



PROTON NUCLEAR MAGNETIC RESONANCE (PMR OR ^1H NMR) SPECTROSCOPY

1.0 INTRODUCTION

Similar to UV-visible and IR spectroscopy, nuclear magnetic resonance (NMR) spectroscopy is also an absorption spectroscopy in which samples absorb electromagnetic radiation in the radio-frequency region (3 MHz to 30,000 MHz) at frequencies governed by the characteristics of the sample. As the name itself implies, **NMR spectroscopy** involves nuclear magnetic resonances which depend on the magnetic property of atomic nuclei. Thus, NMR spectroscopy deals with nuclear magnetic transitions between magnetic energy levels of the nuclei in molecules. NMR signals were first observed in 1945 independently by Purcell at Harvard University and Bloch at Stanford University. The first application of NMR to the study of structure was made in 1951 and ethanol was the first compound thus studied. In 1952, Purcell and Bloch won the Nobel Prize in Physics for their discovery. NMR spectroscopy is more useful for structure elucidation of organic compounds than UV-visible and IR spectroscopy.

There are about 100 isotopes for which NMR spectroscopy is possible, but the most commonly used by organic chemists are proton nuclear magnetic resonance (PMR or ^1H NMR) spectroscopy and carbon-13 (^{13}C NMR) spectroscopy. This chapter deals with PMR spectroscopy.

1.1 THEORY

Some atomic nuclei possess a mechanical spin, *i.e.*, they have angular momentum. The total angular momentum of a spinning nucleus depends on its spin or spin number I (also called as nuclear spin quantum number). The nuclear spin quantum number may have values 0, 1/2, 1, 3/2, 5/2, etc. depending on the mass number and atomic number of the atom as shown in Table 1.1. If the mass number is odd, then spin number I is a half integer ($n + 1/2$, where n is a whole number or zero). If the mass number and the atomic number are both even, the spin number I is zero. If the mass number is even and the atomic number is odd, the I is an integer (1, 2, 3, etc.). Examples of various kinds of nuclei are given in Table 1.1.

The nuclei with either odd mass number or odd atomic number (*i.e.*, nonzero spin number I) possess a mechanical spin and only such nuclei can exhibit a nuclear magnetic resonance spectrum.

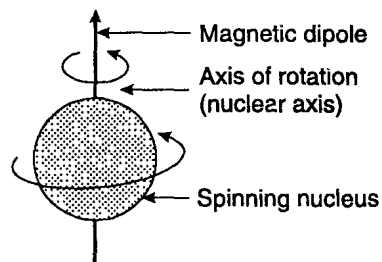


Fig. 1.1. Spinning nucleus and generated magnetic dipole.

Table 1.1 Spin number of I of some nuclei

Mass number	Atomic number	Spin number I	Examples
Odd	Odd or even	$\frac{1}{2}$	^1H , ^{13}C , ^{15}N , ^{19}F , ^{31}P
		$\frac{3}{2}$	^{11}B , ^{35}Cl , ^{37}Cl , ^{79}Br , ^{81}Br
		$\frac{5}{2}$	^{127}I , ^{17}O
Even	Even	Zero (no spin)	^{12}C , ^{16}O , ^{32}S , ^{34}S
Even	Odd	1	^{14}N , ^2H (or D)
		3	^{10}B

It is well known that circulation of a charge generates an electric current which is associated with a magnetic field. Since all atomic nuclei have a positive charge, spinning nuclei generate a magnetic dipole (*i.e.*, north and south poles) along the axis of rotation, *i.e.*, the nuclear axis. Thus spinning nuclei behave like a very small bar magnet with a magnetic moment μ .

In the absence of an external magnetic field, the magnetic nuclei (nuclear magnetic dipoles) are randomly orientated as shown in Fig. 1.2.

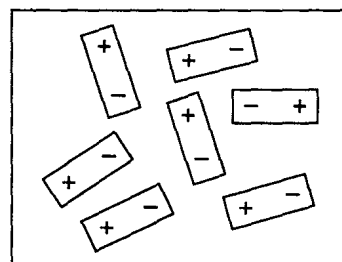


Fig. 1.2. Orientation of nuclear magnetic dipoles in the absence of an external magnetic field.

When a magnetic nucleus with spin number I is placed in a uniform magnetic field H_0 , its magnetic dipole or magnetic moment may assume any one of $2I+1$ orientations with respect to the direction of the applied magnetic field (H_0) and the system is said to be quantized. The most important nuclei for organic chemists are ^1H and ^{13}C . For both of these, $I = 1/2$, hence number of orientations for their magnetic dipoles will be $2 \times \frac{1}{2} + 1 = 2$ (because number of orientations = $2I + 1$). Thus, the magnetic dipoles of nuclei with $I = 1/2$, *e.g.*, ^1H and ^{13}C will align parallel or antiparallel to the applied magnetic field, *i.e.*, with or against the applied magnetic field, respectively, as shown in Fig. 1.3.

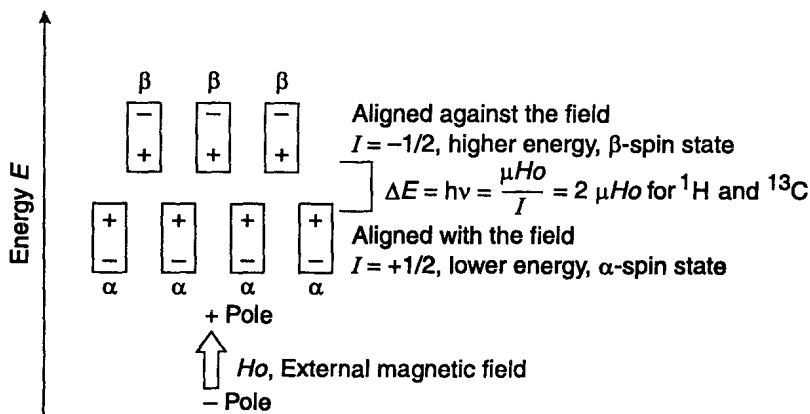


Fig. 1.3. Orientation of nuclear magnetic dipoles in an external magnetic field H_0 .

The alignment with the applied magnetic field is of lower energy and corresponds to the α -spin state (+ 1/2) of the nucleus, and the alignment against the applied magnetic field is of higher energy and corresponds to the β -spin state ($-\frac{1}{2}$) of the nucleus. As the energy difference between the two orientations is very small, the alignment with the field will be slightly more favourable energetically than alignment against the field, and there will be a slight excess of nuclei in the lower energy state, *i.e.*, in the more favourable orientation. It is this very small excess of nuclei in the lower energy state which gives rise to the possibility of introducing transitions between the two orientations, (*i.e.*, observation of NMR phenomenon) if the proper amount of energy is supplied. The function of radiowaves is to supply the energy (ΔE) necessary to change the orientation of the nuclear spin (often called the “flipping” of the spin). The disturbed equilibrium is re-established when this absorbed energy is returned to the environment as heat (Fig. 1.4) through relaxation processes (Section 1.2).

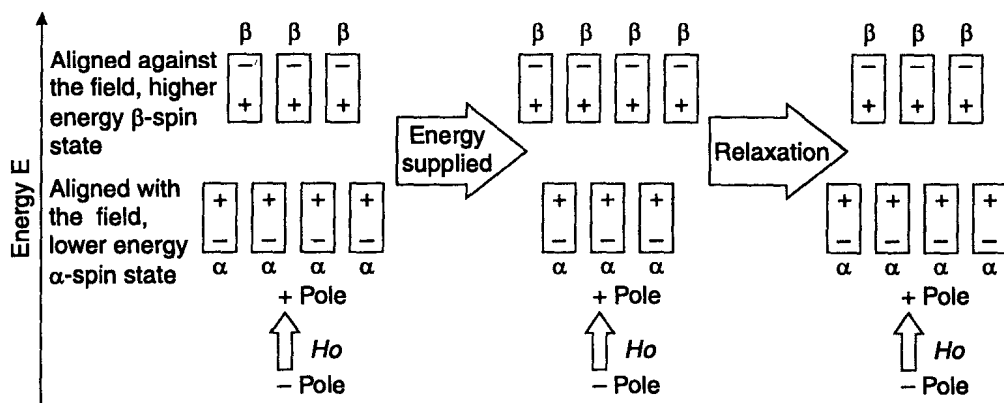


Fig. 1.4. Absorption of energy (ΔE) flips a nuclear spin, converting the lower energy orientation into the higher one.

The energy difference ΔE (*i.e.*, the energy required for a transition) depends on the applied magnetic field H_0 . The following fundamental NMR equation correlates the electromagnetic frequency ν for the transition in a given field H_0 :

$$\nu = \frac{\gamma H_0}{2\pi}$$

or

$$\nu \propto H_0 \tag{1.1}$$

where γ is magnetogyric ratio (or gyromagnetic ratio) which is a fundamental nuclear constant.

The magnetic moment μ of a spinning nucleus behaving like a very small bar magnet is directly proportional to its spin number I . It has been shown that :

$$\gamma = \frac{2\pi\mu}{hI} \tag{1.2}$$

where h is Planck's constant. Magnetogyric ratio, γ , is the proportionality constant between μ and I .

From eqn. 1.1, and 1.2,

$$\begin{aligned} \nu &= \frac{\gamma H_0}{2\pi} = \frac{2\pi\mu}{hI} \cdot \frac{H_0}{2\pi} \\ &= \frac{\mu H_0}{hI} \end{aligned}$$

or

$$h\nu = \Delta E = \frac{\mu H_0}{I} \tag{1.3}$$

For ^1H and ^{13}C , $I = \frac{1}{2}$, hence

$$h\nu = \Delta E = 2\mu H_0$$

or

$$\nu = \frac{2\mu H_0}{h} \quad \dots(1.4)$$

Equation 1.3 shows that the energy required for a transition (ΔE) is directly proportional to the strength of the applied magnetic field (because $\frac{\mu}{h}$ is constant for a given nucleus). This is shown graphically in Fig. 1.5. The stronger the field, the greater will be the tendency of the nuclear magnetic dipoles to remain aligned with it and higher will be the energy required for a transition.

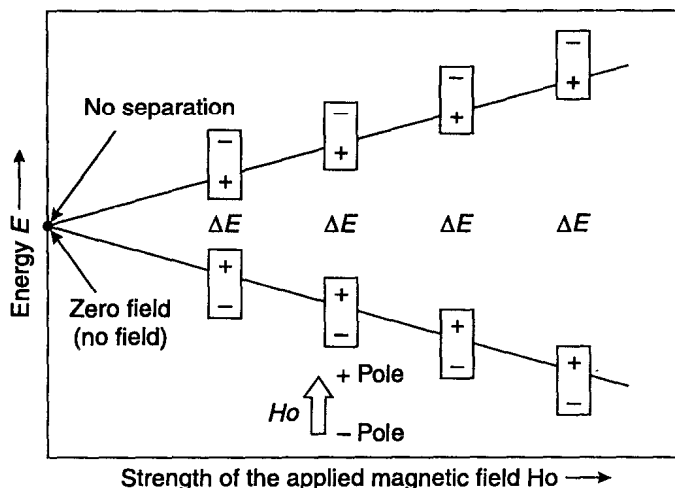


Fig. 1.5. Relationship between the transition energy ΔE and the applied magnetic field H_0 .

The transition from one spin state to the other is called **flipping** of the nuclear spin. The energy involved in this transition is about 10^{-6} kcal/mole. The energy required for resonance depends on the strength of the applied external magnetic field and on the isotope brought into resonance (eqn. 1.3). A frequency of 60 MHz is needed at a magnetic field H_0 of 14,092 gauss of ^1H nuclei (protons) to bring them into resonance (or any other desired combination in the same ratio; this comes from eqn. 1.4). At the same field strength, an electromagnetic radiation of frequency 15 MHz brings ^{13}C nuclei into resonance. These frequencies are in the radio-frequency region of the electromagnetic spectrum. A field strength of 14,092 gauss can be expressed as its equivalent 60 MHz. For flipping the nuclear spin to its higher energy level, most commonly the radio frequency (oscillator frequency) is kept constant and H_0 is varied, although this can also be done by varying the radio frequency and keeping H_0 constant.

According to the theory of electromagnetic radiation, the probability of absorption or emission of energy is equal, i.e., the probability of an upward and a downward transition is equal. Also, a spontaneous transition from a high energy state to a lower energy state is negligible in the radio-frequency region because ΔE is very low (about 10^{-6} kcal/mole). Thus, for all practical purposes NMR is a ground-state phenomenon. Therefore, if two possible spin states in a collection of nuclei were exactly equally populated, the probability of an upward transition (absorption) would be exactly equal to a downward transition (emission) and there would be no NMR effect. Under ordinary conditions in a magnetic field, however, there is slight excess of nuclei in the lower spin state (low energy orientation), i.e., the nuclei take up Boltzmann distribution (under ordinary conditions the

Boltzmann factor is about 0.001%). It is this very small excess of nuclei in the lower energy state which gives rise to net absorption of energy in the radio-frequency region, *i.e.*, the NMR phenomenon.

As the collection of nuclei continually absorbs radio-frequency radiation, the excess of nuclei originally in a lower energy state may diminish and so the intensity of the absorption signal may diminish or vanish entirely. *When the population of nuclei between the two spin states becomes equal, there will be no NMR effect, such a phenomenon is known as saturation.*

1.2 RELAXATION PROCESSES

The radiationless transitions by which a nucleus in an upper spin state returns to a lower spin state are called relaxation processes. These maintain an excess of nuclei in a lower energy state which is the necessary condition for the observation of NMR phenomenon. There are two types of relaxation processes :

- (i) Spin-spin or transverse relaxation or T_1 relaxation
- (ii) Spin-lattice or longitudinal relaxation or T_2 relaxation

(i) Spin-spin or Transverse Relaxation : *It involves mutual exchange of spins by two nuclei in close proximity to each other, i.e., the transfer of energy from one high energy nucleus to another. There is no net loss of energy and this relaxation process shortens the lifetime of an individual nucleus in the higher spin state but does not contribute to the maintenance of the required excess of nuclei in a lower spin state.*

The spectral line width is inversely proportional to the lifetime of the excited state (*i.e.*, higher energy state). The shorter the lifetime of the excited state, the greater is line width. An efficient relaxation process involves shorter time (T_1) and results in broadening of the absorption peak. The spin-spin relaxation contributes to line broadening. Solids and very viscous liquids usually provide properly oriented nuclei in lower spin state which may exchange spins in higher spin states, so spin-spin relaxation times are very short. Thus, the spin-spin relaxation causes line broadening of such a magnitude that NMR spectra of solids become of little interest to organic chemists.

(ii) Spin-lattice or Longitudinal Relaxation : *It involves the transfer of energy from the nucleus in its higher energy state to its environment, i.e., to the molecular lattice (framework of molecules).* The energy in this process is transferred to the components of the lattice as additional translational, rotational and vibrational energy. Thus, the temperature of the system rises slightly, that is why samples are heated up during recording of NMR spectrum. The total energy of the system remains unchanged. *This relaxation process maintains an excess of nuclei in a lower state which is the necessary condition for the observation of NMR phenomenon.*

The spin-lattice relaxation process also contributes to the width of a spectral line. In solids and viscous liquids, molecular motions are greatly restricted, so properly oriented nuclei which may effect spin-lattice relaxation are present relatively infrequently. Thus, most solids and viscous liquids exhibit very long spin lattice relaxation times. Relaxation times for most nonviscous liquids and solids in solution are of the order of one second; this gives rise to a natural line width of about 1 cps. Other factors, like the presence of paramagnetic molecules (*e.g.*, O_2) or ions in the sample also cause the line broadening. Resonance signals for protons attached to an element that has an electric quadrupole moment* will frequently be broadened.

1.3 INSTRUMENTATION

A schematic diagram of an NMR spectrometer is given in Fig. 1.6. The instrument contains the following components :

* Nuclei with a spin number ≥ 1 have a nonspherical charge distribution. This asymmetry is described by an electrical quadrupole moment.

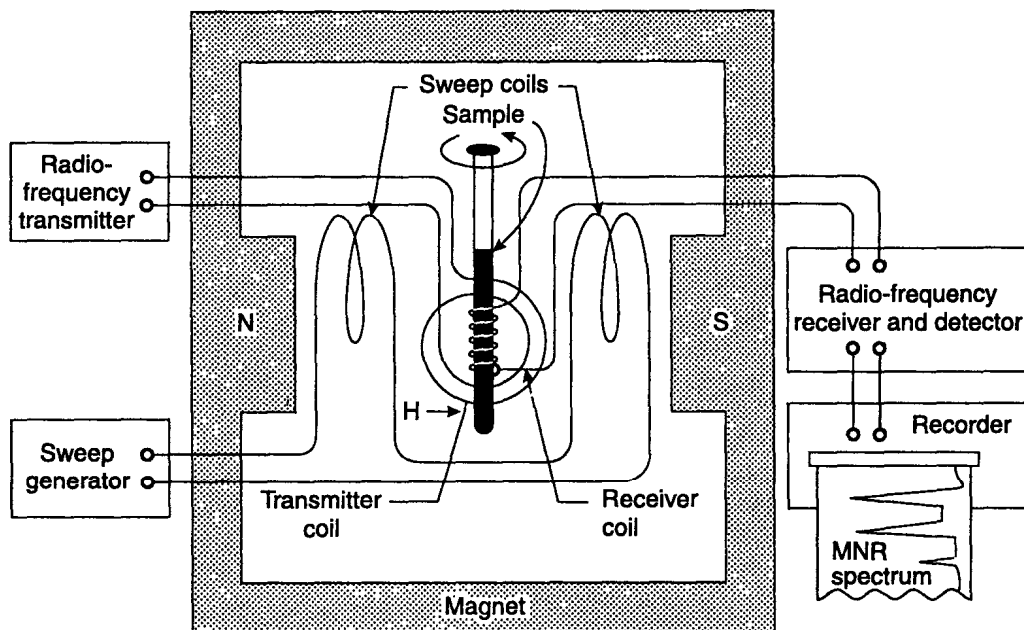


Fig. 1.6. Schematic diagram of an NMR spectrometer.

- (i) A strong magnet with homogeneous field—The strength of its field can be varied continuously and precisely over a relatively narrow range with the help of the sweep generator.
- (ii) A radio-frequency oscillator
- (iii) A radio-frequency receiver and detector
- (iv) A recorder, calibrator and integrator
- (v) A sample holder—It spins the sample to increase the homogeneity of the magnetic field on the sample, and keeps the sample in the proper position with respect to the main magnetic field, the radio frequency oscillator and receiver coils.

The sample under investigation is taken in a glass tube and placed in the sample holder. Most commonly, NMR spectrometers irradiate the sample with a beam of constant radio frequency obtained from the radio-frequency oscillator, while the magnetic field strength is varied with the help of the sweep generator. ΔE varies as the H_0 varies (eqn. 1.3). At the field strength, when ΔE becomes equal to the energy of the incident radio frequency, absorption of energy takes place and transition from a lower spin state to a higher spin state occurs. This causes a tiny electric current to flow in the coil of the radio frequency receiver which is amplified and recorded as a signal on the chart paper by the recorder. An NMR spectrum is recorded as a plot of a series of peaks (signals) corresponding to different applied field strengths against their intensities. *Each peak represents a set (a kind) of protons (in case of a PMR spectrum). The areas under the peaks (the intensities of the peaks) are directly proportional to the number of protons they represent.* An electronic integrator traces a series of steps whose heights are proportional to the peak areas, i.e., the number of protons represented by that particular peak. A typical PMR spectrum is given in Fig. 1.7.

PMR spectra are usually run at 60 MHz (corresponding to field of 14,092 gauss). Now high resolution instruments* are available which operate at 100 MHz (corresponding to the field of 23,486 gauss) or even higher (as high as 500 MHz). By measuring frequency shifts from a reference marker (usually tetramethylsilane, TMS), an accuracy of ± 1 Hz can be achieved.

* Instruments having ability to discriminate among the individual absorptions.

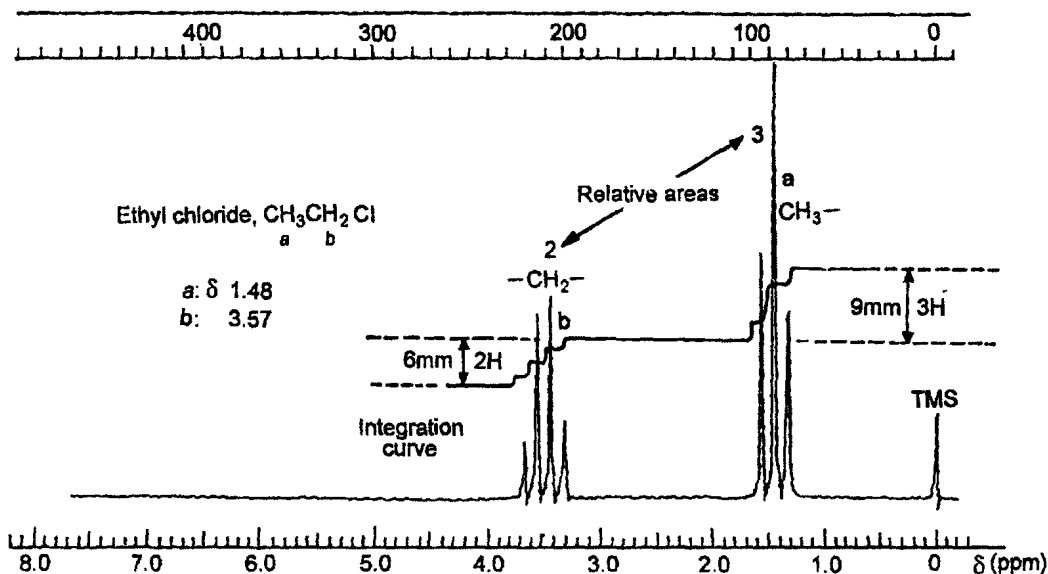


Fig. 1.7. PMR spectrum of ethyl chloride in CDCl_3 at 60 MHz.

1.4 SAMPLE HANDLING

Ordinarily, about 0.4 ml of a neat liquid or 10-50 mg of a liquid or solid dissolved in 0.4 ml of a deuterated solvent is used. The sample is contained in a glass tube with 5 mm outside diameter and about 15 cm length. The ideal solvent should contain no protons, be inexpensive, low boiling, nonpolar and inert. Carbon tetrachloride is an ideal solvent if the compound under study is sufficiently soluble in it. Almost all of the common solvents are available in the deuterated form, *e.g.*, deuterated chloroform CDCl_3 (chloroform-*d*), hexadeuteroacetone CD_3COCD_3 (acetone-*d*₆), hexadeuterodimethyl sulphoxide CD_3SOCD_3 (DMSO-*d*₆), hexadeuterobenzene C_6D_6 (benzene-*d*₆), D_2O , etc. It should be noted that deuterium (^2H or D) has a nuclear magnetic dipole and thus, it should exhibit an NMR signal in the spectrum. Since it does so only under different applied field strength and oscillator frequency, its NMR signal does not appear in the PMR spectra.

1.5 SHIELDING, DESHIELDING AND CHEMICAL SHIFT

Under the influence of the applied magnetic field, electrons surrounding a nucleus start to circulate perpendicular to the applied magnetic field H_0 and so they generate a secondary magnetic field called as induced magnetic field (σH_0) which opposes the applied magnetic field in the region of the nucleus (*e.g.*, proton) (Fig. 1.8). Thus, the nucleus experiences a weaker magnetic field (H_{eff}) than the applied magnetic field (H_0), and it is said to be *shielded*. This type of shielding is termed diamagnetic shielding and its effect is termed as *shielding effect*.

$$H_{\text{eff}} = H_0 - \sigma H_0$$

where σ is screening or shielding constant.

The magnitude of the induced field is directly proportional to the magnitude of the applied field H_0 . *The higher the electron density around the proton, the higher is the diamagnetic shielding.* Circulation of electrons about nearby nuclei generates an induced magnetic field that can either oppose or reinforce the applied field at the proton,

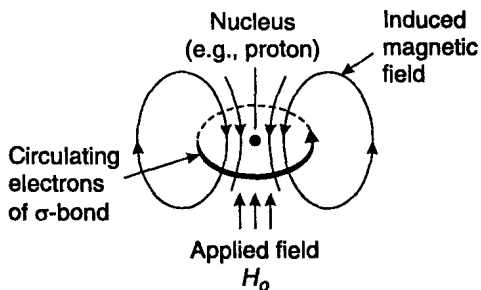


Fig. 1.8. Diamagnetic shielding at nucleus by circulating electrons.

depending on its location in the induced magnetic field (see, anisotropic effect, Section 1.7b). *If the induced field opposes the applied field in the region of proton, then the proton is shielded* as mentioned above. *If the induced field reinforces the applied field, then the field experienced by the proton is greater than the applied field. Such a proton is said to be deshielded and this effect is termed as deshielding effect.* Compared to a naked proton, a shielded proton requires a higher applied field strength, whereas a deshielded proton requires a lower field strength for transition. Thus, shielding shifts the absorption position upfield, whereas deshielding shifts the absorption position downfield and these effects are termed as shielding and deshielding effects, respectively. Such shifts in the NMR absorption positions are called *chemical shifts* because they arise from the circulation of electrons in chemical bonds. The *chemical shift is expressed as the difference between the absorption position of a particular proton and the absorption position of a reference proton.* Due to varying electronic environment of the proton or group of protons their absorption signals appear at different field values. Thus, signals in PMR spectra give information about the different kinds of protons and their environments in molecules.

Why are the NMR absorption positions expressed relative to a reference compound?

The exact frequency values or field values cannot be calibrated with an accuracy of about ± 1 Hz out of about 60×10^6 Hz because the instrument required must be able to discriminate frequencies of the order of one part in 10^8 . Thus, the absolute positions of absorptions cannot be obtained directly from the instrument as in UV and IR spectroscopy. However, relative proton frequencies can be determined with an accuracy of ± 1 Hz. *For this reason, positions of absorption signals are always expressed relative to a reference compound (most commonly tetramethylsilane, TMS), i.e., as chemical shifts.* For practical reasons, the signal from a naked proton is not used as the reference point.

Why is TMS a good reference compound in NMR spectroscopy?

Tetramethylsilane, $(\text{CH}_3)_4\text{Si}$ (TMS), is the most commonly used reference compound because it has following advantages :

- (i) It is chemically inert, hence does not react with compounds under study.
- (ii) It is volatile (b.p. 27°C), hence precious samples may be easily recovered after recording the spectra.
- (iii) It gives a single, sharp and intense absorption peak because its all the twelve protons are equivalent. Thus, its very small amount (1-2 drops) are needed.
- (iv) Its protons absorb at higher field than that of almost all organic compounds, hence overlapping of signals does not occur. The protons of TMS are more shielded due to +I effect of Si which increases electron density around them, hence they absorb at upfield.
- (v) It is not involved in intermolecular association with the sample or solvent, hence the absorption position of its protons remain unchanged.
- (vi) It is soluble in most of the organic liquids.

TMS is usually used as an internal reference. Since it is insoluble in water and D_2O , it cannot be used as internal reference with these solvents. However, it can be used as an external reference, i.e., it is sealed in a capillary and immersed in such solutions.

Sometimes DSS (sodium 2, 2-dimethyl-2-silapentane-5-sulphonate, $(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{SO}_3\text{Na}$, is used as an internal reference in aqueous solutions. This reference compound has disadvantage that it is nonvolatile and has absorptions other than CH_3Si . Any other water-soluble compound may be used as a standard in aqueous solutions, e.g., acetone, dioxane, *t*-butyl alcohol, etc.

1.6 MEASUREMENT OF CHEMICAL SHIFT-NMR SCALE

We can express the chemical shifts in terms of Hz by setting the TMS peak at 0 Hz at the right-hand edge. The magnetic field decreases towards left. When chemical shifts are given in Hz (designated ν), the applied frequency must be specified (e.g., 60, 90, 100, 200, etc. MHz) because the

chemical shift in Hz is directly proportional to the strength of the applied field H_0 and therefore to the applied frequency. The value of Chemical shift in Hz, *i.e.*, ν is $\nu_s - \nu_r$, where ν_s and ν_r are the absorption frequencies of the sample and the reference in Hz, respectively.

Instruments with different field strengths (*e.g.*, 60, 90, 100, 200, etc. MHz) are available, hence it is desirable that chemical shifts be expressed in some form independent of the field strength. *The chemical shifts are commonly expressed in δ unit which is a proportionality and thus dimensionless.* It is independent of the field strength. Chemical shift values in Hz are converted into δ units as follows :

$$\delta \text{ or ppm} = \frac{\text{Chemical shift in Hz (i.e., } \nu)}{\text{Oscillator frequency in Hz}} \times 10^6$$

Oscillator frequency is characteristic of the instrument, *e.g.*, a 60 MHz instrument has an oscillator frequency 60×10^6 Hz. The factor 10^6 is included in the above equation simply for convenience, *i.e.*, to avoid fractional values. Since δ , which is dimensionless, is expressed in parts per million, expression ppm is often used.

Thus, a peak at 60 Hz (ν 60) from TMS at an applied frequency 60 MHz would be at δ 1.00 or 1.00 ppm.

$$\delta \text{ or ppm} = \frac{60}{60 \times 10^6} \times 10^6 = 1.00$$

The same peak at an applied frequency of 100 MHz would be at 100 Hz (ν 100) but would still be at δ 1.00 or 1.00 ppm.

$$\delta \text{ or ppm} = \frac{100}{100 \times 10^6} \times 10^6 = 1.00$$

The δ unit has been criticized because δ values increase in the downfield direction; the reply is that these are really negative numbers. In the other commonly used unit, a value of 10.00 is assigned to TMS peak. This unit expresses chemical shifts in τ value :

$$\tau = 10.00 - \delta$$

It should be noted that δ is treated as a positive number. Shifts at higher field than TMS are rare. If such shifts are present, their δ values are shown with a negative sign and τ values increase numerically, *e.g.*, $\delta - 1.00$ will be equal to τ 11.00. Fig. 1.9 shows various NMR scales.

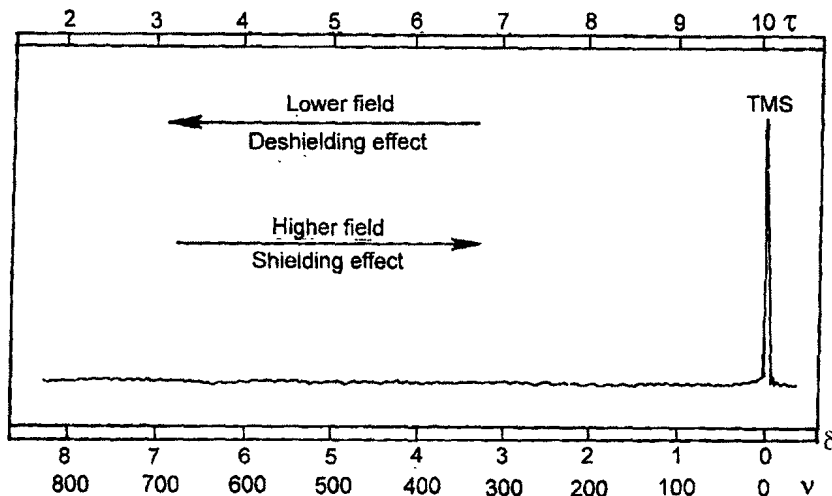


Fig. 1.9. NMR scales.

Example 1. Protons of a compound exhibit an NMR signal at δ 2.5. What will be the value of chemical shift of these protons in Hz if the spectrum is recorded on a 60 MHz spectrometer?

Solution :

$$\delta = \frac{\text{Chemical shift in Hz}}{\text{Oscillator frequency in Hz}} \times 10^6$$

Suppose the chemical shift in Hz is x , therefore according to the question :

$$2.5 = \frac{x}{60 \times 10^6} \times 10^6$$

\therefore

$$x = 2.5 \times 60 = 150 \text{ Hz}$$

Example 2. If the observed chemical shift of a proton is 200 Hz from TMS and instrument frequency is 60 MHz, what is the chemical shift in terms of δ ? Express it in τ value also.

Solution :

$$\delta = \frac{\text{Chemical shift in Hz}}{\text{Oscillator frequency in Hz}} \times 10^6$$

$$= \frac{200}{60 \times 10^6} \times 10^6 = 3.33$$

$$\tau = 10.00 - \delta$$

$$\tau = 10.00 - 3.33 = 6.67$$

The approximate chemical shift ranges of important chemical classes are given in Chart 1.1.

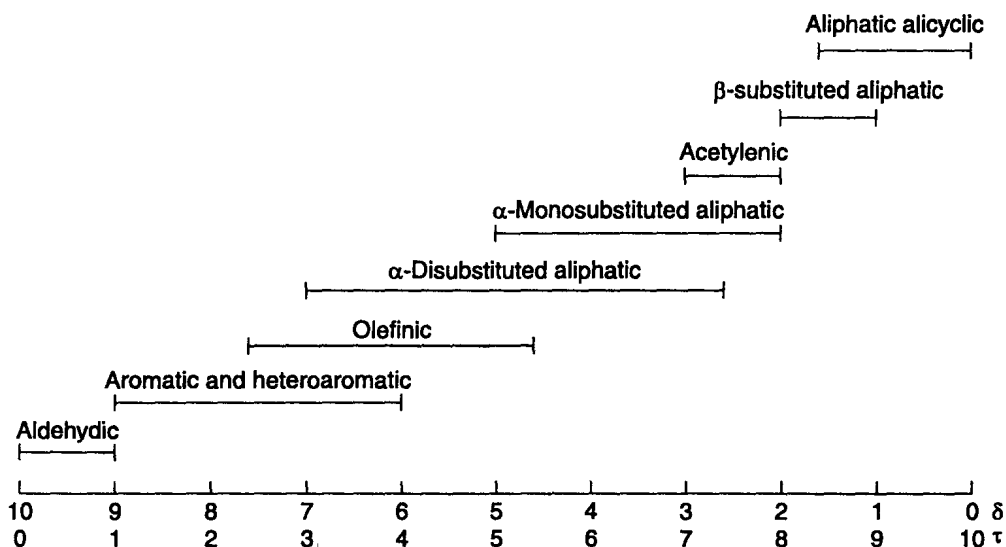


Chart 1.1. General regions of chemical shifts.

1.7 FACTORS AFFECTING CHEMICAL SHIFT

Any factor which is responsible for shielding or deshielding of a proton will affect its chemical shift. The following are the factors which affect the chemical shift :

- Electronegativity-inductive effect
- Anisotropic effects
- Hydrogen bonding
- van der Waals deshielding

(a) **Electronegativity—Inductive Effect :** The degree of shielding depends on the electron density around the proton. The higher the electron density around a proton, the higher the

shielding and the higher the field (lower the δ value) at which the proton, absorbs. Thus, the electron density around a proton successfully correlates with its chemical shift.

A nearby electronegative atom withdraws electron density (due to $-I$ effect) from the neighbourhood of the proton, so the NMR signal of such deshielded proton (the proton surrounded by less electron density) will appear downfield (higher δ value). Thus, the greater the electronegativity of the atom, the greater is the deshielding of the proton. For example, the chemical shifts (in δ un) of protons of methyl halides (CH_3F , CH_3Cl , CH_3Br , CH_3I : 4.26, 3.05, 2.68, 2.16, respectively) are in accordance with the electronegativity of the halogen attached to the methyl group, *i.e.*, the greater the electronegativity of the halogen attached to the methyl group, the lower is the field (higher δ values) at which the PMR signal of its protons appears. Similarly, the chemical shifts of protons of the methyl group attached to carbon, nitrogen and oxygen (*e.g.*, $\text{CH}_3\text{C}-$, $\text{CH}_3\text{N} <$, $\text{CH}_3\text{O} <$: δ -0.9, -2.2, -3.5, respectively) are understandable in view of the electronegativity of C, N and O. The NMR signal of a proton appears at a lower field (higher δ value) as the number of electronegative atoms or group attached to the carbon containing the proton increases. This is because of increasing deshielding of the concerned proton. For example, the chemical shifts of CH_4 , CH_3Cl , CH_2Cl_2 and CHCl_3 protons are δ 0.33, 3.05, 5.28 and 7.24, respectively.

As the distance from the electronegative atom increases, its deshielding effect on the proton decreases, and thus the proton signal appears at a relatively higher field (lower δ value). For example, protons of the methyl groups in CH_3Cl absorb at δ 3.05, whereas the protons of the methyl group in $\text{CH}_3\text{CH}_2\text{Cl}$ absorb at δ 1.48.

(b) Anisotropic Effects : As we have seen above, electronegativity correlates with chemical shifts, However, in some cases, *e.g.*, in the cases of acetylenic, olefinic, aldehydic and aromatic protons, chemical shifts cannot be explained only on the basis of electronegativity. The carbon atom in acetylene is more electronegative than that in ethylene but the acetylenic protons are more shielded than the ethylenic protons, thus acetylenic protons absorb at δ 2.35, whereas ethylenic at δ 4.60. Such anomalies are explained on the basis of anisotropic (direction dependent) effects produced by circulation of π electrons under the influence of the applied magnetic field. These effects depend on the orientation of the molecule with respect to the applied field. Anisotropic effects are in addition to the induced magnetic field generated by the circulation of σ electrons. Generally, the induced magnetic field generated by circulating π electrons is stronger than the generated by σ -electrons.

(i) Acetylenic protons : Acetylene is a linear molecule. A small fraction of rapidly tumbling (moving disorderly) molecules are aligned parallel to the applied magnetic field, hence the electronic circulation within the cylindrical π electron cloud generates an induced magnetic field which opposes the applied field at the acetylenic proton (Fig. 1.10).

Thus, the acetylenic proton is additionally shielded and its signal moves higher field than expected from the electronegativity of the acetylenic carbons.

When acetylene molecules are aligned perpendicular to the applied field, the acetylenic proton falls in the deshielded region and it is

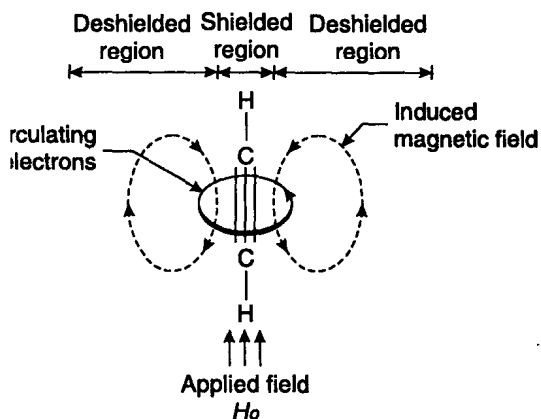


Fig. 1.10. Shielding of acetylenic protons, the molecule aligned parallel to the applied field H_0 .

deshielded (Fig. 1.11). The magnitude of this deshielding is far less than that of the shielding shown in Fig. 1.10 because electrons are much more free to circulate in the direction shown in Fig. 1.10, than in the direction shown in Fig. 1.11.

This is understandable in the light of the fact that π electrons of the triple bond are symmetrical about the bond axis, circulation as shown in Fig. 1.11 will disturb the symmetry. Although only a small fraction of tumbling molecules is aligned parallel to the applied magnetic field, the overall average chemical shift is affected by them, *i.e.*, the acetylenic protons are much more shielded than expected from the electronegativity of the acetylenic carbons and they absorb at higher field.

(ii) **Olefinic protons** : When an alkene molecule is oriented perpendicular to the applied magnetic field H_0 , the induced magnetic field generated by circulating π electrons has the same direction at the olefinic protons as the applied magnetic field (Fig. 1.12).

Thus, the induced magnetic field reinforces the applied field resulting in deshielding of the olefinic protons. Consequently, they absorb at lower field than expected from the electronegativity of olefinic carbons.

(iii) **Aldehydic protons** : When aldehydic group is oriented perpendicular to the applied magnetic field H_0 , the circulation of π electrons generates an induced magnetic field which reinforces the applied magnetic field at the aldehydic proton (Fig. 1.13) resulting in its deshielding similar to that of olefinic protons. Thus, aldehydic protons absorb at much lower field ($\delta \sim 9.5$) due to the combined effects of the high electronegativity of oxygen and anisotropic effects produced by the π electrons of the carbonyl group.

(iv) **Aromatic protons** : Aromatic rings contain cyclic electron clouds of delocalised $(4n + 2)\pi$ electrons (Hückel rule). When a magnetic field is applied perpendicular to the plane of the aromatic ring, circulation of π electrons produces a ring current which induces a magnetic field perpendicular to the plane of the ring. This induced field is in the same direction as the applied field outside the ring but inside the ring it opposes the applied field (Fig. 1.14). Thus, aromatic protons, *e.g.*, the protons of benzene, are highly deshielded, hence appear at lower field. This is called the

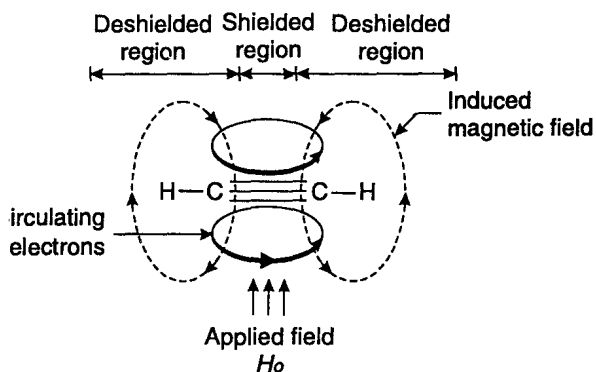


Fig. 1.11. Deshielding of acetylenic protons, the molecule aligned perpendicular to the applied field H_0 .

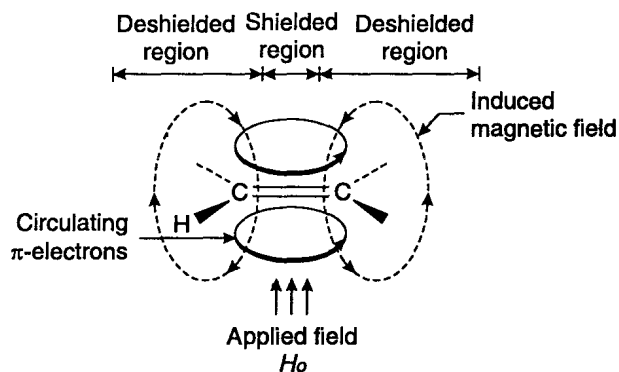


Fig. 1.12. Deshielding of olefinic protons.

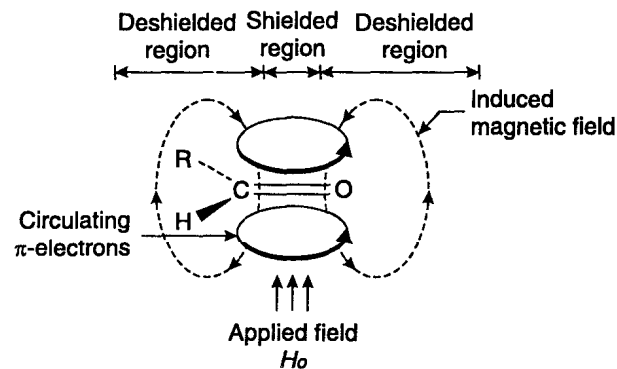


Fig. 1.13. Deshielding of aldehydic protons.

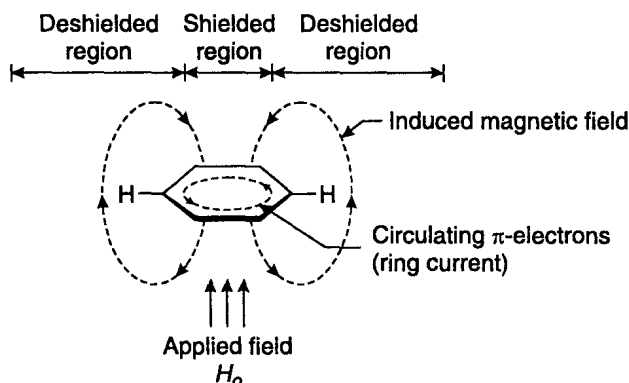
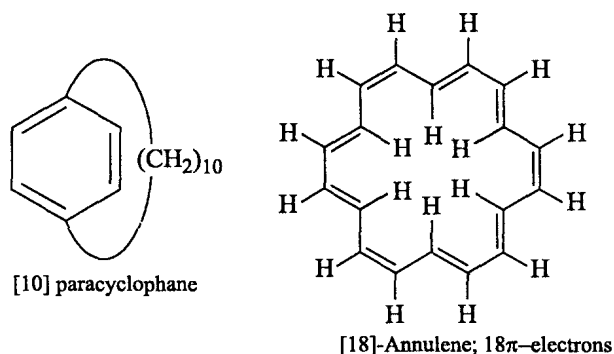


Fig. 1.14. Deshielding of aromatic protons (ring-current effects).

ring-current effect and is used as a very strong evidence for aromaticity. Fig. 1.14 indicates that a proton held above or below the plane of the aromatic ring should be shielded due to the ring current effect. This has actually been found to be the case for some of the methylene protons in 1,4-polymethylenebenzenes, e.g., [10] paracyclophane.

Some of the annulenes furnish interesting example of shielding and deshielding by ring currents. Protons outside the ring of [18]-annulene are strongly deshielded (δ 8.9), whereas those inside the ring are strongly shielded (δ ~1.8).



The shielding and deshielding resulting from aromatic ring currents are stronger than that resulting from the π electrons of olefinic bonds. Thus, olefinic protons absorb between δ 4.6-6.4, whereas aromatic protons absorb between δ 6.0-8.5.

From the above discussion, it is clear that the space around a double bond or an aromatic ring can be divided into shielding and deshielding regions and that protons present in these regions will absorb at a relatively high and low fields, respectively.

The σ electrons of C—C bond also produce anisotropic effects but these are less powerful than that produced by the circulating π electrons, and the axis of the C—C bond is the axis of the deshielding cone in case of the former (Fig. 1.15a). This explains why the protons in the sequence RCH_2 , R_2CH_2 and R_3CH appear progressively downfield. The tertiary proton (R_3CH) falls in the deshielding cones of three C—C bonds, secondary protons (R_2CH_2) fall in the deshielding cones of two C—C bonds and the primary protons (RCH_3) fall in the deshielding cone of only one C—C bond. Thus, the increasing order of their deshielding is $RCH_3 < R_2CH_2 < R_3CH$, i.e., the tertiary proton will absorb at the lowest and the primary at the highest field (Table 1.2). With the help of the deshielding cone (Fig. 1.15a), it can also be explained why an equatorial proton of a conformationally rigid six-membered ring always appears downfield by 0.1–0.7 ppm than the axial proton on the same carbon.

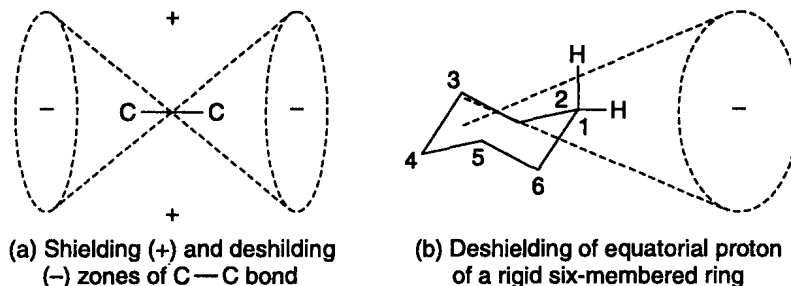


Fig. 1.15. Shielding (+) and deshielding (-) zones of C—C bond.

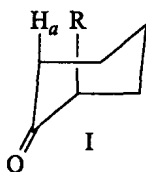
The axial and equatorial protons on C_1 are oriented similarly with respect of $C_1—C_2$ and $C_1—C_6$ bonds but the equatorial protons are within the deshielding cone of the $C_2—C_3$ and $C_5—C_6$ bonds (Fig 1.15b).

It should be noted that anisotropic effects are field effects operating through space, whereas inductive effects operate through the chemical bonds.

(c) Hydrogen Bonding : *Hydrogen bonded protons absorb at a lower field than the non-hydrogen bonded protons.* Due to high electronegativity of the atom to which the proton is hydrogen bonded, the electron density around it is decreased as compared to that around the non-hydrogen bonded proton. Thus, the hydrogen bonded protons are highly deshielded and absorb at a lower field than the non-hydrogen bonded protons. This downfield shift of the absorption depends on the strength of the hydrogen bonding. The stronger the hydrogen bonding, the lower will be the field at which the proton absorbs. *Intermolecular and intramolecular hydrogen bondings can easily be distinguished by PMR spectroscopy because the latter shows no shift in absorption position on changing the concentration of the sample, whereas the absorption position of the former is concentration dependent.* For example, the absorption position of the hydroxyl proton of ethanol is shifted to upfield on diluting the sample with a nonpolar solvent (e.g., carbon tetrachloride) due to breaking of intermolecular hydrogen bonds. Since intramolecular hydrogen bonds are not broken on dilution, intramolecularly hydrogen bonded protons show almost no change in their absorption position on dilution.

Hydrogen bonding explains why and how the chemical shift of the hydroxylic proton depends on concentration, temperature and solvent.

(d) van der Waals Deshielding : In crowded molecules, some protons may occupy sterically hindered position resulting in van der Waals repulsion. In such a case, electron cloud of a bulky group (hindering group) will tend to repel the electron cloud surrounding the proton. Thus, the proton will be deshielded and will absorb at slightly lower field than expected in the absence of this effect. For example, the proton H_a in a conformationally rigid cyclohexanone chair system I present in a steroid skeleton will resonate at lower field when $R=CH_3$ than when $R=H$.



Chemical shifts of protons in various structural environments are given in Table, 1.2. *It should be noted that in otherwise equivalent environments, the order of δ values of methyl, methylene and methyne protons is as follows :*

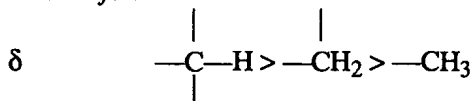


Table 1.2 Chemical shifts of protons in various structural environments

	Type of proton	Chemical shift, δ (ppm)
Primary	RCH_3	0.9
Secondary	R_2CH_2	1.3
Tertiary	R_3CH	1.5
Vinyllic	$C=CH$	4.6–5.9
Acetylenic	$C\equiv C-H$	1.8–3.1
Allylic	$C=C-CH_3$	1.7
Aromatic	$Ar-H$	6–8.5
Benzylic	$Ar-C-H$	2.2–3
Alcohols	$HC-OH$	3.4–4
Ethers	$HC-OR$	3.3–4
Esters	$RCOO-CH$	3.7–4.1
Esters	$HC-COOR$	2–2.2
Acids	$HC-COOH$	2–2.6
Carbonyl compounds	$HC-C=O$	2–2.7
Aldehydic	$RCHO$	9–10
Alcoholic	ROH	1–5.5
Phenolic	$ArOH$	4–12
Enolic	$C=C-OH$	15–17
Carboxylic	$RCOOH$	10.5–12
Amino	$RNH_2, ArNH_2$	1–5
Thiols	RSH	1.1–1.5
Thiophenols	$ArSH$	3–4
Amine salts	\oplus R_3N^+Hr	7.1–7.7
	\oplus $ArNH_3^+$	8.5–9.5
Amines	$HC-NR_2$	2.1–3
Thioethers	$HC-SR$	2.1–2.8
Fluorides	$HC-F$	4–4.5
Chlorides	$HC-Cl$	3–4
Bromides	$HC-Br$	2.5–4
Iodides	$HC-I$	2–4

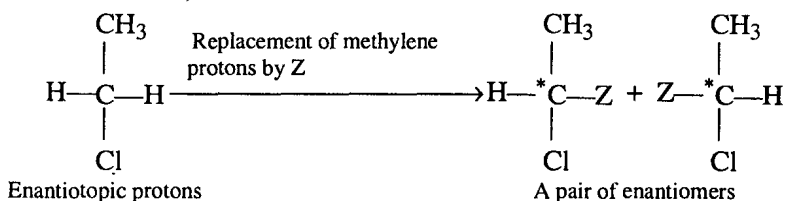
1.8 NUMBER OF PMR SIGNALS—EQUIVALENT AND NONEQUIVALENT PROTONS

The number of signals in a PMR spectrum shows how many kinds of protons are present in a molecule. This is because protons with the same chemical environment absorb at the same field strength, whereas protons with different chemical environments absorb at different field strengths. The protons with the same chemical environment are said to be chemically equivalent. Chemically equivalent protons occupy chemically equivalent position, i.e., they are in identical chemical environments. Chemically equivalent protons are chemical shift equivalent, i.e., they have the same chemical shift.

How can the chemical equivalence of protons be judged?

In a simple method for judging the chemical equivalence of two or more protons, one mentally replaces each proton in turn by some other atom Z. If the replacement results in only one product or enantiomeric products, then the protons are chemically equivalent. We ignore conformers in judging the identity of products. For example, on replacement of a methyl proton by Z, ethyl chloride would give $\text{CH}_2\text{Z}-\text{CH}_2\text{Cl}$, whereas on replacement of a methylene proton it would give CH_3-CHZCl . These are different products, hence we easily judge that the methyl and the methylene protons are not equivalent, *i.e.*, they are **heterotopic**. When we replace any one of the methyl protons by Z, the same product $\text{CH}_2\text{Z}-\text{CH}_2\text{Cl}$ is obtained, hence all the three methyl protons are equivalent (**homotopic**). Thus, we expect only one PMR signal for the three methyl protons and that is the case also. Similarly, both the methylene protons of ethyl chloride are also equivalent, *i.e.*, homotopic.

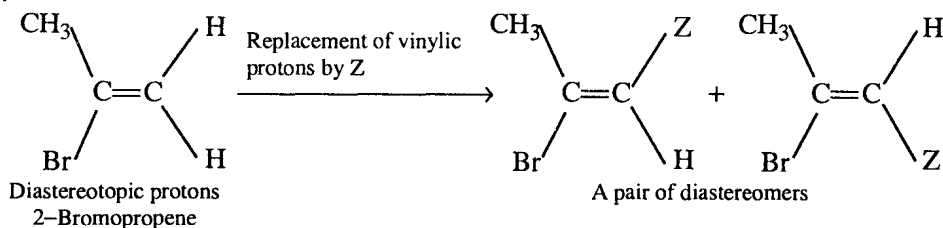
Replacement of the either of the two methylene protons of ethyl chloride by Z gives enantiomeric products (a pair of enantiomers) :



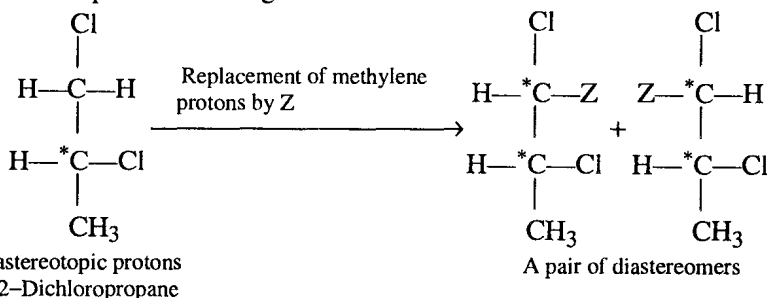
*C is chiral centre.

Such a pair of protons whose replacement gives a pair of enantiomers are called **enantiotopic protons**. These protons have the same chemical shift and exhibit only one PMR signal, *i.e.*, these are equivalent protons.

On the other hand, a pair of protons whose replacement gives a pair of diastereomers are called **diastereotopic protons**. These protons do not have the same chemical shift and show different PMR signals, *i.e.* these are nonequivalent protons. For example, replacement of either of the two vinylic protons of 2-bromopropene by Z gives diastereomeric products (a pair of diastereomers, geometrical isomers) :



Similarly, in 1, 2-dichloropropane the two protons on Cl are diastereotopic, hence are nonequivalent and show separate PMR signals.



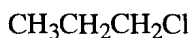
In view of the above discussion, now we are able to recognise various sets of equivalent protons (kinds of protons) and thus **predict the number of PMR signals for molecules**.

Example 1. Indicate the kinds of protons and number of PMR signals in the following compounds :

- (a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$ (b) $\text{CH}_3\text{CHClCH}_3$ (c) CH_3COCH_3

Solution :

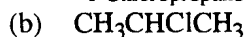
(a) The compound has three kinds of protons labelled as *a*, *b* and *c*, hence it will exhibit 3 PMR signals.



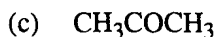
a *b* *c*
3 PMR signals
1-Chloropropane

Protons *c* are enantiotropic, hence equivalent.

Protons *b* are also enantiotropic, hence equivalent.



a *b* *a*
2 PMR signals
2-Chloropropane

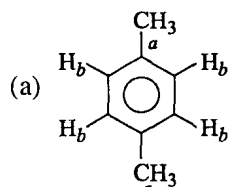


a *a*
1 PMR signal
Acetone

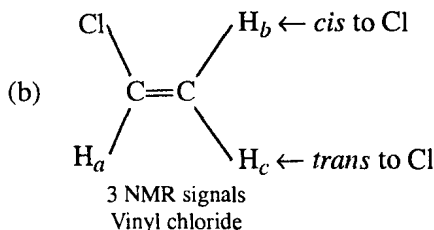
Example 2. Draw the structural formula of each of the following compounds and label all sets of equivalent protons. How many NMR signals do you expect from each of these compounds?

- (a) *p*-xylene (b) Vinyl chloride (c) Cyclobutane
(d) Diethyl ether (e) Two isomers of $\text{C}_2\text{H}_4\text{Cl}_2$

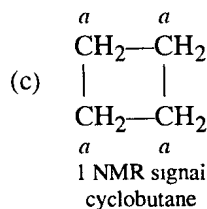
Solution :



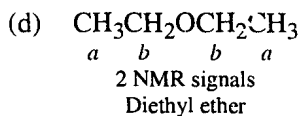
2 NMR signals
p-xylene



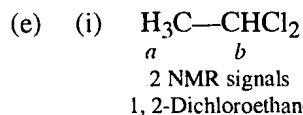
3 NMR signals
Vinyl chloride



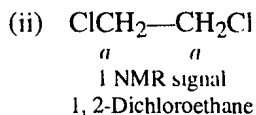
1 NMR signal
cyclobutane



a *b* *b* *a*
2 NMR signals
Diethyl ether



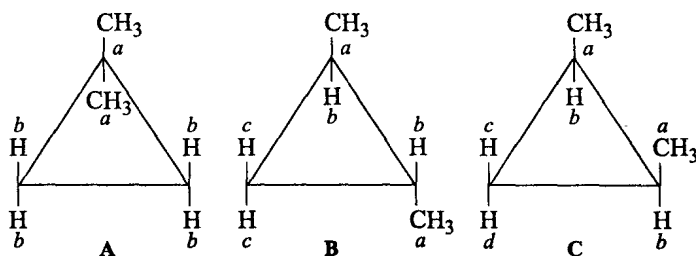
a *b*
2 NMR signals
1, 2-Dichloroethane



a *a*
1 NMR signal
1, 2-Dichloroethane

Example 3. Three isomeric dimethylcyclopropanes A, B and C give 2, 3 and 4 NMR signals, respectively. Draw the stereochemical formulae for A, B and C.

Solution :



In the dimethylcyclopropane *C* the proton *c* is *cis* to CH_3 groups, whereas the proton *d* is *trans* to CH_3 groups, hence these are nonequivalent.

Example 4. Draw the structural formula of each of the following compounds, label the kinds of protons and indicate the expected number of NMR signals.

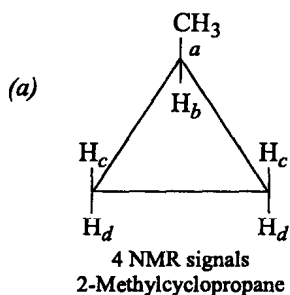
(a) Methylcyclopropane

(b) Mesitylene

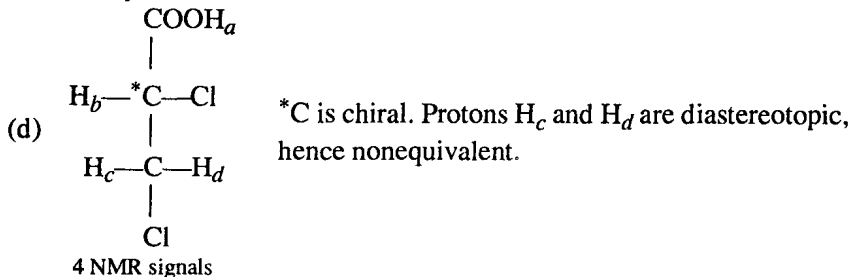
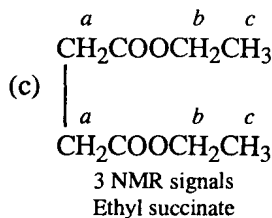
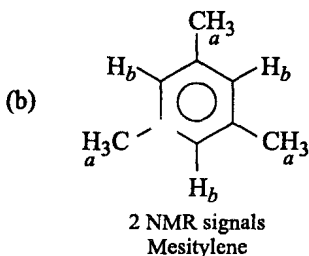
(c) Ethyl succinate

(d) 2, 3-Dichloropropanoic acid

Solution :



Protons *c* are *cis* to the methyl group and protons *d* are *trans* to it, hence they are diastereotopic (nonequivalent).



Strictly speaking, chemically equivalent protons must also be stereochemically equivalent. All the chemically equivalent protons are always chemical shift equivalent but the reverse is not always true. For example, enantiotopic protons are stereochemically nonequivalent (because they give enantiomers on replacement by some other atom or group, and thus they are also chemically

nonequivalent (in strict sense), but they have the same chemical shift. This is because their environments are mirror images of each other and are not different enough for the PMR signals to be noticeably separated. Thus, enantiotopic protons behave as equivalent protons. *It should be noted that PMR spectroscopy neither can distinguish between enantiotopic protons nor between enantiomers in achiral solvents.* However, these can be distinguished by PMR spectroscopy in chiral solvents because chiral solvents interact differently with enantiotopic protons (or enantiomers) making them chemical shift nonequivalent due to the formation of diastereomeric complexes through intermolecular interaction between the solvent and the dissolved substance.

In summary, identical protons (chemically equivalent protons in strict sense) are chemical shift equivalent in any environment, chiral or achiral. Enantiotopic protons are chemical shift equivalent only in achiral solvents. Diastereotopic protons are not chemical shift equivalent in any environment, chiral or achiral.

Magnetically equivalent protons have the same chemical shift and the same coupling constant (J) to every other nucleus in the molecule (see Section 1.13).

1.9 PEAK AREA AND PROTON COUNTING

In a PMR spectrum, various peaks (signals) represent different kinds of protons. *The area under each peak (the intensity of the peak) is directly proportional to the number of protons causing that peak.* Greater the number of protons which flip over at a particular frequency, greater is the energy absorbed and greater is the area under the absorption peak. For the determination of areas under peaks, modern NMR instruments are equipped with an electronic integrator which traces a series of steps at peaks whose heights are proportional the areas of the respective peaks. By measuring the step heights, we arrive at a set of numbers which are in the same ratio as the numbers of different kinds of protons (Fig. 1.17). This set of numbers is converted into a set of smallest whole numbers just as it is done in calculating empirical formulae. The number of protons causing each signal is equal to the whole number for that signal or to some multiple of it. For example, the step heights in Fig. 1.1.7 are 6 mm and 9 mm; the corresponding set of smallest whole numbers will be 1 and 1.5, *i.e.*, the ratio of protons of kinds *b* and *a* is :

$$6 : 9 = 1 : 1.5 = 2 : 3$$

If the molecular formula is known, for example, say it is C_2H_5Cl , then the number of *b* and *a* kinds of protons will be 2 and 3, respectively.

Alternatively, the number of each kind of protons can be counted as follows if the molecular formula C_2H_5Cl is known :

Because $6 + 9 = 15$ mm is equal to 5H

$$\therefore 1 \text{ mm is equal to } \frac{5H}{15} = 0.333H$$

Thus, the number of protons of kind *a* = $9 \times 0.333 = 2.997 = 3H$

$$b = 6 \times 0.333 = 1.998 = 2H$$

In either way we find *a*, 3 H and *b*, 2 H.

Example 5. *A compound shows three signals a, b and c in its PMR spectrum. The heights of integration curve at these signals are 8.8, 2.9 and 3.8 units, respectively. If the molecular formula of the compound is $C_{11}H_{16}$ then count each kind of proton in it.*

Solution : Because $8.8 + 2.9 + 3.8 = 15.5$ units are equal to 16 H

$$\therefore 1 \text{ unit is equal to } \frac{16H}{15.5} = 1.03H$$

Thus, the number of protons of kind

$$a = 1.03 \times 8.8 = 9.1$$

$$b = 1.03 \times 2.9 = 3.0$$

$$c = 1.03 \times 3.8 = 3.9$$

That is, the number of each kind of proton is :

$$a, 9H, b, 3H, c, 4H$$

1.10 SPIN-SPIN SPLITTING—SPIN-SPIN COUPLING

We have already studied that the number of signals in a PMR spectrum is equal to the number of kinds of protons present in the molecule. It has been found that only in some cases one kind of proton is represented by a single peak, *e.g.*, *p*-xylene has two kinds of protons (aromatic and methyl protons) and shows two PMR signals consisting of single peaks, *i.e.*, two singlets. On the other hand, *in most of the cases, instead of a single peak (singlet) for one kind of protons, a group of peaks (a multiplet) is observed in the PMR spectrum. This is called the splitting of NMR signals or the spin-spin splitting.* For example, $\text{CH}_3\text{CH}_2\text{Cl}$ has two kinds of protons and shows two signals, one of which (due to CH_3) is split into three peaks (a triplet) and the other (due to CH_2) into four peaks (a quartet) as shown in Fig. 1.7. Now let us study the origin of a multiplet (a group of peaks) for a particular kind of protons, *i.e.*, the splitting of an NMR signal.

The splitting of NMR signals is caused by spin-spin coupling which is indirect coupling of proton spins through the intervening bonding electrons. The field experienced by the proton is slightly increased if the neighbouring proton (the proton on adjacent carbon or other atoms, *i.e.*, the vicinal proton) is aligned with the applied field; or decreased if the vicinal proton is aligned against the applied field. The absorbing proton thus may experience each of the modified fields and its absorption is shifted up and down fields, and thus the signal is split into a group of peaks (a multiplet).

The nature of the instantaneous spin state is transmitted from one proton to another through the bonding electrons. In a given covalent bond, the net electronic spin magnetic moment is zero because the electron spins are paired. But a nuclear magnetic moment induces a small magnetic polarization of the nearest bonding electrons which in turn induces magnetic polarization of the bonding electrons and so on through the next proton. Thus, the instantaneous spin orientation of one proton is transmitted to another. *Coupling is generally not observable beyond three bonds unless there is ring strain as in small rings, or bridged systems, or bond delocalisation as in aromatic and unsaturated systems. Intermolecular spin-spin coupling is not observed.*

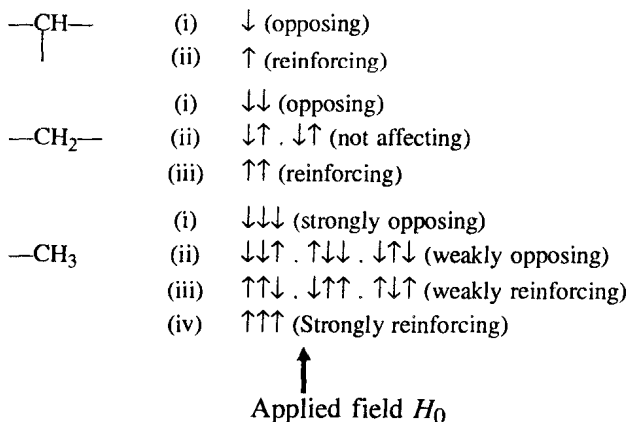


Fig. 1.16. Possible spin orientations (alignments) of the methine $\left(\begin{array}{c} \text{---CH---} \\ | \end{array}\right)$.

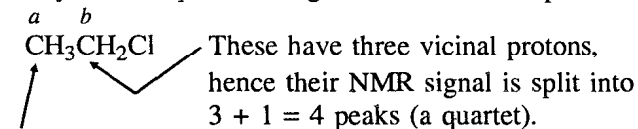
methylene ($-\text{CH}_2-$) and methyl ($-\text{CH}_3$) protons.

Possible spin orientations (alignments) of the methine ($-\text{CH}-$), methylene ($-\text{CH}_2-$) and methyl ($-\text{CH}_3$) protons are shown in Fig. 1.16. The two spin orientations of the methine proton shall affect the absorption position of the vicinal protons in two ways, and thus the signal of the latter is split into two peaks (a doublet) with the intensity ratio 1 : 1 because the probability of the two spin orientations is equal.

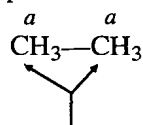
There are three different spin alignments (i-iii) possible for the methylene protons (Fig. 1.16) which shall affect the absorption of the vicinal protons in three ways resulting in the splitting of the signal of the latter into three peaks (a triplet) with the intensity ratio 1 : 2 : 1. The middle peak of the triplet has twice the intensity of the side peaks because it arises due to two spin orientations (ii) equivalent in energy.

Similarly, there are four different spin orientations (i-iv) possible for the methyl protons (Fig. 1.16) which shall affect the absorption of the vicinal protons in four ways and split their signal into four peaks (a quartet) with the intensity ratio 1 : 3 : 3 : 1. Each of the middle two peaks of the quartet has thrice the intensity of each of the two outer most side peaks because it arises due to three orientations (ii and iii) equivalent in energy. The relative intensities of component peaks in a multiplet are directly proportional to the number of nuclear spin orientations of equivalent energy causing different energy levels (Fig. 1.16).

Multiplicity—Number of component peaks (lines) in a multiplet : *It should be noted that spin-spin splitting is observed only between nonequivalent (with different chemical shifts) neighbouring protons.* Equivalent protons do spin-spin couple with one another but splitting is not observed. In general, *the number of component peaks in a multiplet, i.e., the multiplicity = $n + 1$, where n is the number of equivalent protons causing the splitting**. It should be remembered that these equivalent protons must be nonequivalent to the neighbouring protons for splitting of the signal, otherwise there will be no splitting. For example, in $\text{CH}_3\text{CH}_2\text{Cl}$ the three methyl protons are equivalent but they are nonequivalent to the methylene protons and vice versa. Thus, the three methyl protons spin-spin couple with the methylene protons and split their signal into $3 + 1 = 4$ peaks, i.e., the methylene protons appear as a quartet[#]. Similarly, the two methylene protons split the signal of the methyl protons into $2 + 1 = 3$ peaks, i.e., the methyl protons appear as a triplet (Fig. 1.7). On the other hand, the protons of both the methyl groups (all the six protons) in CH_3-CH_3 are equivalent, hence they do not split their signal and all the six protons appear as a single peak (a singlet).



These have two vicinal protons,
hence their NMR signal is split into
 $2 + 1 = 3$ peaks (a triplet)
(Protons a are equivalent and protons
 b are equivalent, but protons a are
nonequivalent to protons b).



Equivalent protons,
hence splitting does
not occur and all the
six protons appears
as a singlet.

If the protons responsible for spin-spin splitting are not equivalent, then the number of peaks (lines) for a particular multiplet will be equal to $(n + 1)$, $(n' + 1)$, $(n'' + 1)$, where n , n' and n'' are the

* The general formula covering all nuclei is $2nI + 1$, where I is the spin number.

Abbreviations, s = singlet; d = doublet; t = triplet; q = quartet and m = multiplet, are generally used

number of different kinds of protons*. For example, in 1, 1-dibromo-3, 3-dichloropropane, $\text{Br}_2\overset{a}{\text{C}}\overset{b}{\text{H}}\overset{c}{\text{C}}\text{H}_2\text{CHCl}_2$, there are three kinds of protons. The methylene protons (b) have two kinds of vicinal protons, *i.e.*, a and c hence the signal for the methylene protons ($-\text{CH}_2-$) appears as a multiplet consisting of $(n+1)(n'+1) = (1+1)(1+1) = 4$ lines, here n and n' are the number of protons of kinds a and c , *i.e.*, 1 each.

Relative intensities of component peaks (lines) of a multiplet : The relative intensities (areas) of the component peaks of multiplet also depend on n (*i.e.*, the number of equivalent protons causing the splitting) and are given by the numerical coefficients of the terms in the expansion of $(x+1)^n$ to the desired value of n :

If $n = 1$, then $(x+1)^1 = x+1$. Thus, the peaks of a doublet have relative intensities 1 : 1.

If $n = 2$, then $(x+1)^2 = x^2 + 2x + 1$. Thus, the peaks of a triplet have relative intensities 1 : 2 :

1.

If $n = 3$, then $(x+1)^3 = x^3 + 3x^2 + 3x + 1$. Thus, the peaks of a quartet have relative intensities 1 : 3 : 3 : 1. Similarly, the relative intensities of component peaks of any $(n+1)$ multiplet can be calculated; the values are given in Table 1.3. The same results can also be obtained from Pascal's triangle where each term coefficient is the sum of the two terms diagonally above it as shown in Table 1.3.

Table 1.3 Relative intensities of various multiplets.

Number of protons responsible for splitting, n	Multiplet	Relative intensity
0	singlet	1
1	doublet	1 : 1
2	triplet	1 : 2 : 1
3	quartet	1 : 3 : 3 : 1
4	pentet (quintet)	1 : 4 : 6 : 4 : 1
5	sextet	1 : 5 : 10 : 10 : 5 : 1
6	septet	1 : 6 : 15 : 20 : 15 : 6 : 1 and so forth

The splitting of a signal is due to different environment of the absorbing protons with respect to the neighbouring protons but not with respect to electrons. The intensities (areas) of a PMR signals depend upon the number of absorbing protons and the multiplicity of a signal depends upon the number of the neighbouring protons.

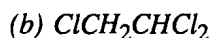
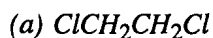
In the above sections, we have seen four general features of PMR spectra :

1. *Number of signals* tells us how many kinds of protons are present in a molecule.
2. *Chemical shifts* tell us about the electronic environment of each kind of protons.
3. *Intensities (areas) of signals* tell us about the ratio of the numbers of each kind of protons present in a molecule.
4. *Spin-spin splitting of signals* into several peaks (multiplets) tells us about the environment of a proton with respect to the neighbouring protons.

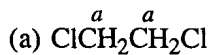
* If different magnetic nuclei are responsible for spin-spin splitting, then the general formula for the multiplicity of a group of equivalent magnetic nuclei A is $(2n_B I_B + 1)(2n_C I_C + 1) \dots$, where n_B and n_C are the number of equivalent magnetic nuclei present and I_B and I_C are their respective spin numbers.

Let us discuss some examples :

Example 6. Predict the number of signals and their multiplicity in the PMR spectra of the following compounds :



Solution :



1, 2 dichloroethane

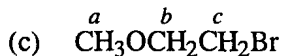
In this compound all the four protons are equivalent, hence it will show only one singlet (no splitting of the signal will occur).



1, 1, 2-trichloroethane

This compound contains two types of protons indicated as *a* and *b*, hence it will show two signals. Protons *a* ($-\text{CH}_2-$) have one vicinal proton (nonequivalent), hence the signal of *a* will be split into $1 + 1 = 2$ peaks, *i.e.*, they will appear as a doublet. Similarly, the proton *b* ($-\text{CH}-$) has

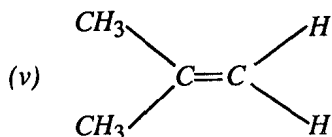
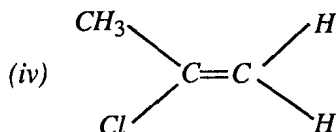
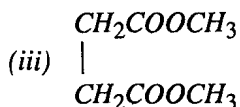
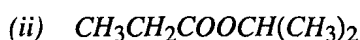
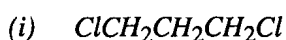
two equivalent vicinal protons *a* which are nonequivalent to *b*, hence its signal will split into $2 + 1 = 3$ peaks, *i.e.*, proton *b* will appear as a triplet.



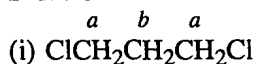
1-bromo-2-methoxyethane

This compound has three kinds of protons indicated as *a*, *b* and *c*, hence it will show three signals. Protons *a* have no vicinal proton, hence their signal will not split and they will appear as a singlet. Protons *b* have two equivalent vicinal protons *c* which are nonequivalent to *b* and vice versa, hence the signal of *b* will split into $2 + 1 = 3$ peaks, and the similar is the case of protons *c*, *i.e.*, protons *b* will appear as a triplet and protons *c* will appear as another triplet.

Example 7. Indicate the kinds of protons and their multiplicity in the ^1H NMR spectra of the following compounds :



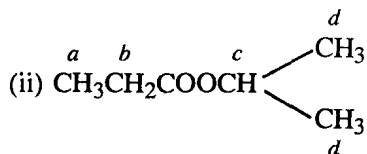
Solution :



There are two kinds of protons, *i.e.*, *a* and *b*, in the compound. Their multiplicity is as follows :

a, triplet

b, quintet



Four kinds of protons, i.e., *a*, *b*, *c* and *d*. Their multiplicity is as follows :

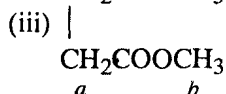
a, triplet

b, quartet

c, septet

d, doublet

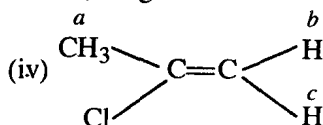
a *b*



Two kinds of protons, i.e., *a* and *b*. Their multiplicity is as follows :

a, singlet

b, singlet



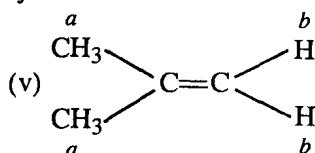
Three kinds of protons, i.e., *a*, *b* and *c*. Their multiplicity is as follows :

a, singlet, because it has no vicinal proton

b, doublet

c, doublet

Protons *b* and *c* also cause splitting of signals because they are nonequivalent and are separated by only two bonds.



Two kinds of protons, i.e., *a* and *b*. Their multiplicity is as follows :

a, singlet, because there is no vicinal proton.

b, singlet, because there is no vicinal proton.

Example 8. Draw the structure of each of the following compounds which meets the given requirements in its PMR spectrum :

(i) $\text{C}_3\text{H}_3\text{Cl}_5$; one doublet and one triplet

(ii) $\text{C}_4\text{H}_{10}\text{O}$; one singlet, one doublet and one septet

(iii) $\text{C}_4\text{H}_8\text{O}_2$; one singlet, one triplet and one quartet

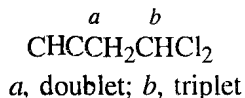
(iv) $\text{C}_3\text{H}_7\text{Cl}$; one doublet and one septet

(v) $\text{C}_4\text{H}_8\text{Cl}_2\text{O}$; two triplets.

Solution :

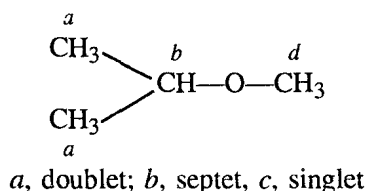
(i) $\text{C}_3\text{H}_3\text{Cl}_5$

The compound shows one doublet and one triplet; this indicates the presence of $-\text{CH}-\text{CH}_2-$ group in the molecule. Thus, the following is the structure with molecular formula $\text{C}_3\text{H}_3\text{Cl}_5$ which fulfils this condition :



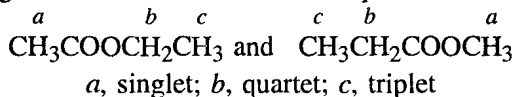
(ii) C₄H₁₀O

The presence of a doublet and a septet indicates (CH₃)₂CH— (isopropyl) group. There is one singlet in the spectrum which shows that a group of protons have no vicinal proton in the molecule. Thus the following is the structure with the above molecular formula which meets the given requirements :



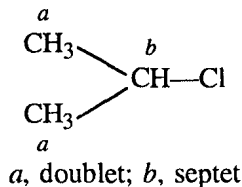
(iii) C₄H₈O₂

The compound shows one triplet and one quartet; this indicates the presence of —CH₂CH₃ group. The compound shows one singlet indicating that a group of three protons (—CH₃) has no vicinal proton. The following structures meet the above requirements :



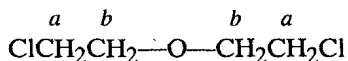
(iv) C₃H₇Cl

The presence of a doublet and a septet indicates (CH₃)₂CH— group. Thus, the structure which meets the given requirements is as follows :



(v) C₄H₈Cl₂O

The compound shows two triplets; this indicates the presence of —CH₂CH₂— group where both the —CH₂— groups are non-equivalent. Thus, the structure which fits the given requirements and the molecular formula is as follows :



1.11 COUPLING CONSTANT (J)

The distance between the centres of two adjacent peaks in a multiplet is called coupling constant or spin-spin coupling constant, and is denoted by *J*. (Fig. 1.17). The values of coupling constants (*J*) are always quoted in Hz or cps and never in δ (ppm) or τ values. The value of *J* (in Hz) remains constant in different applied magnetic fields or radio frequencies used, whereas the values of chemical shifts in Hz are directly proportional to the applied magnetic fields or radio frequencies. This difference between spin-spin splitting and chemical shift affords a method for distinguishing between them. If the spectrum of a compound is recorded at different applied magnetic fields, then the separation of signals (in Hz) due to chemical shift change, whereas separation of two adjacent peaks (in Hz) in a multiplet remains always constant. Thus, if the separation (in Hz) between adjacent peaks does not change, then they are component peaks of a multiplet. On the other hand, if the separation (in Hz)

between the peaks changes on changing the applied field, then they represent different signals. The values of coupling constants (J) between protons generally lies between 0 and 20 Hz.

The separations of peaks (J) in two coupled multiplets are exactly the same, i.e., spin-spin coupling is a reciprocal affair. For example, in the PMR spectrum of 1, 1, 2-trichloroethane (Fig. 1.17), two multiplets (one doublet and one triplet) are observed. The value of J_{ab} (6 Hz) in the doublet is exactly the same as in the triplet. The symbol J_{ab} means the coupling constant for protons a (H_a) split by proton b (H_b) or for H_b split by H_a . Drawing of a splitting diagram (Fig. 1.17) permits us to identify identical spacings between component peaks in the multiplets.

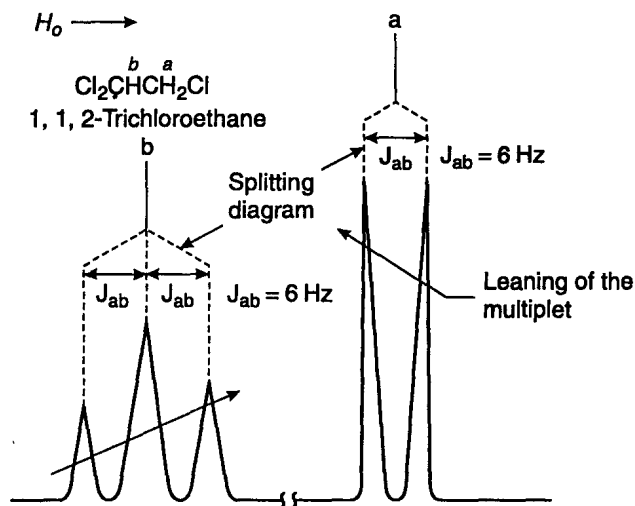
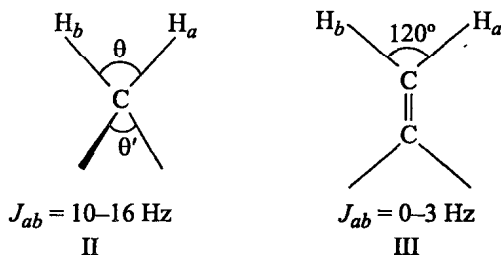


Fig. 1.17. Spin-spin splitting, coupling constant (J), leaning of the coupled multiplets towards one another and splitting diagram.

Factors Affecting Coupling Constant (J) : Coupling constant is a measure of the effectiveness of spin-spin coupling. *The value of coupling constant (J) depends on the number, type and geometrical orientation of bonds separating the coupled nuclei.* We have already noted that J is independent of the applied magnetic field. This is because splitting arises due to instantaneous spin states of the neighbouring protons but not due to flipping of the spin states. *A coupling constant is designated as + or - to permit certain theoretical correlations, but the sign can be ignored except for calculations.* The important factors which affect the magnitude of coupling constants in various types of coupling are given below :

(a) **Geminal coupling :** Protons attached to the same carbon atom are called **geminal protons**. These are separated by two bonds, and when they are non-equivalent, they show spin-spin splitting. Geminal coupling constant (J_{gem}) is usually negative. *Geminal coupling constants increase algebraically on increasing the angle θ between the coupling protons (II and III).* For example, in cyclohexane and cyclopentane rings, the angle θ is similar to the tetrahedral angle ($\theta = 109^\circ$) and J_{gem} is about -12 Hz which is comparable to that of acyclic saturated systems.

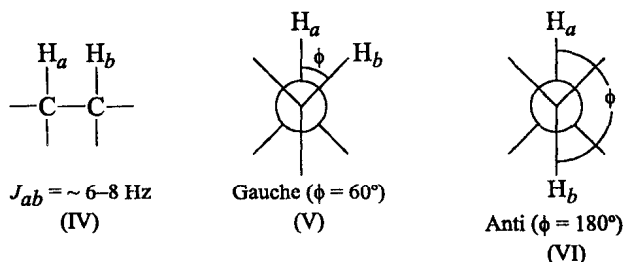


On decreasing the ring size to cyclopropane system, θ' is decreased with consequent increase in θ (II) which becomes $> 109^\circ$, thus the J_{gem} of protons of methylene groups of a cyclopropane ring increases to about -3 Hz. In a terminal methylene group in which the carbon atoms are sp^2 hybridized and $\theta = 120^\circ$ (III), J_{gem} further increases to zero or even becomes positive.

In a system RCH_2X , J_{gem} between CH_2 protons increases algebraically with increasing electronegativity of X . On the other hand, J_{gem} decreases to the carbon atom adjacent to the geminal

protons in 1, 1-dichlorocyclopropane. Such opposite effects of electronegativity illustrate that *changes in J are not simply attributable to the direct inductive effect of the substituent.*

(b) **Vicinal coupling** : Protons attached to adjacent atoms are called **vicinal protons** (IV). These are separated by three bonds. Vicinal coupling constants (J_{vic}) depend on the dihedral angle (angle of rotation) ϕ . J_{vic} is largest when the angle ϕ is 0° or 180° , and has small negative value near 90° . For axial-axial protons in cyclohexanes, where dihedral angle is about 180° (VI), the J_{vic} is approximately 8 Hz, whereas for axial-equatorial and equatorial-equatorial protons, where dihedral angle is about 60° (V), the J_{vic} is about 2 Hz. The relationship between J_{vic} and dihedral angle ϕ is given approximately by theoretically derived Karplus equations (eqns. 1.5 and 1.6) :

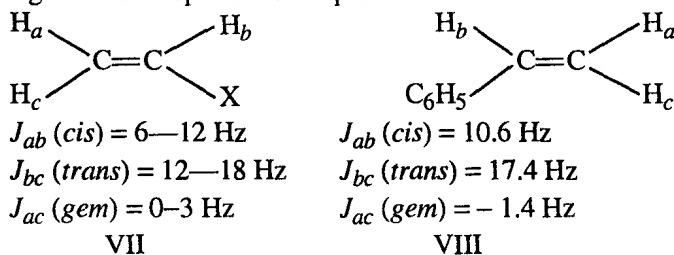


$$J_{vic} = 10 \cos^2 \phi, \text{ for value of } \phi \text{ between } 0 \text{ and } 90^\circ \text{ (eqn. 1.5)}$$

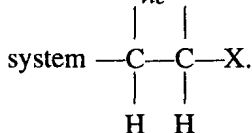
$$J_{vic} = 15 \cos^2 \phi, \text{ for values of } \phi \text{ between } 90^\circ \text{ and } 180^\circ \text{ (eqn. 1.6)}$$

Karplus relationships (eqns. 1.5 and 1.6) are very useful for determining the stereochemistry of organic compounds.

For isomeric olefins, J_{trans} is always greater than J_{cis} , and it is usually observed that $J_{cis} = \sim \frac{2}{3} J_{trans}$. Thus, it is possible to determine the configuration of geometrical isomers of a disubstituted olefin. For monosubstituted olefins (VII) $J_{trans} > J_{cis} > J_{gem}$. Experimental data for styrene (VIII) are given as a specific example.

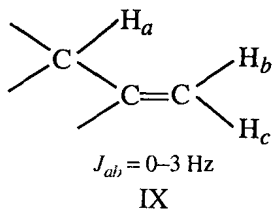


The J_{vic} decreases with increasing electronegativity of X in a freely rotating



(c) **Long-range coupling** : The magnitude of J decreases sharply with distance. It is about 1 Hz for coupling through four covalent bonds. In special cases, observable coupling through five covalent bonds has been reported. Coupling between protons separated by more than three bonds may occur in olefins, acetylenes, aromatics, heteroaromatics, and strained ring systems (small or bridged rings). Such *proton-proton couplings beyond three bonds are called long-range coupling*. Some appreciable long-range coupling are as follows :

(i) **Allylic coupling** : Allylic coupling constants are about 0 to 3 Hz (IX). In conjugated polyacetylenic chains, coupling may occur through as many as nine bonds.



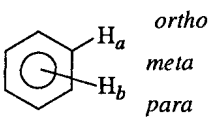
(ii) **Homoallylic coupling** : As might be expected, homoallylic coupling constants are usually very small (about 0—2 Hz).

(iii) **Aromatic coupling** : *Meta* coupling in benzene ring is 1—3Hz, and *para* 0—1 Hz. *Ortho* coupling in benzene ring is 6—10 Hz. It should be noted that the *ortho* coupling is not a long-range coupling because here the coupled protons are separated by only three bonds. Coupling constants in heteroaromatics assume similar values.

Protons spin-spin coupling constants of some common systems are given in Table 1.4.

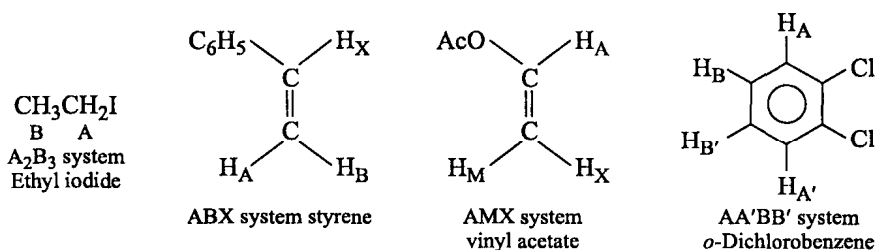
Table 1.4 Proton spin-spin coupling constants

Type	J_{ab} Hz	Type	J_{ab} Hz
	10—16		0—3
	6—8		6—12
	~ 0		12—18
	8—10		0—3
ax.-ax.	2—3		4—10
ax.-eq.	2—3		0—2
eq.-eq.			10—13

Type	J_{ab} Hz	Type	J_{ab} Hz
		$\begin{array}{c} \\ H_a - C - C \equiv C - H_b \\ \end{array}$	2—3
		$\begin{array}{c} \qquad \\ H_a - C - C \equiv C - C - H_b \\ \qquad \end{array}$	2—3
			6—10 1—3 0—1

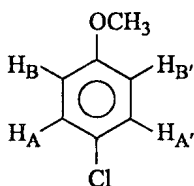
1.12 NOMENCLATURE OF SPIN SYSTEMS

A spin system is a group of coupled protons. A spin system may not include a whole molecule. For example, the ethyl protons in ethyl isopropyl ether constitute one spin system and the isopropyl protons another. By convention, protons of a spin system which are separated by small chemical shift are designated with the letters *A*, *B* and *C* (usually in order of decreasing δ value), and those far away in chemical shift from these with the letters *X*, *Y* and *Z*, whereas those intermediate in chemical shift with the letters *M*, *N* and *O*. In brief, the protons widely differing in chemical shift ($\Delta\nu/J = 6$) are assigned letters widely separated in the alphabet, e.g., *A*, *M* and *X*. The protons with about the same chemical shifts are assigned letters adjacent to one another in the alphabet. The number of protons of each kind is denoted by a subscript number. For example, A_2B system means the spin system has two kinds (*A* and *B*) of protons; there are two protons of kind *A*, and the protons of this spin system are separated by small chemical shift. A_2B denotes a strongly coupled 3-spin system. The nuclei which are chemically equivalent but magnetically nonequivalent are differentiated by primes, e.g., $AA'XX'$ is a 4-spin system, where *A* and *A'* (as well as *X* and *X'*) are the protons which are chemically equivalent but magnetically nonequivalent. The above nomenclature of spin systems is illustrated by the following examples :



1.13 MAGNETIC EQUIVALENCE

Magnetically equivalent nuclei (e.g. protons) have the same chemical shift and the same coupling constant (*J*) to every other nucleus in the spin system. All the magnetically equivalent nuclei are



chemically equivalent but the reverse is not always true. For example, protons H_A and $H_{A'}$ in *p*-chloroanisole are chemical shift equivalent. Protons H_A and $H_{A'}$ are coupled to proton H_B (or $H_{B'}$) with different geometry (through different bond angles and bond distances), hence have different coupling constants. Thus, protons H_A and $H_{A'}$ are magnetically non-equivalent, protons H_B and $H_{B'}$, when treated in the same way, are also found to be magnetically nonequivalent. The system is $AA'BB'$. Spin systems which contain groups of chemically equivalent protons which are magnetically nonequivalent cannot be analysed by first order method.

1.14 PROTONS ON HETEROATOMS—PROTON EXCHANGE REACTIONS

Protons on a heteroatom differ from protons on a carbon atom in following ways :

- (i) they are exchangeable,
- (ii) they are subject to hydrogen bonding, and
- (iii) they are subject to partial or complete decoupling by electrical quadrupole effects of some heteroatoms.

We have already discussed the effect of hydrogen bonding on chemical shift in Section 1.7c. Now we shall discuss the effect of proton exchangeability on PMR signals.

Let us take the example of ethanol. Under ordinary conditions, ethanol (neat, acidified) shows a triplet at δ 1.17 due to methyl protons, a quartet at δ 3.62 due to methylene protons and a singlet at δ 5.37 due to hydroxylic proton (Fig. 1.18).

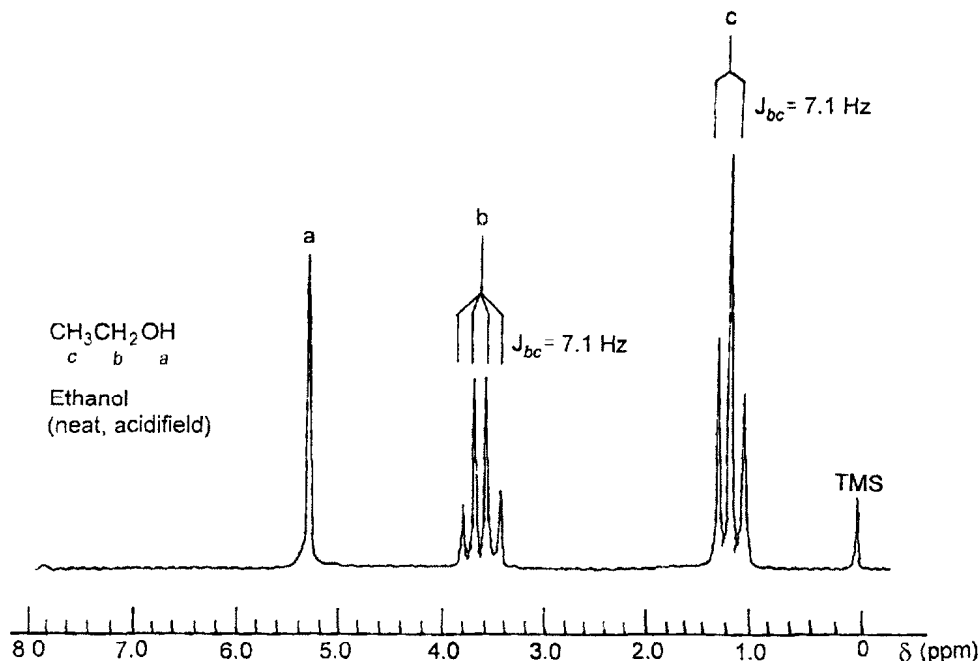


Fig. 1.18. PMR spectrum of ethanol (neat, acidified) at 60 MHz.

Spectrum of pure anhydrous ethanol (Fig. 1.19) exhibits :

- (i) a triplet for $-\text{CH}_3$ protons at δ 1.17,
- (ii) a multiplet consisting of eight lines for $-\text{CH}_2-$ protons at δ 3.62. The $-\text{CH}_2-$ protons are under the influence of two kinds of protons ($-\text{CH}_3$ and $-\text{OH}$). Thus, the multiplet for $-\text{CH}_2-$ protons consists of $(n + 1)(n' + 1) = (3 + 1)(1 + 1) = 8$ lines, and

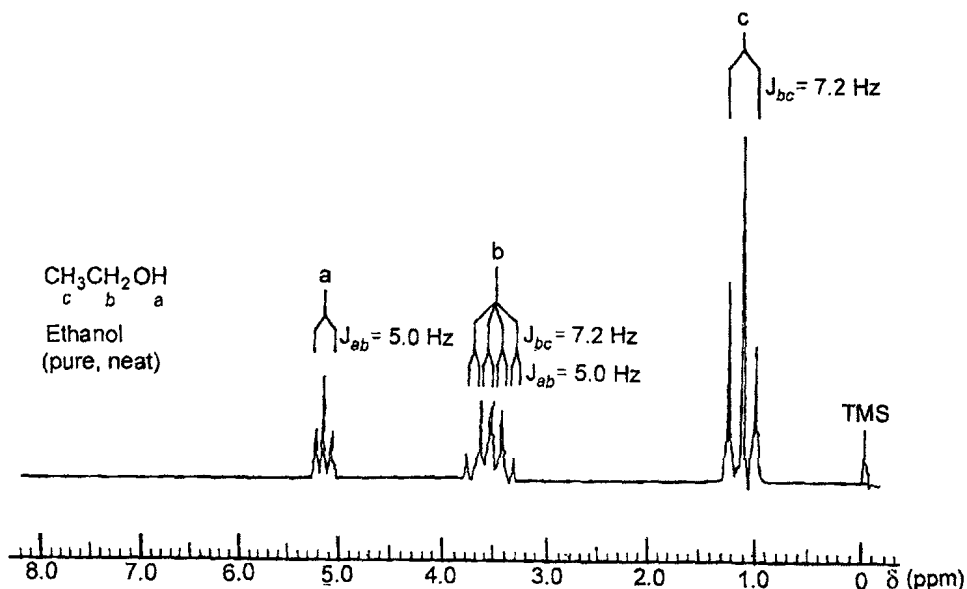
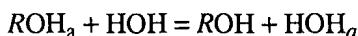


Fig. 1.19. PMR spectrum of pure, neat ethanol at 60 MHz.

- (iii) a triplet for —OH proton at δ 5.28. The —OH appears as a triplet because of its coupling with —CH₂— protons.

The above observations can be explained on the basis that the *proton exchange reaction (chemical exchange)* becomes faster in the presence of water or acidic or basic impurity.



Similarly, the exchange of —OH protons among ethanol molecules also occurs. The rate of proton exchange reactions increases with increasing temperature. The proton exchange in the presence of water or at high temperature or in acidic or basic medium is faster than the NMR transition time. Thus, a particular proton does not reside on a particular oxygen atom long enough to “see” the three spin states of methylene protons or to show its two spin states to the methylene protons, so the expected spin-spin coupling is not observed. *Rapid chemical exchange causes spin-spin decoupling.*

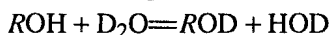
When the rate of chemical exchange is made very slow by the removal of water, acidic or basic impurities, the expected couplings are observed, *i.e.*, —CH₂— protons appear as a multiplet consisting of 8 lines and —OH protons as a triplet. The rate of proton exchange can also be made slower by lowering the temperature or through strong solvation by using highly polar solvents like dimethyl sulphoxide (DMSO, CH₃SOCH₃) or acetone.

Protons attached to other heteroatoms, such as N, S, etc., also behave like hydroxylic protons. Protons of —OH, —NH₂, —SH, etc. groups have no characteristic chemical shift ranges, as their chemical shifts depend on concentration, solvent and temperature. However, such groups are identified by exchange with D₂O which causes their signals to disappear from the spectrum (Section 1.15).

It should be noted that even when exchange is very slow, the signals due to N—H proton is broadened by quadrupolar interaction with nitrogen. Nuclei with $I \geq 1$ have an electric quadrupole moment, the magnitude of which is a measure of the nonspherical nature of the electric charge distribution within the nucleus. The NMR signals for protons attached to a nucleus which has an electric quadrupole moment are broadened, *i.e.*, splitting is not observed. The greater the magnitude of the electric quadrupole moment, the more is the broadening of the signal.

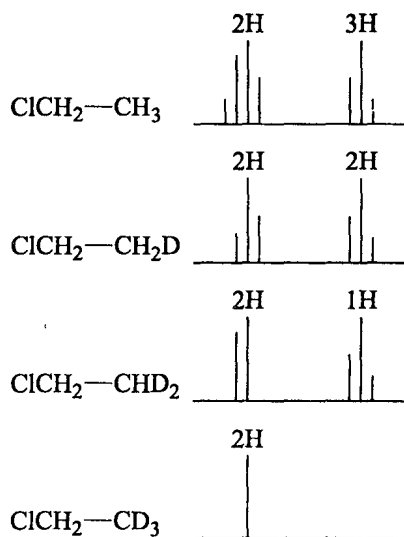
1.15 DEUTERATION—DEUTERIUM EXCHANGE AND DEUTERIUM LABELLING

The protons of —OH, —NH₂, —SH, etc. groups are exchangeable with D₂O.



Thus, such groups are identified by exchange with D₂O which causes their signal to disappear from the spectrum. This exchange reaction is similar to proton exchange reactions (Section 1.14) and is called deuterium exchange reaction. For detecting the protons exchangeable with D₂O, either the PMR spectrum is recorded in D₂O or a few drops of D₂O is added to the sample. For example, in case of an alcohol on D₂O exchange, the proton signal due to the alcoholic —OH will disappear and instead, a signal due to HOD proton will appear in the PMR spectrum.

Deuterium is easily introduced into a molecule and its presence in a molecule is not detected in the PMR spectrum because it absorbs at a different field strengths. Deuterium couples only slightly with the proton, hence it does not split its signal. Deuterium labelling also simplifies PMR spectra as illustrated by the example of ethyl chloride.



As the methyl hydrogens are replaced by deuterium, the multiplicity of the methylene signal changes from a quartet (3 + 1) to a triplet (2 + 1) to a doublet (1 + 1) and finally to a singlet as shown above.

1.16 INTERPRETATION (ANALYSIS) OF SIMPLE (FIRST ORDER) NMR SPECTRA

While interpreting an NMR spectrum to obtain structurally useful information one must analyse it and correlate the NMR parameters with structure. The process of deriving the NMR parameters δ and J from multiplets is known as the analysis of the NMR spectrum.

First Order (Simple) Spectra : When the chemical shifts are large compared to the coupling constants ($\Delta\nu/J^*$ is greater than about 10), δ and J values may be measured directly from the spectrum, and spectra of this type are known as *first order spectra*. Nuclei (*e.g.*, protons) which give rise to such spectra are said to be *weakly coupled*. First order spectra can usually be interpreted by using the

* $\Delta\nu$ is the difference in chemical shifts (in Hz) between two groups of coupled protons.

following splitting rules (already discussed in Sections 1.10 and 1.11) which are features of these spectra :

1. The number of component peaks in a multiplet is given by $n + 1$, where n is the number of equally coupled protons causing the splitting. The general formula which covers all the nuclei is $2nI + 1$, where n is the number of the coupling nuclei, with spin I .
2. The relative intensities of the component peaks of a multiplet are given by coefficients of the terms in binomial expansion of $(x + 1)^n$ for nuclei with $I = \frac{1}{2}$.
3. The centre of the multiplet gives the resonance position of the nucleus, and hence its chemical shift.
4. In the case of only two different groups of coupling nuclei, the separation between the component peaks of the multiplet are equal and correspond to the coupling constant.

A large number of PMR spectra are first order spectra, and can be analysed by inspection and direct measurement in terms of the above rules. The chemical shift separation $\Delta\nu$ (in Hz) increases as the strength of applied magnetic field increases, but the value of J remains constant, and so $\Delta\nu/J$ ratio is increased. Thus, a large proportion of PMR spectra become first order spectra at high applied magnetic fields. It should be noted that NMR instruments operating at high magnetic fields (i.e., at high radio frequencies) give better resolution and relatively easily interpretable spectra.

Interpretation of first order (simple) NMR spectra : Let us take the example of the PMR spectrum of ethyl bromide shown in Fig. 1.20. The signal at δ 0.00 is due to the internal reference

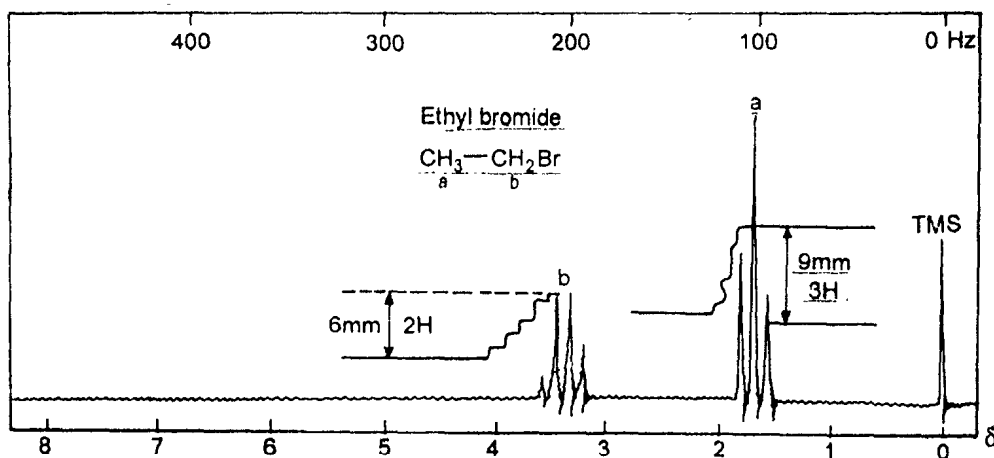


Fig. 1.20. PMR spectrum of ethyl bromide.

TMS. The downfield quartet centered at δ 3.42 is due to methylene protons because they are more deshielded than the methyl protons by the bromine. The methyl protons appear as a triplet centred at δ 1.66, i.e., upfield. The integration curve shows relative peak areas of 2 : 3 corresponding to the number of protons causing the peak. The spacing between the component peaks of both the multiplets are equal and have the value ~ 9 Hz, i.e., $J_{ab} = \sim 9$ Hz. The chemical shift separation is $3.57 - 1.48 = 2.09$ δ , i.e., $\Delta\nu = 2.09 \times 60 = 125.4$ Hz (the spectrum has been recorded at 60 MHz, hence δ 1 = 60 Hz). Thus $\Delta\nu/J$ is about 14, a large enough ratio for first order analysis. The system is A_2X_3 (Section 1.12). The leaning of the two coupled signals towards each other even at such a high $\Delta\nu/J$ ratio may be noticed, which shows that the multiplets are not perfectly symmetrical, i.e., there is no exact intensity ratio of 1 : 2 : 1 for the triplet and 1 : 3 : 3 : 1 for the quartet. It should be remembered that such minor deviations from ideality are almost always apparent.

The following are some more examples of interpretation of simple PMR spectra :

1. 1, 1, 2-Tribromoethane :

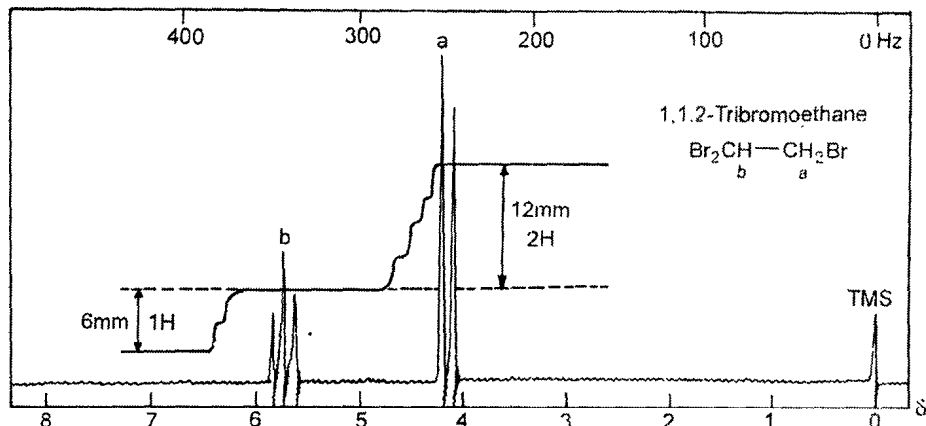


Fig. 1.21. PMR spectrum of 1, 1, 2-tribromoethane.

- (i) A doublet centred at δ 4.15, equivalent to 2H, indicates the methylene protons (*a*).
- (ii) The methine proton (*b*) being adjacent to two bromine atoms, appears as a triplet centred at δ 5.72, equivalent to 1H.

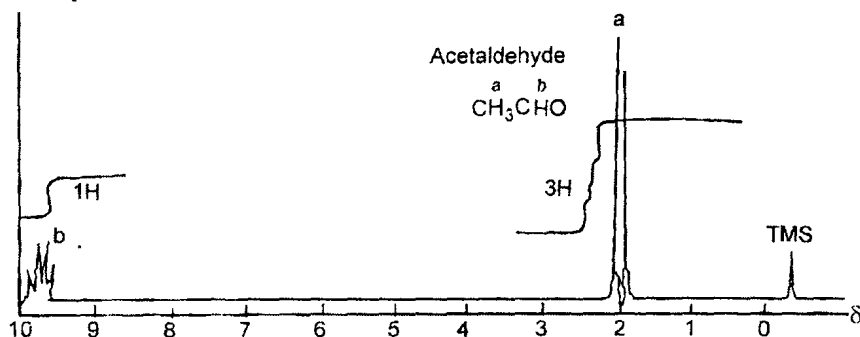


Fig. 1.22. PMR spectrum of acetaldehyde.

2. Acetaldehyde :

- (i) A doublet ($J_{ab} = 2.8$ Hz) centred at 2.15 δ , equivalent to 3H, represents methyl protons (*a*).
- (ii) A quartet ($J_{ab} = 2.8$ Hz) centred at 9.68 δ , equivalent to 1H, indicates the aldehydic proton (*b*).

3. Ethyl acetate :

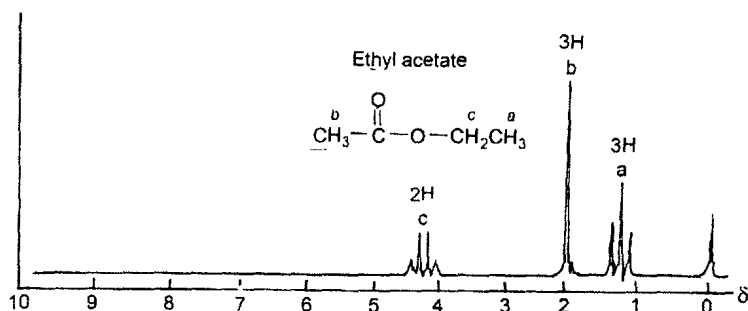


Fig. 1.23. PMR spectrum of ethyl acetate.

- (i) A triplet at δ 1.23 ($J = 7.1$ Hz), equivalent to 3H, indicates the methyl protons (*a*).
- (ii) A singlet at δ 1.97, equivalent to 3H, indicates the methyl protons (*b*).
- (iii) A quartet at δ 4.06 ($J = 7.1$ Hz), equivalent to 2H, indicates the methylene protons (*c*).

4. Toluene :

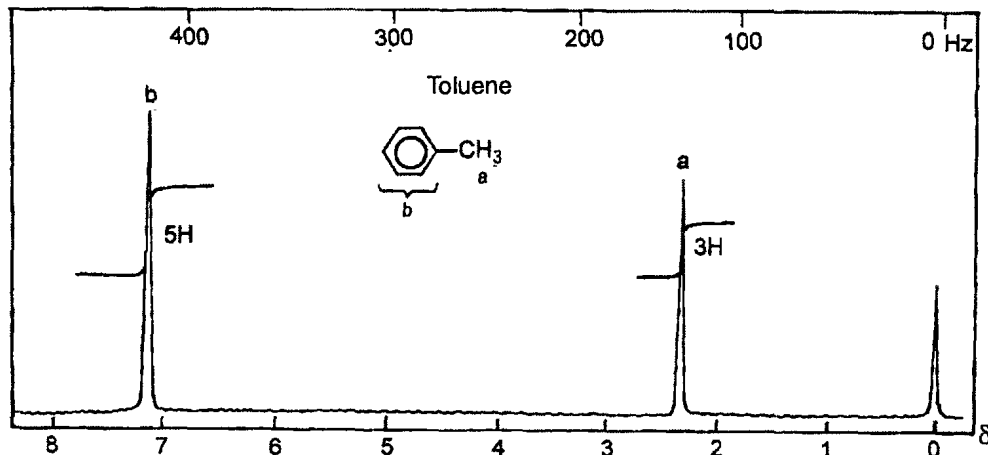


Fig. 1.24. PMR spectrum of toluene.

- (i) A singlet at δ 2.31 equivalent to 3H indicates the methyl protons (*a*).
- (ii) The signals due to five protons (*b*) of the phenyl ring appear at the same place (δ 7.10). It is characteristic of five aromatic protons of a monosubstituted benzene with a non-electronegative substituent. Strictly speaking, there are three kinds of aromatic protons in toluene but in practice their coupling constants are approximately equal therefore their signals overlap to give a singlet.

5. Ethanol : For the interpretation of the PMR spectrum of ethanol, see Section 1.14.

6. Acetophenone :

- (i) A singlet at δ 2.47, equivalent to 3H, represents the methyl protons (*a*) attached to the benzoyl group.
- (ii) Two separate downfield multiplets at δ 7.50 and 7.90 exhibit respectively the aromatic protons *b* and *c*. The *ortho* protons *c* are deshielded by the diamagnetic anisotropic effect of the $C=O$ group. The upfield multiplet is due to the three *b* protons.

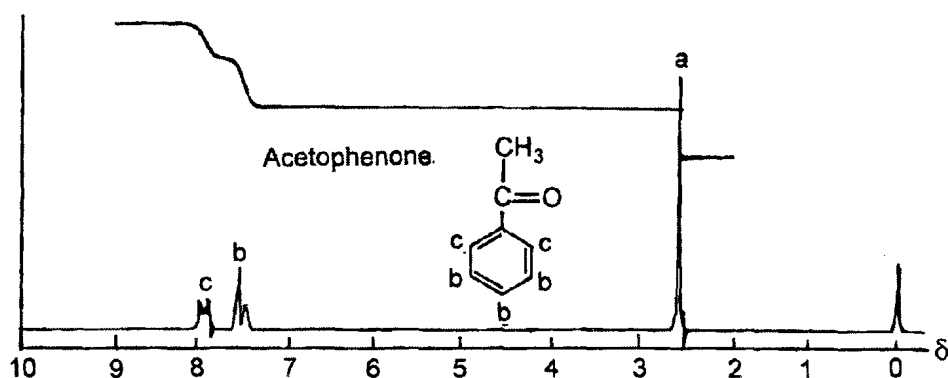


Fig. 1.25. PMR spectrum of acetophenone.

7. Benzoic acid :

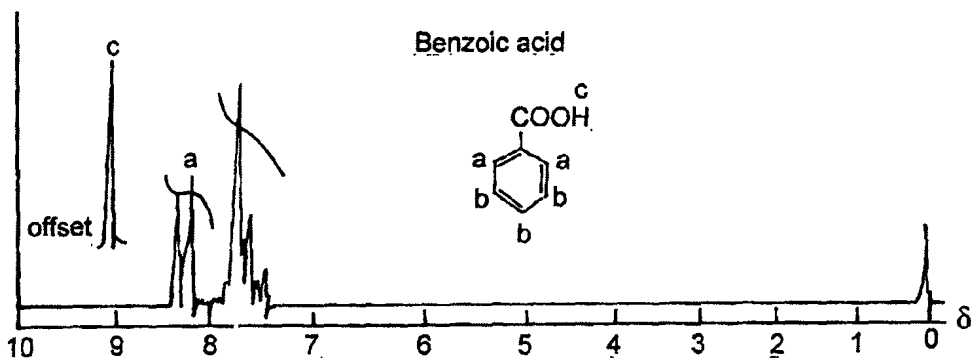


Fig. 1.26. PMR spectrum of benzoic acid.

- (i) A multiplet at 7.50 – 7.70 δ , equivalent to 3 H, is due to the aromatic protons *b*.
- (ii) A multiplet at 8.10 – 8.30 δ , equivalent to 2 H, is due to the aromatic protons *a*.
- (iii) A singlet at 12.70 δ , equivalent to 1 H, is due to the carboxylic acid (COOH) proton *c*. This proton is exchangeable with deuterium on treatment with D_2O .

8. Acetamide :

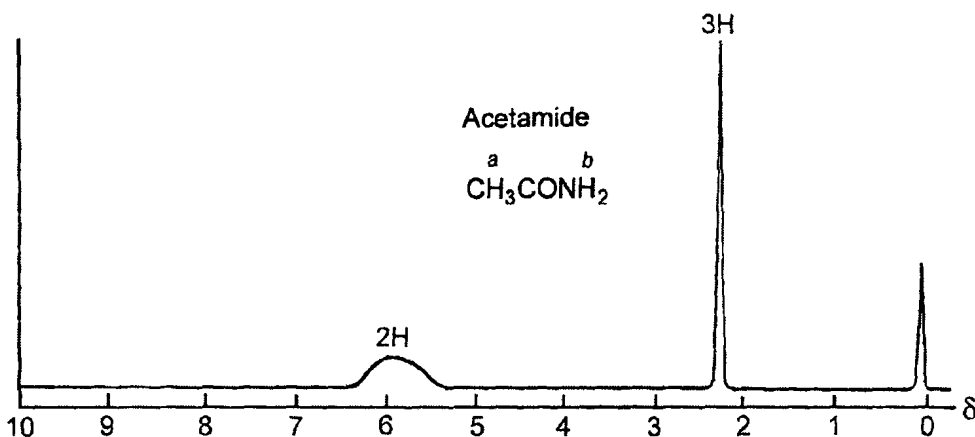


Fig. 1.27. PMR spectrum of acetamide.

- (i) A singlet at δ 2.00, equivalent to 3 H represents the methyl protons (*a*).
- (ii) A broad singlet at δ 6.15, equivalent to 2 H, indicates the protons *b* on nitrogen. The protons on nitrogen often appear as a broad peak due to electric quadrupole moment of the nitrogen nucleus. These protons exchange with D_2O .

1.17 APPLICATIONS OF PMR SPECTROSCOPY

PMR spectroscopy is an important tool in the hands of organic chemists for getting structural information. It is also useful in stereochemical studies. An organic molecule consists of carbon—hydrogen skeleton, and thus NMR spectroscopy is especially useful in the study of this structural feature of the molecule. The important applications of PMR spectroscopy besides obtaining routine structural information, are summarized on the next page :

(a) **Identification of Structural Isomers :** Structural isomers can easily be distinguished by PMR spectroscopy, for example :

- (i) CH_3OCH_3 and $\text{CH}_3\text{CH}_2\text{OH}$: In dimethyl ether, all the six protons are equivalent, hence its PMR spectrum will show only one singlet. In ethanol, there are three kinds of protons, hence its PMR spectrum will exhibit three signals; one triplet due to the methyl protons, one quartet due to the methylene protons and one singlet due to the hydroxylic proton.
- (ii) 1, 1-Dichloroethane (CH_3CHCl_2) and 1, 2-dichloroethane ($\text{ClCH}_2\text{CH}_2\text{Cl}$) : 1, 1-Dichloroethane has two kinds of protons, hence it will exhibit two signals in its PMR spectrum; one doublet and one quartet due to CH_3- and $-\underset{\text{|}}{\text{CH}}-$ groups, respectively. In 1,2-dichloroethane all the four protons are equivalent, hence its PMR spectrum will show only one singlet.

(b) **Detection of Aromaticity** : As we have seen in Section 1.7b (iv), aromatic protons are highly deshielded due to the circulating π electrons (ring current) and appear at very low field (δ 6–8.5). From this, the aromatic character of a compound under study can be predicted.

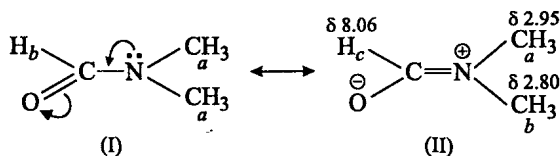
(c) **Detection of Hydrogen Bonding** : Intermolecular and intramolecular hydrogen bondings can be detected by PMR spectroscopy because both shift the absorption position of the hydrogen bonded proton to downfield. Besides, both types of hydrogen bonding can also be distinguished, as the intermolecular hydrogen bonding is concentration dependent, while the intramolecular hydrogen bonding is not concentration dependent (Sec.1.7c).

(d) **Distinction Between *Cis-Trans* Isomers and Conformers** : PMR spectroscopy can easily distinguish *cis* and *trans* isomers because the concerned protons have different values of chemical shifts as well as coupling constants (Section 1.11b). For example :



Similarly, the axial and equatorial positions of protons or groups carrying protons and various conformations of a molecule can be distinguished on the basis of different values of their coupling constants, chemical shifts and peak areas.

(e) **Detection of Partial Double Bond Character** : In certain cases, it can be detected by PMR spectroscopy whether a particular single bond in a molecule has acquired partial double bond character. One of the most thoroughly studied example is the hindered rotation about the C—N bond in simple amides, e.g., N, N—dimethylformamide (DMF). There is hindered rotation about C—N bond because it has acquired partial double bond character through resonance as shown below :

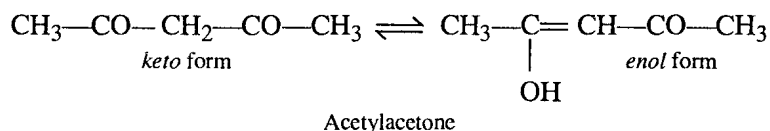


The hindered rotation, i.e., the partial double bond character of C—N bond in DMF is demonstrated by the presence of two doublets in its PMR spectrum at δ 2.80 ($J=0.6$ Hz) and 2.95 ($J=0.3$ Hz) due to the two methyl groups at room temperature. This is because the methyl groups have become nonequivalent in structure (II) due to the presence of C—N double bond. At elevated temperatures, the rapid rotation about the C—N bond makes both the methyl groups equivalent and only one signal (doublet) is observed for both the methyl groups.

(f) **Quantitative Analysis** : The fact that areas under the peaks are directly proportional to the number of protons causing the respective peaks is the basis for the quantitative analysis by NMR

spectroscopy. For quantitative analysis, the components of the mixture must be known and each component must give at least one signal which is well separated from the other signals in the spectrum. Impure samples may be determined by the addition of a known pure compound as an internal standard. If the reactants and products are known, then the rate of the reaction may be determined.

Automatic integration of NMR signals affords an easy and rapid quantitative means for determining the ratio of compounds in a mixture provided that at least one signal from each constituent is free from overlap by other signal(s). The estimation of the keto-enol ratio in acetylacetone will illustrate the quantitative analysis of a mixture.



In the PMR spectrum of acetylacetone, the height of the integration curve at the methylene (—CH₂—) signal was found to be 10 mm and that at the methine (=CH—) signal was 22 mm. Let us calculate the % of keto and enol forms in the sample.

The methylene group of the keto form $\equiv 2\text{H} \equiv 10$ mm

The methine group of the enol form $\equiv 1\text{H} \equiv 22$ mm

Therefore,

$$2\text{H} \equiv 44 \text{ mm}$$

$$\% \text{ of the keto form} = \frac{10}{44 + 10} \times 100 = 18.5\%$$

$$\% \text{ of the enol form} = \frac{44}{44 + 10} \times 100 = 81.5\%$$

PMR spectroscopy has also been used for the quantitative analysis of the mixtures of diastereomers as well as for determining the enantiomeric excess (*e.e.*), *i.e.*, optical purity.

1.18 CONTINUOUS WAVE (CW) AND FOURIER TRANSFORM (FT) NMR SPECTROSCOPY

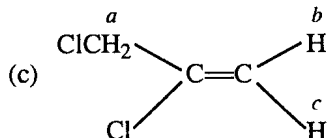
The common method for obtaining NMR spectra is to irradiate the sample with a constant radio frequency while changing (sweeping) the applied magnetic field (field sweep). Alternatively, NMR spectrometers operate at a constant magnetic field while the radio frequency is varied (frequency sweep). Both the methods give the same NMR spectrum. This commonly used technique is called *continuous wave (CW) NMR spectroscopy*.

In a recent method for obtaining NMR spectra, the sample is irradiated with an intense pulse of all radio frequencies in the desired range (*e.g.*, covering all ¹H frequencies) at once while keeping the magnetic field constant. All the nuclei under study absorb at their individual frequencies and are flipped to their higher energy spin states. This results in an interferogram (called as *free induction decay*, *FID* or *time-domain* spectrum) which cannot be interpreted directly. The *time-domain* spectrum is converted into ordinary *frequency-domain* spectrum (showing the intensity of absorption against frequency) by performing a mathematical operation known as *Fourier transformation*. This technique is called *pulsed-Fourier transform nuclear magnetic resonance (FT-NMR) spectroscopy*. It gives good spectra even with very small quantities of samples (less than a milligram). The principal advantage of FT-NMR spectroscopy is a great increase in sensitivity per unit time of experiment. It is the increase in sensitivity brought about by the introduction of FT-NMR spectroscopy which has allowed the routine observation of ¹³C NMR spectra.

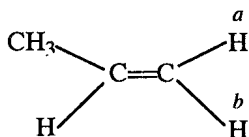

VERY SHORT ANSWER QUESTIONS


- What are the spin number (I) and the allowed spin states of each of the following atoms?
 (a) ${}^2_1\text{H}$ (D) (b) ${}^{13}_6\text{C}$ (c) ${}^{14}_7\text{N}$ (d) ${}^{19}_9\text{F}$ (e) ${}^{17}_8\text{O}$
- Give the relative decreasing order of δ value of 1° , 2° and 3° protons of alkanes as compared to CH_4 protons.
- Arrange the following compounds in increasing order of deshielding of their methyl protons.
 $\text{CH}_3\text{—CH}_3$, CH_3F , CH_3OCH_3 , $(\text{CH}_3)_3\text{N}$

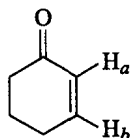
- Indicate the types of protons in methylcyclobutane.
- Predict the number of signals and their multiplicity in the PMR spectra of the following compounds :
 (a) $\text{Br—CH}_2\text{—CH}_2\text{—Br}$ (b) $\text{CH}_3\text{—CCl}_2\text{—CH}_2\text{Cl}$



- Will protons a and b in the following compound will cause splitting of their signals due to spin-spin coupling?



- Write the geometrical isomers of $\text{C}_2\text{H}_2\text{BrCl}$. How distinguish them using PMR spectroscopy?
- A compound with molecular formula $\text{C}_7\text{H}_5\text{Cl}_3\text{O}$ shows a three-proton singlet at δ 3.9 and two one-proton doublets ($J = 8$ Hz) at δ 6.76 and 7.3. Identify the compound.
- In which of the following the —OH proton of ethanol have the lower chemical shift in δ value?
 (a) Pure ethanol (b) 1.0 M ethanol in CCl_4
 (c) 0.1 M ethanol in CCl_4 (d) 2.0 M ethanol in CCl_4
- How will you distinguish *cis*- and *trans*-stilbenes with the help of PMR spectroscopy?
- A hydrocarbon with molecular mass 102 shows two PMR signals : δ 7.4 (5H) and 3.08 (1H). Deduce the structure of the compound.
- The PMR spectrum of a mixture of methyl iodide and *tert*-butyl iodide shows two singlets at δ 2.20 and 1.8 with relative integrals 5 : 1. What is the mole per cent of each compound in the mixture?
- In the following compound whether proton H_a or H_b will absorb at lower field. Explain.

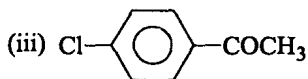
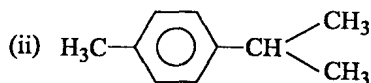
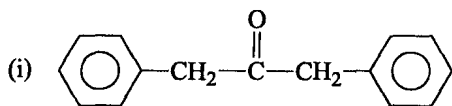


14. Predict the number of signals in the PMR spectra of the following compounds :
- (a) Allyl bromide (b) Vinyl bromide
 (c) *cis*-1, 2-Dibromoethene (d) *trans*-1, 2-dibromoethene
 (e) Mesitylene
15. Indicate the kinds of protons and their integral ratio in the following compounds :
- (a) Ethanol (b) Butanone (c) Crotonic acid (d) *p*-Xylene (e) *n*-Butane



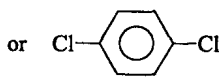
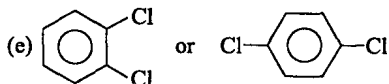
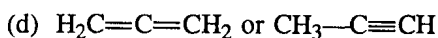
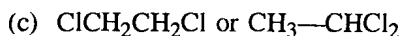
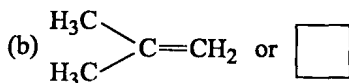
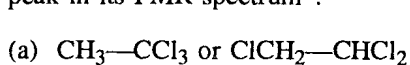
1. Give the relative positions of the PMR signals and their multiplicity in each of the following compounds :
- (i) $\text{CH}_3\text{CH}_2\text{COCH}_3$ (ii) $\text{CH}_3\text{CH}_2\text{CHO}$
 (iii) $\text{CH}_3\text{CH}_2\text{OOCCH}_2\text{CH}_2\text{COOCH}_2\text{CH}_3$ (iv) $(\text{CH}_3)_2\text{CHCOOH}$

2. Comment on the number of signals and their splitting, if any, in the PMR spectra of the following compounds :

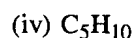
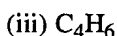
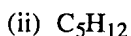
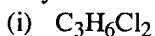


3. In an organic compound, the three kinds of protons appear at 60, 100 and 180 Hz when the spectrum is recorded at 60 MHz NMR spectrometer. What will be their relative positions (in Hz) when 90 MHz spectrometer is used ?
4. Propose the structure for the compounds that fit the following ^1H NMR data :
- (i) $\text{C}_5\text{H}_{10}\text{O}$ (ii) $\text{C}_4\text{H}_7\text{BrO}$
 δ 0.95, 6H, doublet δ 2.11, 3H, singlet
 δ 2.10, 3H, singlet δ 3.52, 2H, triplet, $J = 6$ Hz
 δ 2.43, 1H, multiplet δ 4.40, 2H, triplet, $J = 6$ Hz

5. Which member of each of the following pairs of the structural isomers is expected to exhibit a singlet peak in its PMR spectrum ?



6. Draw the structure of a compound with each of the following molecular formulae that will show only one PMR signal :



7. An organic compound has molecular formula $\text{C}_3\text{H}_7\text{Br}$. Its PMR spectrum is shown in Fig. 1.28. Deduce the structure of the compound.

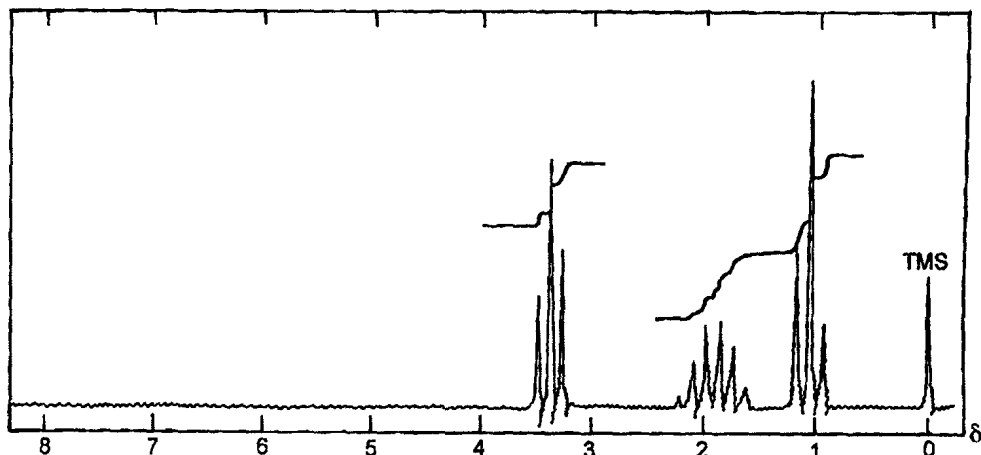
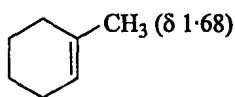
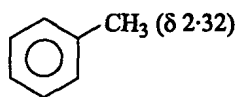


Fig. 1.28.

8. The PMR spectrum of an organic compound C_8H_9Br shows a quartet at 5.5δ , a doublet at 2.0δ and an unsymmetrical multiplet at $\sim 7.4 \delta$ in the intensity ratio 1 : 3 : 5, respectively. Deduce the structure of the compound.
9. Using PMR spectroscopy, how will you distinguish the following pairs?
 - (i) 1,2-Dimethoxyethane and 1,1-dimethoxyethane
 - (ii) *Cis*-1-chloropropene and *trans*-1-chloropropene
 - (iii) Acetone and methyl acetate.
10. An organic compound having molecular formula $C_5H_{11}Cl$ gave the following 1H NMR data :
 δ 1.0 (*t*, 3H) 1.5 (*s*, 6H) and 1.8 (*q*, 3H)
 Deduce the structure of the compound.
11. A proton H_a is coupled to four equivalent neighbouring protons H_b . What will be the multiplicity and relative intensity of the component peaks in signal of H_b ?
12. Analyse the following compounds on the basis of 1H NMR spectroscopy :
 (a) CH_3-CH_2-Br (b) $CH_3-CHCl-CH_3$ (c) $CH_3-O-CH_2-CH_3$
13. Comment on the given δ values of the methyl protons in the following compounds :



1-Methylcyclohexene



Toluene

14. Explaining the following spectral data, deduce the structure of an organic compound with molecular mass 120, and containing C, H and O :
 UV : λ_{max} 278 and 319 nm.
 IR : Significant absorption bands at 3070–3010, 2970–2860, 1685, 1605, 1580 and 1450 cm^{-1} .
 PMR : δ 2.1 (*s*, 3H) and 7.5 (*m*, 5H).
15. An organic compound $C_8H_{14}O_4$ gave the following spectral data :
 UV : No significant absorption above 210 nm.
 IR : Significant absorption bands at 1735 and 2950 cm^{-1} .
 1H NMR : δ 1.2 (*t*, $J = 7\text{ Hz}$, 6H), 2.6 (*s*, 4H) and 4.2 (*q*, $J = 7\text{ Hz}$, 4H)
 Explaining the spectral data, deduce the structure of the compound.
16. An organic compound with molecular formula $C_3H_5ClO_2$ gave the following spectral data :
 UV : No significant absorption above 210 nm.

IR : A broad band in the range of 2500–3300 cm^{-1} centring around 2900 cm^{-1} , and a strong intensity band at 1705 cm^{-1} .

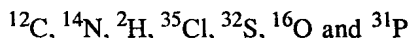
$^1\text{H NMR}$: Two triplets at δ 2.8 and 3.8 and a singlet at δ 12 are found in the intensity ratio 2 : 2 : 1. Deduce the structure of the compound and explain the spectral data.

17. An organic compound $\text{C}_4\text{H}_7\text{N}$ gave the following spectral data :
UV : No significant absorption above 200 nm.
IR : Significant absorption bands at 2940, 2270 and 1460 cm^{-1} .
PMR : δ 2.72 (septet, $J = 6.7$ cps) and 1.33 (doublet, $J = 6.7$ cps) in the intensity ratio 1 : 6. Explaining the spectral data, deduce the structure of the compound.
18. Explain the following spectral data given by an organic compound $\text{C}_9\text{H}_{10}\text{O}_2$ and deduce the structure of the compound :
UV : λ_{max} 257 nm, ϵ_{max} 194.
IR : Significant absorption bands at 3040, 2950, 1740, 1480, 1440, 1220, 750 and 700 cm^{-1} .
PMR : δ 1.96 (3H, s), 5.00 (2H, s) and 7.22 (5H, s).
19. Rationalizing the following spectral data, deduce the structure of a compound with molecular formula $\text{C}_3\text{H}_7\text{NO}$.
UV : λ_{max} 238 nm, ϵ_{max} 10500.
IR : Significant absorptions at 3428, 2941–2857, 1681 and 1452 cm^{-1} .
 $^1\text{H NMR}$: δ 1.9 (3H, s), 2.7 (3H, s) and 8.13 (1H, s)
20. A compound with molecular formula $\text{C}_6\text{H}_{12}\text{O}$ gave the following spectral data :
UV : λ_{max} 280 nm, ϵ_{max} 25.
IR : Significant bands at 1715 and 2900 cm^{-1} .
PMR : Two singlets at δ 1.0 and 2.0 in the intensity ratio 3 : 1. Explaining the spectral data, deduce the structure of the compound.
21. An organic compound C_9H_{12} gave the following spectral data :
UV : λ_{max} 268 nm, ϵ_{max} 480.
IR : Significant absorption bands at 3065–2910, 1608 and 1473 cm^{-1} .
PMR : δ 2.26 (9H, s) and 6.70 (3H, s)
Explaining the spectral data, derive the structure of the compound.
22. An organic compound $\text{C}_3\text{H}_5\text{NO}$ is transparent in the UV spectrum. Its IR spectrum shows bands at 2860–2940, 2250 and 1460 cm^{-1} . It shows two PMR singlets at δ 4.22 and 3.49 in the intensity ratio 2 : 3. Explaining the spectral data, deduce the structure of the compound.
23. An organic compound $\text{C}_7\text{H}_8\text{O}$ gave the following spectral data :
UV : λ_{max} 255 nm, ϵ_{max} 202.
IR : Significant absorption bands at 3400, 3065, 2890, 1500 and 1455 cm^{-1} .
 $^1\text{H NMR}$: δ 3.90 (s, 1H), 4.60 (s, 2H) and 7.26 (s, 5H)
Deduce the structure of the compound and explain the spectral data.
24. An organic compound with molecular mass 58 is transparent above 200 nm in its UV spectrum. It shows absorption bands at 2940–2860 and 1460 cm^{-1} in its IR spectrum. The PMR spectrum of the compound exhibits signals at δ 4.75 (t, $J = 7.1$ cps) and 2.75 (quintet, $J = 7.1$ cps) in the intensity ratio 2 : 1. Derive the structure of the compound and explain the spectral data.
25. An organic compound with molecular formula $\text{C}_7\text{H}_{12}\text{O}_4$ gave the following spectral data :
UV : No significant absorption band above 210 nm.
IR : Significant absorption band at 2940–2860, 1740, 1460, 1260 and 1050 cm^{-1} .
PMR : δ 1.3 (t, $J = 7.2$ Hz), 2.5 (s) and 4.2 (q, $J = 7.2$ Hz) in the intensity ratio 3 : 1 : 2, respectively. Rationalizing the above spectral data, deduce the structure of the compound.

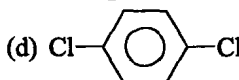
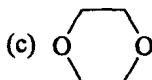
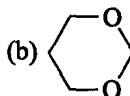
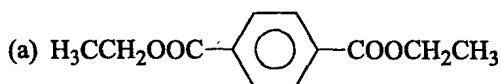


PROBLEMS FOR SELF ASSESSMENT

1. For which of the following isotopes NMR spectroscopy is possible and why?



2. Predict the number of signals and their relative intensities in the low resolution PMR spectra of the following compounds :
- (a) Toluene (b) Propanal (c) Propionamide
3. What is chemical shift? Giving examples, discuss the factors which affect the magnitude of the chemical shift.
4. Explain spin-spin coupling and splitting of signals with examples.
5. Predict the number of signals and their multiplicity in the PMR spectra of the following compounds :



6. Write notes on the following :
- (a) Shielding and deshielding
 (b) Relaxation processes
 (c) Coupling constant
 (d) Why are the NMR absorption positions expressed relative to a reference compound?
 (e) Why is TMS a good reference compound in NMR spectroscopy?
7. In PMR spectroscopy, what information can be obtained from the following?
- (a) Number of signals (b) Chemical shifts (c) Areas under peaks (d) Splitting of signals
 (e) Coupling constants
8. Give a structure consistent with each of the following sets of NMR data:
- (a) $\text{C}_3\text{H}_5\text{Cl}_3$: δ 2.20 singlet, 3H; δ 4.02, singlet, 2H
 (b) $\text{C}_{10}\text{H}_{14}$: δ 1.30, singlet, 9H; δ 7.28, singlet, 5H
 (c) $\text{C}_{10}\text{H}_{14}$: δ 0.88, doublet 6H; δ 1.86, multiplet, 1H; δ 2.45; doublet, 2H; δ 7.12, singlet, 5H.
9. Predict the number of signals and their relative intensities in the PMR spectra of the following isomers :
- (a) Acetone and propanal (b) Ethylbenzene and *p*-xylene
 (c) 2-Pentanone and 3-pentanone
10. What is cause of different chemical shifts for various hydrogens in NMR spectroscopy? Why are chemical shifts generally expressed in δ or τ values instead of in cps (Hz)?
11. A compound $\text{C}_{10}\text{H}_{13}\text{Cl}$ gave the following NMR data :
- δ 1.57, singlet, 6H
 δ 3.07, singlet, 2H
 δ 7.27, singlet, 5H
- Deduce the structure of the compound.
12. Using PMR spectroscopy, how will you distinguish each of the following isomeric pairs :
- (i) Maleic acid and fumaric acid

- (ii) 1-Chloropropane and 2-chloropropane
 (iii) Intermolecular hydrogen bonding and intramolecular hydrogen bonding
13. Explain the following :
- Acetylenic protons absorb at higher field than olefinic protons.
 - The hydroxylic proton of ethanol does not split the PMR signal of its methylene protons in the presence of a trace of acid.
 - No signal for deuterium is observed in the PMR spectrum of a compound, *e.g.*, $\text{CD}_3\text{CH}_2\text{CH}_3$.
14. An organic compound has molecular formula $\text{C}_3\text{H}_6\text{Br}_2$. Its PMR spectrum is given in Fig. 1.29. Interpret the spectrum and assign the structure to the compound.

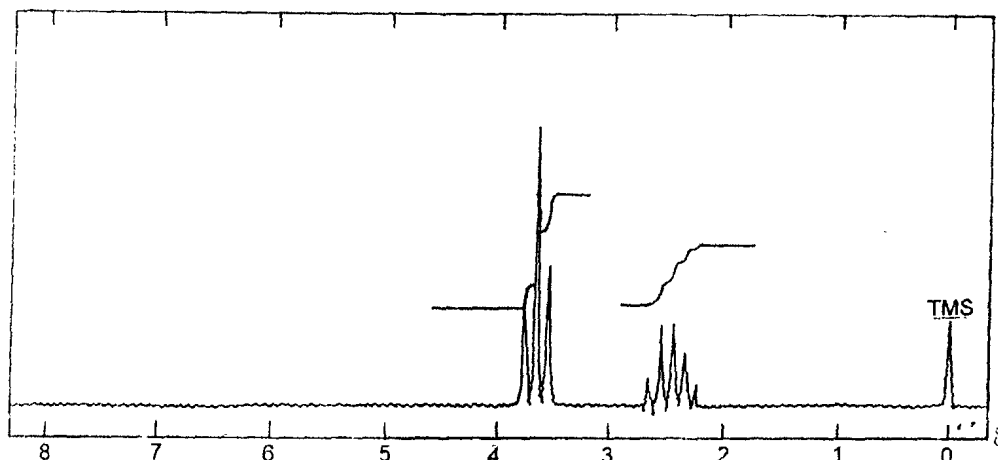


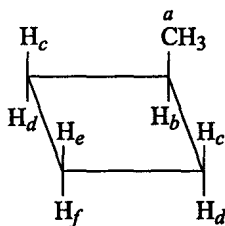
Fig. 1.29.

15. The following ^1H NMR absorptions were recorded as detailed below and are listed in Hz from TMS standard. Convert the absorption values into δ units :
- 451 Hz at 60 MHz spectrometer
 - 430 Hz at 90 MHz spectrometer
 - 543 Hz at 100 MHz spectrometer
16. A compound has molecular formula $\text{C}_3\text{H}_8\text{O}$. Its IR spectrum shows a strong absorption band at 3380 cm^{-1} with no other characteristic band. The PMR spectrum of the compound displayed signals δ 1.2 (d, 6H), 3.8 (septet, 1H) and 4.9 (s, 1H). Deduce the structure of this compound.
17. Using PMR spectroscopy, how will you distinguish the following isomeric compounds :
- 1,4-Dioxane and 1,3-dioxane
 - t*-Butyl bromide and 1-bromo-2-methylpropane
 - 1-Butyne and 2-butyne
18. Propose a structure consistent with the ^1H NMR data of each of the following compounds :
- $\text{C}_4\text{H}_{10}\text{O}$: δ 1.28 (s, 9H), 1.35 (s, 1H)
 - $\text{C}_4\text{H}_{10}\text{O}_2$: δ 3.25 (s, 6H), 3.45 (s, 4H)
 - $\text{C}_{10}\text{H}_{13}\text{Cl}$: δ 1.57 (s, 6H), 3.07 (s, 2H), 7.27 (s, 5H)
19. If the observed chemical shift of a proton is 315 Hz from TMS at a 90 MHz NMR spectrometer, what is the chemical shift in terms of δ ? Express it in τ value also.
20. A compound containing C, H, O and Cl shows a strong IR absorption band near 1710 cm^{-1} and a broad band near 2800 cm^{-1} . Its PMR spectrum displays two triplets at δ 2.8 and 3.8 and a singlet at about δ 12 in the intensity ratio 2 : 2 : 1, respectively. Deduce the structure of the compound.

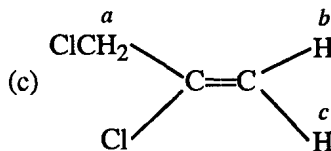
21. A compound C_8H_{10} exhibited the following PMR signals :
- (i) a triplet (3H) at δ 1.22 (ii) a quartet (2H) at δ 2.62
 (iii) a singlet (5H) at 7.12
 Deduce the structure of the compound.
22. (a) How PMR spectroscopy is useful in detection of aromaticity?
 (b) Discuss the use of deuterium exchange and deuterium labelling in PMR spectroscopy.
23. A compound having the molecular formula $C_{10}H_{14}$ gave the following 1H NMR data :
 (i) δ 0.88 (9H, s), and (ii) δ 7.28 (5H, s).
 Assign the structural formula to the compound.
24. An organic compound C_4H_8O gave the following spectral data :
 UV : λ_{max} 274 nm, ϵ_{max} 17
 IR : A significant bond at 1705 cm^{-1}
 1H NMR : δ 1.07 (t, $J = 7.2$ Hz, 3H); 2.12 (s, 3H); 2.48 (q, $J = 7.2$ Hz, 2H).
 Explaining the spectral data, deduce the structure of the compound.

ANSWERS TO VERY SHORT ANSWER QUESTIONS

1. (a) $I = 1$, spin states : -1, 0, +1
 (b) $I = 1/2$, spin states : -1/2, +1/2
 (c) $I = 1$, spin states : -1, 0, +1
 (d) $I = 1/2$, spin states : -1/2, +1/2
 (e) $I = 5/2$, spin states : -5/2, -3/2, -1/2, +1/2, +3/2, +5/2
2. $R_3CH > R_2CH_2 > RCH_3 > CH_4$
3. $CH_3-CH_3 < (CH_3)_3N < CH_3OCH_3 < CH_3F$
4. Six types of protons :

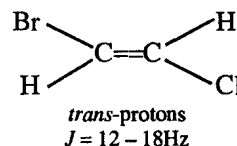
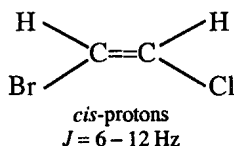
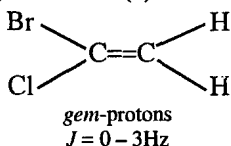


5. (a) One singlet (b) Two singlet

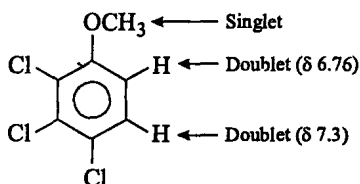


Three signals, one singlet due to protons *a* and two doublets one each for proton *b* and *c*.

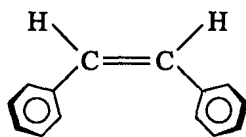
6. Yes. Because they are not equivalent and are separated from each other only by two bonds.
7. C_2H_2BrCl has three geometrical isomers which can be distinguished on the basis of their different coupling constants (J).



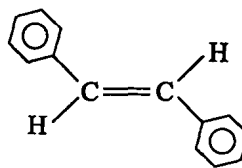
8. (i) A three-proton singlet at δ 3.9 show the presence of a methoxy ($-\text{OCH}_3$) group.
 (ii) Two one-proton doublets at δ 6.76 and 7.3 ($J = 8$ Hz) indicate that these are *o*-protons. The rest of the three substituents are chlorine atoms. Thus the compound is :



9. (c)
 10. In *cis*- and *trans*-stilbenes the olefinic protons are equivalent, hence do not couple to split their signals. Thus, these two isomers cannot be distinguished on the basis of J values. However, they can be distinguished on the basis of chemical shifts of olefinic protons. In *trans*-isomer the olefinic protons absorb at lower field (δ 6.99) than that of the *cis*-isomer (δ 6.49).

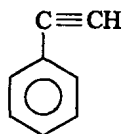
*cis*-stilbene

δ 6.49 (the aromatic rings are tilted, hence there is no van der Waals repulsion to cause deshielding of the olefinic protons)

*trans*-stilbene

δ 6.99 (each olefinic proton lies in the plane of the two phenyl rings, hence is deshielded due to van der Waals repulsion)

11. The absorption of 5 protons at δ 7.4 indicates the presence of a phenyl group (mol. mass 77). The rest of the mass ($102 - 77 = 25$) should be a hydrocarbon substituent containing two carbon atoms and one hydrogen atom. Since the proton absorbs at δ 3.08, it must be an acetylenic proton. Thus, the structure of the compound is :



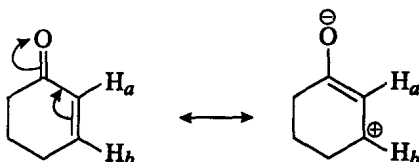
12. Methyl protons in CH_3I are more deshielded than that of *tert*-butyl iodide, hence protons of CH_3I absorb at δ 2.2 while that of *tert*-butyl iodide at δ 1.8. For every three protons in CH_3I there are nine protons in $(\text{CH}_3)_3\text{CI}$. Thus,

$$\frac{5 \text{ protons of } \text{CH}_3\text{I} \times 1/3/\text{proton}}{1 \text{ protons of } (\text{CH}_3)_3\text{CI} \times 1/9/\text{proton}} = \frac{15 \text{ molecules of } \text{CH}_3\text{I}}{1 \text{ molecule of } (\text{CH}_3)_3\text{CI}}$$

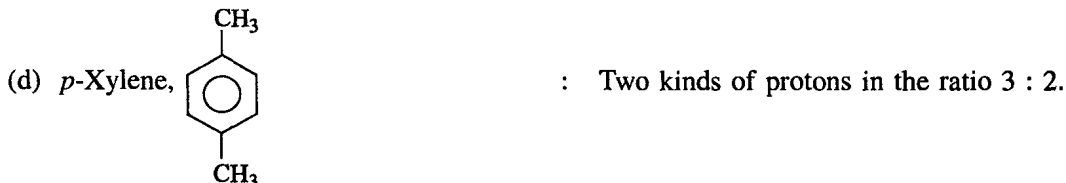
$$\text{Mole fraction of } \text{CH}_3\text{I} = \frac{15}{15 + 1} = \frac{15}{16} = 0.938$$

Thus, the sample contains 93.8 mole percent of CH_3I and rest, *i.e.*, 6.2 mole per cent of $(\text{CH}_3)_3\text{CI}$.

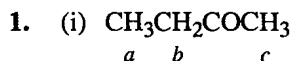
13. H_b will absorb at lower field because due to resonance electron density decreases at the carbon to which the proton H_b is attached, hence it gets deshielded.



14. (a) 4 (b) 3 (c) 1 (d) 1 (e) 1
15. (a) Ethanol, $\text{CH}_3\text{CH}_2\text{OH}$: Three kinds of protons in the ratio 3 : 2 : 1.
 (b) Butanone, $\text{CH}_3\text{COCH}_2\text{CH}_3$: Three kinds of protons in the ratio 3 : 2 : 3.
 (c) Crotonic acid, $\text{CH}_3-\text{CH}=\text{CH}-\text{COOH}$: Four kinds of protons in the ratio 3 : 1 : 1 : 1.

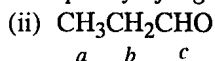


SOLUTIONS OF PROBLEMS



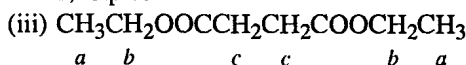
On moving downfield, the sequence of signals is; protons *a*, then *c* and then *b*.

Multiplicity of signals : Protons *a*, triplet; *b*, quartet and *c*, singlet.



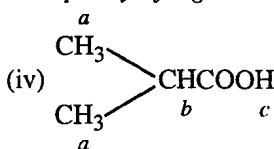
On moving downfield, the sequence of signals is : *a*, then *b* and *c*.

Multiplicity of signals : Protons *a*, triplet; *b*, multiplet consisting of eight lines [(3 + 1)(1 + 1) = 8], and *c*, triplet.



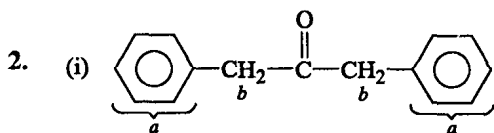
On moving downfield, the sequence of signals is : protons *a*, then *c* and then *b*.

Multiplicity of signals : Protons *a*, triplet; *b*, quartet and *c*, singlet.

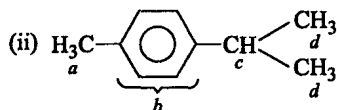


On moving downfield, the sequence of signals is : *a* then *b* and *c*

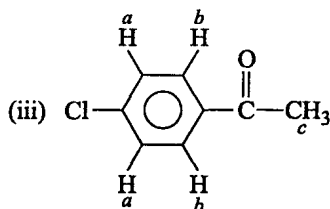
Multiplicity of signals : Protons *a*, doublet; *b*, septet and *c*, singlet.



In certain cases, environments of chemically nonequivalent protons are not different enough for the signals to be noticeably separated, and in such cases we may see fewer signals than we predict. For example, in aromatic compounds with non-electronegative substituents the ortho, meta and para protons have nearly the same chemical shifts, and hence for NMR purposes they are nearly equivalent, i.e., exhibit only one signal (singlet). This is the situation in the present case, thus all the five phenyl protons (*a*) are nearly equivalent and appear as a singlet. This compound shows two singlets; one due to the phenyl protons (*a*) and the other due to the methylene protons (*b*).



This compound contains four kinds of protons, hence will exhibit four PMR signals. Protons *a*, a singlet; protons *b*, a singlet; proton *c*, a septet because it has six neighbouring protons ($6 + 1 = 7$, septet); protons *d* have one neighbouring proton, hence they will appear as a doublet ($1 + 1 = 2$, doublet).



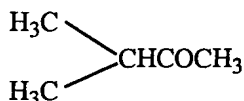
In this compound, protons *b* which are *ortho* to the carbonyl group will have quite different chemical shift compared to protons *a* which are *ortho* to the chloro group. Thus, this compound has three kinds of protons and will exhibit three signals. Protons *a* have one neighbouring proton, hence will appear as a doublet ($1 + 1 = 2$, doublet). Similarly, protons *b* will also appear as a doublet. The methyl protons (*c*) have no neighbouring proton, hence will appear as a singlet.

3. The chemical shift in Hz is directly proportional to the strength of the applied magnetic field (and therefore, to the applied frequency). Thus,

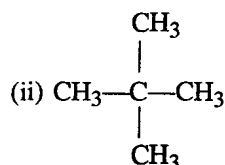
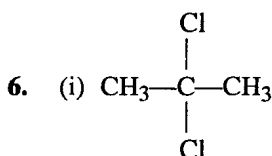
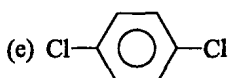
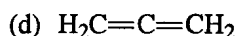
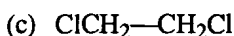
$$(i) \frac{60}{60} \times 90 = 90 \text{ Hz} \quad (ii) \frac{100}{60} \times 90 = 150 \text{ Hz} \quad (iii) \frac{180}{60} \times 90 = 270 \text{ Hz}$$

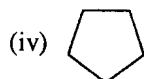
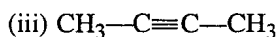
4. (i) The compound with molecular formula $C_5H_{10}O$ shows a doublet due to six protons. This indicates that these six protons are equivalent and the carbons bearing them are attached to a $-\text{CH}-$ group, *i.e.*, the molecule has $(\text{CH}_3)_2\text{CH}-$ group; the $-\text{CH}-$ proton appears as a

multiplet (septet). One singlet due to three protons indicates that the compound contains a methyl group which has no proton on the atom to which it is attached. Thus, the structure for the compound which fits the above data is :

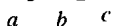


- (ii) The compound $C_4H_7\text{BrO}$ shows two triplets with the same coupling constant ($J = 6 \text{ Hz}$) showing that it contains two nonequivalent adjacent methylene groups coupled with each other ($-\text{CH}_2-\text{CH}_2-$). The presence of a three proton singlet indicates the presence of a methyl group which has no proton on the atom to which it is attached. Thus, the structure for the compound is :

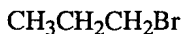




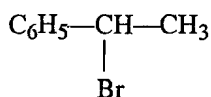
7. The PMR spectrum of the compound shows three signals, viz., two triplets and one sextet, hence it contains three kinds of protons. On moving upfield the successive heights of the integration curves at the signals are 8 mm, 8 mm and 12 mm, i.e., the ratio of the number of each kind of protons is 1 : 1 : 1.5. Since the molecular formula of the compound is $\text{C}_3\text{H}_7\text{Br}$, the number of each kind of protons is 2H, 2H and 3H. This indicates that the compound has $\text{CH}_3\text{CH}_2\text{CH}_2\text{—}$ group and thus, its structure is $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$.



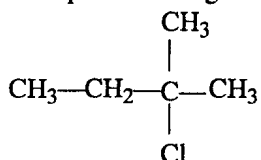
The protons *a* appear as an upfield triplet, while protons *c* as a downfield triplet. The protons *b* appear as a sextet. However, the protons *b* might be expected to exhibit twelve lines, i.e., $(3 + 1)(2 + 1) = 12$ because they are coupled with two equivalent groups of three protons *a* and two protons *c*. In practice, J_{ab} is approximately equal to J_{bc} and therefore overlapping of lines occurs as shown in Fig. 1.28 and thus, a sextet is observed. Since $J_{ab} = J_{bc}$, we can say that the *b* protons have five equivalent neighbouring protons, hence appear as a sextet, i.e., $5 + 1 = 6$. Thus, the structure of the given compound is :



8. The molecular formula of the compound is $\text{C}_8\text{H}_9\text{Br}$ and the intensity ratio of the different kinds of protons present is 1 : 3 : 5, therefore, the number of each kind of protons will be 1H, 3H and 5H. The presence of an unsymmetrical multiplet at $\sim 7.4 \delta$ due to 5H shows the presence of a phenyl group ($\text{C}_6\text{H}_5\text{—}$), and the presence of a quartet due to 1H and a doublet due to 3H indicates the presence of —CH—CH_3 group. Thus, the structure of the given compound is :



9. (i) 1,2-Dimethoxyethane ($\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3$) will exhibit two singlets due to protons *a* and *b*, while 1,1-dimethoxyethane, ($\text{CH}_3\text{O})_2\text{CHCH}_3$, will exhibit one singlet due to protons *a*, one quartet due to protons *b* and one doublet due to protons *c*.
- (ii) *Cis*-1-chloropropene and *trans*-1-chloropropene can be distinguished on the basis of their coupling constants. The *cis* isomer will have lower coupling constant ($J_{cis} = 6\text{--}12 \text{ Hz}$) than the *trans* isomer ($J_{trans} = 12\text{--}18 \text{ Hz}$).
- (iii) Both the methyl group in acetone (CH_3COCH_3) are equivalent, hence it will show only one singlet. In methyl acetate ($\text{CH}_3\text{COOCH}_3$) the two methyl groups are nonequivalent, hence it will show two singlets.
10. The ^1H NMR spectrum of the compound exhibits a three proton triplet and a two proton quartet which indicate the presence of the $\text{CH}_3\text{CH}_2\text{—}$ group. The appearance of a six proton singlet shows the presence of two equivalent $\text{CH}_3\text{—}$ groups which must be attached to a carbon containing no hydrogen. Thus, the structure of the compound having molecular formula $\text{C}_5\text{H}_{11}\text{Cl}$ is :



11. Multiplicity = $n + 1$

In the present case $n = 4$, hence $4 + 1 = 5$, *i.e.*, H_a will appear as a quintet. The relative intensity of component peaks in its signal will be $1 : 4 : 6 : 4 : 1$, which can be derived using Pascal's triangle or the expression $(x + 1)^n$.

12. (a) $\overset{a}{\text{CH}_3}\text{—}\overset{b}{\text{CH}_2}\text{—Br}$. Two signals ($a : b = 3 : 2$). CH_3 will appear at a higher field than CH_2 . Protons a appear as a triplet ($1 : 2 : 1$) and protons b as a quartet ($1 : 3 : 3 : 1$).

(b) $\overset{a}{\text{CH}_3}\text{—}\overset{b}{\text{CHCl}}\text{—}\overset{a}{\text{CH}_3}$. Two peaks ($a : b = 6 : 1$). CH_3 (a) will appear at a higher field than CH (b). Protons a exhibit a doublet ($1 : 1$) and proton b a heptet ($1 : 6 : 15 : 20 : 15 : 6 : 1$).

(c) $\overset{a}{\text{CH}_3}\text{—O—}\overset{b}{\text{CH}_2}\text{—}\overset{c}{\text{CH}_3}$. Three peaks ($3 : 2 : 3$). Protons a (singlet), b (quartet, $1 : 3 : 3 : 1$) and c (triplet, $1 : 2 : 1$). On moving downfield, the sequence of signals : c, a, b .

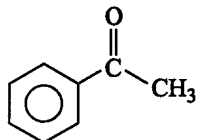
13. The deshielding effect induced by the ring current in the benzene ring system extends beyond the hydrogens directly attached to the aromatic ring, thus the methyl protons on toluene appear downfield as compared to the protons of methyl group attached to the double bond in 1-methylcyclohexene.

14. UV : λ_{max} 278 and 319 nm indicate the presence of a carbonyl (an aldehydic or ketonic) group and an aromatic ring.

IR : Absorption bands at $3070\text{--}3010$ and $2970\text{--}2860\text{ cm}^{-1}$ are due to aromatic and alkyl C—H stretch, respectively. The band at 1685 cm^{-1} may be due to the aromatic ketonic $>\text{C}=\text{O}$ group. The absorption bands at 1605, 1580 and 1450 are characteristic of an aromatic ring.

PMR : The presence of a five proton multiplet at δ 7.5 indicates the presence of a phenyl group and the three proton singlet at δ 2.1 shows the presence of a methyl group.

The above discussion clearly shows that the compound contains $\text{C}_6\text{H}_5\text{—}$, $\text{C}=\text{O}$ (ketonic) and $\text{CH}_3\text{—}$ structural units which amount to 120 mass units, *i.e.*, the molecular mass of the compound. Thus, the structure of the compound is :

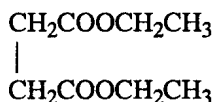


15. UV : The absence of absorption band above 210 nm indicates the absence of conjugation, aldehydic and ketonic carbonyl groups and an aromatic ring.

IR : Absorption bands at 1735 and 2950 cm^{-1} indicate the presence of an ester ($>\text{C}=\text{O}$) and alkyl group, respectively.

$^1\text{H NMR}$: The presence of a six proton triplet at δ 1.2 and a four proton quartet at δ 4.2 (both having $J = 7\text{ Hz}$) indicates the presence of two equivalent CH_3CH_2 groups. The four proton singlet at δ 2.6 is due to a $\text{—CH}_2\text{CH}_2\text{—}$ group with equivalent protons. Thus, the compound contains two equivalent CH_3CH_2 group and one $\text{—CH}_2\text{CH}_2\text{—}$ group.

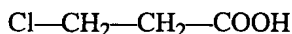
On the basis of the spectral data, as explained above, and the given molecular formula $\text{C}_8\text{H}_{14}\text{O}_4$, the deduced structure of the compound is :



16. UV : The absence of absorption band above 210 nm indicates the absence of conjugation, aldehydic and ketonic carbonyl groups and an aromatic ring.

IR : The presence of a broad band in the range of $2500\text{--}3300\text{ cm}^{-1}$ indicates the presence of an alkyl C—H and —OH groups, and the strong band at 1705 cm^{-1} may be due to —COOH group.

^1H NMR : The presence of two triplets at δ 2.8 and 3.8 shows the presence of two adjacent and nonequivalent —CH₂— groups, *i.e.*, —CH₂—CH₂— group. The presence of a very low field singlet at δ 12 indicates the presence of a carboxylic proton. These are found in the intensity ratio 2 : 2 : 1. Thus, the compound contains —Cl, —CH₂CH₂— and —COOH groups, and its structure is :

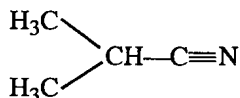


This structure is strictly in accordance with the given spectral data as explained above.

17. **UV :** The absence of absorption band above 200 nm indicates the absence of conjugation, aldehydic and ketonic carbonyl groups and an aromatic ring.

IR : The absorption bands at 2270, 2940 and 1460 cm^{-1} are due to $\text{C}\equiv\text{N}$, alkyl C—H and C—C stretching, respectively.

PMR : A septet and a doublet with the same value of coupling constant ($J = 6.7\text{ cps}$) suggest the presence of an isopropyl group $(\text{CH}_3)_2\text{CH—}$. This corresponds to C_3H_7 . The remaining one C and one N constitute a $\text{C}\equiv\text{N}$ group as also indicated by the IR band at 2270 cm^{-1} . Thus, the compound contains $(\text{CH}_3)_2\text{CH—}$ and $\text{C}\equiv\text{N}$ structural units, and its structure is :

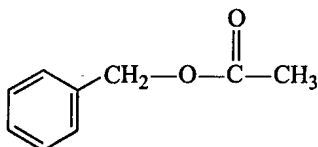


18. **UV :** λ_{max} 257 nm, ϵ_{max} 194 indicate the presence of an aromatic ring.

IR : Absorption bands at 3040, 1480, 1440, 700 and 750 cm^{-1} indicate the presence of monosubstituted benzene ring. The presence of a band at 1740 together with another band at 1220 cm^{-1} is characteristic of an acetate. The band at 2950 cm^{-1} is due to an alkyl C—H stretching.

PMR : The presence of five proton singlet at δ 7.22 is due to aromatic protons. The singlet nature of this peak shows that the compound is a monosubstituted benzene derivative and that the substituent has nearly the same electronegativity as the ring carbon. A three proton singlet at δ 1.96 indicates the presence of a $\text{CH}_3\text{—}$ group on a carbonyl group. The other two proton singlet shows the presence of a CH_2 group and its chemical shift (δ 5.00) is in accordance with its attachment to a benzene ring on one side and oxygen atom on the other side.

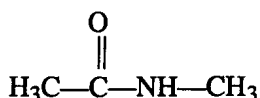
Thus, the following is the structure of the compound consistent with its given molecular formula and spectral data :



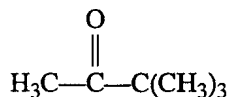
19. **UV :** The absorption at λ_{max} 238 nm, ϵ_{max} 10500 is characteristic of conjugation.

IR : The band at 2941–2857, 3428 and 1452 cm^{-1} are due to alkyl C—H, N—H and C—C stretching, respectively. The band at 1681 cm^{-1} is due to $\text{C}=\text{O}$ stretching which is in conjugation with the lone pair of electrons of nitrogen atom.

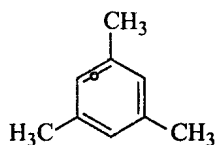
^1H NMR : Two singlets, each due to three protons, indicate the presence of two methyl groups, one of which at δ 2.7 may be due to a methyl group attached to the nitrogen atom. The low field (δ 8.13) one proton singlet is due to —NH—. Thus, the structure of the compound is :



20. **UV** : λ_{\max} 280 nm with ϵ_{\max} 25 indicates the presence of an aldehydic or ketonic C=O group.
IR : Absorption bands at 1705 and 2900 cm^{-1} may be assigned to ketonic C=O and alkyl C—H, respectively.
PMR : The two singlets are in the intensity ratio 3 : 1 and the molecular formula of the compound is $\text{C}_6\text{H}_{12}\text{O}$, hence the singlets are due to 9 and 3 protons, respectively. This indicates that the compound has three equivalent CH_3 groups and one more CH_3 group which is non-equivalent to these CH_3 groups.
 Thus, the compound has the following structure, which explains all the given spectral data.



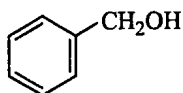
21. **UV** : λ_{\max} 268, ϵ_{\max} 480 indicate the presence of an aromatic ring.
IR : Absorption bands at 3065–2910 cm^{-1} may be due to aromatic and saturated C—H stretching. The bands at 1608 and 1473 cm^{-1} are due to C=C and C—C stretchings, respectively.
PMR : The singlet at δ 6.79 indicates the presence of three aromatic protons, and the singlet at δ 2.26 is due to nine alkyl protons. Thus, there is a benzene ring containing three methyl groups and the compound has the following structure.



22. The compound is transparent in the UV spectrum indicating the absence of conjugation, aldehydic and ketonic carbonyl groups and an aromatic ring. The IR bands at 2860–2940, 2250 and 1460 cm^{-1} are due to alkyl C—H, C≡N and C—C stretches, respectively. The two PMR singlets are due to CH_2 and CH_3 because the molecular formula of the compound has five protons and the PMR singlet intensity ratio is 2 : 3. Thus, the structure of the compound is :



23. **UV** : The absorption at λ_{\max} 255 nm, ϵ_{\max} 202 indicate the presence of an aromatic ring.
IR : Significant absorption bands at 3400, 3065 and 2890 cm^{-1} are due to —OH, aromatic C—H and alkyl C—H, respectively. The bands at 1500 and 1455 cm^{-1} are due to C—C stretching.
 ^1H NMR : The one proton singlet at δ 3.9 is due to —OH proton and the two proton singlet at δ 4.6 is due to a — CH_2 — group attached to an aromatic ring on one side and an electronegative atom oxygen on the other side. The five proton singlet at δ 7.26 is due to a phenyl group. According to these spectral data the compound has the following structure :



24. **UV** : The compound is transparent above 200 nm in its UV spectrum. This indicates the absence of conjugation, aldehydic and ketonic carbonyl group and an aromatic ring.
IR : Absorption bands at 2940–2860 and 1460 cm^{-1} are due to an alkyl C—H and C—C stretching, respectively.
PMR : The presence of a triplet at δ 4.75 and a quintet at δ 2.7 having the same J value (7.1 cps) shows the presence of a — CH_2 — CH_2 — CH_2 — grouping in which the middle — CH_2 — is non-equivalent to the terminal — CH_2 — groups. The molecular mass of the compound is 58 and that of the — CH_2 — CH_2 — CH_2 — unit is 42, hence the remaining mass 16 indicates the presence of an oxygen atom in the molecule. The above discussion leads to the following structure of the molecule :



25. **UV** : The absence of absorption band above 210 nm indicates the absence of conjugation, aldehydic and ketonic carbonyl groups and an aromatic ring.

IR : Absorption bands at 2940–2860 and 1740 cm^{-1} are due to alkyl C—H and ester C=O, respectively. Absorption at 1460 is due to C—C and that at 1260 and 1050 cm^{-1} are attributable to C—O stretchings.

PMR : The triplet at δ 1.3 and quartet at δ 4.2 with the same coupling constant ($J = 7.2$ Hz) indicate the presence of CH_3CH_2 - group. From the molecular formula $\text{C}_7\text{H}_{12}\text{O}_4$ and the intensity ratio 3 : 1 : 2 it is clear that the triplet is due to 6H, singlet is due to 2H and the quartet is due to 4 H. This shows that, there are two CH_3CH_2 -groups and one $-\text{CH}_2-$ groups in the molecule. The chemical shift of the singlet (δ 2.5) shows that the $-\text{CH}_2-$ group is attached to a C=O group. On the basis of the above rationalization of spectral data, the following structure of the compound is deduced :

