5

Proton Nuclear Magnetic Resonance (PMR or ^{1}H NMR) Spectroscopy

5.1 Introduction

Similar to the UV 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 Prucell at Harvard and Bloch at Stanford. The first application of NMR to the study of structure was made in 1951 and ethanol was the first compound thus studied. In 1952, Prucell and Bloch won the Nobel Prize in Physics for their discovery.

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

5.2 Theory

Nuclei of some isotopes 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). Each proton and neutron has its own spin and I is a resultant of these spins, i.e. vector combination of proton and neutron spins. Unfortunately, the laws governing this combination are not yet known, hence the spin of a particular nucleus cannot be predicted in general. However, the observed spins can be rationalized and some empirical rules have been formulated which are given in Table 5.1. The spin number I may have values $0, \frac{1}{2}, 1, \frac{3}{2}, \frac{5}{2}$ etc. depending on the mass number and atomic number of the atom as shown in Table 5.1. Nuclei composed of even number of protons and neutrons have no net spin ($I = 0$) because their spins are paired off.

The isotopes with either odd mass number or odd atomic number possess a mechanical spin and only such isotopes can exhibit a nuclear magnetic resonance spectrum.

Table 5.1 Spin number of some isotopes

Mass number	Atomic number	Spin number I		Examples
Odd	Odd or even	$\frac{1}{2}$	Half-integer	^{1}H, ^{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	0 (no spin)		^{12}C, ^{16}O, ^{32}S, ^{34}S
Even	Odd	1	Integer	^{14}N, ^{2}H (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 tiny bar magnet with a magnetic moment μ.

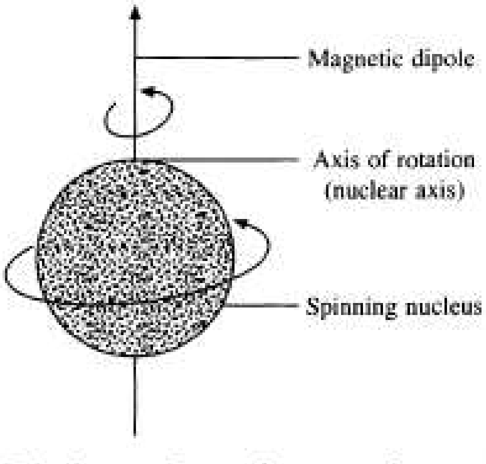

Fig. 5.1 Spinning nucleus and generated magnetic dipole

In the absence of an external magnetic field, the magnetic nuclei (nuclear magnetic dipoles) are randomly orientated, i.e. the nuclear spin is of no consequence (Fig. 5.2).

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 ^{1}H and ^{13}C. For both of these $I = \frac{1}{2}$. Hence, number of orientations for their magnetic dipoles will be $2 \times \frac{1}{2} + 1 = 2$ (because number of orientations $= 2I + 1$).

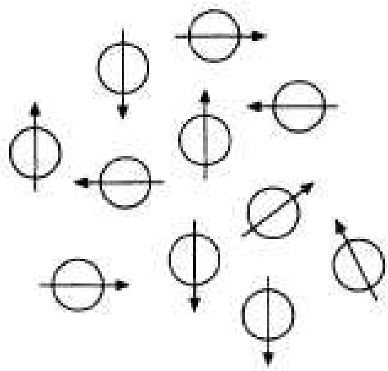

Fig. 5.2 Orientation of nuclear magnetic dipoles in the absence of an external magnetic field

Thus, the magnetic dipoles of nuclei with $I = \frac{1}{2}$, e.g. ^{1}H and ^{13}C will align parallel or antiparallel to the applied magnetic field, i.e. with or against the applied magnetic field, respectively (Fig. 5.3).

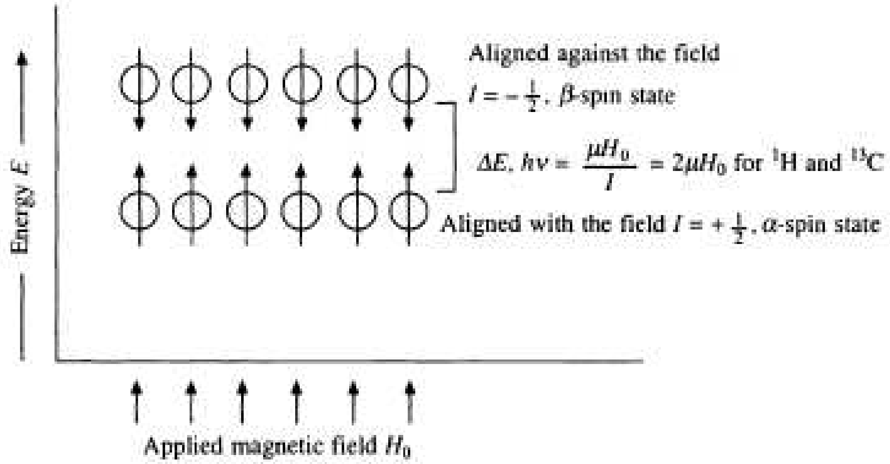

Fig. 5.3 Orientation of nuclear magnetic dipoles in an external magnetic field H_0

The alignment with the applied magnetic field is of lower energy and corresponds to the α-spin state ($+\frac{1}{2}$) 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.

The energy difference ΔE (i.e. the energy required for a transition) has been shown to be a function of 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

$$\nu = \frac{\gamma H_0}{2\pi} \tag{5.1}$$

or

$$\nu \propto H_0$$

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 tiny bar magnetic is directly proportional to its spin number I. It has been shown that

$$\gamma = \frac{2\pi\mu}{hI} \tag{5.2}$$

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

From Eqs. (5.1) and (5.2)

$$\nu = \frac{\gamma H_0}{2\pi} = \frac{2\pi\mu}{hI} \cdot \frac{H_0}{2\pi} = \frac{\mu H_0}{hI}$$

or

$$h\nu = \Delta E = \frac{\mu H_0}{I} \tag{5.3}$$

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

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

or

$$\nu = \frac{2\mu H_0}{h} \tag{5.4}$$

Equation (5.3) shows that the energy required for a transition ΔE is directly proportional to the strength of the applied magnetic field (because μ/I is constant for a given nucleus). This is shown graphically in Fig. 5.4. The stronger the field, 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.

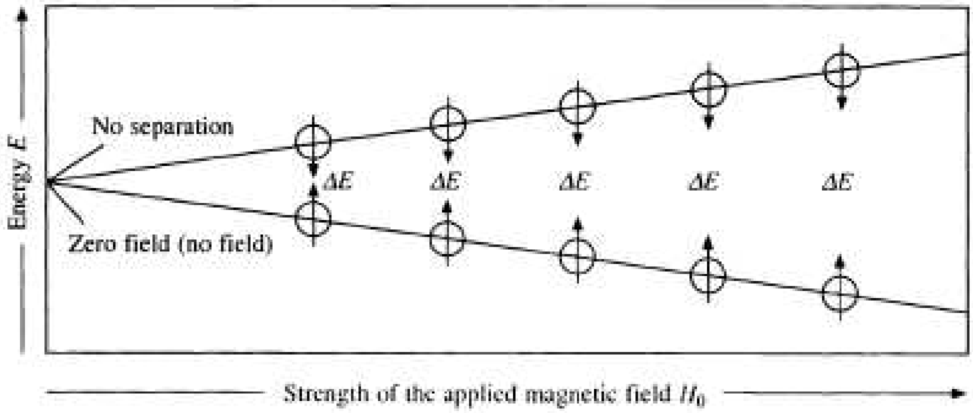

Fig. 5.4 Relationship between the transition energy ΔE and the applied magnetic field H_0

(i) Process of Absorption of Energy

If the axis of the nuclear magnet is not oriented exactly parallel or antiparallel to the applied magnetic field, then there will be a certain force by the applied magnetic field to so orient it. Since the nucleus is spinning, the effect is that its rotational axis draws out a circle perpendicular to the applied field, i.e. the nucleus starts precessing. This precession is similar to the gyroscopic motion of a common top which precesses if spun with an initial axis of rotation different from earth's gravitational field.

The nuclei aligned in such a way that their magnetic axes make an angle with the axis of the applied magnetic field H_0 are responsible for the process of absorption or emission of energy, i.e. for the NMR phenomenon. Fig. 5.5 shows a nucleus precessing in a magnetic field H_0.

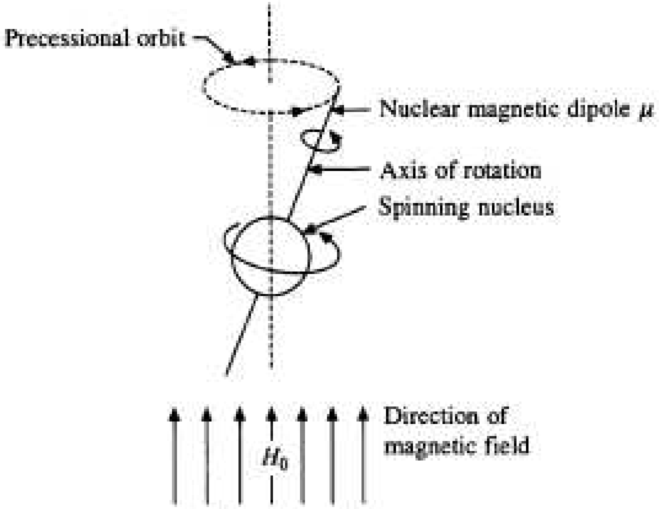

Fig. 5.5 A nucleus precessing in a magnetic field H_0

The precessional angular velocity $\omega_0 = \gamma H_0$.
From the fundamental NMR Eq. (5.1)

$$\gamma H_0 = 2\pi\nu$$

Therefore,

$$\omega_0 = 2\pi\nu$$

The value of this frequency ν inserted is called *precessional frequency*. The precessional angular velocity is quantized. Thus, the difference between angular velocities in the ground state and excited state corresponds to a precise frequency (i.e. energy) equal to the precessional frequency. Thus, the precessional frequency of spinning nucleus is exactly equal to the frequency of electromagnetic radiation necessary to induce a transition from one nuclear spin state to another. The transition corresponds to a change in the angle that the nuclear magnet makes with the applied magnetic field. This change can be brought about through the application of electromagnetic radiation whose magnetic vector component H_1 is rotating in a plane perpendicular to the applied magnetic field H_0 (Fig. 5.6).

When the frequency of the rotating magnetic field and the precessional frequency of the nucleus become equal, they are said to be in resonance, and absorption or emission of energy by the nucleus can occur.

The transition from one spin state to the other is called *flipping* of the precessing nucleus. 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 (Eq. (5.3)). A frequency of 60 MHz is needed at a magnetic field H_0 of 14,092 gauss for ^1H nuclei

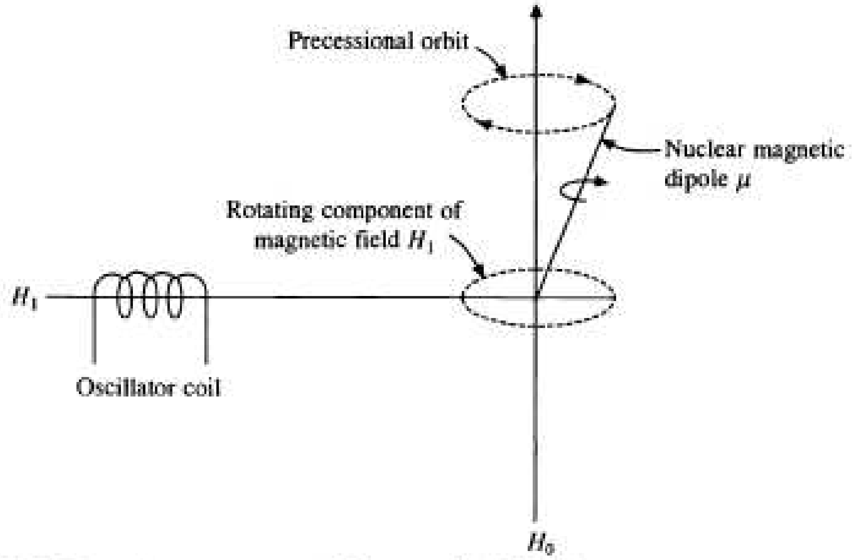

Fig. 5.6 Rotating component of magnetic field H_1 generated by an oscillator

(protons) to bring them into resonance (or any other desired combination in the same ratio; this comes from Eq. (5.4). 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 nucleus 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. Hence, 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 become equal, there will be no NMR effect, such a phenomenon is known as *saturation*.

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. The two types of relaxation processes are:

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

(a) Spin-spin (or Transverse) Relaxation

It involves mutual exchange of spins by two precessing nuclei in close proximity to each other. Each precessing nucleus is associated with a magnetic vector component rotating in a plane perpendicular to the main field. When two nuclei are in close proximity, this small rotating magnetic field is the same as is required to induce a transition in the neighbouring nucleus, 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 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, hence 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.

(b) 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 molecular lattice contains precessing nuclei all of which are undergoing translational, rotational and vibrational motions. Hence, a variety of small magnetic fields is present in the lattice. A particular small magnetic field, properly oriented in the lattice, can induce transition in a particular precessing nucleus from an upper state to a lower state. 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 non-viscous 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.

5.3 Instrumentation

The schematic diagram of a NMR spectrometer containing the following components is given in Fig. 5.7:

(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.

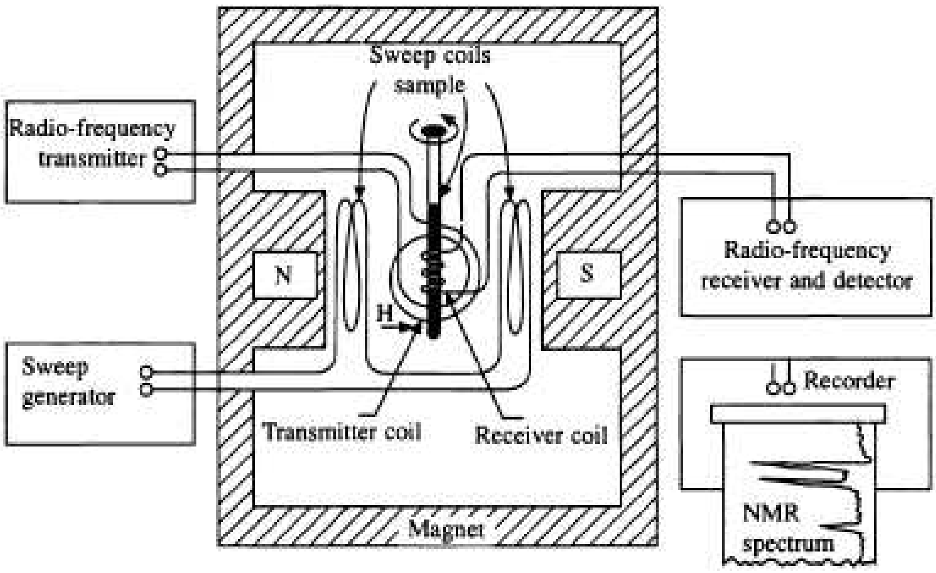

Fig. 5.7 Schematic diagram of a NMR spectrometer

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.

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

ΔE varies as the H_0 varies (Eq. 5.3). 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. A 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. 5.8.

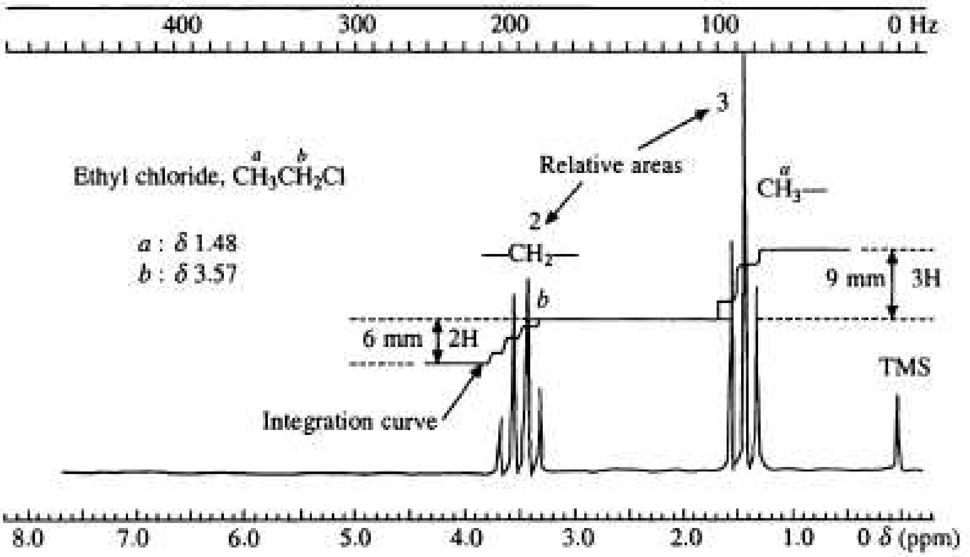

Fig. 5.8 PMR spectrum of ethyl chloride in $CDCl_3$ at 60 MHz

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

5.4 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

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*Instruments having ability to discriminate among the individual absorptions.

the deuterated form, e.g. deuterated chloroform CD_3Cl (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. Note that deuterium (^2H or D) has a nuclear magnetic dipole and thus, it should exhibit a 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.

5.5 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 *induced magnetic field* (σH_0) which opposes the applied magnetic field in the region of the nucleus, e.g. proton (Fig. 5.9). 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*, i.e.

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

where σ is screening or shielding constant.

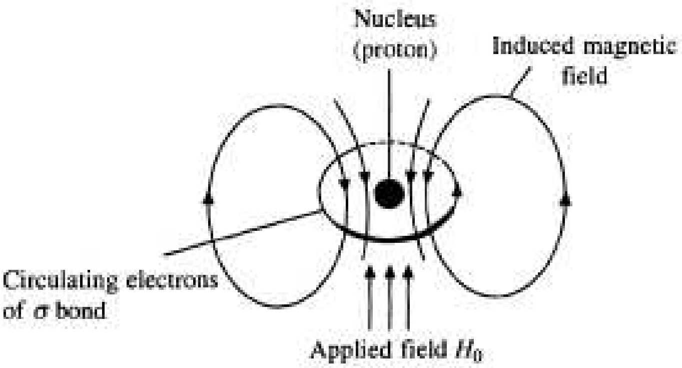


Fig. 5.9 Diamagnetic shielding of nucleus by circulating electrons

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, depending on its location in the induced magnetic field (see Section 5.7(ii)). 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 $(CH_3)_4Si$(TMS) is the most commonly used reference compound because of the 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 all its twelve protons are equivalent. Thus, very small quantity (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 the DSS (sodium 2,2-dimethyl-2-silapentane-5-sulphonate, $(CH_3)_3SiCH_2CH_2CH_2SO_3Na$), is used as an internal reference in aqueous solutions. The disadvantage of this reference compound is 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.

5.6 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 ν are given in Hz, 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 ν in Hz 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, i.e. ν are converted into δ units as follows:

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

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 values as

$$\tau = 10.00 - \delta$$

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. 5.10 shows NMR scale at 60 MHz and 100 MHz.

Example 1. Protons of a compound exhibit a 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

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

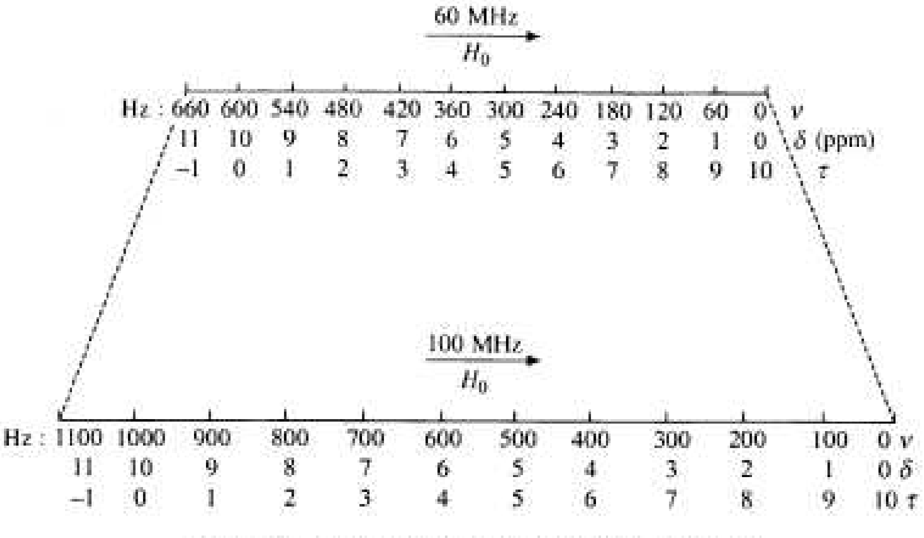


Fig. 5.10 NMR scale at 60 MHz and 100 MHz

Suppose the chemical shift in Hz is x. Therefore,

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

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

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.

Solution

$$\delta = \frac{\text{Chemical shift in Hz}}{\text{Oscillator frequency in Hz}} \times 10^6 = \frac{200}{60 \times 10^6} \times 10^6 = 3.33$$

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

The approximate chemical shift ranges of important chemical classes are given in Chart 5.1.

5.7 Factors Affecting Chemical Shift

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

(i) Electronegativity-inductive effect
(ii) Anisotropic effects
(iii) Hydrogen bonding
(iv) van der Waals deshielding

(i) 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 higher

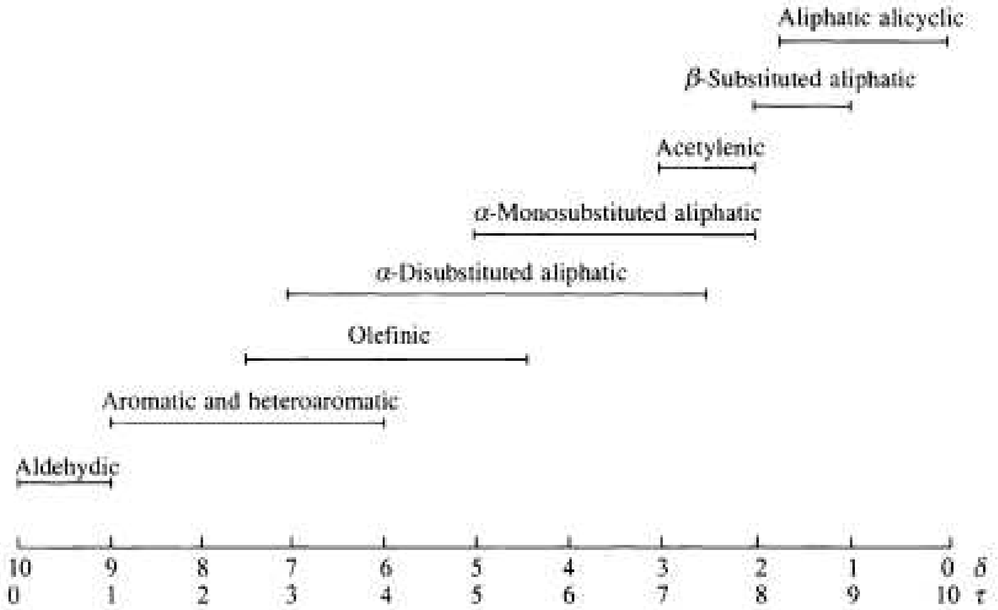


Chart 5.1 General regions of chemical shifts

is 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 neighborhood 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 electronegativiy of the atom, the greater is the deshielding of the proton. For example, the chemical shifts (in δ unit) 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. $H_3C—$, $H_3C—N\langle$, $CH_3O—$: $\delta \approx 0.9, \approx 2.2, \approx 3.5$, 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 groups 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 CH_3CH_2Cl absorb at δ 1.48.

(ii) Anisotropic Effects

As discussed above, electronegativity correlates with chemical shifts. However, in some cases, e.g. in 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 $\delta 2.35$, whereas ethylenic absorbs at $\delta 4.60$. 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 that generated by σ electrons.

(a) 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 could generate an induced magnetic field which opposes the applied field at the acetylenic proton (Fig. 5.11).

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

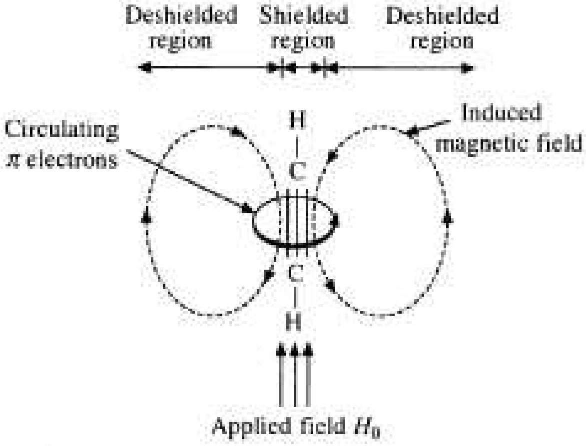


Fig. 5.11 Shielding of acetylenic protons, the molecule aligned parallel to the applied field H_0

When acetylene molecules are aligned perpendicular to the applied field, the acetylenic proton falls in the deshielded region and it is deshielded (Fig. 5.12). The magnitude of this deshielding is far less than that of the shielding (Fig. 5.11) because electrons are much more free to circulate in the direction shown in Fig. 5.11 than the direction shown in Fig. 5.12.

This is understandable in the light of the fact that π electrons of the triple bond are symmetrical about the bond axis, and the circulation as shown in Fig. 5.12 will disturb the symmetry. Although only a small fraction of tumbling molecules are aligned parallel to the applied magnetic field, the overall average chemical shift is affected by them, i.e. the acetylenic protons are much more

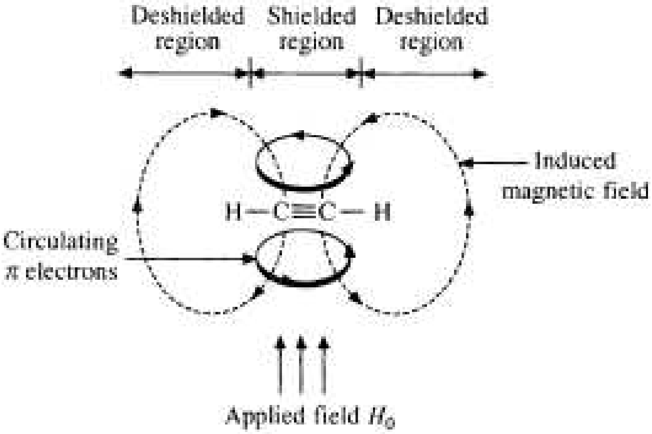


Fig. 5.12 Deshielding of acetylenic protons, the molecule aligned perpendicular to the applied field H_0

shielded than expected from the electronegativity of the acetylenic carbons and they absorb at higher field.

(b) 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. 5.13).

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.

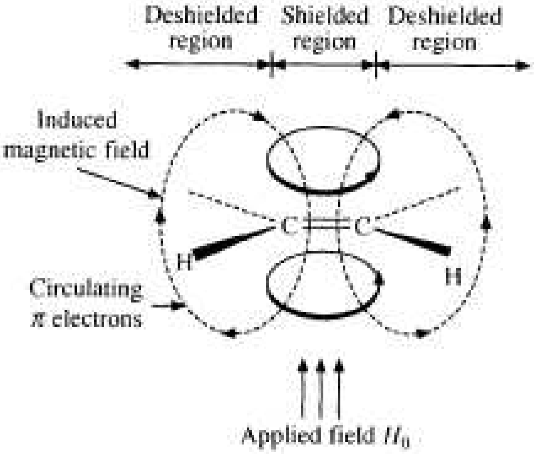


Fig. 5.13 Deshielding of olefinic protons

(c) Aldehydic Protons

When an 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. 5.14) resulting in its deshielding similar to that of olefinic protons. Thus, aldehydic protons absorb at much lower field (δ ~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.

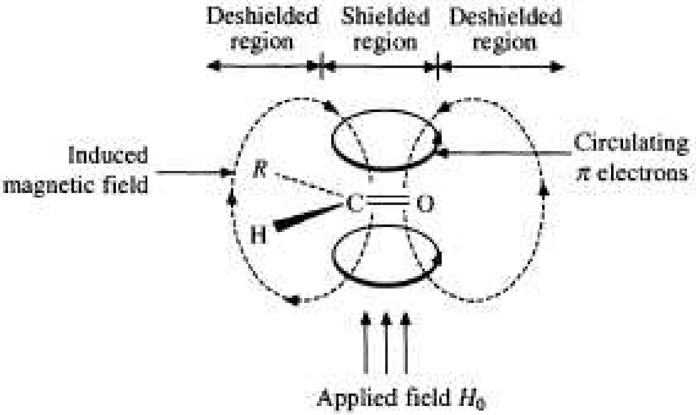


Fig. 5.14 Deshielding of aldehydic protons

(d) Aromatic Protons

Aromatic rings contain cyclic electron clouds of delocalized $4n + 2\pi$ 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. 5.15). Thus, aromatic protons, e.g. the protons of benzene, are highly deshielded, and hence appear at lower field. This is called the *ring-current effect* and is used as a very strong evidence for aromaticity.

Fig. 5.15 shows 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.

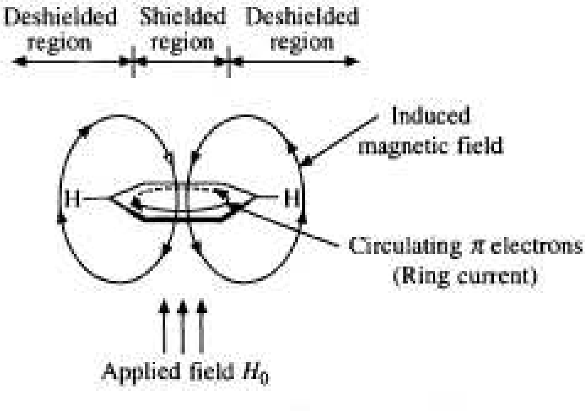
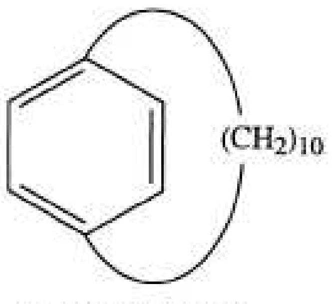
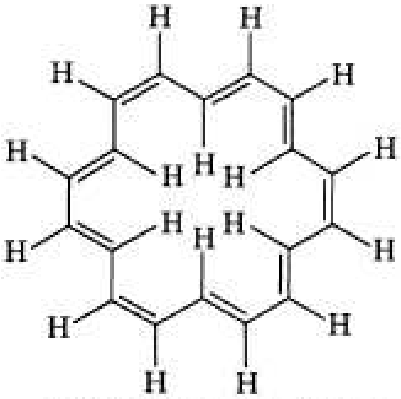


Fig. 5.15 Deshielding of aromatic protons (ring-current effects)

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).



[10] paracyclophane



[18]-Annulene; 18π electrons

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 and 6.4, whereas aromatic protons absorb between δ 6.0 and 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 (Fig. 5.16) and that protons present in these regions will absorb at a relatively high and low field, respectively. The boundary between shielding and deshielding regions resembles the surface of a double cone as shown in Fig. 5.16. For a carbonyl group, the situation is similar to alkenes (Fig. 5.16 (a)).

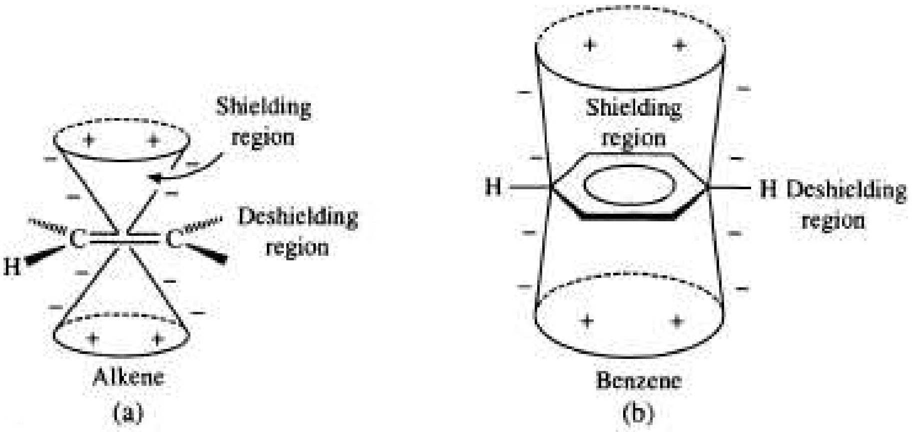
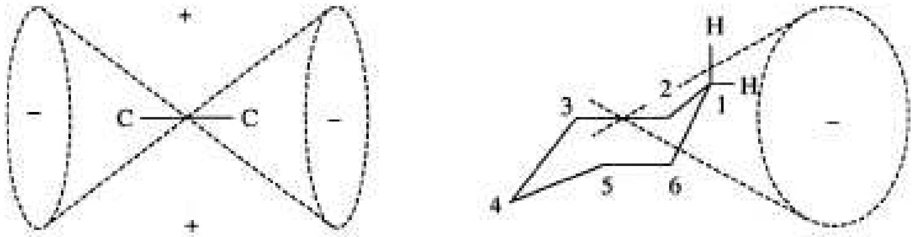


Fig. 5.16 Shielding (+) and deshielding (–) zones of π-bonded systems

The σ electrons of C—C bond also produce anisotropic effects but these are less powerful than that produced by circulating π electrons, and the axis of the C—C bond is the axis of the deshielding cone in the former (Fig. 5.17 (a)). This explains why the protons in the sequence RCH_3, 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) 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 5.2). With the help of the deshielding cone (Fig. 5.17(b), 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.



(a) Shielding (+) and deshielding (−) zones of C—C bond

(b) Deshielding of equatorial proton of a rigid six-membered ring

Fig. 5.17 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 proton is within the deshielding cone of the C_2—C_3 bond (and C_5—C_6 bond).

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

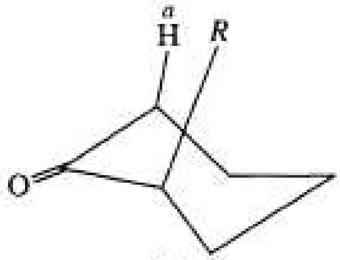
(iii) Hydrogen Bonding

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 show 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.

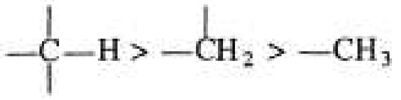
(iv) van der Waals Deshielding

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 $\overset{a}{\mathrm{H}}$ in a conformationally rigid cyclohexanone chair system (I) present in a steroid skeleton will resonate at lower field when $R = CH_3$ than when $R = H$.



(I)

Chemical shifts of protons in various structural environments are given in Table 5.2. It should be noted that in otherwise equivalent environments, the order of δ values of methyl, methylene and methyne protons is as follows:



$$-\overset{|}{\underset{|}{C}}-H > -\overset{|}{C}H_2 > -CH_3$$

Table 5.2 Chemical shifts of protons in various structural environments

	Type of proton*	Chemical shift, δ (ppm)
Primary	$R\mathbf{CH_3}$	0.9
Secondary	$R_2\mathbf{CH_2}$	1.3
Tertiary	$R_3\mathbf{CH}$	1.5
Vinylic	$C{=}\mathbf{CH}$	4.6–5.9
Acetylenic	$C{\equiv}C{-}\mathbf{H}$	1.8–3.1
Allylic	$C{=}C{-}\mathbf{CH_3}$	1.7
Aromatic	$Ar{-}\mathbf{H}$	6–8.5
Benzylic	$Ar{-}C{-}\mathbf{H}$	2.2–3
Alcohols	$\mathbf{H}C{-}OH$	3.4–4
Ethers	$\mathbf{H}C{-}OR$	3.3–4
Esters	$RCOO{-}C\mathbf{H}$	3.7–4.1
Esters	$\mathbf{H}C{-}COOR$	2–2.2
Acids	$\mathbf{H}C{-}COOH$	2–2.6
Carbonyl compounds	$\mathbf{H}C{-}C{=}O$	2–2.7
Aldehydic	$RC\mathbf{H}O$	9–10
Alcoholic	$RO\mathbf{H}$	1–5.5
Phenolic	$ArO\mathbf{H}$	4–12
Enolic	$C{=}C{-}O\mathbf{H}$	15–17
Carboxylic	$RCOO\mathbf{H}$	10.5–12
Amino	$RN\mathbf{H_2}$, $ArN\mathbf{H_2}$	1–5
Thiols	$RS\mathbf{H}$	1.1–1.5
Thiophenols	$ArS\mathbf{H}$	3–4
Amine salts	$R_3\overset{+}{N}\mathbf{H}$	7.1–7.7
	$Ar\overset{+}{N}\mathbf{H_3}$	8.5–9.5
Amines	$\mathbf{H}C{-}NR_2$	2.1–3
Thioethers	$\mathbf{H}C{-}SR$	2.1–2.8
Fluorides	$\mathbf{H}C{-}F$	4–4.5
Chlorides	$\mathbf{H}C{-}Cl$	3–4
Bromides	$\mathbf{H}C{-}Br$	2.5–4
Iodides	$\mathbf{H}C{-}I$	2–4

*Indicated in bold.

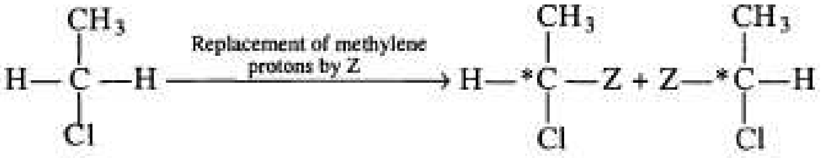
5.8 Number of PMR Signals: Equivalent and Nonequivalent Protons

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 positions, 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?

The simple method to judge the chemical equivalence of two or more protons, is to mentally replace 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 $CH_2Z—CH_2Cl$, whereas on replacement of a methylene proton it would give $CH_3—CH_2ZCl$. These are different products, hence we easily judge that the methyl and the methylene protons are not equivalent. When we replace any one of the methyl protons by Z, the same product $CH_2Z—CH_2Cl$ is obtained, hence all the three methyl protons are equivalent. Thus, we expect only one PMR signal for the three methyl protons and that is also the case.

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

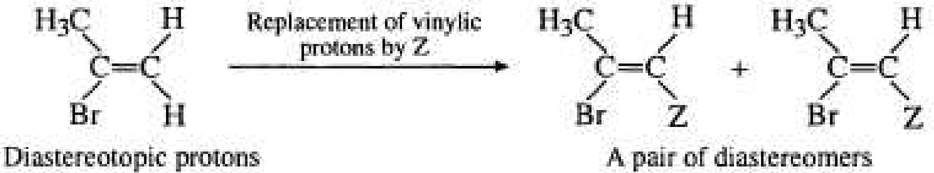


Enantiotopic protons
*C is chiral center

A pair of enantiomers

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.

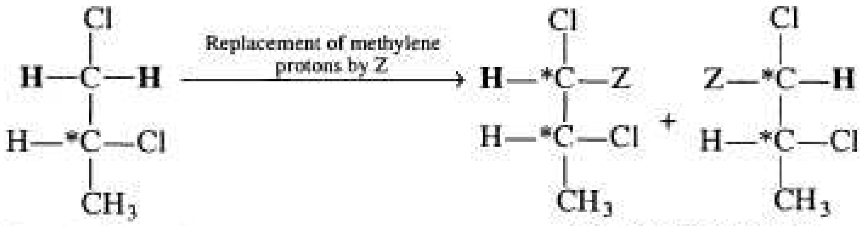
On the other hand, a pair of protons whose replacement gives a pair of diastereomers are called *diastereotopic protons*. These protons do not have the same chemical shift and show different PMR signals, i.e. these are nonequivalent protons. For example, replacement of either of the two vinylic protons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



Diastereotopic protons
2-Bromopropene

A pair of diastereomers

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



Diastereotopic protons
1,2-Dichloropropane

A pair of diastereomers

In view of the above discussion, now we are able to recognize 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) $CH_3CH_2CH_2Cl$ (b) $CH_3CHClCH_3$ (c) CH_3COCH_3

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

$\overset{a}{C}H_3\overset{b}{C}H_2\overset{c}{C}H_2Cl$ Protons *c* are enantiotopic, hence equivalent
3 PMR signals
1-Chloropropane

(b) $\overset{a}{C}H_3\overset{b}{C}HCl\overset{a}{C}H_3$
2 PMR signals
2-Chloropropane

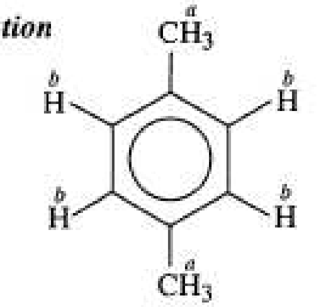
(c) $\overset{a}{C}H_3COC\overset{a}{H}_3$
1 PMR signal
Acetone

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 $C_2H_4Cl_2$

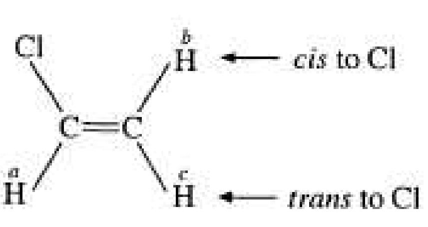
Solution

(a)



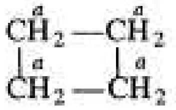
2 NMR signals *p*-xylene

(b)



3 NMR signals vinyl chloride

(c)



1 NMR signal
Cyclobutane

(d) $\overset{a}{C}H_3\overset{b}{C}H_2O\overset{b}{C}H_2\overset{a}{C}H_3$

2 NMR signals
Diethyl either

(e) (i) $\overset{a}{H}_3C—C\overset{a}{H}Cl_2$

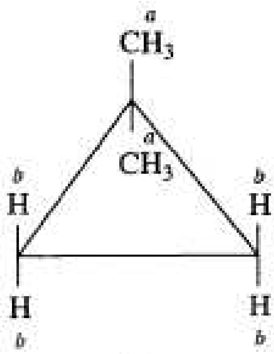
2 NMR signals
1,1-Dichloroethane

(ii) $ClC\overset{a}{H}_2—C\overset{a}{H}_2Cl$

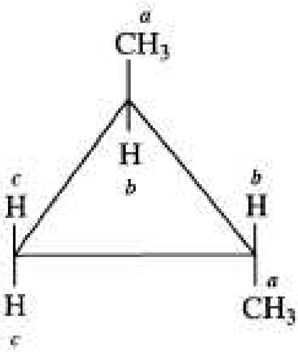
1 NMR signal
1,2-Dichloroethane

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*.

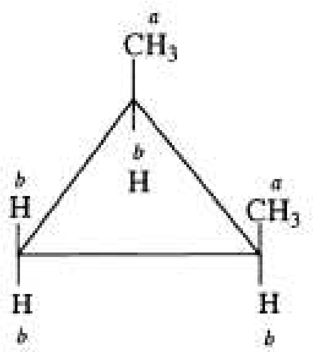
Solution



A



B



C

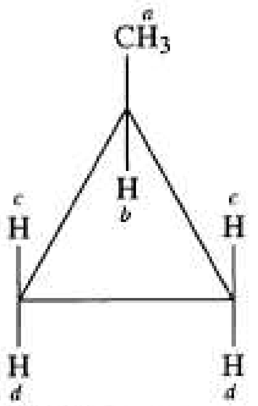
In the dimethylcyclopropane *C* the proton *c* is *cis* to CH_3 groups, whereas the proton *d* is *trans* to CH_3 groups. Hence these are nonequivalent.

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

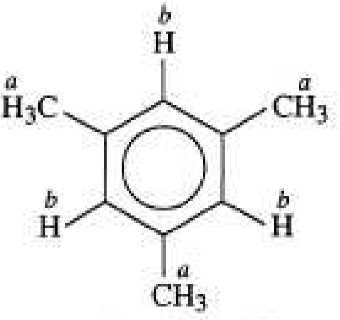
(a)



4 NMR signals
2-Methylcyclopropane

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

(b)



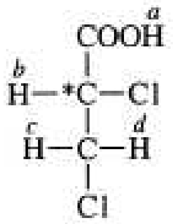
2 NMR signals mesitylene

(c) $\overset{a}{\text{CH}}_2\text{COO}\overset{b}{\text{CH}}_2\overset{c}{\text{CH}}_3$

$\overset{a}{\text{CH}}_2\text{COO}\overset{b}{\text{CH}}_2\overset{c}{\text{CH}}_3$

3 NMR signals
Ethyl succinate

(d)



$$\begin{array}{c} \overset{a}{\text{COOH}} \\ | \\ \overset{b}{\text{H}}-{}^{*}\text{C}-\text{Cl} \\ | \\ \overset{c}{\text{H}}-\text{C}-\overset{d}{\text{H}} \\ | \\ \text{Cl} \end{array}$$

C$_2$ is chiral. Protons $\overset{c}{\text{H}}$ and $\overset{d}{\text{H}}$ are diastereotopic, hence nonequivalent.

4 NMR signals
2,3-Dichloropropanoic acid

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 can neither 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.

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, i.e. chiral or achiral.

Magnetically equivalent protons have the same chemical shift and the same coupling constant J to every other nucleus in the spin system (see Section 5.14).

5.9 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 to 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. 5.8). 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. 5.8 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 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

Hence,
$$1\text{ mm} = \frac{5\text{H}}{15} = 0.333\text{H}$$

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

$$b = 6 \times 0.333 = 1.998 = 2\text{H}$$

In either way we find $a = 3\text{H}$ and $b = 2\text{H}$.

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 16H

Hence,
$$1\text{ unit} = \frac{16\text{H}}{15.5} = 1.03\text{H}$$

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

$$a = 9\text{H}, \quad b = 3\text{H}, \quad c = 4\text{H}$$

5.10 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) 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, CH_3CH_2Cl 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. 5.8. Now let us study the origin of a multiplet (a group of peaks) for a particular kind of proton, 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 neighboring 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 downfields, 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 delocalization as in aromatic and unsaturated systems. Intermolecular spin-spin coupling is not observed.

Possible spin orientations (alignments) of the methine ($\text{—}\underset{|}{\text{CH}}\text{—}$), methylene ($\text{—}CH_2\text{—}$) and methyl ($\text{—}CH_3$) protons are shown in Fig. 5.18. 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 possible (Fig. 5.18, (i)-(iii)) for the methylene protons 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 (Fig. 5.18, (ii)) equivalent in energy.

Similarly, there are four different spin orientations possible (Fig. 5.8, (i)-(iv)) for the methyl protons 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 outermost side peaks because it arises due to three orientations (Fig. 5.18, (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. 5.18).

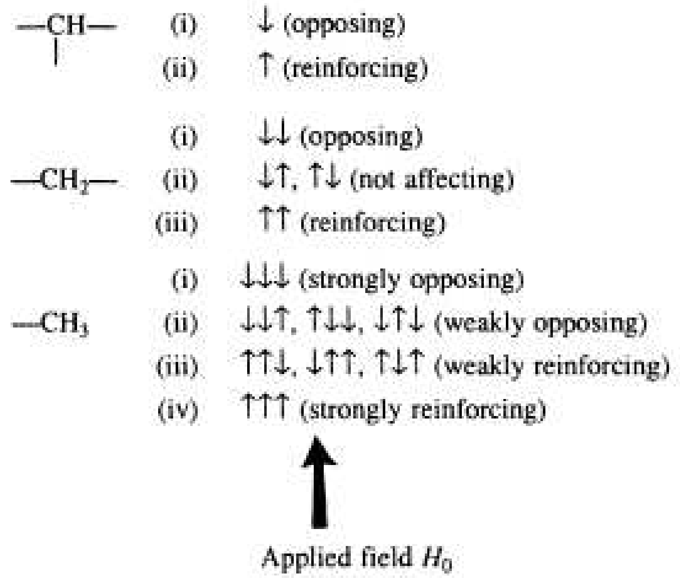


Fig. 5.18 Possible spin orientations (alignments) of the methine (—CH—), methylene (—CH$_2$—) and methyl (—CH$_3$) protons

(i) Multiplicity-Number of Component Peaks (Lines) in Multiplet

It should be noted that spin-spin splitting is observed only between nonequivalent (with different chemical shifts) neighboring 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 neighboring protons for splitting of the signal, otherwise there will be no splitting. For example, in CH_3CH_2Cl 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. 5.18). 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 three vicinal protons, hence their NMR signal is split into 3 + 1 = 4 peaks (a quartet)

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

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

---

*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.

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 number of different kinds of protons.* For example, in 1,1-dibromo-3,3-dichloropropane, $Br_2C\overset{a}{H}C\overset{b}{H}_2C\overset{c}{H}Cl_2$, 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 ($—CH_2—$) 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.

(ii) Relative Intensities of Component Peaks (Lines) of a Multiplet

The relative intensities (areas) of the component peaks of a 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 Fig. 5.19. The same results can also be obtained from Pascal's triangle.

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 (quintett)	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

Fig. 5.19 Relative intensities of various multiplets

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

---

*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 $(2n_BI_B + 1)$ $(2n_CI_C + 1)\ldots$, 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.

protons and the multiplicity of a signal depends upon the number of the neighboring protons.

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

1. Number of signals showing 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 giving the ratio of the numbers of each kind of protons present in a molecule.
4. Spin-spin splitting of signals into several peaks (multiplets) showing the environment of a proton with respect to the neighboring protons.

Some of the examples are:

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

(a) $ClCH_2CH_2Cl$ (b) $ClCH_2CHCl_2$ (c) $CH_3OCH_2CH_2Br$

Solution

(a) $\mathrm{ClC}\overset{a}{\mathrm{H}}_2\mathrm{C}\overset{a}{\mathrm{H}}_2\mathrm{Cl}$

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).

(b) $\mathrm{ClC}\overset{a}{\mathrm{H}}_2\mathrm{C}\overset{b}{\mathrm{H}}\mathrm{Cl}_2$

1,1,2-trichloroethane

This compound contains two types of protons indicated as *a* and *b*. Hence, it will show two signals. Proton *a* ($-CH_2-$) has one vicinal proton (nonequivalent). Thus, the signal of *a* will be split into 1 + 1 = 2 peaks, i.e. they will appear as a doublet. Similarly, the proton *b* ($-\underset{|}{\mathrm{C}}\mathrm{H}-$) has two equivalent vicinal protons *a* which are nonequivalent to *b*. Thus, its signal will split into 2 + 1 = 3 peaks, i.e. proton *b* will appear as a triplet.

(c) $\mathrm{C}\overset{a}{\mathrm{H}}_3\mathrm{OC}\overset{b}{\mathrm{H}}_2\mathrm{C}\overset{c}{\mathrm{H}}_2\mathrm{Br}$

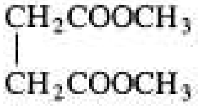
1-bromo-2-methoxyethane

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. Thus, 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. Similar is the case of protons *c*, i.e. protons *b* will appear as a triplet and protons *c* as another triplet.

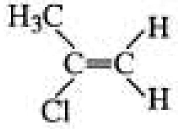
Example 7. Indicate the types of protons and their multiplicity in the ^{1}H NMR spectra of the following compounds:

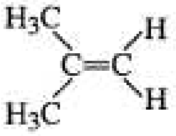
(i) $ClCH_2CH_2CH_2Cl$

(ii) $CH_3CH_2COOCH\,(CH_3)_2$

(iii) 

$$\begin{array}{l} CH_2COOCH_3 \\ | \\ CH_2COOCH_3 \end{array}$$

(iv) 

(v) 

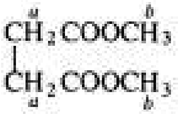
Solution

(i) $Cl\overset{a}{C}H_2\overset{b}{C}H_2\overset{a}{C}H_2Cl$

There are two types of protons *a* and *b* in this compound. Their multiplicity is *a* (triplet) and *b* (quintet).

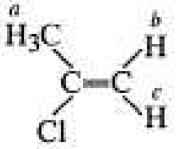
(ii) 

There are four kinds of protons *a*, *b*, *c* and *d*. Their multiplicity is *a* (triplet), *b* (quartet), *c* (septet) and *d* (doublet).

(iii) 

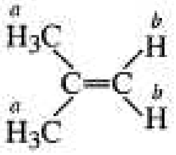
$$\begin{array}{l} \overset{a}{C}H_2COO\overset{b}{C}H_3 \\ | \\ \underset{a}{C}H_2COO\underset{b}{C}H_3 \end{array}$$

There are two kinds of protons *a* and *b*. Their multiplicity is *a* (singlet) and *b* (singlet).

(iv) 

There are three kinds of protons *a*, *b* and *c*. Their multiplicity is *a* (singlet) because it has no vicinal proton, *b* (doublet) and *c* (doublet).

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

(v) 

There are two kinds of protons *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) $C_3H_3Cl_5$; one doublet and one triplet
- (ii) $C_4H_{10}O$; one singlet, one doublet and one septet
- (iii) $C_4H_8O_2$; one singlet, one triplet and one quartet
- (iv) C_3H_7Cl; one doublet and one septet
- (v) $C_4H_8Cl_2O$, two triplets

Solution

(i) $C_3H_3Cl_5$

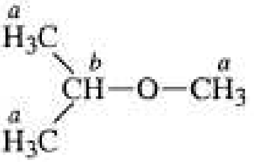
The compound shows one doublet and one triplet. This indicates the presence of —CH—CH$_2$— group in the molecule. Thus, following structure with molecular formula $C_3H_3Cl_5$ fulfils this condition:

$$Cl_3C\overset{a}{CH_2}\overset{b}{CH}Cl_2$$

a (doublet) and *b* (triplet).

(ii) $C_4H_{10}O$

The presence of a doublet and a septet indicates $(CH_3)_2CH$— (isopropyl) group. There is one singlet in the spectrum which shows that a group of protons have no vicinal proton in the molecule. Thus, following structure with the above molecular formula meets the given requirements:



a (doublet) and *b* (septet).

(iii) $C_4H_8O_2$

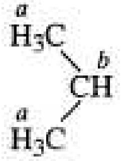
The compound shows one triplet and one quartet which indicates the presence of $—CH_2CH_3$ group. The compound shows one singlet indicating that a group of three protons ($—CH_3$) has no vicinal proton. The following structures meet the above requirements:

$$\overset{a}{CH_3}COO\overset{b}{CH_2}\overset{c}{CH_3} \quad \text{and} \quad \overset{c}{CH_3}\overset{b}{CH_2}COO\overset{a}{CH_3}$$

a (singlet), *b* (quartet), *c* (triplet).

(iv) C_3H_7Cl

The presence of a doublet and a septet indicate $(CH_3)_2CH$— group. Thus, the structure which meets the given requirements is



a (doublet) and b (septet).

(v) $C_4H_8Cl_2O$

This compound shows two triplets which indicates the presence of $—CH_2CH_2—$ group where both the $—CH_2—$ groups are non-equivalent. Thus, the structure which fits the given requirements and the molecular formula is

$$ClC\overset{a}{H}_2C\overset{b}{H}_2—O—C\overset{b}{H}_2C\overset{a}{H}_2Cl$$

5.11 Coupling Constant (*J*)

The distance between the centres of two adjacent peaks in a multiplet is called *coupling constant* or *spin-spin coupling constant J* (Fig. 5.20). 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 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 between adjacent peaks does not change, then they are component peaks of a multiplet. On the other hand, if the separation between the peaks changes on changing the applied field, then they represent different signals. The values of coupling constants J between protons generally lie 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. 5.20) 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, where J_{ab} is the coupling constant for protons a ($\overset{a}{H}$) split by proton b ($\overset{b}{H}$) or for $\overset{b}{H}$ split by $\overset{a}{H}$. Drawing of a splitting diagram (Fig. 5.20) permits us to identify identical spacings between component peaks in the multiplets.

(i) Factors Affecting *J*

Coupling constant is a measure of the effectiveness of spin-spin coupling. The value of 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 because splitting arises due to instantaneous spin states of the neighboring protons and not due to flipping of the spin states. A

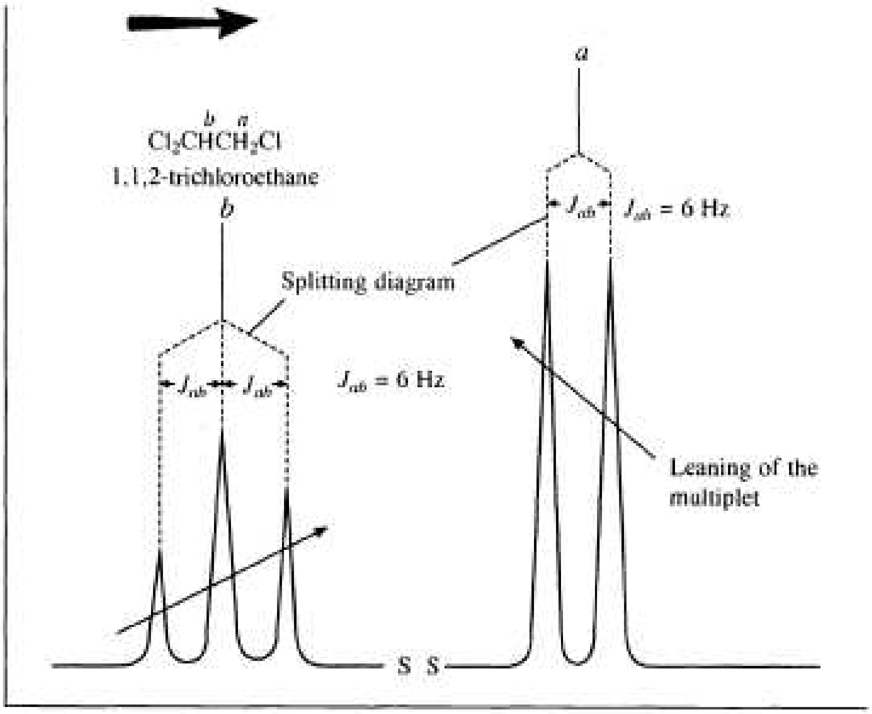
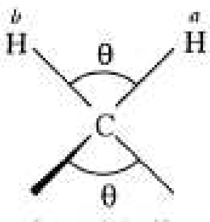


Fig. 5.20 Spin-spin splitting, coupling constant *J* leaning of the coupled multiplets towards one another and splitting diagram

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 couplings are discussed as follows.

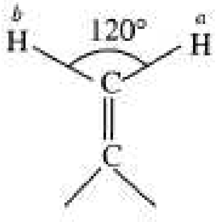
(a) Geminal Coupling

Protons attached to the same carbon atom are called *geminal protons*. These are separated by two bonds, and when they are nonequivalent, they show spin-spin splitting. Geminal coupling constant J_{gem} is usually negative and increases 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 (θ = 109°) and J_{gem} is about –12 Hz which is comparable to that of acyclic saturated systems.



J_{ab} = 10-16 Hz

(II)



J_{ab} = 0-3 Hz

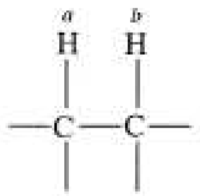
(III)

On decreasing the ring size to cyclopropane system, θ' is decreased with consequent increase in θ (II) which becomes > 109°. 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 $\theta = 120°$ (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 algebraically with increasing electronegativity of a substituent attached 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.

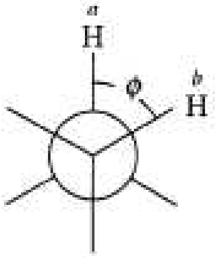
(b) Vicinal Coupling

Protons attached to adjacent atoms are called *vicinal protons* (IV). These are separated by three bonds. Vicinal coupling constants J_{vic} which depend on the dihedral angle (angle of rotation) ϕ are 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 as



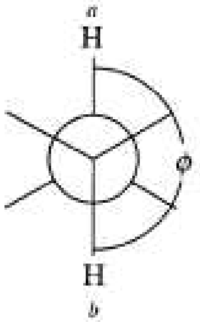
J_{ab} = ~6-8 Hz

(IV)



Gauche (ϕ = 60°)

(V)



Anti (ϕ = 180°)

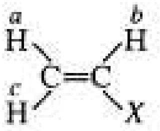
(VI)

$$J_{vic} = 10\cos^2\phi, \text{ for values of } \phi \text{ between 0 and } 90° \tag{5.5}$$

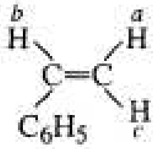
$$J_{vic} = 15\cos^2\phi, \text{ for values of } \phi \text{ between 90 and } 180° \tag{5.6}$$

Karplus relationships (Eqs. (5.5) and (5.6)) are very useful for determining the stereochemistry of organic compounds.

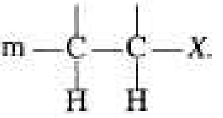
For isomeric olefins, J_{trans} is always greater than J_{cis}, and it is usually observed that $J_{cis} = \sim\frac{2}{3}J_{trans}$. Thus, it is possible to determine the configuration of geometrical isomers of a disubstituted olefin. For monosubstituted olefins (VII), $J_{trans} > J_{cis} > J_{gem}$.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



J_{ab} (*cis*) = 6-12 Hz
J_{bc} (*trans*) = 12-18 Hz
J_{ac} (gem) = 0-3 Hz
(VII)



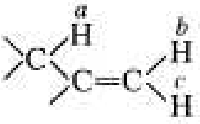
J_{ab} (*cis*) = 10.6 Hz
J_{bc} (*trans*) = 17.4 Hz
J_{ac}(gem) = −1.4 Hz
(VIII)

The J_{vic} decreases with increasing electronegativity of X in a freely rotating system  $—\underset{H}{\overset{|}{\underset{|}{C}}}—\underset{H}{\overset{|}{\underset{|}{C}}}—X$.

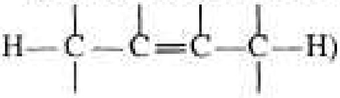
(c) Long-range Coupling

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 couplings*. Some appreciable long-range couplings are as follows:

(1) 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.



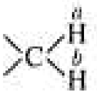
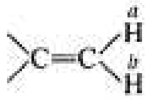
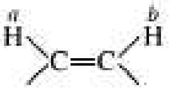
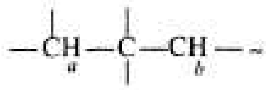
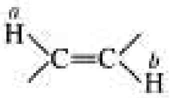
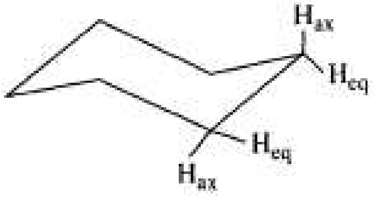
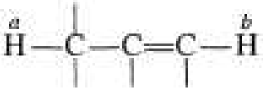
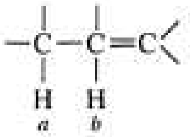
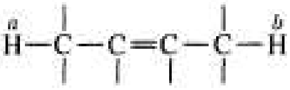
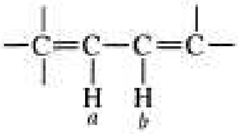
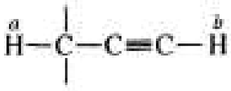
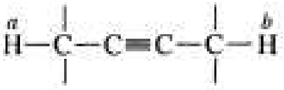
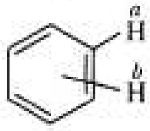
J_{ab} = 0-3 Hz
(IX)

(2) Homoallylic coupling. As might be expected, homoallylic coupling ( $H—\overset{|}{\underset{|}{C}}—\overset{|}{C}=\overset{|}{C}—\overset{|}{\underset{|}{C}}—H$) constants are usually very small (about 0-2 Hz).

(3) Aromatic coupling. *Meta* coupling in benzene ring is 1-3 Hz, 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.

Proton spin-spin coupling constants of some common systems are given in Table 5.3.

Table 5.3. Proton spin-spin coupling constants

Type	J_{ab} (Hz)	Type	J_{ab} (Hz)
	10–16		0–3
 (free rotation)	6–8		6–12
	-0		12–18
			0–3
ax–ax ax–eq eq–eq	8–10 2–3 2–3		4–10
			0–2
			10–13
			2–3
			2–3
		 *ortho* *meta* *para*	6–10 1–3 0–1

5.12 Analysis (Interpretation) of NMR Spectra

To obtain structurally useful information, we must analyze the NMR spectrum and correlate the NMR parameters with structure. The process of deriving the NMR parameters δ and J from multiplets is called *analysis of the NMR spectrum.*

(i) First Order Spectra

When the chemical shifts are large compared to the coupling constants ($\Delta v/J$[*] 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 following splitting rules (Sections 5.10 and 5.11) 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. Center 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 analyzed by inspection and direct measurement in terms of the above rules. The chemical shift separation Δv (in Hz) increases as the strength of applied magnetic field increases, but the value of J remains constant, and thus $\Delta v/J$ ratio is increased. Hence, 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.

As an example of the analysis of first order NMR spectra, let us analyze the PMR spectrum of ethyl chloride shown in Fig. 5.8. The signal at δ 0.00 is due to the internal reference TMS. The downfield quartet

$$\mathrm{C}\overset{a}{\mathrm{H}}_3\mathrm{C}\overset{b}{\mathrm{H}}_2\mathrm{Cl}$$

centered at δ 3.57 is due to methylene protons as they are more deshielded than the methyl protons by the chlorine. The methyl protons appear as a triplet centered at δ 1.48, i.e. upfield. The integration curve show 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} = ~9 Hz. The chemical shift separation is 3.57–1.48 = 2.09 δ, i.e. $\Delta v = 2.09 \times 60 = 125.4$ Hz (the spectrum has been recorded at 60 MHz, hence $\delta 1 = 60$ Hz). Thus $\Delta v/J$ is about 14, a large enough ratio for first order analysis. The system is A_3X_2 (Section 5.13). The leaning of the two coupled signals towards each other even at such a high $\Delta v/J$ ratio may be noticed, which shows that the

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[*] Δv is the difference in chemical shifts (in Hz) between two groups of coupled protons.

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.

(ii) Second Order (More Complex) Spectra

When the chemical shifts of coupled protons are of approximately the same magnitude as the coupling constants, the NMR spectra cannot be analyzed by inspection and direct measurement in terms of the simple splitting rules summarized above. Such spectra are more complex and are known as *second order spectra*. Nuclei which give rise to second order spectra are said to be *strongly coupled*. Second order spectra may be recognized by the following features:

1. Often more lines are present than are predicted by $(2nI + 1)$ rule used for first order spectra.
2. Even in the case of only two different groups of coupling nuclei, the lines of a particular multiplet are not equally separated.
3. The relative intensities of the peaks of a multiplet are not given by coefficients of the terms in binomial expansion of $(x + 1)^n$.
4. The chemical shifts and coupling constant both cannot be measured directly from the spectrum. However, in certain cases one of these parameters may be obtained by inspection.

In second order spectra, mathematical analysis of the spectral data is required to obtain values for the chemical shifts and the coupling constants. In principle, any NMR spectrum, however complicated, can be analyzed by quantum mechanical calculations performed by a computer.

(a) Distortion of Multiplets

As $\Delta\nu/J$ becomes smaller the coupled multiplets approach one another, the inner peaks increase in intensity and the outer peaks decrease. Thus, there is a leaning of coupled multiplets towards one another (Fig. 5.20). Generally, a multiplet points upward towards the signal of the protons which causes the splitting. Now the center of the multiplet does not give the resonance position, i.e. the chemical shift of the protons(s) causing that multiplet. In such cases the chemical shift position is at the 'center of gravity'. Fig. 5.21 shows this type of distortion of two doublets. The chemical shift position can be calculated by the following formula, where the peak positions 1, 2, 3 and 4 from left to right (Fig. 5.22), are in Hz from reference

$$(1 - 3) = (2 - 4) = \sqrt{(\Delta\nu)^2 + J^2}$$

The chemical shift positions (in Hz) of each kind of protons are $\pm\frac{1}{2}\Delta\nu$ from the mid-point of the pattern.

5.13 Nomenclature of Spin Systems

A spin system, which is a group of coupled protons, 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

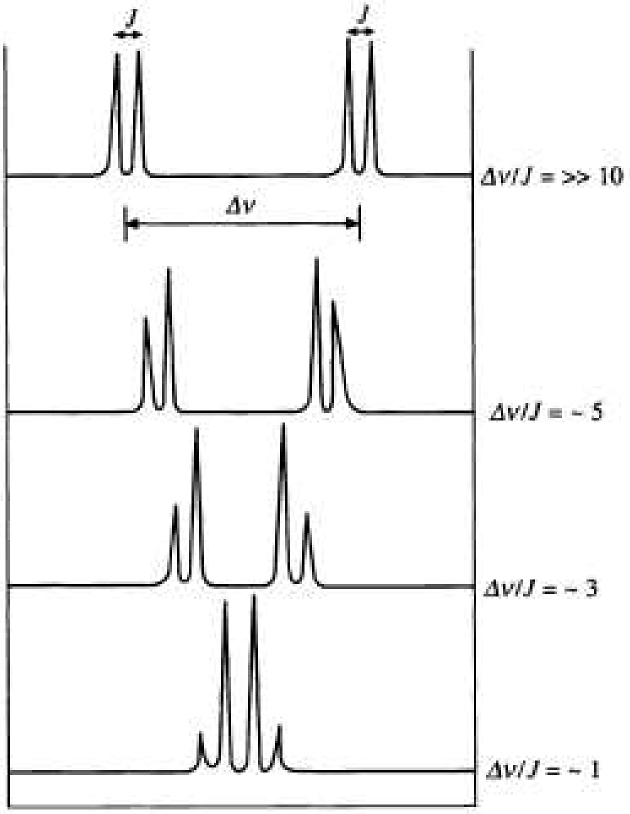


Fig. 5.21 **As Δv/J becomes smaller, the doublets approach one another, the inner two peaks increase in intensity and the outer two peaks decrease**

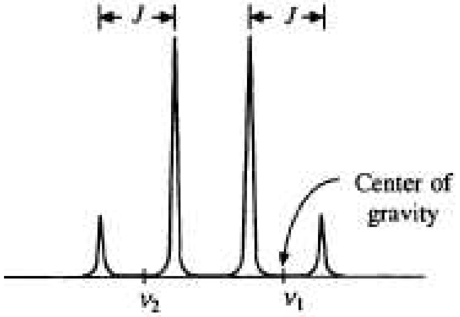
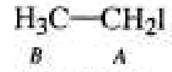


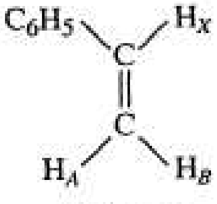
Fig. 5.22 **When Δv/J ratio is low, centers of gravity (ν_2 and ν_1) are chemical shift positions instead of linear mid-points**

system which are separated by small chemical shifts are denoted by *A*, *B* and *C* (usually in order of decreasing δ value), and those far away in chemical shift from these by *X*, *Y* and *Z*, whereas those intermediate in chemical shift by *M*, *N* and *O*. In brief, the protons widely differing in chemical shift by ($\Delta\nu/J$ = 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. 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.

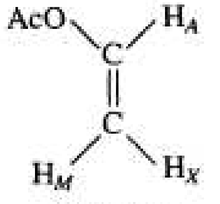
The nuclei which are chemically equivalent but magnetically nonequivalent are differentiated by primes, e.g. *AA′XX′* is a 4-spin system, where *A* and *A′* (as well as *X* and *X′*) are the protons which are chemically equivalent but magnetically nonequivalent. The above nomenclature of spin systems is illustrated by the following examples:



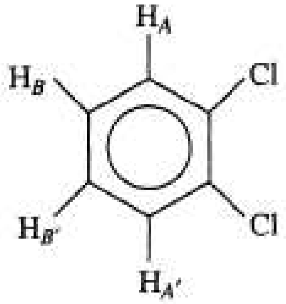
A_2B_3 system
Ethyl Iodide



ABX system
Styrene



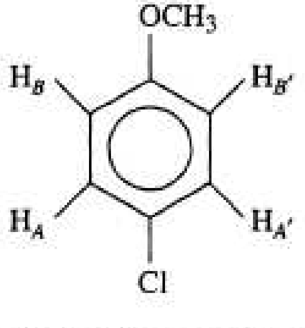
AMX system
Vinyl acetate



AA′BB′ system
o-Dichlorobenzene

5.14 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 nonequivalent, 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 analyzed by first order method.

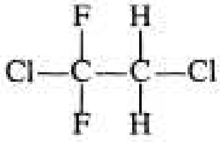


5.15 Spin-Spin Coupling of Protons with Other Nuclei

As shown in Section 5.2, any nuclei which has $I > 0$ is capable of exhibiting a NMR spectrum. Different nuclei (e.g. ^1H, D, ^{13}C, ^{19}F etc.) require different oscillator frequencies for exhibiting NMR in a given magnetic field. For example, in a magnetic field of 14,092 gauss, ^1H, D, ^{13}C and ^{19}F nuclei resonate at 60.000, 9.211, 15.085 and 56.446 MHz, respectively. Thus, under a given set of conditions for NMR of a particular nucleus, signals due to other nuclei are not observed in the spectrum. Proton may couple with any nucleus (having $I > 0$) to which it is covalently bonded.

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. Thus, the signals of protons coupled with deuterons, which have only small quadrupole moment, are not appreciably broadened. The coupling constant for a proton with deuteron (J_{HD}) in the situation $-\underset{|}{C}HD$ is ~2 Hz and in the situation $-\overset{|}{C}H\overset{|}{C}D-$, it is less than 1 Hz. The signals of protons coupled with nitrogen nucleus are almost always broadened because of the intermediate value for its electric quadrupole moment. Protons do not couple with halogen atoms (except fluorine) on adjacent atoms or on the same atom, because the very large quadrupole moments of the halogen atoms cause spin-spin decoupling of adjacent protons.

Fluorine (^{19}F) nucleus has $I = \frac{1}{2}$ and does not have electric quadrupole moment. Thus, ^{19}F nuclei can efficiently couple with each other as well as with protons. Hence, the splitting of their signals occurs (J_{HCF} = ~ 60 Hz; J_{HCCF} = ~ 20 Hz). For example, in 1,2-dichloro-1,1-difluoroethane, the coupling of two equivalent protons with fluorine nuclei gives a triplet in the spectrum



$$Cl-\overset{F}{\underset{F}{C}}-\overset{H}{\underset{H}{C}}-Cl$$

1,2-dichloro-1,1-difluoroethane

We know that spin-spin splitting is a reciprocal affair. Hence, if a spectrum contains a multiplet then it must be accompanied by at least one more multiplet. Thus, appearance of only one triplet (one multiplet only) in the PMR spectrum of 1,2-dichloro-1,1-difluoroethane looks rather surprising. However, it is easily understandable because different nuclei require different radio frequency for exhibiting NMR in a given magnetic field. Thus, under the PMR conditions another triplet due to two fluorine atoms is not observed in the PMR spectrum of 1,2-dichloro1,1-difluoroethane. Similarly, in the ^{19}F NMR spectrum of this compound, only a triplet due to the two fluorine atoms will be observed and the triplet due to the two protons will not be observed. ^{13}C gives rise to observable $^{13}C—H$ coupling ($J\,^{13}C—H$) = ~100-250 Hz; $J\,^{13}CCH$ = ~40 Hz), especially in spectra recorded at high amplitude. Peaks resulting from coupling with ^{13}C are called ^{13}C satellite peaks. These weak peaks appear symmetrically on either side of the much stronger signals of $^{12}C—H$ groups.

Unlike PMR spectra, NMR spectra of nuclei which have large electric quadrupole moments have very broad bands rather than sharp peaks. The spread in resonance frequencies of other nuclei and the magnitude of the coupling constants are very large when compared with the corresponding values for PMR spectra. Similar to the PMR spectroscopy, NMR spectra of other nuclei also provide structural information about compounds.

5.16 Protons on Heteroatoms: Proton Exchange Reactions

Protons on a heteroatom differ from protons on a carbon atom as they are:

(i) exchangeable.
(ii) subject to hydrogen bonding.
(iii) subject to partial or complete decoupling by electrical quadrupole effects of some heteroatoms (Section 5.15).

We have already discussed the effect of hydrogen bonding on chemical shift in Section 5.7 (iii). 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. 5.23). Spectrum of pure anhydrous ethanol (Fig. 5.24) exhibits

(i) a triplet for —CH$_3$ protons at δ 1.17.
(ii) a multiplet consisting of eight lines for —CH$_2$— protons at δ 3.62. The —CH$_2$— protons are under the influence of two kinds of protons (—CH$_3$ and —OH). Thus, the multiplet for —CH$_2$— protons consists of $(n + 1)(n' + 1) = (3 + 1)(1 + 1) = 8$ lines.
(iii) a triplet for —OH proton at δ 5.28. The —OH appears as a triplet because of its coupling with —CH$_2$— protons.

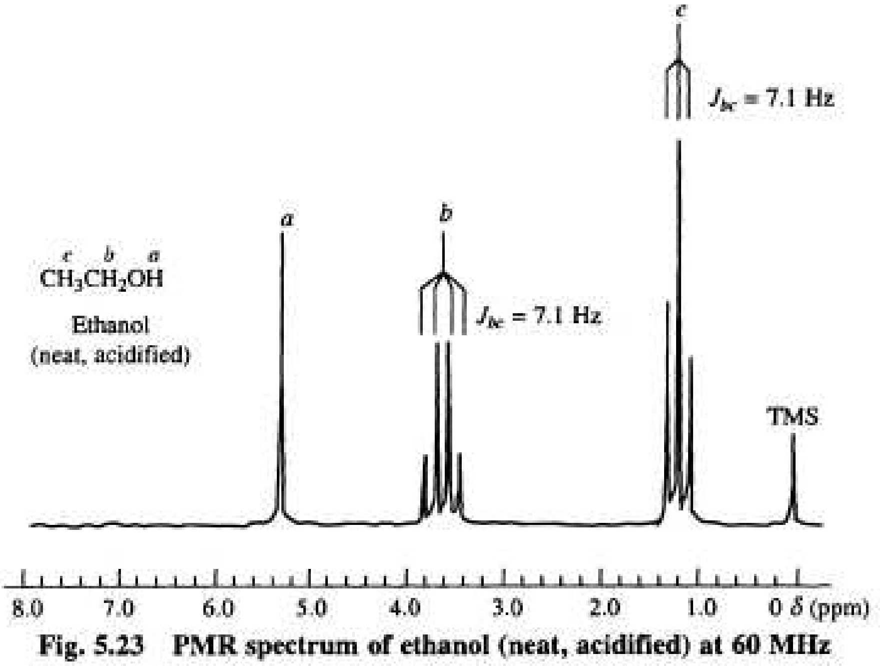


Fig. 5.23 PMR spectrum of ethanol (neat, acidified) at 60 MHz

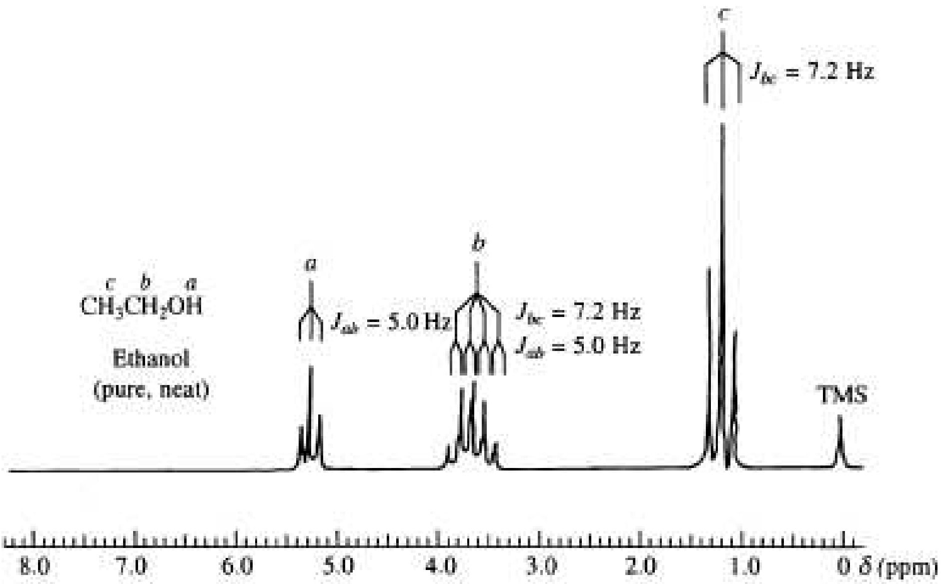


Fig. 5.24 PMR spectrum of ethanol (pure, neat) at 60 MHz

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

$$\mathrm{RO\overset{a}{H} + HOH = ROH + HO\overset{a}{H}}$$

Similarly, the exchange of —OH protons among ethanol molecules also occurs. The rate of proton exchange reactions increases with increasing temperature. 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. Thus, 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. —CH_2— 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 through strong solvation by using highly polar solvents like dimethyl sulphoxide (DMSO, CH_3SOCH_3) or acetone.

Since the rate of chemical exchange increases with increasing temperature, spin-spin decoupling can sometimes be observed by raising the temperature of the sample. On the other hand, spin-spin coupling can sometimes be observed by lowering the temperature of the sample. For example, the PMR spectrum of methanol at very low temperature (−40°C) shows a quartet for hydroxyl proton and a doublet for methyl protons. This indicates that the chemical exchange is very slow at −40° C as compared to the NMR transition time. When the temperature is raised to +31°C, the signals for —CH_3 and —OH protons appear as sharp singlets. This indicates that the rate of chemical exchange at +31°C is faster than the NMR transition time. At –4°C, the component peaks of both the multiplets coalesce to give relatively broad singlets. This shows that at this temperature, the rate of chemical exchange is intermediate.

Fast chemical exchange will usually occur when two hydroxylic species are present, like in solutions of ethanol-water or acetic acid-water. In such solutions, only one PMR signal is observed for hydroxylic protons of both the species present although individually they have different chemical shifts. The signal appears at an average concentration dependent position according to the following formula:

$$\delta_s = N_a\delta_a + N_b\delta_b$$

where δ_s is the chemical shift of hydroxylic protons in the solution, N_a the mole fraction of the hydroxylic proton a, N_b the mole fraction of the hydroxylic proton b, δ_a the chemical shift of unexchanged hydroxylic proton a and δ_b chemical shift of unexchanged hydroxylic proton b.

It helps in the quantitative analysis of mixtures like ethanol-water; acetic acid-water etc. If a single compound contains both carboxyl and hydroxyl groups, proton exchange usually causes these groups to appear as a single signal.

Protons attached to other heteroatoms, such as N, S etc., also behave like hydroxylic protons. Protons of —OH, —NH_2, —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 D_2O which causes their signals to disappear from the spectrum (Section 5.17(iii)).

It should be noted that even when exchange is very slow, the signal due to N—H proton is broadened by quadrupolar interaction with nitrogen. However, the N—H proton splits the signal of the proton on an adjacent carbon. For example, in the spectrum of ethyl N-methylcarbamate ($CH_3NHCOOCH_2CH_3$), the N—H proton shows a broad signal centered at δ~5.16, and the signal of N—CH_3 protons at δ2.78 ($J = -5$ Hz) is split into a doublet by the N—H proton. The ethoxy (—OCH_2CH_3) protons give the usual triplet at δ1.23 and quartet at δ4.14.

5.17 Simplification of Complex NMR Spectra

The complete analysis of a NMR spectrum becomes difficult when signals overlap and thus, useful information is buried due to complexity of the spectrum. For example, if several closely related methylene groups are present in a molecule, their signals may overlap and may not be clearly recognized. Sometimes, an intense, broad and unresolved signal due to several methylene groups is observed at about δ 1-2 which is called as the *methylene envelope*. When there is not much difference between the chemical shifts and coupling constants, more complex (second order) spectra are obtained. The important methods for simplifying a NMR spectrum to get the maximum information are discussed as follows.

(i) High Field Strengths

We have noted that the chemical shift in Hz is directly proportional to the applied magnetic field, whereas the value of coupling constant in Hz remains constant in different applied magnetic fields. On increasing the field strength the chemical shift separation Δv (Hz) increases, but the value of J (Hz) remains constant. Thus, the multiplets which are overlapped at lower field are expected to separate out at high field strengths. In this way, the NMR spectrometers operating at high magnetic fields (i.e. at high radio frequencies) give better resolution and relatively easily interpretable spectra.

(ii) Spin-Spin Decoupling (Double Irradiation or Double Resonance)

Spin-spin coupling between neighboring nuclei splits their signals into multiplets and the analysis of the splitting patterns is useful for structure determination of compounds. However, in certain cases, the splitting patterns and spectra are so complex that for the simplification of spectra, spin-spin decoupling is desired.

Irradiation of a nucleus or a group of equivalent nuclei at their resonance using a second strong radio frequency oscillator results in the removal of all couplings arising from the irradiated nuclei called *spin-spin decoupling* (spin decoupling or double irradiation or double resonance) because an additional radio frequency is used. Such an irradiation imparts extra energy which causes rapid transitions between the different spin states of the irradiated group of nuclei. Thus, neighboring nuclei (e.g. protons) cannot see different spin states (but they can see only an average view of spin states) of the irradiated nuclei and consequently spin-spin couplings are effectively removed. This is very similar to spin-spin decoupling through rapid proton exchange reaction (Section 5.16).

Let us take the example of PMR spectrum of ethanol (Fig. 5.25) where methyl protons appear as a triplet due to the spin-spin splitting by the methylene protons. If the methylene protons are irradiated strongly with an additional radio frequency at their resonance, then they change their spin states very rapidly. Thus, the methyl protons can see only an average of the possible spin orientations of the methylene protons and the coupling will be removed. Consequently, the triplet resulting from the methyl protons collapses to a singlet and appears at its

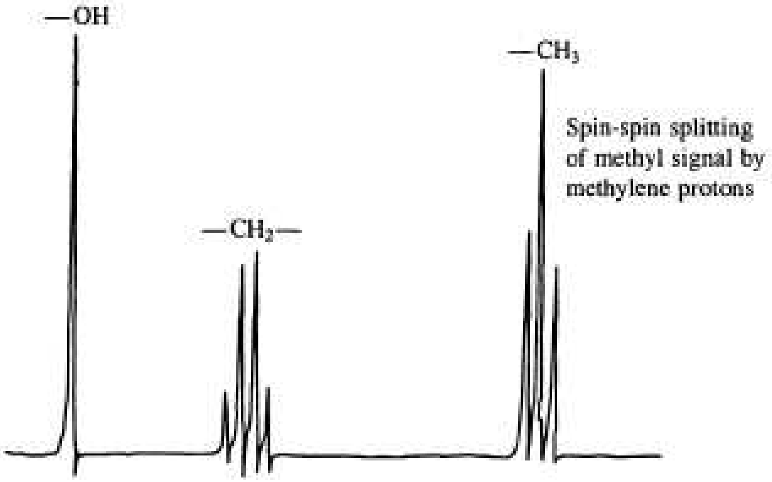


Fig. 5.25 PMR spectrum of acidified ethanol

usual position and the methylene absorption is eliminated (Fig. 5.26). The disappearance of the methylene absorption is due to saturation (Section 5.2). Similarly, when the methyl protons are irradiated, the quartet resulting from the methylene protons collapses to a singlet and the methyl absorption is eliminated.

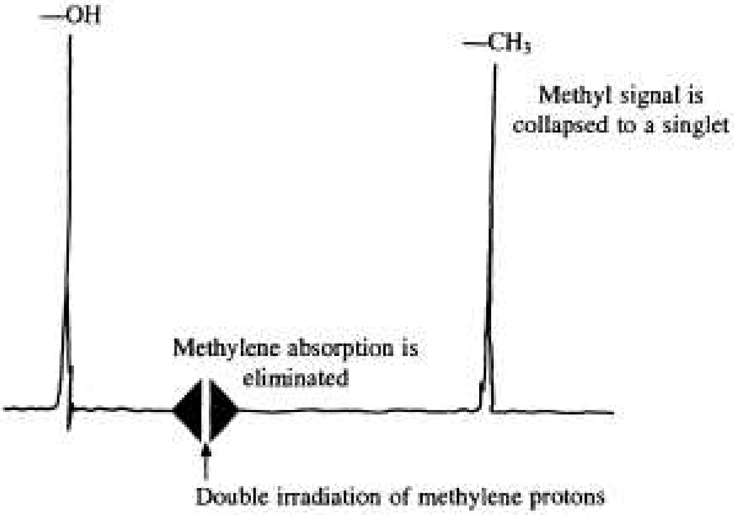


Fig. 5.26 PMR spectrum of acidified ethanol on double irradiation of methylene protons

Since strong irradiation is used for decoupling, this technique is not suitable when the chemical shifts positions for the coupling multiplets are closer than ~20 Hz at 100 MHz. In such cases, another technique *spin tickling* is applicable. Spin tickling involves irradiation of a nucleus with a much less intense radiation than required for spin-spin decoupling. This results in an increase in the number of lines in the coupled multiplets.

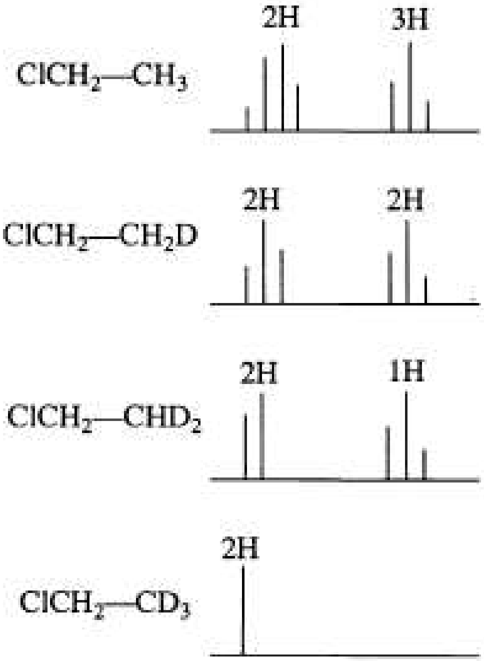
(iii) Deuteration-Deuterium Exchange and Deuterium Labelling

The protons of —OH, —NH_2, —SH etc. groups are exchangeable with D_2O. Thus, such groups

$$ROH + D_2O \rightleftharpoons ROD + HOD$$

are identified by exchange with D_2O which causes their signal to disappear from the spectrum. This exchange reaction is similar to proton exchange reactions (Section 5.16), and is called *deuterium exchange reaction*. For detecting the protons exchangeable with D_2O, either the PMR spectrum is recorded in D_2O or a few drops of D_2O are added to the sample. For example, in the case of an alcohol on D_2O 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.

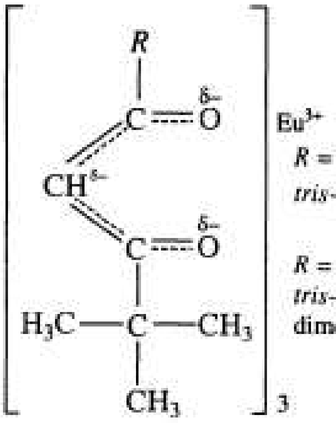
Deuterium is easily introduced into a molecule and its presence in a molecule is not detected in the PMR spectrum because it absorbs at different field strengths (Section 5.14). Deuterium couples only slightly with the proton, hence it does not split its signal. Deuterium labelling also simplifies PMR spectra as illustrated by the example of ethyl chloride.



As 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.

(iv) Use of Shift Reagents

Shift reagents were first introduced by Hinckley in 1969. Shift reagents provide a useful method for spreading out normally overlapped PMR absorption patterns without increasing the strength of the applied magnetic field. The shift reagents are usually enolic β-dicarbonyl complexes of a rare earth (lanthanide) metal and these complexes are mild Lewis acids. Following are the structures of more commonly used shift reagents $Eu(dpm)_3$ and $Eu(fod)_3$:



R = *t*-butyl = $Eu(dpm)_3$
tris-(dipivalomethanato) europium

$R = C_3F_7—$ = $Eu(fod)_3$
tris-1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionatoeuropium

The use of such shift reagents is illustrated in Fig. 5.27 in which the PMR spectrum of 1-hexanol is simplified by addition of $Eu(dpm)_3$. Fig. 5.27(a) shows the PMR spectrum of 1-hexanol in the absence of the shift reagent. In this spectrum, the only interpretable signal is that of the methylene group (a triplet at δ 3.8) adjacent to OH and the terminal methyl (a distorted triplet at δ 0.9). The protons of the remaining methylene groups are buried in the methylene envelope (between δ 1.2-1.8). Upon addition of the shift reagent Eu(dpm)$_3$, the signals of the methylene groups closer to the OH group are shifted downfield resulting in a separate signal for each of the methylene groups (Fig. 5.27(b)). Thus, the spectrum is simplified almost to the first order.

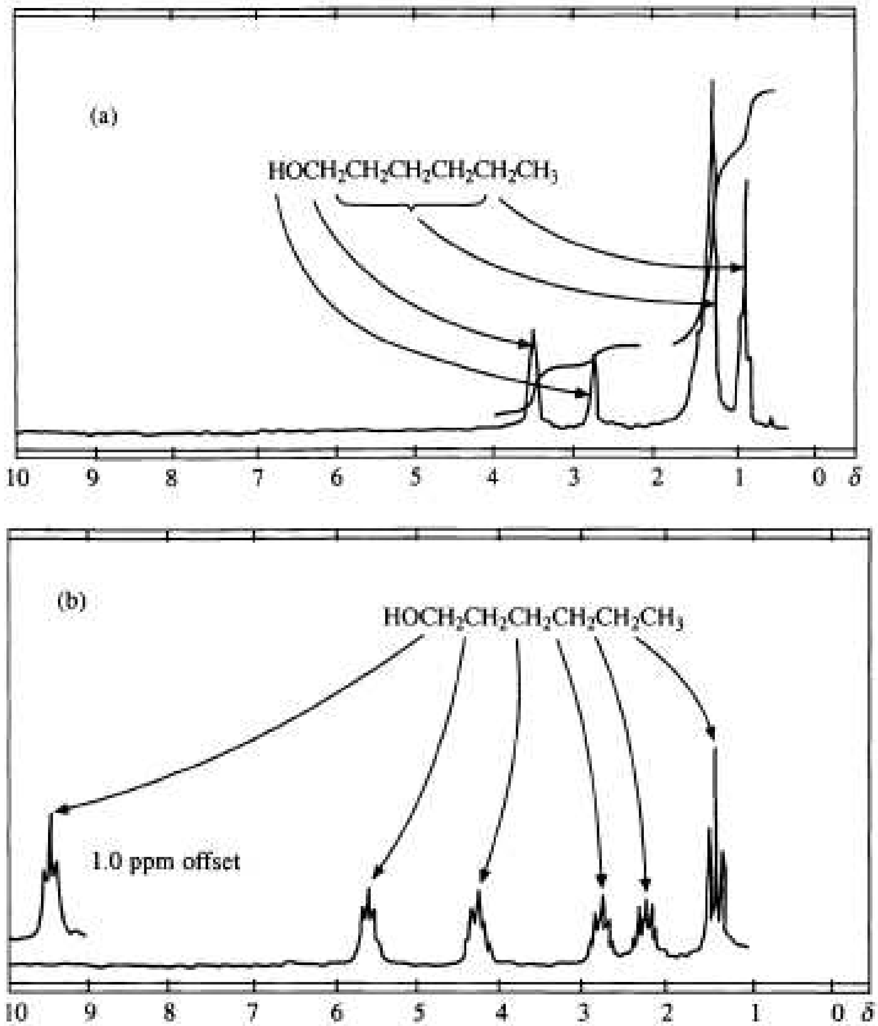


Fig. 5.27 PMR spectrum of 1-hexanol at 100 MHz: (a) in the absence of the shift reagent and (b) after addition of the shift reagent Eu(dpm)$_3$

The signal due to the hydroxylic proton is shifted to low field to be observed. In the shift reagents, the lanthanide ion can increase its coordination through bonding interaction with lone pair of electrons of the groups like OH, NH$_2$, C=O, —O—, COO*R*, CN etc. present in the organic compound under study.

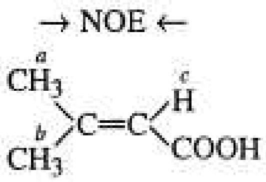
The metal ion of the shift reagent is a paramagnetic moiety which causes marked changes in the observed chemical shifts of the protons present in the substrate. Hence, the name *shift reagent*. Europium complexes generally produce downfield shifts, whereas praseodymium complexes produce upfield shifts.

5.18 Nuclear Overhauser Effect (NOE)

This effect is a change in the intensity of absorption of a nucleus on double irradiation of another nucleus. In this case, less intense radiation is used than that in spin tickling (Section 5.17(ii)). Usually, an increase of a few per cent (theoretically up to 50%) in the intensity of absorption is observed between protons which are in close spatial proximity. NOE tells whether two nuclei (e.g. protons) are in close spatial proximity or not. It is useful in the study of stereochemical relationships within molecules. NOE is observable only over very short distances, generally 2-4 Å. Since NOE involves the interaction of magnetic nuclei through space, the number of intervening bonds between the concerned protons has no significance. NOE does not lead to spin-spin coupling. It must be clearly understood that spin-spin coupling and NOE are different phenomena and that the coupling interaction takes place via the bonds separating the nuclei, whereas the NOE is transmitted through space and originates from the relaxation process.

NOE has its origin in the relaxation process. The double irradiation upsets the Boltzmann equilibrium by producing the saturation condition (Section 5.2), i.e. we eliminate the population difference across some transitions by double irradiation. Thus, other parts attempt to maintain the Boltzmann equilibrium of the total system by spin relaxation resulting in the change of their intensity of absorption. A nucleus in higher energy spin state may undergo spin relaxation by transferring its energy to an adjacent nucleus with lower energy spin state. The efficiency of this spin relaxation is directly related to the distance between the two nuclei.

Let us take the example of 3-methyl-2-butenoic acid (X). If the vinyl hydrogen ($\overset{c}{\text{H}}$) is irradiated, then the intensity of the signal due to the methyl group *a*, which is *cis* to $\overset{c}{\text{H}}$, becomes greater than that due to the *trans* methyl group *b*. On irradiation of the *cis* methyl group *a*, $\overset{c}{\text{H}}$ shows an increase of 17% in the intensity of its absorption, whereas the irradiation of relatively distant *trans* methyl groups *b* does not affect the intensity of the $\overset{c}{\text{H}}$ absorption.



(X)

5.19 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 as follows.

(i) Identification of Structural Isomers

Structural isomers can easily be distinguished by PMR spectroscopy. For example

(i) CH_3OCH_3 and CH_3CH_2OH

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. Thus, 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 ($ClCH_2CH_2Cl$)

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 $—\underset{|}{C}H—$ groups, respectively. In 1,2-dichloroethane all the four protons are equivalent. Hence, its PMR spectrum will show only one singlet.

(ii) Detection of Aromaticity

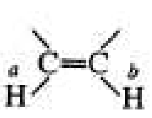
As shown in Section 5.7(ii)(d), aromatic protons are highly deshielded due to the circulating π electrons (ring current) and appear at very low field (δ 6-8.5). From this, the aromatic character of a compound under study can be predicted.

(iii) Detection of Hydrogen Bonding

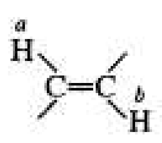
Intermolecular and intramolecular hydrogen bondings can be detected by PMR spectroscopy because both shift the absorption position of the hydrogen-bonded proton to downfield. Besides, both types of hydrogen bonding can also be distinguished, as the intermolecular hydrogen bonding is concentration-dependent, while the intramolecular hydrogen bonding is not concentration-dependent (Section 5.7(iii)).

(iv) 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 5.11(b). For example



J_{cis} = 6-12 Hz

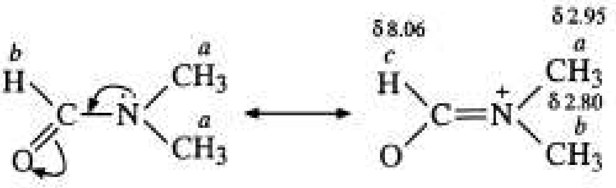


J_{trans} = 12-18 Hz

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.

(v) 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:



(XI) (XII)

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 (XII) 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.

(vi) 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 afford 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 acetyl acetone will illustrate the quantitative analysis of a mixture.

$$\underset{\text{Keto form}}{H_3C{-}CO{-}CH_2{-}CO{-}CH_3} \rightleftharpoons \underset{\text{Enol form}}{H_3C{-}\underset{\displaystyle OH}{\underset{|}{C}}{=}CH{-}CO{-}CH_3}$$

Acetylacetone

In the PMR spectrum of acetylacetone, the height of the integration curve at the methylene (—CH_2—) 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 = 2H = 10 mm
The methine group of the enol form = 1H = 22 mm
Therefore, 2H = 44 mm

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

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

Quantitative analysis of the mixtures like ethanol-water; acetic acid-water etc. has already been discussed in Section 5.16. PMR spectroscopy has also been used for the quantitative analysis of the mixtures of diastereomers as well as for determining the enantiomeric excess (ee), i.e. optical purity.

5.20 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 *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 ^{13}C NMR spectra.

5.21 Some Solved Problems

Problem 1. Give the relative positions of the PMR signals and their multiplicity in each of the following compounds:

(i) $CH_3CH_2COCH_3$ (ii) CH_3CH_2CHO
(iii) $CH_3CH_2OOCCH_2CH_2COOCH_2CH_3$ (iv) $(CH_3)_2CHCOOH$

Solution

(i) $\overset{a}{C}H_3\overset{b}{C}H_2CO\overset{c}{C}H_3$

On moving downfield, the sequence of signals is protons *a*, then *c* and *b*.
Multiplicity of signals: Protons *a* (triplet), *b* (quartet) and *c* (singlet).

(ii) $\overset{a}{C}H_3\overset{b}{C}H_2\overset{c}{C}HO$

On moving downfield, the sequence of signals is proton *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).

(iii) $\overset{a}{C}H_3\overset{b}{C}H_2OOC\overset{c}{C}H_2\overset{c}{C}H_2COO\overset{b}{C}H_2\overset{a}{C}H_3$

On moving downfield, the sequence of signals is protons *a*, then *c* and *b*.
Multiplicity of signals: Protons *a* (triplet), *b* (quartet) and *c* (singlet).

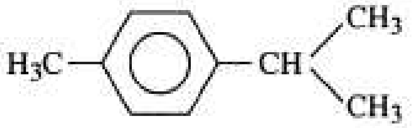
(iv)

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

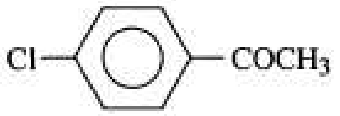
Problem 2. Comment on the number of signals and their splitting, if any, in the PMR spectra of the following compounds:

(i)

(ii)

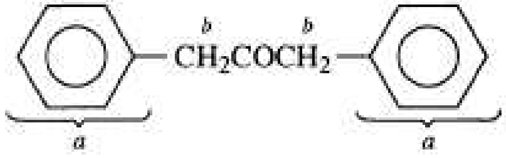


(iii)



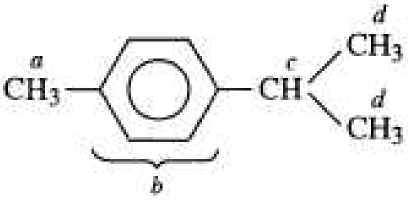
Solution

(i)



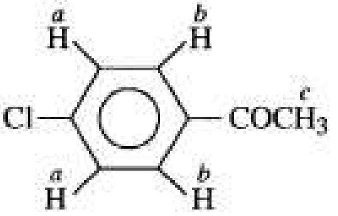
In certain cases, environments of chemically nonequivalent protons are not different enough for the signals to be noticeably separated, and in such cases we may see fewer signals than we predict. For example, in some (but not all) aromatic compounds the *ortho*, *meta* and *para* protons have nearly 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 proton *a* and the other due to the methylene proton *b*.

(ii)



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

(iii)



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 neighboring proton, hence will appear as a doublet (1 + 1 = 2). Similarly, protons *b* will also appear as a doublet. The methyl proton *c* has no neighboring proton, hence will appear as a singlet.

Problem 3. In an organic compound, 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?

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

(i) $\frac{60}{60} \times 90 = 90\text{ Hz}$

(ii) $\frac{100}{60} \times 90 = 150\text{ Hz}$

(iii) $\frac{180}{60} \times 90 = 270\text{ Hz}$

Problem 4. Propose the structure for the compounds that fit the following ^{1}H NMR data:

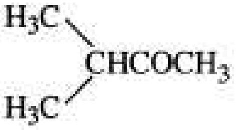
(i) $C_5H_{10}O$

δ 0.95, 6H, doublet
δ 2.10, 3H, singlet
δ 2.43, 1H, multiplet

(ii) C_4H_7BrO

δ 2.11, 3H, singlet
δ 3.52, 2H, triplet, $J = 6$ Hz
δ 4.40, 2H, triplet, $J = 6$ Hz

Solution (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 $-\underset{|}{\mathrm{C}}\mathrm{H}-$ group, i.e. the molecule has $(CH_3)_2CH-$ group; the $-\underset{|}{\mathrm{C}}\mathrm{H}-$ 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



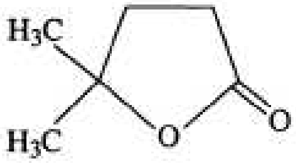
$(H_3C)_2CHCOCH_3$

(ii) The compound C_4H_7BrO shows two triplets with the same coupling constant ($J = 6$ Hz) showing that it contains two nonequivalent adjacent methylene groups coupled with each other ($-CH_2-CH_2-$). 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

$$BrCH_2CH_2COCH_3$$

Problem 5. A compound $C_6H_{10}O_2$ shows a significant IR bond at 1770 cm^{-1}, and three ^1H NMR signals at τ 5.8, 7.5 and 9.1 with relative intensity 1 : 1 : 3, respectively. Deduce the structure of the compound.

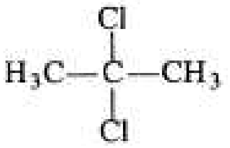
Solution. The presence of an IR bond at 1770 cm^{-1} indicates that the compound is a lactone (cyclic ester). It shows three ^1H NMR signals. Hence, there are three kinds of protons in the compound. Since the total number of protons is 10 and the intensity ratio is 1 : 1 : 3, the number of each kind of protons is 2, 2 and 6, i.e. the compound has two nonequivalent CH_2 and two equivalent CH_3 groups. Thus, the structure of the compound is



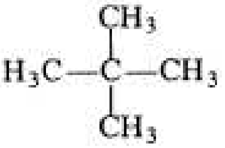
Problem 6. Draw the structure of a compound with each of the following molecular formulae that will show only one PMR signal:

(i) $C_3H_6Cl_2$ (ii) C_5H_{12} (iii) C_4H_6 (iv) C_5H_{10}

Solution

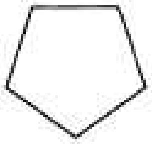
(i) 

$H_3C-\overset{Cl}{\underset{Cl}{C}}-CH_3$

(ii) 

$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$

(iii) $H_3C-C=C-CH_3$

(iv) 

Problem 7. An organic compound has molecular formula C_3H_7Br. Its PMR spectrum is shown in Fig. 5.28. Deduce the structure of the compound.

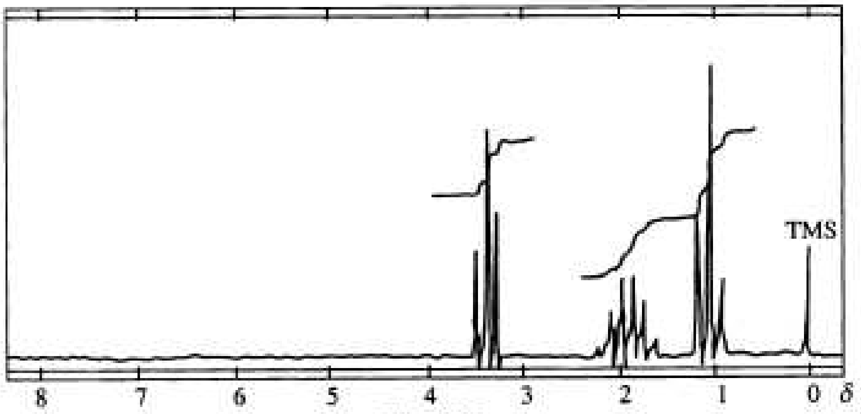


Fig. 5.28

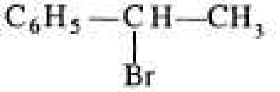
Solution. The PMR spectrum of the compound shows three signals, viz. two triplets and one sextet, hence it contains three kinds of protons. On moving upfield the successive heights of the integration curves at the signals are 8 mm, 8 mm and 12 mm, i.e. the ratio of the number of each kind of protons is 1 : 1 : 1.5. Since the molecular formula of the compound is C_3H_7Br, the number of each kind of protons is 2H, 2H and 3H. This indicates that the compound has $CH_3CH_2CH_2$— group and thus, its structure is $\overset{a}{CH_3}\overset{b}{CH_2}\overset{c}{CH_2}Br$.

The proton *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. 5.28 and thus, a sextet is observed. Since $J_{ab} = J_{bc}$, we can say that the *b* protons have five equivalent neighboring protons, hence appear as a sextet, i.e. $5 + 1 = 6$. Thus, the structure of the given compound is:

$$CH_3CH_2CH_2Br$$

Problem 8. The PMR spectrum of an organic compound C_8H_9Br shows a quartet at 5.5 δ, a doublet at 2.0 δ and an unsymmetrical multiplet at ~7.4 δ in the intensity ratio 1: 3: 5, respectively. Deduce the structure of the compound.

Solution. The molecular formula of the compound is C_8H_9Br and the intensity ratio of 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 ~7.4 δ due to 5H shows the presence of a phenyl group (C_6H_5—), and the presence of a quartet due to 1H and a doublet due to 3H indicates the presence of $-\underset{|}{C}H-CH_3$ group. Thus, the structure of the given compound is



$$C_6H_5-\underset{\substack{|\\ Br}}{C}H-CH_3$$

Problem 9. Using PMR spectroscopy, how will you distinguish the following pairs?

(i) 1,2-dimethoxyethane and 1,1-dimethoxylethane
(ii) *cis*-1-chloropropene and *trans*-1-chloropropene
(iii) Acetone and methyl acetate.

Solution (i) 1,2-dimethoxyethane ($C\overset{a}{H}_3OC\overset{b}{H}_2C\overset{b}{H}_2OC\overset{d}{H}_3$) will exhibit two singlets due to protons *a* and *b*, while 1,1-dimethoxyethane ($(C\overset{a}{H}_3O)_2C\overset{b}{H}C\overset{c}{H}_3$ will exhibit one singlet due to proton *a*, one quartet due to proton *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} = 6-12 Hz) than the *trans* isomer (J_{trans} = 12-18 Hz).

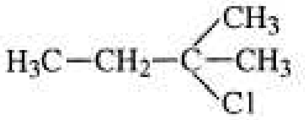
(iii) Both the methyl group in acetone (CH_3COCH_3) are equivalent, hence it will show only one singlet. In methyl acetate (CH_3COOCH_3) the two methyl groups are nonequivalent, hence it will show two singlets.

Problem 10. An organic compound having molecular formula $C_5H_{11}Cl$ gave the following ^1H NMR data:

δ1.0 (*t*, 3H), 1.5 (*s*, 6H) and 1.8 (*q*, 3H)

Deduce the structure of compound.

Solution. The ^1H NMR spectrum of the compound exhibits a three proton triplet and a two proton quartet which indicate the presence of the CH_3CH_2— group. The appearance of a six proton singlet shows the presence of two equivalent CH_3— groups which must be attached to a carbon containing no hydrogen. Thus, the structure of the compound having molecular formula $C_5H_{11}Cl$ is



Problem 11. Fig. 5.29 shows the PMR spectrum of a compound having molecular formula $C_8H_{10}O$. Deduce the structure of the compound.

Solution. The PMR spectrum of the compound shows four signals, viz. two singlets, one doublet and one quartet. Hence, it contains four kinds of protons.

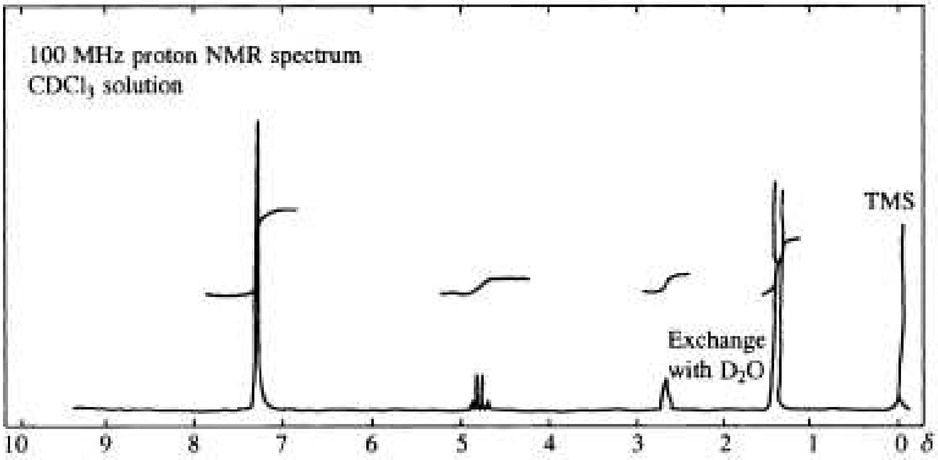
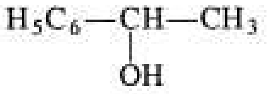


Fig. 5.29

On moving upfield, the successive heights of the integration curves at the signals are 15 mm, 3 mm, 3 mm, and 9 mm, i.e. the ratio of the number of each kind of protons is 5 : 1 : 1 : 3. Since the molecular formula of the compound is $C_8H_{10}O$, the number of each kind of protons is 5H, 1H, 1H and 3H.

The appearance of a five proton singlet at ~7.2 δ indicates the presence of a phenyl (C_6H_5—) group. The presence of a three proton doublet and one proton quartet shows the presence of a CH_3CH group. The proton (1H) causing a singlet is exchangeable with D_2O which shows the presence of a hydroxyl group. Thus, the structure of the compound consistent with the above observations is



$$H_5C_6\text{—}\underset{\displaystyle OH}{\underset{|}{CH}}\text{—}CH_3$$

PROBLEMS

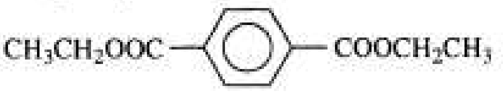
1. For which of the following isotopes NMR spectroscopy is possible and why?

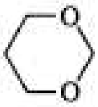
   ^{12}C, ^{14}N, ^{2}H, ^{35}Cl, ^{32}S, ^{16}O and ^{31}P

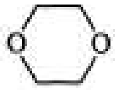
2. Discuss the process of absorption of energy during the nuclear magnetic transitions.
3. Predict the number of signals and their relative intensities in the low resolution PMR spectra of the following compounds:

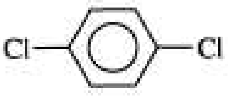
   (a) Toluene (b) Propanal (d) Propionamide

4. What is chemical shift? Giving examples, discuss the factors which affect the magnitude of the chemical shift.
5. Explain spin-spin coupling and splitting of signals with examples.
6. Predict the number of signals and their multiplicity in the PMR spectra of the following compounds:

   (a) 

(b) 

(c) 

(d) 

7. Write notes on:

(a) Shielding and deshielding (b) Relaxation processes (c) Coupling constant

8. (a) Why are the NMR absorption positions expressed relative to a reference compound?

(b) Why is TMS a good reference compound in NMR spectroscopy?

9. 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

10. In an *AX* spectrum, the four lines were observed at δ 5.8, 5.7, 1.1 and 1.0 (measured from TMS with an instrument operating at 100 MHz). What are the chemical shift positions (in δ) of the *A* and *X* nuclei, and the coupling constant (in Hz) between them?

11. Give a structure consistent with each of the following sets of NMR data:

(a) $C_3H_5Cl_3$: δ 2.20 singlet, 3H; δ 4.02, singlet 2H
(b) $C_{10}H_{14}$: δ 1.30, singlet, 9H; δ7.28, singlet 5H
(c) $C_{10}H_{14}$: δ 0.88, doublet, 6H; δ 1.86, multiplet, 1H; δ 2.45; doublet, 2H; δ 7.12, singlet, 5H.

12. 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

13. What is the 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?

14. A compound $C_{10}H_{13}Cl$ gave the following NMR data:

δ 1.57, singlet, 6H; δ 3.07, singlet, 2H; δ 7.27, singlet, 5H

Deduce the structure of compound.

15. Write explanatory notes on :

(a) Shift reagents
(b) Spin-spin decoupling
(c) Nuclear Overhauser Effect (NOE)

16. Using PMR spectroscopy, how will you distinguish the following pairs:

(i) Maleic acid and fumaric acid
(ii) 1-chloropropane and 2-chloropropane
(iii) Intermolecular hydrogen bonding and intramolecular hydrogen bonding

17. Explain the following:

(a) Acetylenic protons absorb at higher field than olefinic protons.

(b) The hydroxylic proton of ethanol does not split the PMR signal of its methylene protons in the presence of a trace of acid.

(c) No signal for deuterium is observed in the PMR spectrum of a compound, e.g. $CD_3CH_2CH_3$.

18. An organic compound has molecular formula $C_3H_6Br_2$. Its PMR spectrum is given in Fig. P5.1. Interpret the spectrum and assign the structure to the compound.

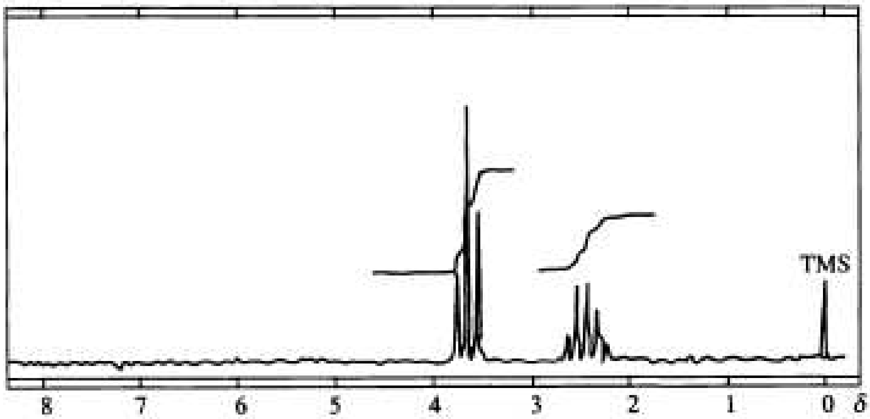


Fig. P5.1

19. Discuss the characteristic features of the first order PMR spectra. How can the more complex (second order) PMR spectra be simplified for obtaining more information?

20. Write notes on:

(a) Chemical and magnetic equivalence of protons.
(b) Factors affecting coupling constants.

21. The following ^1H NMR absorptions were recorded and are listed in Hz from TMS standard. Convert the absorption values into δ units.

(i) 451 Hz at 60 MHz spectrometer
(ii) 430 Hz at 90 MHz spectrometer
(iii) 543 Hz at 100 MHz spectrometer

22. A compound has molecular formula C_3H_8O. 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 (*s*, 1H) and 4.9 (*s*, 1H). Deduce the structure of this compound.

23. (a) Give an account of vicinal and geminal couplings in PMR spectroscopy.
(b) Write a note on chemical exchange and spin-spin decoupling.

24. Using PMR spectroscopy, how will you distinguish the following isomeric compounds:

(i) 1,4-dioxane and 1,3-dioxane
(ii) *t*-butyl bromide and 1-bromo-2-methyl propane
(iii) 1-butyne and 2-butyne

25. Propose a structure consistent with the ^1H NMR data of each of the following compounds:

(a) $C_4H_{10}O$: δ 1.28 (*s*, 9H), 1.35 (*s*, 1H)
(b) $C_4H_{10}O_2$: δ 3.25 (*s*, 6H), 3.45 (*s*, 4H)
(c) $C_{10}H_{13}Cl$: δ1.57 (*s*, 6H), 3.07 (*s*, 2H), 7.27(*s*, 5H)

26. If the observed chemical shift of a proton is 315 Hz form TMS at a 90 MHz NMR spectrometer, what is the chemical shift in terms of δ? Express it in τ value also.

27. The PMR spectrum of a compound C_8H_{10} is given in Fig. P5.2. Analyse the spectrum and assign the structure to the compound.

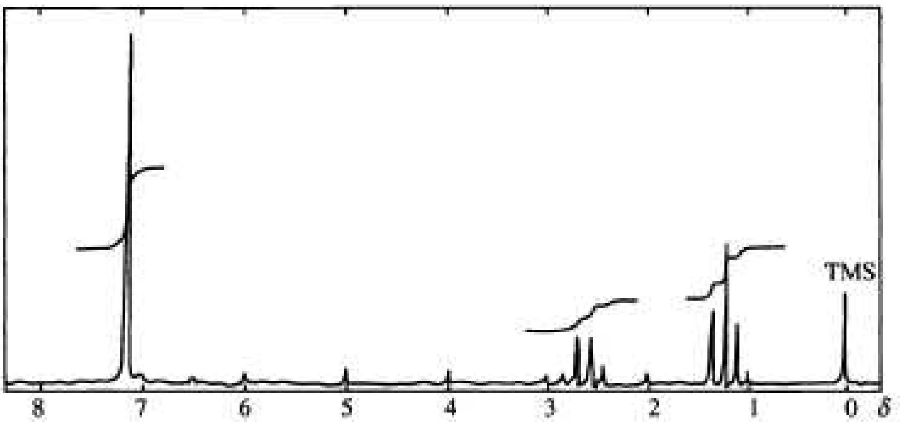


Fig. P5.2

28. 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.

29. A pale yellow organic compound with molecular formula $C_6H_5NO_3$ exhibited an unsymmetrical multiplet in the region 1.8-2.9 τ (4H) and a singlet at 0.1 τ (1H) in its NMR spectrum. Deduce the structure of the compound.

30. (a) How is PMR spectroscopy useful in the detection of aromaticity?

(b) Discuss the use of deuterium exchange and deuterium labelling in PMR spectroscopy.

31. Fig. P5.3 shows PMR spectrum of a compound $C_8H_{10}O$. Interpret the spectrum and assign the structure to the compound.

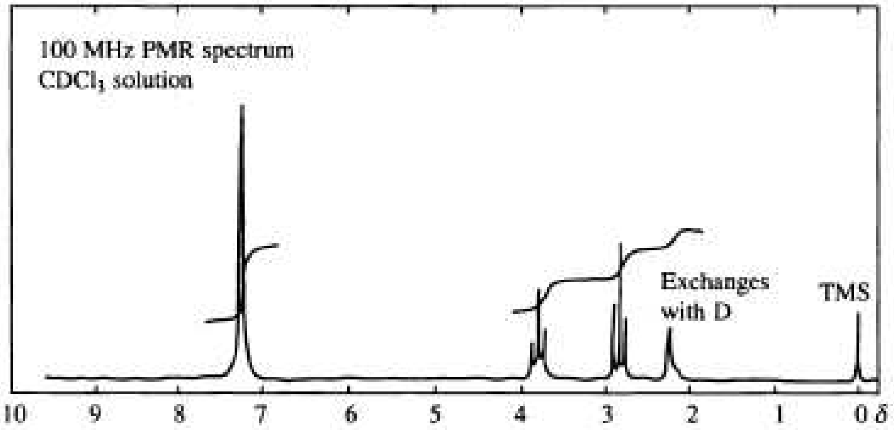


Fig. P5.3

32. Cyclohexane gives only one PMR signal (singlet) at the room temperature, whereas at –100°C it gives two sharp singlets. Explain this observation.

(Hint: At room temperature the interconversions of the two equivalent chair conformations is so fast that the PMR spectrometer sees protons in their average environment and records them as a singlet. At −100°C the time between interconversions is long enough for the spectrometer to record the PMR of the molecule as one conformation or the other, and thus one singlet for the six axial and the other for the six equatorial protons are observed.)

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