NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Nuclear magnetic resonance (NMR) is a spectroscopic method that is even more important to the organic chemist than infrared spectroscopy. Many nuclei may be studied by NMR techniques, but hydrogen and carbon are most commonly available. Whereas infrared (IR) spectroscopy reveals the types of functional groups present in a molecule, NMR gives information about the number of magnetically distinct atoms of the type being studied. When hydrogen nuclei (protons) are studied, for instance, one can determine the number of each of the distinct types of hydrogen nuclei as well as obtain information regarding the nature of the immediate environment of each type. Similar information can be determined for the carbon nuclei. The combination of IR and NMR data is often sufficient to determine completely the structure of an unknown molecule.

NUCLEAR SPIN STATES

Many atomic nuclei have a property called spin**:** the nuclei behave as if they were spinning. In fact, any atomic nucleus that possesses either *odd* mass, *odd* atomic number, or both has a quantized spin angular momentum and a magnetic moment. The more common nuclei that possess spin include $_1{}^1$H, $_2{}^1$H, $_{13}{}_6$C, $_{14}{}_7$N, $_{17}{}_8$O, and $_{19}{}_9$F. Notice that the nuclei of the ordinary (most abundant) isotopes of carbon and oxygen, $_{12}{}_6$C and $_{16}{}_8$O, are not included among those with the spin property. However, the nucleus of the ordinary hydrogen atom, the proton, does have spin. For each nucleus with spin, the number of allowed spin states it may adopt is quantized and is determined by its nuclear spin quantum number I. For each nucleus, the number I is a physical constant, and there are $2I + 1$ allowed spin states with integral differences ranging from $+I$ to $\square I$. The individual spin states fit into the sequence

$+I, (I \square 1), \ldots , (\square I + 1), \square I$

For instance, a proton (hydrogen nucleus) has the spin quantum number $I = \downarrow 1$

$_2\downarrow$ and has two allowed spin states $[2(\downarrow_1{}_2\downarrow) + 1 = 2]$ for its nucleus: $\square\downarrow_1{}_2\downarrow$ and $+\downarrow_1{}_2\downarrow$. For the chlorine nucleus, $I = \downarrow_3{}_2\downarrow$ and there are four allowed spin states .

In the absence of an applied magnetic field, all the spin states of a given nucleus are of equivalent energy (degenerate), and in a collection of atoms, all of the spin

states should be almost equally populated, with the same number of atoms having each of the allowed spins.

Principle of NMR

To understand the principle of nmr let us consider the moition of the spining top .when the spining top is distrubuted a little ,its spining axis will trace out a circle perpendicular to the earths field .such amoition is called precession.
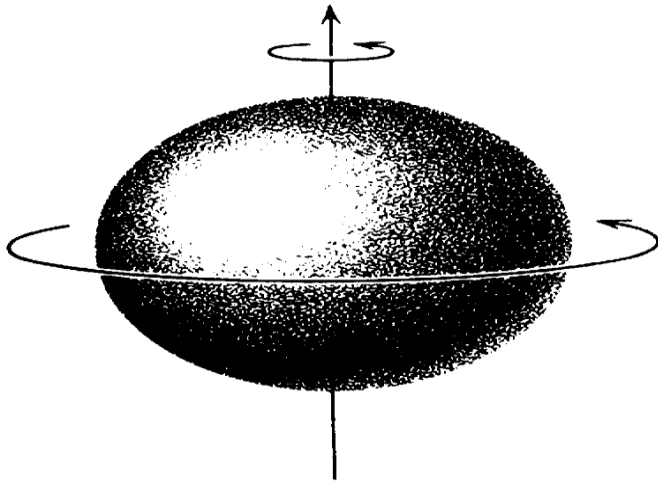
FIGURE 4.1. Spinning charge on proton generates magnetic dipole.
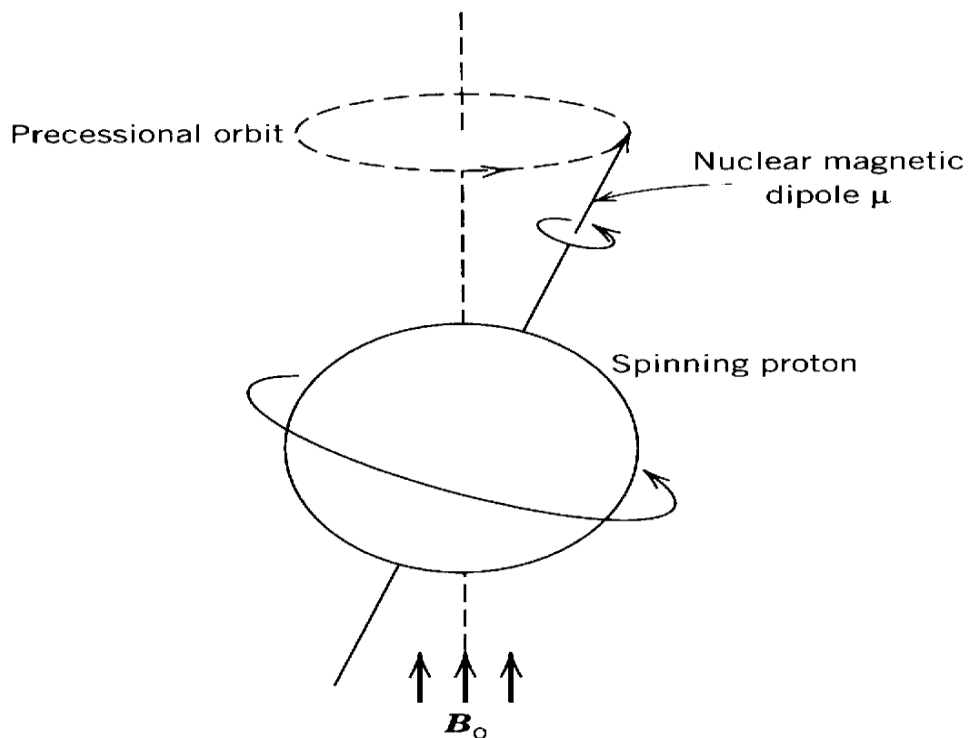
FIGURE 4.3. Classical representation of a proton precessing in a magnetic field of magnitude B_0 in analogy with a precessing spinning top.

In a similar way when anuclear magnet is placed in an external magnetic feild ,it will experience a torque (force perpendicular to the axis of the nuclear magnet which will tend to align it with the feild .Since the nuclear magnet is spining ,it will not align with the external magnet feild , but will precess around it.with a certain angular frequency ωcalled the precessional frequency .stronger the feild the feild , higher the precessional frequency

Since the proton has two allowed spin states (I=+1/2 and I= -1/2) it canprecess in two orientations – one aligned with the applied feild (lower enerdy) and the other with the applied feild (higher energy).

When the precessional frequency of thr nucleus is exactly equal to the frequency of the electromagnetic radiation ,the asbsorption occurs and the nuclie in lower energy state flip to higher energy state .when this occurs the nucleus and the radio frequency are in resonance and this resonance is due to the magnetic properties of the nuclie ,it is called nmr.

The exact amount of energy needed for resonance depends up on the external magnetic field and on the nucleus irradiated

$$\Delta E = h\nu = \Upsilon h/2\pi . H_0$$

INSTRUMENTATION OF NMR

NMR spectrophotometermakes use of a magnet,a radio-frequency, a detector and an amplifier. The detection system is used to note that energy is being transferred from the radio –frequency beam to nucles.

The sample under investigation is taken in a glass tube which is placed between the polefaces of a magnet.A radio-frequency source (v=60mega cycles sec) is made to fall on the sample. It can be done by feeding energy (Radio frequency source) into a coil wound round the sample tube.A signal is detected if the nuclei in the sample resonates with the source,i-e., E, energy required to flip the protion is the same as that of the source.Energy is transferred from the source via nuclei to the detector coil. The output from the detector can be fed to a cathode ray oscillograph or to a strip chart recorder after amplication* etc.

Protons beieng in different electronic environments cant resonate at exactly 60 mega cycles sec . for practical purposes, radio-frequency source is held steady at the said frequency and field strength is varied by placing small electromagnet to the pole faces of the main magnet. By increasing the current flowing through these electromagnets, the total field strength is increased .

As the field strength increases, the precessional frequency of each proton increases until resonance radio-frequency source takes place.As aproton (or a set of equivalent protons) comes to resonance, the signalfrom the detector produces a peak on the chart paper. The nmr spectrum consists of series of series of peaks that correspond to different applied field strengths. Each peak means a set of protons.
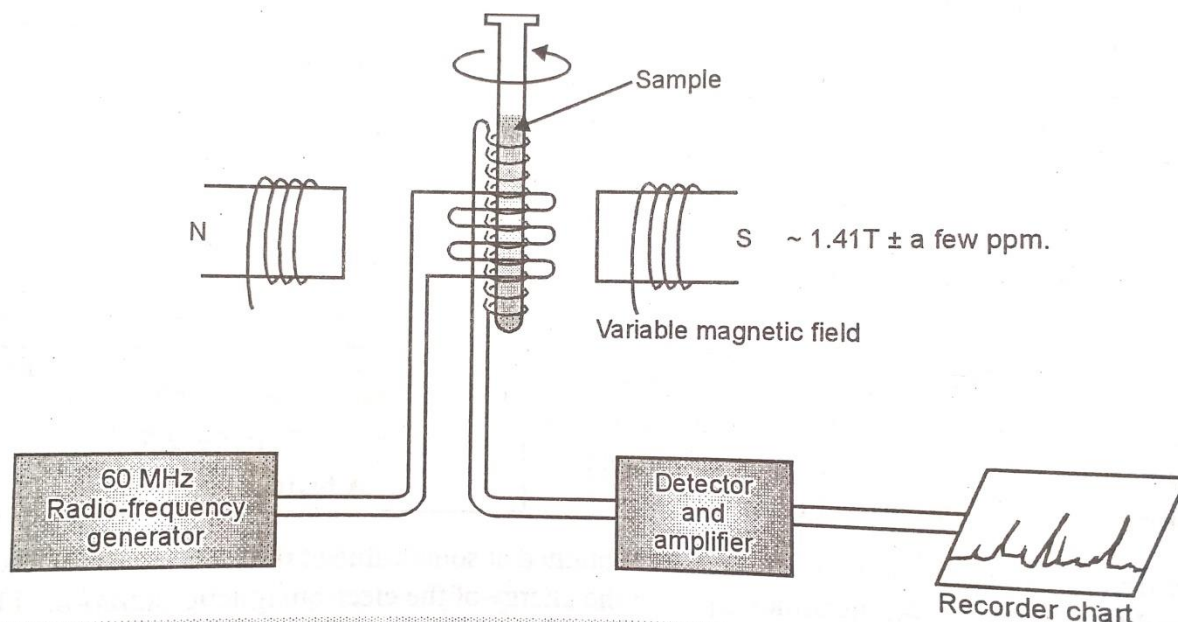

Positionof signals—shielding and deshielding

When a molecule is placed in a magnetic field to get its PMR spectrum, the applied magnetic field causes the circulation of electrons surrounding the protons. This circulation of electrons produces a secondary magnetic field called the induced magnetic field.This induced magnetic field may either oppose or reinforce the applied magnetic field.For example, circulation of electrons in sigma—bonds surrounding the protons, generates an induced fieldwhich opposes the applied magnetic field.
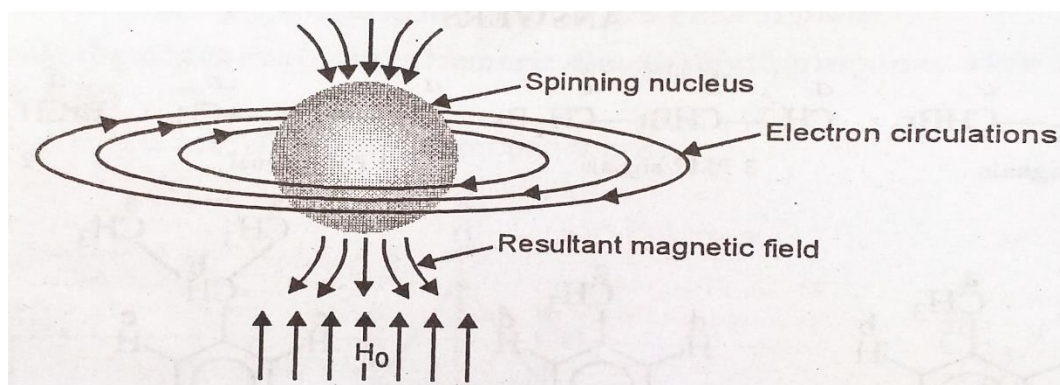
On the other hand, circulation of electrons particularly the π-electrons generates an induced field which may either oppose or reinforce the applied field acting upon a proton depending upon its location in the induced field. For example, circulation of π-electrons in benzene derivatives produces an induced field which reinforces the applied field.
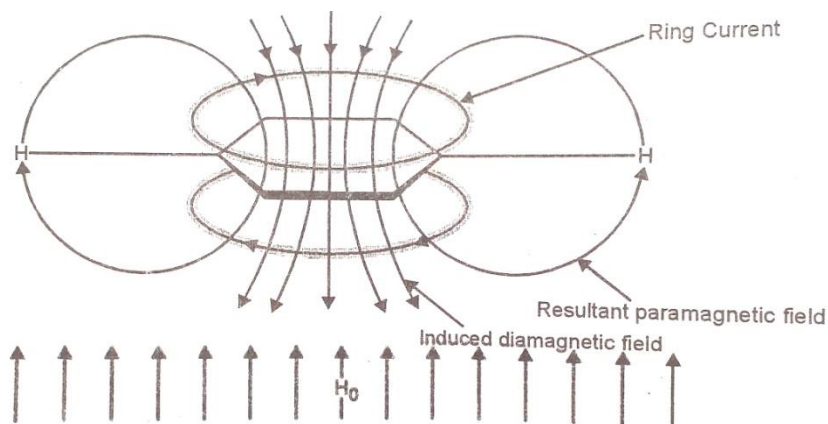
When the induced field opposes the applied field, the actual acting on the proton decreases and the proton is said to be shielded. In order, to get an absorption sisignal from the shielded proton decreaces and the proton is said to be shielded.In order to get an absorption signal from the shielded proton , the applied feild has to be increased somewhat to reach the same effective feild strength at which absorption occurs .Thus sheiklding shifts the absorption up field.On the other hand whebn the induced field reinforces the applied field ,the actual field acting on the proton increases an d the proton is said to be desheilded.

SPIN–SPIN SPLITTING

We have discussed the manner in which the chemical shift and the integral (peak area) can give nformation about the number and types of hydrogens contained in a molecule. A third type of information to be found in the NMR spectrum is that derived from the spin–spin splitting phenomenon. Even in simple molecules, one finds that each type of proton rarely gives a single resonance peak. For instance, in 1,1,2-trichloroethane there are two chemically distinct types of hydrogens

On the basis of the information given thus far, one would predict two resonance peaks in the NMR spectrum of 1,1,2-trichloroethane, with an area ratio (integral ratio) of 2:1. In reality, the high-resolution NMR spectrum of this compound has five peaks: a group of three peaks

(called a **triplet**) at 5.77 ppm and a group of two peaks (called a **doublet**) at 3.95 ppm. Figure 3.25 shows this spectrum. The methine (CH) resonance (5.77 ppm) is said to be split into a triplet, and the methylene resonance (3.95 ppm) is split into a doublet. The area under the three triplet peaks is 1, relative to an area of 2 under the two doublet peaks. This phenomenon, called **spin–spin splitting,** can be explained empirically by the so-called **_n_ + 1 Rule.** Each type of proton "senses" the number of equivalent protons (_n)_ on the carbon atom(s).

next to the one to which it is bonded, and its resonance peak is split into _(n_ + 1) components. Examine the case at hand, 1,1,2-trichloroethane, utilizing the _n_ + 1 Rule. First the lone methine hydrogen is situated next to a carbon bearing two methylene protons.

THE CHEMICAL SHIFT AND SHIELDING

Nuclear magnetic resonance has great utility because not all protons in a molecule have resonance at exactly the same frequency. This variability is due to the fact that the protons in a molecule are surrounded by electrons and exist in slightly different electronic (magnetic) environments from one another. The valence-shell electron densities vary from one proton to another. The protons are **shielded** by the electrons that surround them. In an applied magnetic field, the valence electrons of the protons are caused to circulate. This circulation, called a **local diamagnetic current,** generates a counter magnetic field that opposes the applied magnetic field. Figure 3.10 illustrates this effect, which is called **diamagnetic shielding** or **diamagnetic anisotropy.**

Circulation of electrons around a nucleus can be viewed as being similar to the flow of an electric current in an electric wire. From physics, we know that the flow of a current through a wire induces a magnetic field. In an atom, the local diamagnetic current generates a secondary, induced magnetic field that has a direction opposite that of the applied magnetic field.

EQUIVALENT AND NON EQUIVALENT PROTONS

Protons with different environments absorb at different field strength ,while protons which the same environment absorb at the same applied field strength..A set of protons are said to be equivalent if they have the same environment and non equivalent if they have the different environment .Since each set of equivalent protons produces a different signal, therefore the number of signals in an NMR spectrum tells us as to how many different sets of equivalent protons or how many types of protons are present in a molecule .

In most of the cases ,it is possible to predict the different types of protons in a molecule simply by looking at the molecule .but this is not always easy .therefore,we must devise a method by which we can accurately tell as to how many kinds of protons are present in a molecule .

Let us now illustrate this method by considering a few examples.

(1) The molecule of ethyl chloride (CH_3—CH_2—C1) contains three methyl and two methylene protons. Replacement of a methyl proton would give ZCH_2—CH_2C1 and replacement of a methylene proton will give CH_3—CHZ—C1.These are obviously different products. Therefore methyl protons are not equivalent to methylene protons. However, it may be noted that the three methyl protons are equivalent amongst themselves since the replacement of any one of them gives the same products i-e. ZCH_2—CH_2C1.
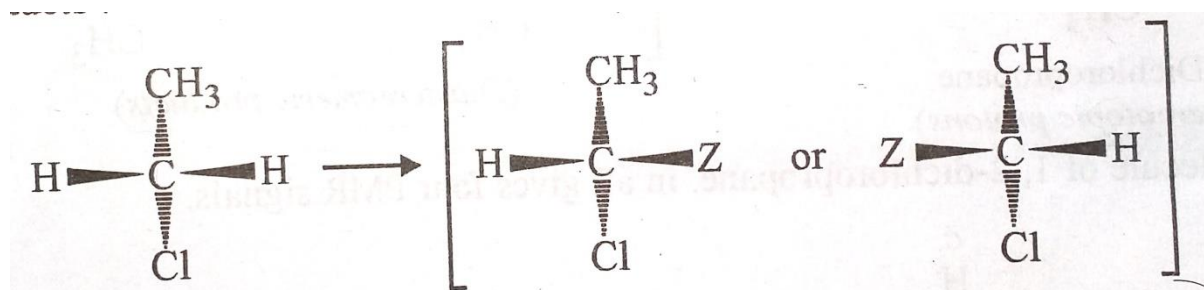
On the other hand , replacement of either of the two methylene protons would give of the two enantiomeric products:

(2) Let us now consider a molecule of 2-bromopropene. It has three methyl and two vinylic protons. The three methyl protons are obviously equivalent among themselves since replacement of each one of them gives the same product. On the other hand, replacement of either of the vinylic protons produces one of pair of diastereomeric products

2–Bromopropene   Deasterromers
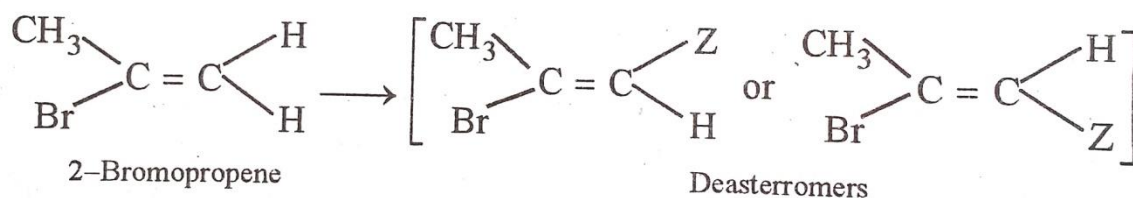
Coupling constant. The distance between two adjacent peaks in a multiplet is called couling constant .It is a quantitive measure of the effectiveness of the spin-spin coupling.It is denoted by the term J and the coupling constant between two protons marked ^{Ha} and H^b is represented by J_{ab} .the value of the coupling is represent in terms of Hertz.

If a compound has two mutually coupled protons ,then the coupling due to splitting of one proton by the other is same asthe coupling constant due to splitting of the second proton by the first .In other words mutually coupled protons have the same numerical value of the coupling constant.

Magnitude of the coupling constant

The magnitude of the coupling constant depends up on the number and the kind of interveining bonds and the spatial relations between the protons is as under.

1.**Geminal protons**.For equivalent proton attached to the same carbo atom i.e, germinal protons j varies with bond angle and over all structure of the molecule from 0-20 Hz.For example .,

2.Vinical coupling.For proton attached to adjacent carbons atoms i.e, vicinal protons,j value varies from 2-18Hz depending up on positions of protons in space and the structure of the molecule.
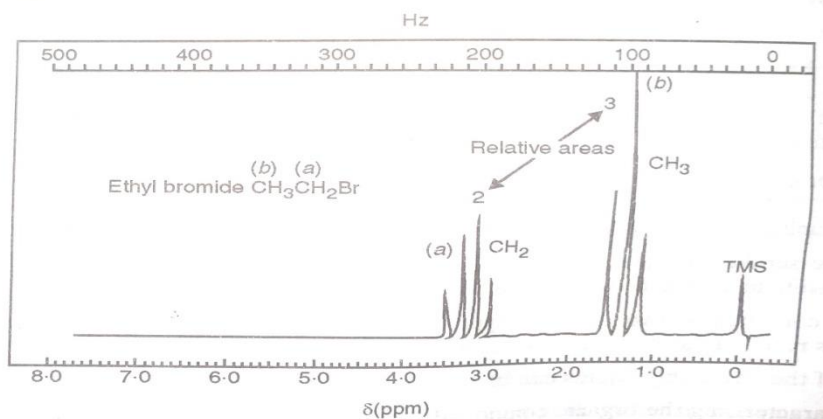

3.Vinylic protons.In vinylic protons when restriction of bonds is restricted due to double bonds , the cis protons have j= 6-12, while the trans proton have j=11-18

PMR OF SOME COMPOUNDS

ETHYLBROMIDE

1. Ethyl bromide CH_3CH_2Br
PMR Spectrum

Data obtained.the spectrum contains two peaks

 (a) Triplet δ 1.7,3H (CH_3)

 (b) Quartet δ 3.42H (CH_2)

Iterpretation of the data .On the right hand side of the spectrum there is standarad peak for TMS of δ 0.00

Ethyl bromide contains two types of protrons a and b .Due to negative effect of bromine atoms the a, protons are desheilded and give a signakl at low faield the quartet $^\delta$ 3.4 is from magnetically equivalent methylene protons which are coupled with three protons resulting in a down field quartlet because of desheilding effect of bromine

The b, protons are shielded by three C-H bonds and two methylene protons to give a signal in a high magnetic field

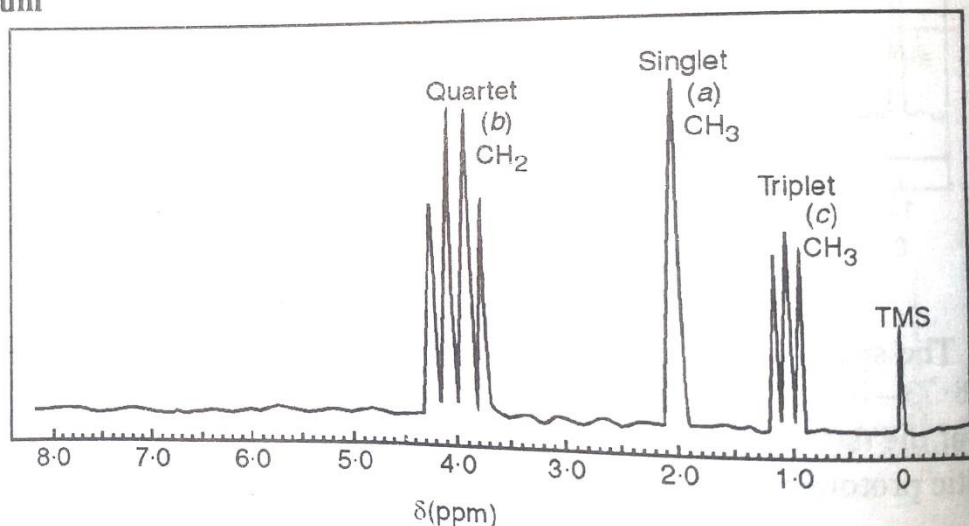# 1,1,2.Tribromoethane

5. 1, 1, 2-Tribromoethane, $CH_2Br - CHBr_2$
PMR Spectrum
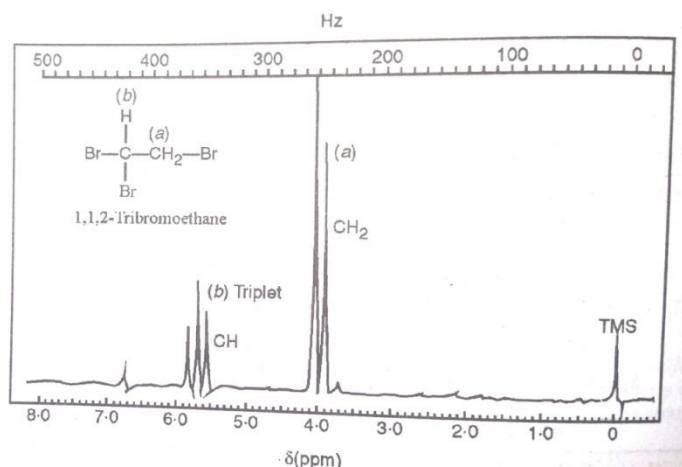
PMR OF ETHYL ACETATE

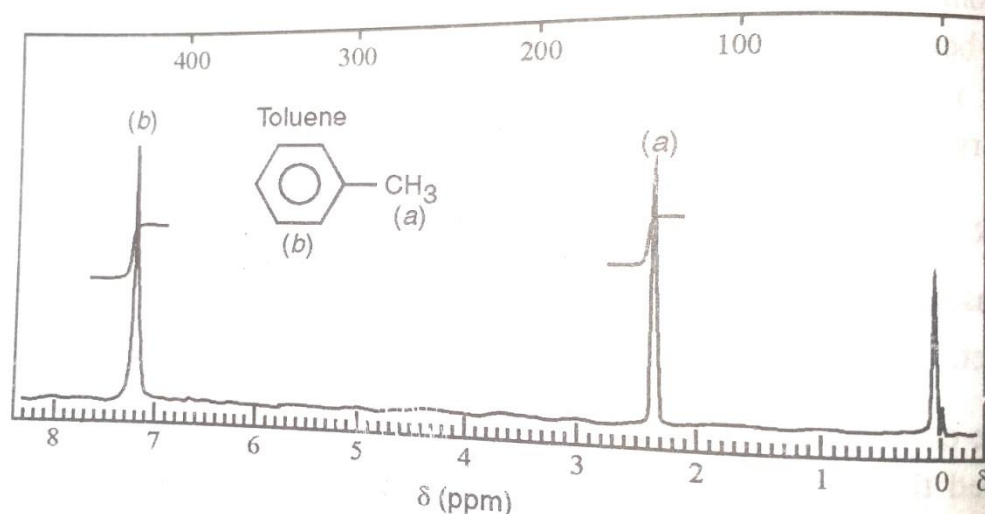11. Ethyl acetate $(CH_3-\overset{\overset{O}{\|}}{C}-OCH_2CH_3)$
PMR Specetrum

PMR OF TOLUENE

8. Toluene ⬡—CH₃
PMR Spectrum

Toluene

PMR OF ETHANOL

CH_3-CH_2-OH
  a   b   c
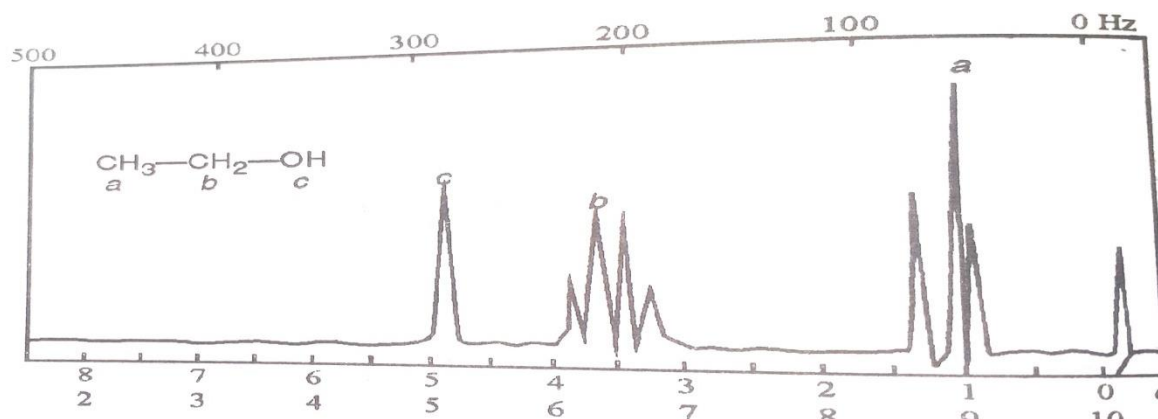
APPLICATIONS OF PMR SPECTROSCOPY

PMR spectroscopy has been extremely useful in the study of organic chemistry. Some of its important applications are discussed below;

1.IDENTIFICATION OF SUBSTANCES. Lie IR spectrum, PMR spectrum can also be used as a fingerprint of the substances. If the PMR spectru of a given sample is exactly the same as that of a known compound, the given compound must be identical with the knwon compound.

2.DERTERMINATION OF MOLECULAR STRUCTURE. PMR spectra are often very complex. But this this complexity is not a disadvantage butis often useful in determing the molecular structure since it makes the spectra characterteristic.

3.**Identification of reaction products**.whwere ever in reaction ,two or more products are theortically possible.PMR spectroscopy has been used to identity the actual product .

4.**Distinction between geometrical isomers** .PMR spectroscopy can be used to distinguish between cis and trans isomers the distinction is based up on the magnitude of coupling constant.

5.**Distinction between inter and intramolecular hydrogen bonding** .During H-bonding transfer of electrons occurs from the hydrogen atom to the neighboring electronegative atoms .As a result hydrogen bonded hydrogen gets deshielded.