m_2}{m_1} = \frac{65 \times 65}{91} = 46.4$$

A metastable peak in case of toluene appears at 46.4 in the mass spectrum.

Factors influencing chemical shift

Following are the factors which influence the chemical shift.

- Inductive effect
- Van der Waal's deshielding
- Anisotropic effect
- Hydrogen bonding.

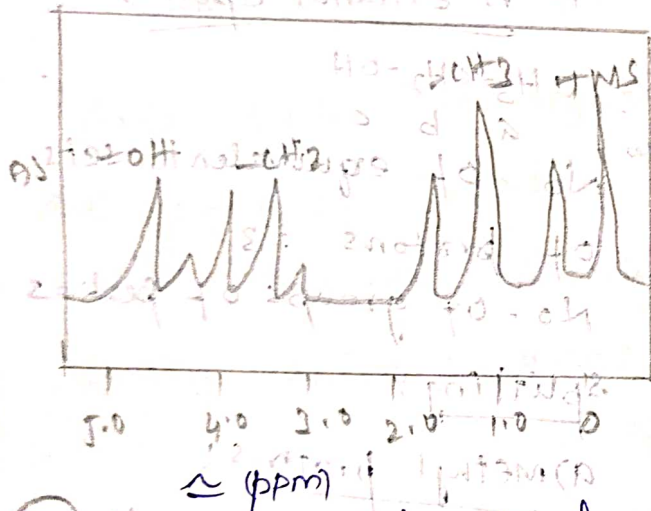
a) Inductive effect:

A proton is said to be deshielding if it is attached with an electronegative atom or group or rather the electronegativity of the atom greater is deshielding caused to the proton. If the deshielding is more for a proton, then its δ value will be more.

So according to rule 3 given above, the methylene NMR signal will be split into eight $[(n_A + 1)(n_B + 1) = (3 + 1)(1 + 1) = 4 \times 2 = 8]$. The area ratio will be 1:7:21:35:35:21:7:1

c) Hydroxyl proton

It has an adjacent methylene group with two equivalent protons. The OH NMR signal will be split into the area ratio will be 1:2:1



AS = Absorption signal.

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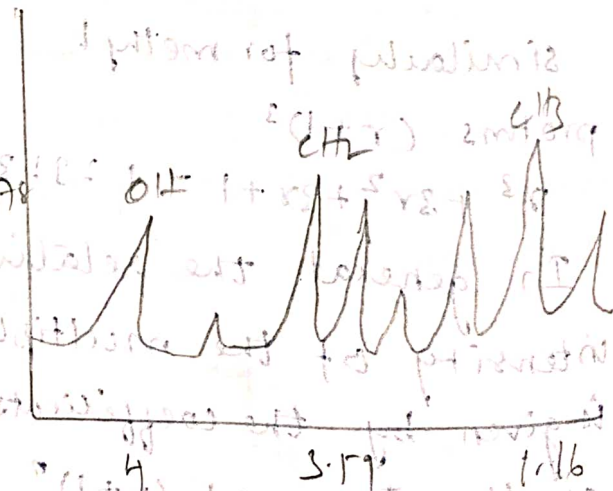
have an adjacent methylene group with two equivalent

protons so the methyl NMR signal will be split into three. The intensity ratio will be 1:2:1.

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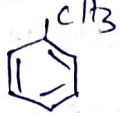
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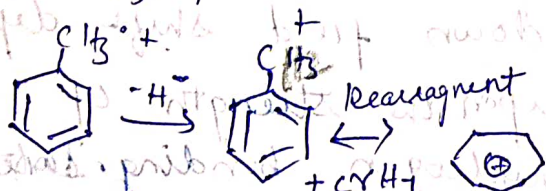
No. of equivalent sets of protons = 2
 No. of groups of peaks = 2

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As the various protons are separated by more than two bonds they don't interact so no splitting takes place.

Consider the mass spectrum of toluene two strong peaks at m/e 91 and at m/e 67 are formed. The peak at m/e 91 is due to the formation of tolylium cation (stable) which loses a molecule of acetylene (C_2H_2 mass units) to

give C_5H_7^+ + C (m/e 67)



Toluene $\xrightarrow{-\text{H}}$ Benzyl cation \leftrightarrow $\text{C}_6\text{H}_5\text{CH}_2^+$ ($m/e=91$)

Suppose the transition C_7H_7 (91) to C_5H_7 (67) occurs in the second field free region. Then a metastable peak is formed. The position of the broad metastable peak is determined as

$$m^* = \frac{m_2}{m_1} = \frac{67 \times 67}{91} = 46.4$$

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- Anisotropic effect
- Hydrogen bonding.

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A proton is said to be deshielding if it is attached with an electronegative atom or group or greater the electronegativity of the atom greater is deshielding caused to the proton. If the deshielding is more for a proton, then its δ value will be also be more.

Two signals are expected for each of the two compounds. Deshielding for protons 'a' in compound (i) is more than that for similar protons in compound (ii).

As the distance from the electronegative atom increases, the deshielding effect due to it diminishes. Protons 'b' are comparatively less deshielded and hence will resonate at comparatively lower value of $\delta_a > \delta_b$.

b) Van der Waals deshielding:

Electron cloud of bulky group will tend to repel the electron cloud surrounding the proton. Thus such a proton will be deshielded and will resonate at slightly higher value of δ than expected in the absence of this effect.

c) Anisotropic effects

Refer (space effect)

The deshielding effect on protons attached to C is higher than that can be accounted for by inductive effect alone. Aldehydic and aromatic protons are much more deshielded. Alkyne protons appear at relatively low value of δ . The value

of δ (chemical shift) in each case can be justified by explaining the manner in which the π electrons circulate under the influence of the applied field. Induced circulation of π electrons generates induced magnetic field which is diamagnetic around carbon atom and paramagnetic in the region of the alkene protons. Thus the protons will feel greater field strength and hence resonance occurs at lower applied field.

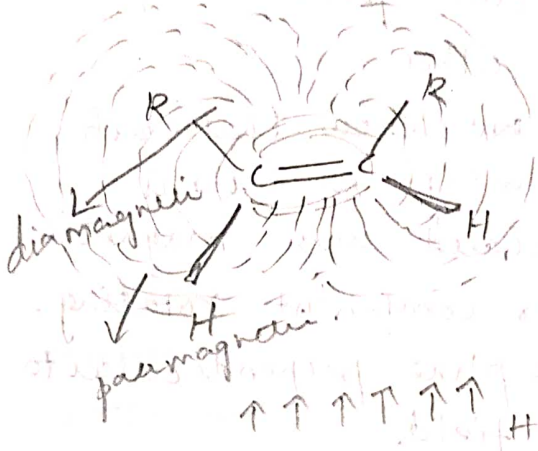
d) Hydrogen bonding:

The hydrogen bonded proton being attached to a highly electronegative atom will have smaller electron density around it. Boiling less shielded. The field felt by such a proton will be more and hence resonance will occur deshielded. The down field shift depends upon the strength of hydrogen bonding. Intra molecular and inter molecular hydrogen bonding can be easily distinguished.

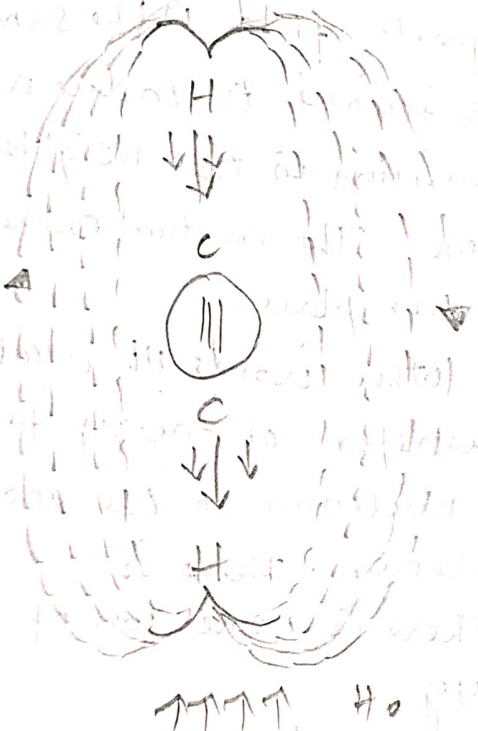
as the latter does not show change in concentration.

Deshielding of ethylenic

protons:

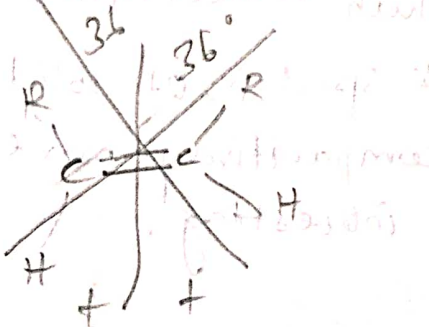


Alkyner:

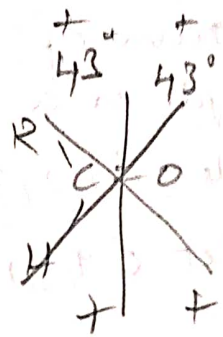


Shielding of acetylene

protons

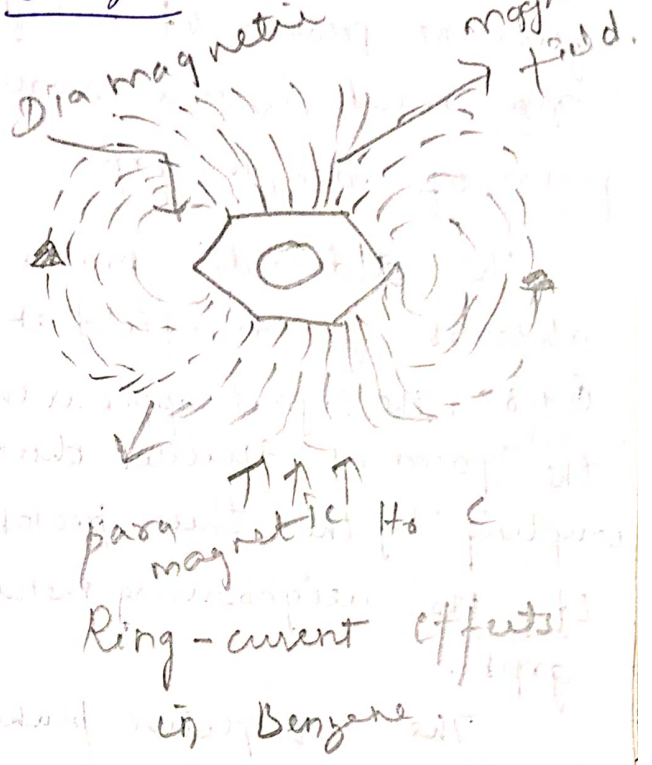


a) alkene



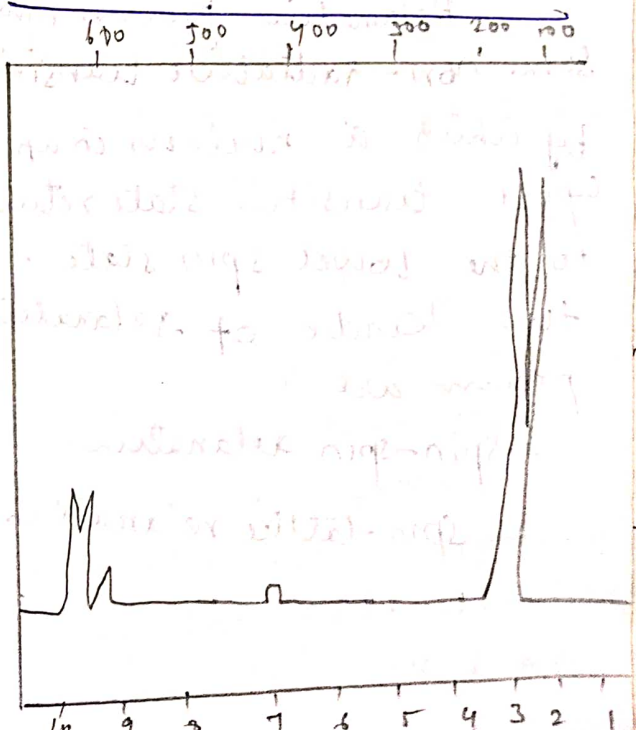
b) carbonyl:

benzene:



NMR spectrum in simple organic molecule.

3. Acetaldehyde, CH3CHO



The spectrum of acetaldehyde is as follows

- a) Double, $\delta 2.2, 3H (CH_3)$
- b) Quartet $\delta 9.8, 1H (C^{\overset{O}{\parallel}}H)$

Explanation: The double at $\delta 2.2$ is due to the equivalent protons of methyl group coupled with a single proton of aldehyde group.

The aldehydic proton absorbs far downfield at $\delta 9.8$. The signal appears in the form of quartet due to coupling by the three protons of the neighbouring methyl group.

The respective peaks appear in the ratio 3:1

Relaxation process:

Relaxation process involves some non-radiative transition by which a nucleus in an upper transition state returns to the lower spin state. Two kinds of relaxation process are:

- * Spin-spin relaxation
- * Spin-lattice relaxation.

Spin-spin relaxation:

* It is due to the mutual exchange of spins by two precessing nuclei which are in close proximity to each other.

* We know that each precessing nucleus is associated with magnetic vector component rotating in a plane perpendicular to the field.

* If this small rotating magnetic field is the same as is required to induce a transition in the neighbouring protons. The mutual exchange is taken place.

* In other words it involves the transfer of energy from one nucleus to the another nucleus. There is

* There is no net loss of energy.

* The spread of energy among the nuclei ~~are~~ concerned results in line broadening which makes nmr.

* Spectra of solids comparatively more interesting.



Spin-lattice relaxation:

* It involves the transfer of energy from the nucleus in its higher energy state to the molecular lattice.

* The energy is transferred to the components of the lattice state as the additional translational, vibrational and rotational energy.

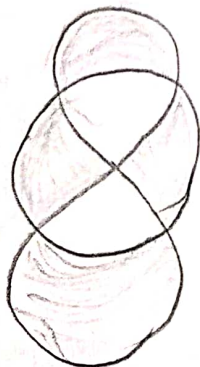
* The total energy of the system remains the same.

* An efficient relaxation process involves a short time and results in the broadening of absorption peaks.

* Smaller time of the excited state greater is the line width.

* This mechanism is not effective in solid. The

* This process keeps the excess of nuclei in the lower energy state which is necessary condition for nuclear magnetic resonance phenomenon.

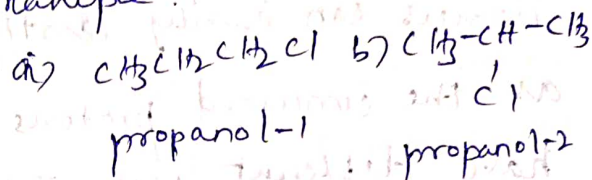


Application of NMR

* Identification of structural isomers

NMR is widely used for investigating the details of an unknown compound.

example:



* Detection of hydrogen bonding:

Intermolecular hydrogen bonding shifts the absorption for a proton downfield. The extent of hydrogen bonding varies with the solvent concentration of the solution and temperature. This in two types can be detected by NMR.

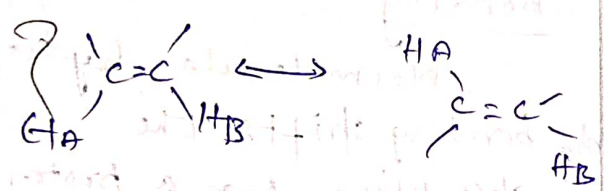
Detection of Aromaticity:

Protons attached to the benzoyl polynuclear are extremely deshielded due to circulating electron following Hückel's rule. As the result of this the signal for the aromatic proton appears at very low field than benzene. This kind of

Aromaticity character investigation under.

* distinction b/w cis-trans isomers of and conformers

The cis and trans isomers can easily distinguished as the concerned protons have different valency of the chemical shift.



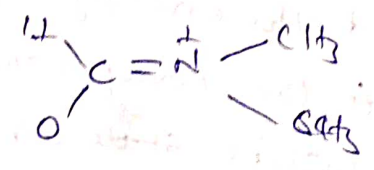
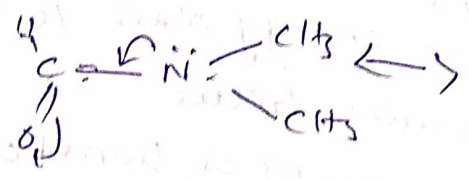
* Detection of electronegative atom or group

It is known as the presence of an electronegative atom or group in the neighbourhood of the proton cause signal downfield. we can investigate that.

* Detected some double bond character due to resonance.

In some compounds the molecule acquires a

little double bond due to resonance we can find that with NMR



* Important in a quantitative analysis:

NMR spectroscopy is gaining importance for the quantitative analysis of the compound.

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