

UNIT - II

2.1. Nuclear Magnetic Resonance Spectroscopy

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2.1. Nuclear Magnetic Resonance Spectroscopy

2.1.1. General Introduction :

Nuclear magnetic resonance spectrometry is basically absorption spectrometry just like UV or IR spectroscopy under appropriate conditions in a magnetic field, a sample can absorb electromagnetic radiation in the radio frequency (rf) region. A plot of frequencies of this absorption peaks versus peak intensities constitutes an NMR spectrum. All nuclei carry a charge and in some nuclei this charge 'spins' on the nuclear axis, and this circulation of nuclear charge generates a magnetic dipole along the axis. The angular momentum of the spinning charge can be described in terms of spin numbers

(I) and they have values of $0, \frac{1}{2}, 1, \frac{3}{2},$ etc... The spin number (I) can be determined from the atomic mass and atomic number.

	Atomic mass	Atomic number	Example (I)
Half-integer	odd	odd or even	${}^1_1\text{H}(\frac{1}{2}), {}^{17}_8\text{O}(\frac{5}{2}), {}^{15}_7\text{N}(\frac{1}{2})$
integer	Even	odd	${}^2_1\text{H}(1), {}^{14}_7\text{N}(1), {}^{10}_5\text{B}(3)$
Zero	Even	Even	${}^{12}_6\text{C}(0), {}^{16}_8\text{O}(0), {}^{34}_{16}\text{S}(0)$

Several nuclei (eq ${}^1_1\text{H}, {}^3_1\text{H}, {}^{13}_6\text{C}, {}^{15}_7\text{N}, {}^{19}_9\text{F}, {}^{31}_{15}\text{P}$) have spin number I of $\frac{1}{2}$ and a uniform spherical charge distribution. Nuclei with spin number I of 1 or higher have non spherical charge distribution. Such a magnetically active nucleus is placed in an external magnetic field, the nuclei, tiny bar magnets, will take up definite orientation which are quantized. The number of possible orientations will be given the equation $N = 2I + 1$, where I is the spin number of nucleus under consideration. Each orientation is associated with definite energy and the energy of each state can be defined. The energy difference between adjacent levels can be given by this expression $\Delta E = h\nu$

h = Planks constant

ν = Frequency of electromagnetic radiation

It is found that $\omega = \nu H_0$

ω = angular processional velocity

H_0 - Applied field in gauss

ν - Gyromagnetic ratio = $\frac{2\pi\mu}{hI}$

μ = Magnetic moment of the nuclei

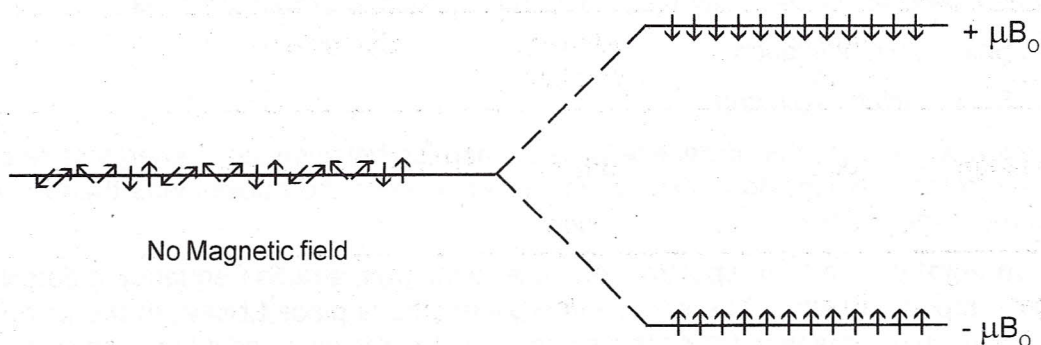
I = Spin number of the spinning magnetic

According to the fundamental NMR equation which correlates electromagnetic frequencies with the magnetic field we say $\nu H_0 = 2\pi \nu$

ν = Frequency of electromagnetic radiation.

The value of the frequency ν = inserted is called precessional frequency.

For a nucleus with $I = \frac{1}{2}$ this number of possible orientations in a magnetic field will be $2I + 1$ (^1H , ^{13}C , ^{19}F) and taking up one of the two orientations with respect to the external field



- i) Alignment with the field and
- ii) Alignment against the field

When a proton is pressing this aligned orientation, it can pass into the opposed orientation by absorbing energy. From the high energy opposed orientation it comes back to the low energy aligned orientation by losing energy.

The transition from one energy state to the other is called flipping of the proton. The transition between two energy states can be brought about by the absorption of quantum of electromagnetic radiation in the radiowave region with energy $h\nu$. The energy required to bring about the transition depends upon the strength of this external field. Stronger the field greater will be the tendency of the nuclear magnet to remain lined up with it and higher frequency of radiation needed to flip the proton to the higher energy state.

We know that $\nu = \frac{\nu H_0}{2\pi}$

ν = Frequency in cycles per sec or Hz

H_0 = Strength of the magnetic field in gauss

γ = Nuclear constant or Gyromagnetic ratio and is equal to 26750 for ten proton.

At 14092 gauss (1.4T) this energy required to cause flipping corresponds to electromagnetic radiation of frequency 60 million cycles per second or 60 MHz. When we irradiate this precession nuclei with a beam of electromagnetic radiation of desired frequency, then the low energy nuclei will absorb it and move to higher energy state. The precession proton will absorb energy from the radio frequency region only if the precession frequency is the same as the frequency of the radio frequency beam, then the nucleus and radio frequency beam are in resonance. Hence it is called nuclear magnetic resonance.

Relaxation Process : When the population in the two energy states becomes equal, equilibrium is established and thereafter no further absorption of energy by the nuclei. However, there is a process known as relaxation which retain the small excess population in the lower energy state through out the irradiation process.

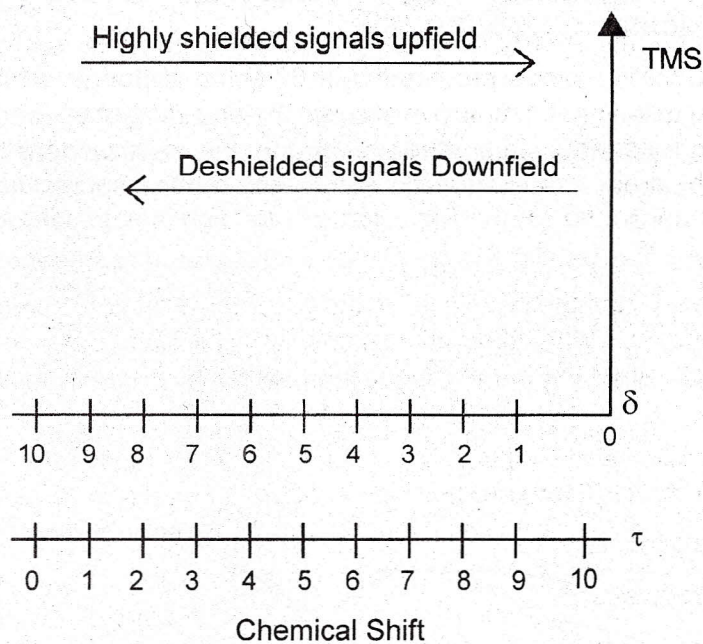
Relaxation process involve non-radiative transitions by which a nucleus in an upper transition state return to lower spin state. There are two kinds of such relaxation process.

- i) Spin – Spin relaxation
- ii) Spin – lattice relaxation

In the former process the nuclei energy is exchanged between lower energy state and higher energy state in the surrounding nuclei. In this latter process the nuclei loose their energy to the surroundings, to the lattices.

Instrumentation : In NMR spectrophotometer a magnet, a radio frequency, a detector and an amplifier are important parts. The sample in a glass tube is placed between the pole faces of a magnet. A R_f source is made to fall on this sample. A signal is detected if the nuclei resonates with the source, i.e. energy required to flip the proton is the same as that of the source. The spectrum can be obtained either by CW scan or pulse FT. Generally protons in a molecule being in different electronic environments cannot resonate at the same frequency. For practical purposes the radio frequency source is held constantly and field strength is varied. Peaks are measured by an electronic integrator that traces the height proportional to the peak area. Peak positions are measured in frequency units from a reference peak.

Chemical shift : The nucleus is shielded to a small extent by its electron cloud and whose density varies with this environment. This variation gives rise to different absorption positions usually within the range of about 750 Hz in a magnetic field corresponding to 60 MHz. The electrons under the influence of a magnetic field will circulate, and will generate their own magnetic field opposing the applied field, and hence the shielding effect. The degree of shielding depends on the density of ten circulating electrons and also on the inductive effect of other groups attached to this carbon atoms. The difference in the absorption position of a particular proton from the absorption position of a reference proton is called as chemical shift of that particular proton. Generally Tetramethylsilane is useful as reference compound.

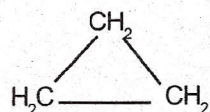


Chemical shift for various types of protons

Types of protons

Chemical shift in PPM

Cyclopropane



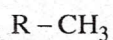
δ

τ

0.2

9.8

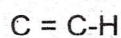
Primary



0.9

9.1

Vinyllic



4.6-5.8

5.4-4.2

Acetylenic



2-3.5

8-6.5

Aromatic



6-9.0

4-1.0

Flourides



4-4.5

6-5.5

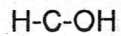
Chlorides



3-4

7-6

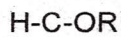
Alcohols



3.4-4

6.6-6

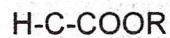
Ethers



3.3-4

6.7-6

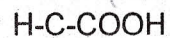
Esters



2-2.2

8-7.8

Acids



2-2.5

8-7.5

Aldehydic



9-10

1-0

Hydroxly



1-5.5

9-4.5

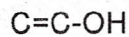
Pheolic



4-12

6 to -2

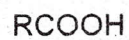
Enolic



15-17

-5 to -7

Carboxylic



10.5-12

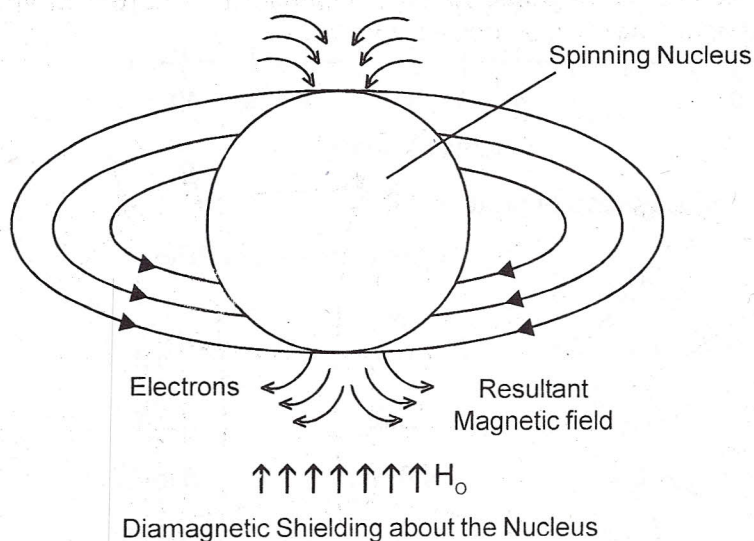
-0.5 to -2

2.1.2. Shielding and deshielding effects :

Hydrogen nuclei in a molecule are surrounded by the electronic charge which shields the nucleus from the influence of the applied field. Thus to overcome the shielding effect and to bring the protons to resonance, greater external field is required. Clearly greater the electron density around the proton, greater will be induced secondary magnetic field which opposes the applied field and thus, greater external field will cause protons absorption. The extent of shielding is represented in terms of shielding parameter α . When absorption occurs, the field H felt by the proton is represented as

$$H = H_0(1 - \alpha) \text{----- (1)}$$

Where H_0 is the applied field strength. Clearly the field felt by proton does not correspond to the applied field.



Greater the value of α greater will be the value of applied field strength which has to be applied to get the effective field required for absorption

$$V = \frac{\nu H}{2\pi} \text{----- (2)}$$

From 1 and 2

$$\nu = \frac{\nu H_0(1 - \alpha)}{2\pi}$$

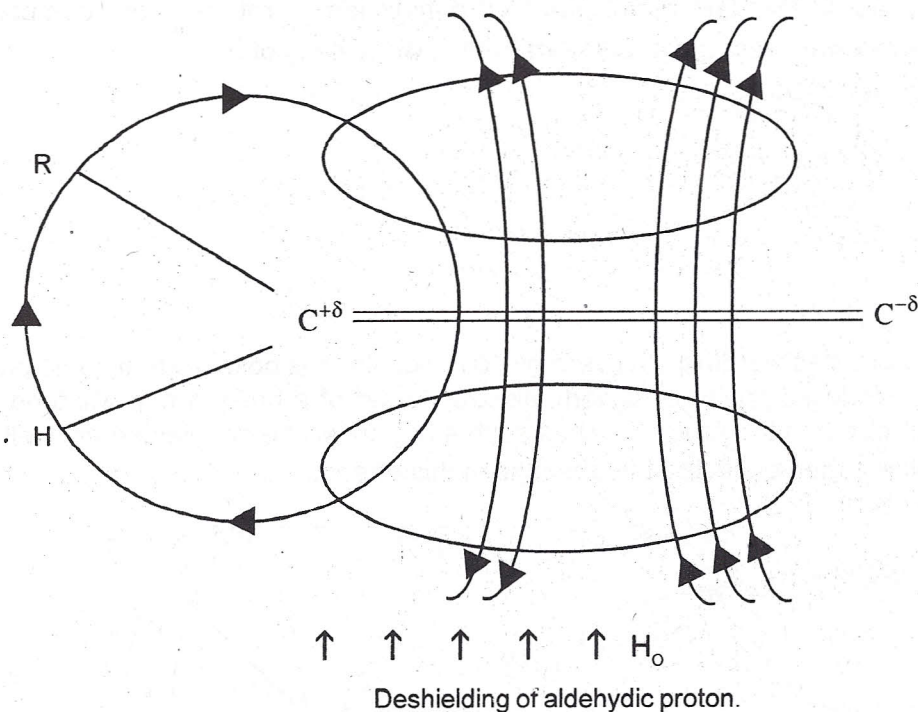
From this relation, it is clear that the protons with different electronic environments or with different shielding parameter can be brought into resonance in two ways.

- 1) The strength of the external field is kept steady and the radio frequency is constantly varied.
- 2) The radio frequency is kept steady and the strength of the applied field is constantly varied.

The constant radio – frequency shielding shift the absorption upfield in the molecule where there is a spherical distribution of electrons around the proton. It is called positive shielding, presence of the electronegative atoms or groups cause reduction in electron density around the proton (deshielding) and thus absorption is shifted downfield (decreases) the diamagnetic and the paramagnetic effects from the neighbouring atoms and also the effects from the interatomic currents which results in the proton absorption shift.

It has been found that the absorption depends upon the manner in which the π electrons circulate under the influence of the applied field in case of ethene oriented at right angles to the direction of the applied field, the induced magnetic field is diamagnetic around the carbon atoms and is paramagnetic in the region of protons. Thus protons feel more magnetic field and hence absorption occurs at low field. Similarly, aldehydic protons appear at low field.

In the case of acetylene, the proton experience a diamagnetic shielding effect. The induced magnetic field at the protons is diamagnetic but paramagnetic at the carbon atom. Thus, protons are said to be shielded and hence absorption occurs upfield.

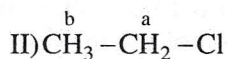
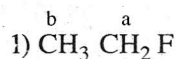


In case of olefins, acetylenes aldehydes, ketones, acids, esters, nitrides etc, if the proton is present in the positive region, it will be shielded and absorption occurs upfield. On the otherhand if the proton lies in the negative region, its absorption is downfield. In the case of benzene and other aromatic compounds strong diamagnetic currents are induced by the applied field this causes paramagnetic shielding at the aromatic protons and thus, absorption occurs downfield on the otherhand any group which is present above or below the plane of the aromatic nucleus will be shielded and absorption for such a proton occurs upfield ring current effect as is seen in benzene and other aromatic compounds is absent in saturated hydrocarbons.

Factors influencing chemical shift : Following are the factors which influence the chemical shift

- Inductive effect
- Vanderwaal's deshielding
- Anisotropic effects
- Hydrogen bonding

a) Inductive effect : A proton is said to be deshielded if it is attached with a electronegative atom or group. Greater the electronegativity of the atom, greater is the deshielding caused to the proton. If the deshielding is more for a proton, then its δ value will also be more consider the following compounds.

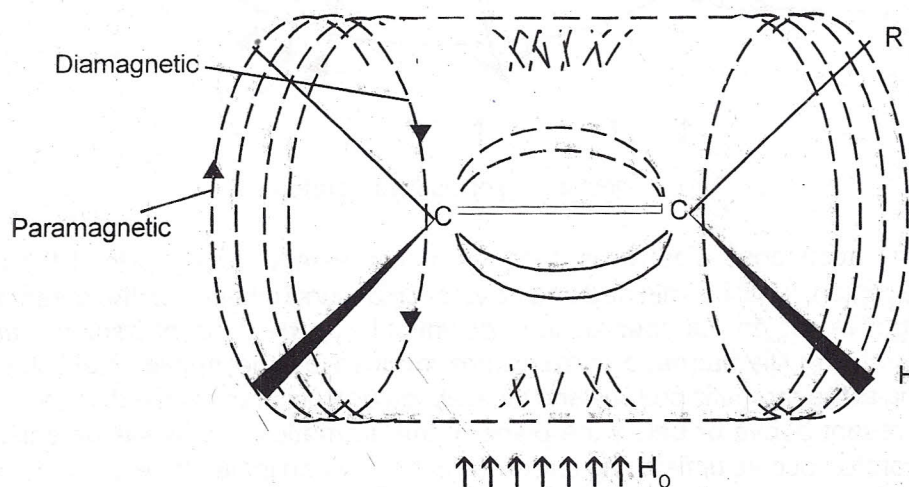


Two signals are expected for each of the two compounds. Deshielding for protons 'a' is compound (I). Is more than that for similar proton in compound (II). As the distance from the electronegative atom decreases, the deshielding effect due to it diminishes. Protons b are comparatively less deshielded and hence will resonate at comparatively lower values of δ .

Tau value for CH_3 protons

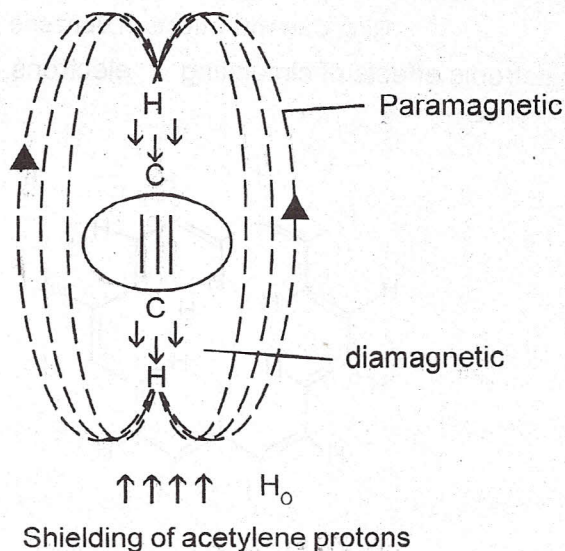
Compound	δ Value
$\text{CH}_3 \text{ F}$	4.25
$\text{CH}_3 \text{ Cl}$	3.1
$\text{CH}_3 \text{ Br}$	2.64

b) Vanderwaal's deshielding : In overcrowded molecules it is possible that some proton may be occupying slightly hindered position. Clearly electron cloud of a bulky group will tend to repel the electron cloud surrounding the protons. Thus such a proton will be deshielded and will resonate at slightly higher value δ than expected the absence of this effect.

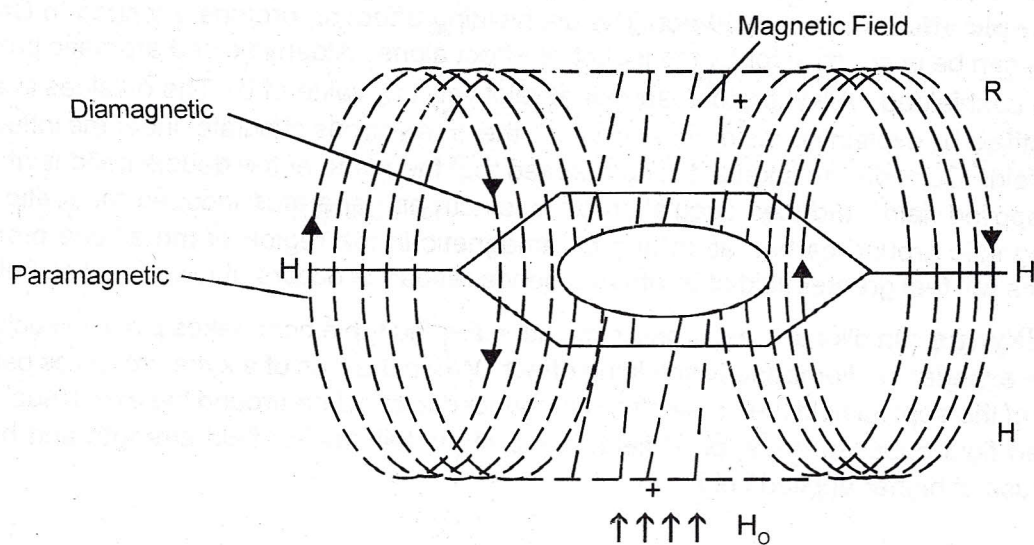


c) Anisotropic effects : (Space effect) The deshielding effect on protons attached to C=C is higher than that can be accounted for by the inductive effect alone. Aldehydic and aromatic protons are much more deshielded. Alkyl protons appear at relatively low value of δ . The δ values in each case can be justified by explaining the manner in which the π electrons circulate under the influence of the applied field. Consider an alkene it is so oriented that the plane of the double bond is at right angles to 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.

2.1.3. Alkynes : In alkynes, electronic circulation around triple bond takes place in such way that the protons experience diamagnetic shielding effect. When the axis of alkyne group lies parallel to the direction of the applied field the π electrons are induced to circulate around the axis in such way that the induced field opposes the applied field thus protons feel smaller field strength and hence resonance occurs at higher applied field.

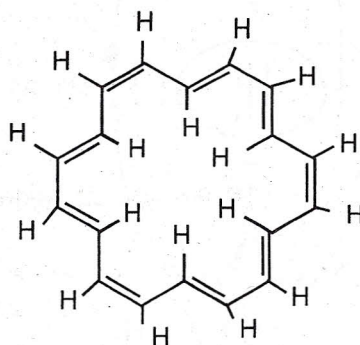


Benzene : In case of benzene, loops of π electrons are delocalised cylindrically over the aromatic ring. These loops of electrons are induced to circulate in the presence of applied field producing ring current. The induced current is diamagnetic in the center of the ring and is paramagnetic outside the ring. Thus the aromatic protons experience a magnetic field greater in magnitude than the applied field such protons are said to be deshielded and hence, smaller applied field will be required to bring them to resonance. It may be noted that the protons held above and below the plane of the ring resonate at low δ value. In a molecule of toluene, the methyl protons resonate at 2.34 δ where as a methyl group attached to an acyclic alkene of the ring current in an aromatic compound as compared to the deshielding influence caused by conjugated alkene group. An excellent example of shielding and deshielding by ring currents, is given by some of the annulenes. The proton outside the ring of (18) annulenes are strongly deshielded and these inside the ring are strongly shielded.



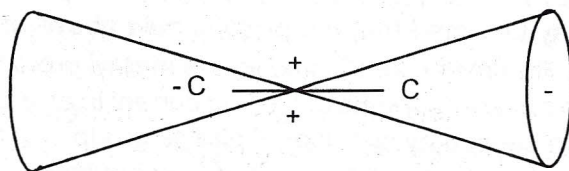
Ring Current - effects in Benzene

Compared to the anisotropic effects of circulating π electrons, the sigma



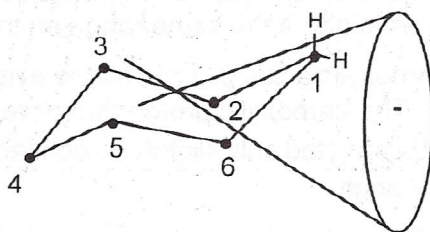
[18] Annulene

electrons of C-C bond produce a small effect. The axis of C-C bond is the axis of the deshielding cone.



Shielding (+) and deshielding (-) zone of C-C

The above figure account for the deshielding effect of successive alkyl substituents on the proton attached to a carbon atom. Thus the protons absorb downfield in the order, RCH_3 , R_2CH_2 , R_3CH . Also an equatorial proton is found to absorb further downfield by 0.7-0.1 ppm than the axial proton on the same carbon in a rigid six membered ring. The axial and equatorial protons on C_1 are oriented in the same way, with respect to C_1-C_2 and C_1-C_6 but the equatorial proton is within the deshielding conc of C_2-C_3 and C_5-C_6 bands.



Deshielding of equatorial protons of rigid six membered ring

Fig : Chemical shift range of different hydrogens.

Protons on Heteroatoms : Protons on a heteroatom differ from protons on a carbon atom in that (1) they are exchangeable, (2) they are subject to hydrogen bonding and (3) they are subject to partial or complete decoupling by electrical quadrupole effects of some heteroatoms.

2.1.4. Protons on Oxygen :

2.1.4.1. Alcohols : Unless special precautions are taken the spectrum of neat ethanol usually shows the hydroxylic proton as a slightly broadened peak at δ 5.35. At the commonly used concentration of about 5-20% in a non polar solvent, such as carbon tetrachloride or deuterio chloroform, the hydroxylic peak is found between δ 2 and δ 4. One extrapolation to infinite dilution or in the vapour phase, the peak is near 0.5. δ A change in solvent or temperature will also shift the hydroxylic peak.

Hydrogen bonding explains why the shift position of the hydroxylic proton depends on concentration, temperature and solvent. Hydrogen bonding decreases the electron density around the proton, and thus moves the protons absorption to lower field. The extent of intermolecular hydrogen bonding is decreased by dilution with a nonpolar solvent and with increased temperature, polar solvent introduce the additional complication of hydrogen bonding between the hydroxylic proton and the solvent. Intramolecular hydrogen bonds are less effected by their environment than intermolecular hydrogen bonds.

2.1.4.2. Phenols : The behavior of a phenolic proton resembles that of an alcoholic proton. The phenolic proton peak is usually a sharp singlet and its range, depending on concentration, solvent and temperature, is generally downfield ($\delta \sim 7.5 - \delta \sim 4.0$) compared with the alcoholic proton the concentration dependance of the OH peak. A carbonyl group in the ortho position shifts the phenolic proton absorption downfield to the range about (δ 12.0 - $\delta \sim 10.0$) because of intramolecular hydrogen bonding. Thus o-hydroxy acetophenone shows a peak at about δ 12.05 almost completely in variant with concentration. The much weaker intermolecular hydrogen bonding in o-chlorophenol explains

its shift range, which is broad compared with that of O-hydroxy acetophenone but narrow compared with that of phenol.

2.1.4.3. Enols : Enols are usually stabilised by intramolecular hydrogen bonding, which varies from very strong in aliphatic β -diketones to weak in cyclic α -diketone. The enolic proton is downfield relative to alcohol protons and, in the case of the enolic form of some β diketones, may be found as far downfield as δ 16.6. The enolic proton peak is frequently broad at room temperature because of slow exchange. Furthermore, the keto-enol conversion is slow enough so that absorption peaks of both forms can be observed, and the equilibrium maintained. When strong intramolecular bonding is not involved, the enolic proton absorbs in about the same range as the phenolic proton.

2.1.4.4. Carboxylic acids : Carboxylic acids exist as stable hydrogen-bonded dimers in non-polar solvents even at high dilution. The carboxylic proton therefore absorbs in a characteristically narrow range $\delta \sim 13.2$. $\delta \sim 10.0$ and is affected only slightly by concentration. Polar solvents partially disrupt the dimer shift the peak accordingly.

The peak width at room temperature range from sharp to broad, depending on the exchange rate of the particular acid. The carboxylic proton exchanges quite rapidly with protons of water and alcohols to give a single peak whose position depends on concentration. Sulfhydryl or enolic protons do not exchange rapidly with carboxylic protons and individual peaks are observed.

2.1.4.5. Protons on Nitrogen : The ^{14}N nucleons has a spin number of 1 and in accordance with the formula $2I+1$, should cause a proton attached to it and a proton on an adjacent carbon atom to show three equally intense peaks. These are two factors, however, that complicate the picture the rate of exchange of the proton on the nitrogen atom and the electrical quadrupole moment of the ^{14}N nucleons.

The proton on a nitrogen atom may undergo rapid, intermediate or slow exchanges. If the exchanges is rapid the NH proton decoupled from the N atom and from the protons on adjacent carbon atoms. The NH peak is therefore a sharp singlet, and the adjacent CH protons are not split by NH. Such is the case of most aliphatic amines. If the NH exchange rate is low, the NH peak is still broad because the electrical quadrupole moment of the nitrogen nucleus induces a moderately efficient spin relaxation and thus, an intermediate life time for the spin states of the nitrogen nucleus. The proton thus sees three spin states of the nitrogen nucleus which are changing at a moderate and the proton responds by giving a broad peak. In this case, coupling of the NH proton to the adjacent protons is observed. Such is the case for pyrroles, imidazoles, secondary and primary amides, and carbamates.

The H-N-C-H coupling takes place through the C-H, C-N and N-H bonds, but coupling between nitrogen and protons on adjacent carbon atoms is negligible. The proton-proton coupling is observed in the signal due to hydrogen on carbon. The N-H proton signal is severely broadened by the quadrupolar interaction. Ethyl N-methyl carbamate $\text{CH}_3\text{NHC(=O)CH}_2\text{CH}_3$ the NH proton shows a broad absorption

centered about δ 5.16 and N-CH₃ absorption at δ 2.78 is split into a doublet ($J \sim 5\text{H}_2$) by the NH proton. The ethoxy protons are represented by the triplet at δ 1.23 and the quartet at δ 4.14. The small peak at δ 2.67 is an impurity. Aliphatic and cyclic amine NH protons absorb from $\sim\delta$ 3.0 – 0.5 aromatic amines absorb from $\sim\delta$ 5.0 – 3.0

2.1.4.6. Protons on Sulfur : Sulfhydryl protons usually exchange at a low rate so that at room temperature they are coupled to protons on adjacent carbon atoms or do they exchange rapidly with hydroxyl, carboxylic, or enolic protons on the same or on other molecules. However, exchanges is rapid enough that shaking for a few minutes with deuterium oxide replaces sulfhydryl protons with deuterium. The absorption range for aliphatic sulfhydryl protons or δ 1.6 – δ 1.2 for aromatic sulfhydryl protons δ 3.6. – δ 2.8 concentration, solvent and temperature affect the position within these ranges.

2.1.5. Protons on or near Halogens :

Chlorine, bromine, and iodine nuclei are completely decoupled from protons directly attached or an adjacent carbon atoms, because of strong electrical quadruple moments.

The ^{19}F atom has a spin number of $\frac{1}{2}$ and complies straggly with protons the rules for coupling of protons with fluorine are the same as for proton - proton coupling. The proton fluorine coupling constants are some what larger, and long - range effects are frequently found. The ^{19}F nucleus can be observed at 56.4 MH_2 . Its spin is split by proton and fluorine spins, and the multiplicity rules are the same as these observed in proton spectra.

2.1.6. Chemical Exchange :

In a molecule, if a proton shuttles between two magnetic environments at a rate which is much faster in comparison with the nmr transition time then the resonance observed for that proton will be simply that of the average effective field in the two environments thus only one resonance will be observed, although the proton will shuttle in the different magnetic environments. We know that the –OH proton in water has different chemical shift as compared to that of the –OH proton in acetic acid in water at an average position according to the following formula.

$$N_a\delta_a + N_b\delta_b$$

Where

N_a = Mole fraction of the proton a.

N_B = Mole fraction of the proton b

δ_a = Chemical shift of unexchanged proton a

δ_b = Chemical shift of unexchanged proton b

This clearly shows that the rate at which the –OH proton exchanges between water and acetic acid is much faster than the nuclear transition time.

The phenomenon of chemical exchange can be explained by considering the nmr spectrum of anhydrous ethanol and also the spectrum of ethanol containing small quantities of water.

In the case of pure anhydrous ethanol $\overset{a}{\text{CH}}_3 - \overset{b}{\text{CH}}_2 - \overset{c}{\text{OH}}$ three signals are observed.

- 1) a triplet for CH_3 protons at 8.827 due to coupling with CH_2 protons

- 2) a multiplet consisting of eight lines for $-\text{CH}_2-$ protons at 6.38 δ . The $-\text{CH}_2-$ protons are under the influence of two kinds of proton in different chemical environments. Thus, the multiplet consists of $(n+1)(n'+1) = (3+1)(1+1) = 8$ lines
- 3) a triplet for $-\text{OH}$ proton at 4.72. The OH proton appears as a triplet because of coupling to $-\text{CH}_2-$ protons

Now if we scan the spectrum of ethyl alcohol containing water, the OH signals appear as a singlet and its coupling with adjacent $-\text{CH}_2-$ does not take place.

The alcohol containing some amount of water, a singlet is observed for the hydroxyl proton. The position of the singlet peak for the OH proton is slightly shifted depending upon the water content in alcohol and hence, it helps in the quantitative analysis of ethanol - water, acetic acid - water mixtures.

The spin decoupling can usually be observed at 1) high temperature and 2) by using highly polar solvents for the polar samples.

The spectrum of methanol (CH_3OH) at very low temperature (-40°C) shows a quartet for hydroxyl proton and a doublet for methyl protons. This shows that the chemical exchange is very slow at -40°C as compared to the nmr transition time. But, if the temperature is raised to $+31^\circ\text{C}$, multiplets CH_3 and $-\text{OH}$ protons collapse to the sharp singlets. Thus shows that the rate of chemical exchange becomes faster than the nmr transition time.

2.1.7. Suggested Readings

10. Some Modern methods of Organic Synthesis, W. Carruthers, Cambridge University Press.
11. Advanced Organic Chemistry, Reactions Mechanisms and Structure, J. March. John Wiley
12. Advanced Organic Chemistry Part B, F.A. Carey and R.J. Sundberg, Plenum Press 1.
13. Spectrometric Identification of Organic Compounds, R. M. Silverstein, G.C. Bassler and T. C. Morrill, John Wiley.
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