Organic Spectroscopy

Principles and Applications

Second Edition

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Narosa

4.8 EQUIVALENCE AND NON-EQUIVALENCE OF PROTONS

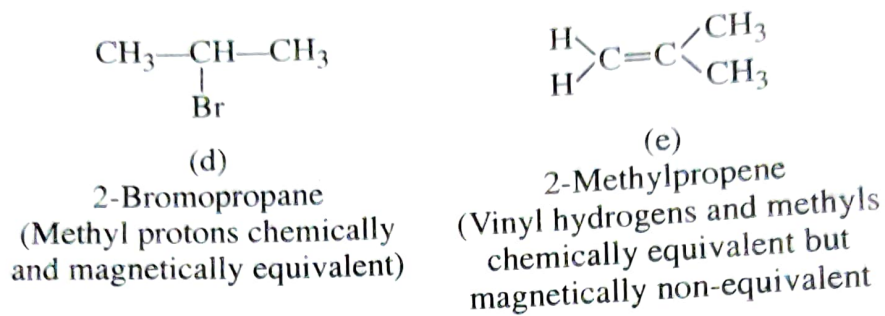## 4.8.1 Magnetic equivalence and non-equivalence of protons

Two nuclei are said to be magnetically equivalent if they exhibit the same chemical shift and the same coupling constant to every other nucleus in the molecule. In other words, magnetically equivalent protons possess the same frequency (isochronous) and only one characteristic spin-spin interaction with the nuclei of a neighbouring group. They are usually also chemically equivalent but there may be subtle differences. This is explained by taking into consideration, the following examples:

(i) The protons of a methyl group are magnetically equivalent since, as a consequence of the rotation about the C–C bond, all the three protons have the same time-averaged chemical environment and therefore the same resonance frequencies. The coupling constant to the protons of a neighbouring CH_2 or CH group is likewise necessarily identical for each of the three protons as the three conformations a, b and c are of equal energy and therefore equally populated. The geometric relation between the individual methyl protons and their neighbours, which determines the magnitude of the coupling constant, thus becomes identical for each of the three methyl protons.

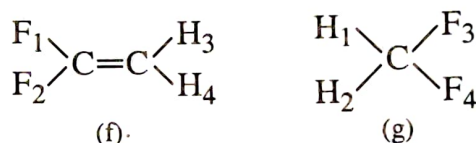(a)   (b)   (c)
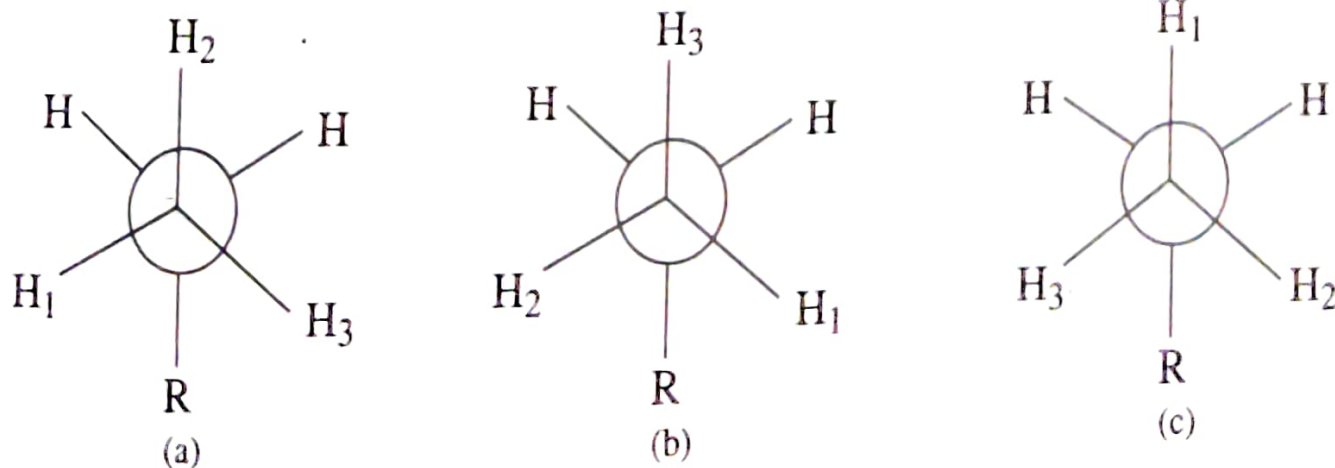
However, in case of *t*-butyl group, it is possible to reduce the rate of rotation about the bond to the next carbon by cooling to low temperatures to such an extent that chemically different methyl groups can be distinguished in the NMR spectrum.

(ii) The methyl protons in 2-bromopropane (d) are chemically and magnetically equivalent whereas in 2-methylpropene (e), the two methyl groups are magnetically non-equivalent because they do not have the same coupling constant with respect to the same hydrogen and consequently magnetically non-equivalent.

$$CH_3—CH—CH_3$$
$$|$$
$$Br$$

(d)
2-Bromopropane
(Methyl protons chemically
and magnetically equivalent)

$$\begin{array}{c} H \\ H \end{array}C{=}C\begin{array}{c} CH_3 \\ CH_3 \end{array}$$

(e)
2-Methylpropene
(Vinyl hydrogens and methyls
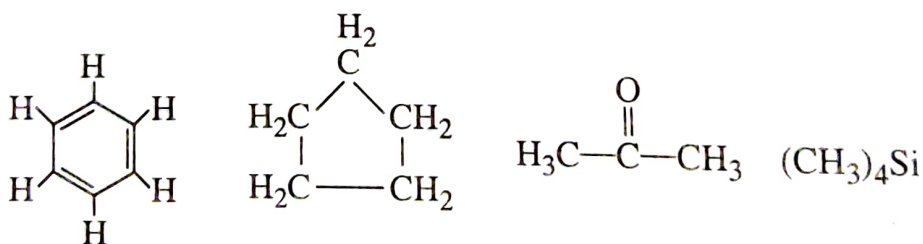chemically equivalent but
magnetically non-equivalent

(iii) Similarly the protons in 1,1-difluoroethylene (f) as well as the two fluorine nuclei are chemically equivalent but magnetically non-equivalent for two different coupling constants are observed that is $J_{1,3} \neq J_{1,4}$ or $J_{cis} \neq J_{trans}$. In difluoromethane (g), on the other hand, the protons as well as the fluorine nuclei, are magnetically equivalent ($J_{1,3} = J_{1,4} = J_{2,3} = J_{2,4}$).

$$\begin{array}{c} F_1 \\ F_2 \end{array}C{=}C\begin{array}{c} H_3 \\ H_4 \end{array}$$

$$\begin{array}{c} H_1 \\ H_2 \end{array}C\begin{array}{c} F_3 \\ F_4 \end{array}$$

(f).   (g)

4.8.2   Chemically equivalent protons

Protons in chemically identical environments would often exhibit the same chemical shift. Thus, all the protons in tetramethylsilane (TMS), benzene, cyclopentane or acetone will give rise to a single absorption peak in their PMR spectra. The protons are said to be chemically equivalent.

$$H_3C—\overset{\overset{O}{\|}}{C}—CH_3 \quad (CH_3)_4Si$$

(Molecules giving rise to only one NMR absorption peak: (all protons chemically equivalent)

On the other hand, molecules which have sets of equivalent protons, chemically distinct from one another, may give rise to an absorption peak pertaining to each set.

$$H_2C—COOCH_3 \quad H_3C—COOCH_3$$
$$|$$
$$H_2C—COOCH_3 \quad H_3C—O—CH_2Cl$$
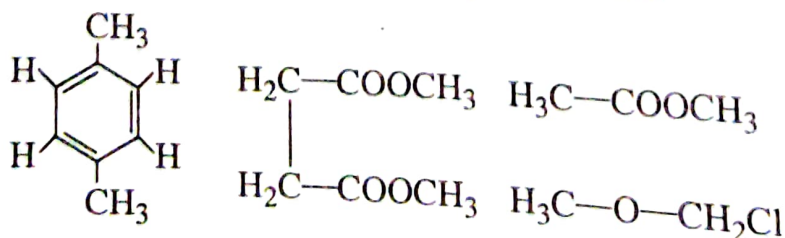
Molecules giving rise to two NMR absorption peaks: (two sets of chemically equivalent protons)

The NMR spectrum of phenylacetone exhibits three chemically distinct types of protons. Chemically equivalent nuclei are, however, not necessarily magnetically equivalent.

7.2δ (5-protons)
2.1δ (3-protons)
3.6 δ (2-protons)
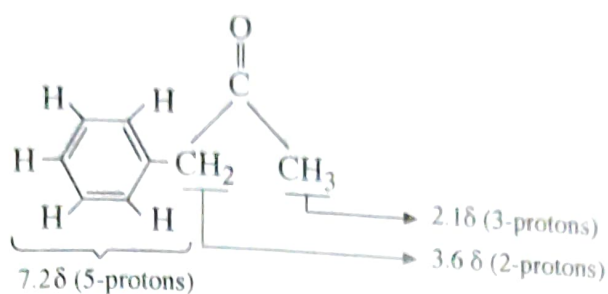
4.8.3 Spin-spin coupling or spin-spin splitting

The coupling interaction between two or more protons, most often through the bonds, results in splitting of the spectral lines. This is called spin-spin coupling. It is related to the number of possible combinations of the spin orientations of the neighbouring protons.

The magnitude of the spin coupling interaction between protons in general decreases as the number of bonds between the coupled nuclei increases. The coupling constant is finally reduced to the order of magnitude of the natural line width so that a splitting is no longer observed. This is illustrated by comparing the PMR spectrum of benzyl acetate with that of ethyl formate (Fig. 4.10).
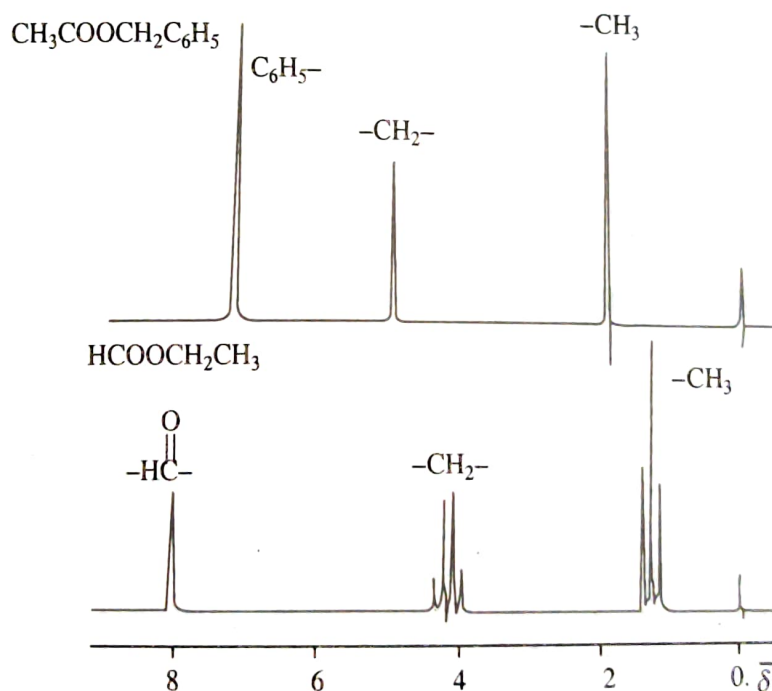

Fig. 4.10   PMR spectra of benzyl acetate and ethyl formate.

Figure 4.10 exhibits not only a difference in the position of the resonance signals but also a difference in the multiplicity of the signals. In the case of benzyl acetate, singlets are observed for both the methyl and methylene protons while in ethyl formate the same protons give rise to a triplet and quartet respectively, each with a rather distinct intensity distribution. The cause of this fine structure is spin-spin coupling. It is brought about by a magnetic interaction between individual

protons that is not transmitted through space but rather by the bonding electrons through which the protons are indirectly connected.

Figure 4.11 shows schematic representation of the nuclear spin-spin interaction through bonding electrons in the HF molecule and in a CH_2 group. The lower energy state corresponds to the antiparallel arrangement of nuclear and magnetic moments. Pauli principle and Hund's rule are applicable for the transmission of polarization of orbitals. Thus, the magnetic polarization for orbitals involved in bonding is antiparallel while that for degenerate orbitals, that is, the hybrid orbitals at a carbon atom, is parallel.
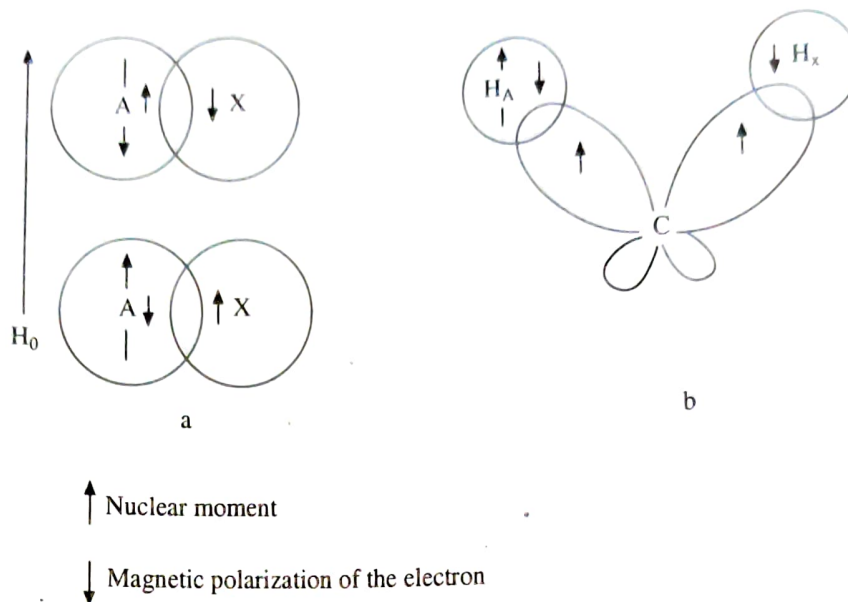

↑ Nuclear moment

↓ Magnetic polarization of the electron

Fig. 4.11 Schematic representation of nuclear spin-spin interaction through the bonding electrons (a) in the HF molecule and (b) in a CH_2 group.

4.8.4 Multiplicity of splitting and relative intensity of lines in a multiplet

4.8.4.1 MULTIPLICITY OF SPLITTING

The degree of multiplicity, that is, the number of lines observed in the NMR signal for a group of protons, and intensity distribution of lines within a multiplet may be derived from the relative probabilities of different spin arrangement of nuclei in each group. This is illustrated by taking into consideration the example of ethyl group in ethyl formate (Fig. 4.10). The number of lines in each group, that is, their multiplicity, is larger by just one than the number of protons in the neighbouring groups. The fact that the three protons of the methyl group can exist in four different magnetic states leads to the observed quartet for the resonance of the methylene protons in which 1 : 3 : 3 : 1 intensity distribution is a result of the relative probabilities of the different spin combinations of the nuclei (Fig. 4.12). Completely analogous considerations apply for the structure of the methyl protons resonance.

The simple rules governing spin-spin splitting is described as follows:

(i) A group of n equivalent protons in the neighbour will split an NMR signal into $n + 1$ peaks.

(ii) When two neighbouring groups of protons are present such that the chemical shift pertaining to the second group is different from that of the protons in the first group, the effect of the second group must be considered separately. Thus, if a nucleus H_M has two chemically different neighbouring nuclei H_A and H_X, the signal for H_M would be split into a doublet of doublet. A triplet would be observed only if J_{AM} and J_{AX} were by chance identical.
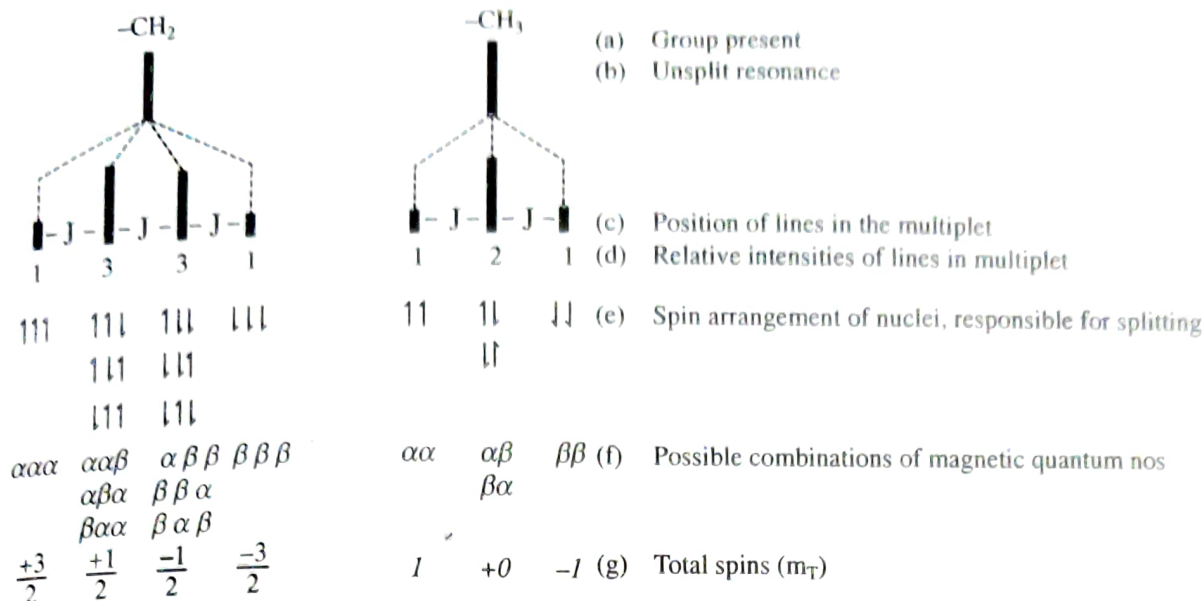
Fig. 4.12   Spin-spin splitting diagram for ethyl group.

(iii) If a proton has, as neighbours, sets n_a, n_b, n_c . . . of chemically equivalent protons, the multiplicity of its resonance will be $(n_a + 1)(n_b + 1)(n_c + 1)$ . . .

(iv) When the nucleus, involved in spin-spin coupling, has a spin quantum number I greater than 1/2, the multiplicity and the intensity distribution of the splitting pattern deviates from the rules given above. For example, a neighbouring deuteron ($I = 1$) splits a proton signal into a triplet, the lines of which have equal intensity. This is due to the fact that the possible orientation of the deuteron's spin relative to an external field, namely $m_I = + 1$, 0 and -1 are in practice equally probable. In general, the multiplicity of an NMR signal caused by n neighbouring nuclei is given by $2nI + 1$.

4.8.4.2   RELATIVE INTENSITY OF LINES IN A MULTIPLET

The relative intensities of lines within a multiplet are given by coefficients of the binomial expression $(x + 1)^n$ or by the use of Pascal's triangle, where each term coefficient is the sum of the two terms diagonally above it, as described below:

Number of equivalent protons responsible for splitting	Multiplicity of observed signals	Intensity distribution of lines within the multiplet
0	Singlet	1
1	Doublet	1 1
2	Triplet	1 2 1
3	Quartet	1 3 3 1
4	Quintet	1 4 6 4 1
5	Sextet	1 5 10 10 5 1

4.8.5   Coupling constants

The coupling constant is a measure of the coupling interaction (spin-spin coupling or splitting) between the nuclei. The spacing between the lines within a coupled multiplet is constant. This constant distance called the coupling constant, is denoted by J and expressed by Hertz (Hz).

The coupling constant, J, is determined in the spectrum by measuring the separation of adjacent lines in the multiplet under consideration. The observed splitting must then also be found in the multiplet of the neighbouring group of protons. This is illustrated in the Fig. 4.13 for the three aromatic protons of 2, 4-dinitrophenol.

The spectrum clearly reveals that the magnitude of J decreases as the number of bonds between the coupled nuclei increases, i.e. $J_{ac} < J_{ab} < J_{bc}$. The coupling constant is a function of several factors, the most important of which are the following:

(a) *Number of bonds separating the nuclei*
This is illustrated by the following examples:
    (i) The coupling constants are attenuated with increasing number of bonds. For example $J_0 > J_m > J_p$.

J_{ao} (ortho) = 6 – 10 Hz
J_{am} (meta) = 1 – 3 Hz
J_{ap} (para) = 0 – 1 Hz
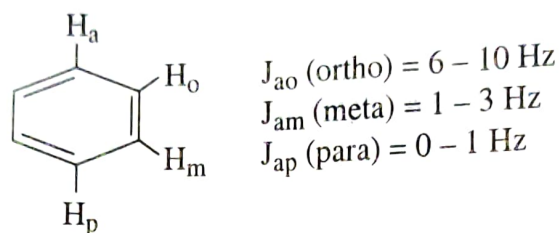
(ii) Long range coupling over more than three bonds is generally observed in unsaturated systems in which the π-electrons prove to be effective transmitters of magnetic information.

(iii) Spin-spin coupling interaction can be transmitted through hetero-atoms in groups of the type H–C–O–H and H–C–N–H.
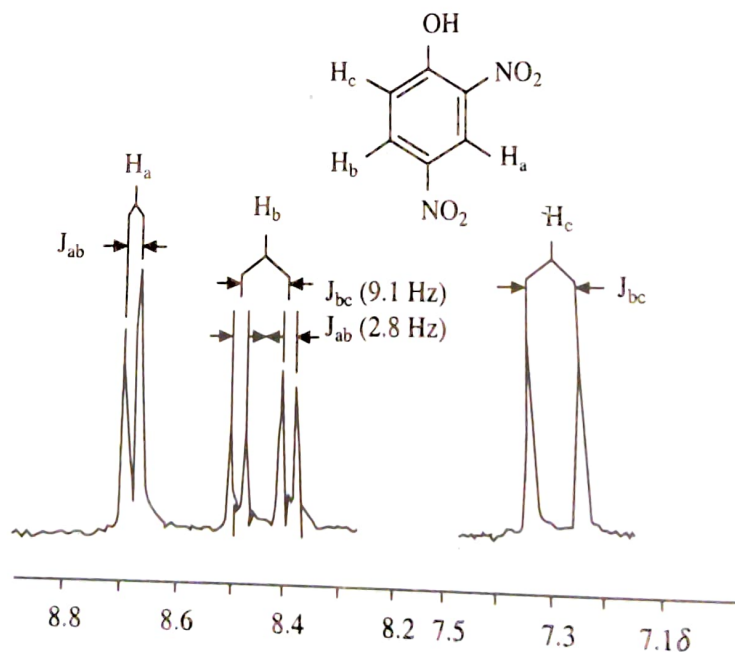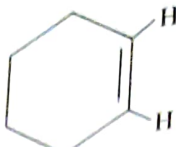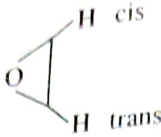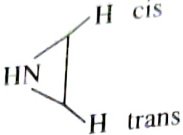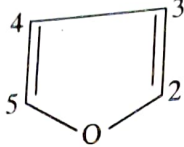

Fig. 4.13 100 MHz PMR spectrum of 2, 4-dinitrophenol.

(b) *Geometry of the coupling path, i.e. stereochemistry of the molecule*
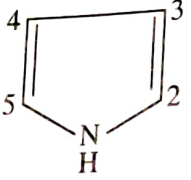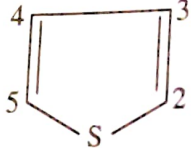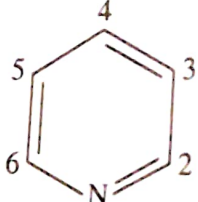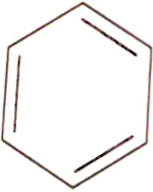Some typical values of H–H coupling constants in organic compounds are recorded in the Table 4.7. The data clearly reveals that the magnitude of coupling constants for protons in general lies in the range 5–17 Hz and that these parameters are very sensitive to the geometry of the coupling path, i.e.,

Table 4.7 *Proton spin-spin coupling constants (Hz)*

S. No.	Structural unit	J (Hz)
1.	$C{\Big\langle}^H_H$	12–15
2.	–CH–CH (free rotation)	6–8
3.	$\overset{H}{\diagdown}C{=}C\diagdown^H$	11–18
4.	$\overset{H}{\diagdown}C{=}C\diagup^H$	6–14
5.	$-C{=}C{\Big\langle}^H_H$	0–4
6.	$C{=}C{\Big\langle}^{CH}_H$	4–10
7.	$O{=}C{\Big\langle}^{CH}_H$	1–3
8.	HC=C–CH	0.5–3
9.	HC≡C–CH	2–3
10.	CH–C=C–CH	0–3
11.	CH–C≡C–CH	2–3
12.	C=CH–HC=C	9–13
13.	cyclopropane H cis / H trans	6–12 / 4–8
14.	cyclobutane H cis / H trans	6–11 / 5–9
15.	cyclopentane H cis / H trans	7–11 / 2–8
16.	cyclohexane H a, a / a, e / H e, e	8–14 / 0–7 / 0–5
17.	cyclopentene =CH	5–7

18.

4–5

19.

H cis

3.2

H trans

6.3

H cis

20.

3.8

H trans

2.0

J 2, 3	3.5
J 3, 4	0.9
J 2, 4	1.6
J 2, 5	

21.

22.

J 2, 3	2.6
J 3, 4	3.4
J 2, 4	1.4
J 2, 5	2.1

23.

J 2, 3	5.2
J 3, 4	3.6
J 2, 4	1.3
J 2, 5	2.7

24.

J 2, 3	5.5
J 3, 4	7.5
J 2, 4	1.9
J 2, 5	0.9
J 3, 5	1.6
J 2, 6	0.4

25.

J ortho	6–10
J meta	1–4
J para	0–2

the stereochemistry of the molecule. For example J_{trans} is, in general, greater than J_{cis}. In cyclopropane, however, $J_{trans} < J_{cis}$. Similarly in cyclohexane $J_{aa} > J_{ee}$.

4.8.5.1   Positive and negative coupling constant

An alternate way of looking at the phenomenon of spin coupling is to consider the energy level diagram of a two spin system. When a nucleus A is coupled to the nucleus X, then the following four different orientations of nuclear spins of A and X with respect to the applied field H_o, as shown in the fig. 4.13a are possible.

(a) Both A and X are parallel to H_o,

(b) A can be parallel to H_o while X can be antiparallel,

(c) A can be antiparallel to H_o while X can be parallel, and

(d) Both A & X can be antiparallel with respect to H_o

In the absence of spin spin coupling, these transitions A_1 and A_2 will occur for the nucleus A. Since both transitions are of equal energy, a single resonance line results. In the presence of spin-spin coupling, however the eigen values of the spin system are altered as shown in the fig. 4.13b. The states (ii) and (iii) in which the spins of A and X are antiparallel to each other are by convention the stable arrangements and come quantity the eigen value of both (ii) and (iii), due to spin-spin coupling are lowered while those of (i) and (iv) are raised (destabilized). This means that the transition (A_1') and (A_2') are no longer of the same energy but instead A_1' becomes greater than A_2' Consequently, there will be two different values of the applied field at which the nucleus A will come to resonance resulting in the formation of a doublet. A similar consideration applies to X, which will also appear as a doublet.

It may be mentioned that the protons attached to adjacent carbon atom tend to have antiparallel nuclear moments with respect to one another in the lowest energy state. The coupling constants between such protons are generally positive. On the other hand, protons attached to the same carbon atom tend to have their nuclear moments parallel to one another in the lower energy state (fig. 4.11b) the coupling constant between such geminal methylene protons are usually negative.

In the case of non-aromatic annulenes containing $4n\pi$ electrons, e.g., [16]-annulenes, quantum mechanics predicts a paramagnetic ring current effect (paramagnetic anisotropy) instead of the diamagnetic effect which results in the opposite situation, i.e. inner protons are deshielded and outer ones are shielded.

It may be mentioned that the ring current effects are only discernible in planner conjugated cyclic molecules. In nonpolar molecules e.g. cyclooctatetraene (Fig.) which is tube shaped, the delocalization of π-electrons is severely restricted, and the protons of cyclooctatetraene therefore resonate in the normal olefinic region (δ 5.80).
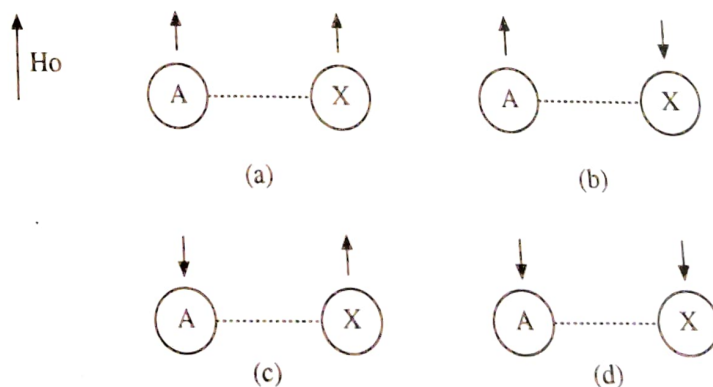

Fig. 4.13a   Relative orientations of the spins of nuclei A and X with respect to applied field H_0.

4.8.6 Integration

It is the process by which relative areas under spectral peaks, proportional to the number of equivalent protons giving the signal, are measured. The NMR instrument integrates the area as follows:

When there is no signal, it draws a horizontal line. When the signal arrives, the line ascends and levels off as the signal ends. The relative distance from plateau to plateau gives the relative area.
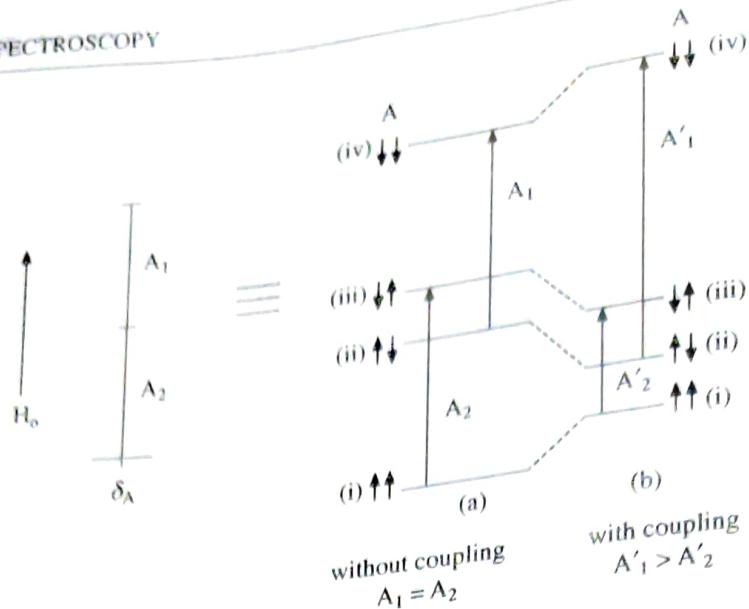
Fig. 4.13b **Effect of spin-spin coupling on the eigenvalues of coupled nuclei: (a) without spin-spin coupling (b) with spin-spin coupling.**

Thus, the integration process exhibits only the relative number of protons. This has been illustrated by the integrated PMR spectrum of benzyl acetate (Fig. 4.14).
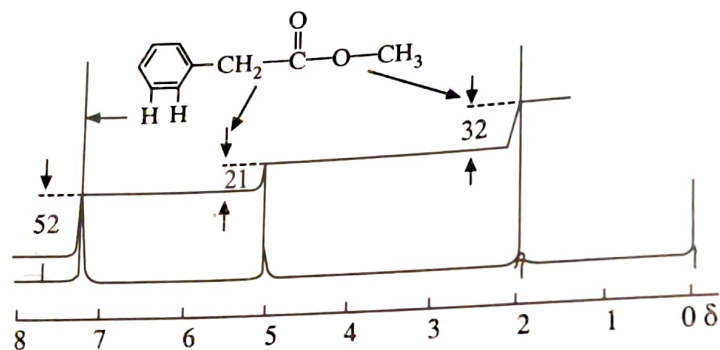

Fig. 4.14 **Integrated PMR spectrum of benzyl acetate.**

The integration of resonance signals has been used to determine the constitution of mixtures or percentage of an impurity present. For example, the mass M_A of component A in a mixture can be determined if an amount M_B of a known compound B is added to a weighed sample of the mixture and the signals assigned to A and B are integrated. The mass of A is then given by the following relation:

$$m_A = m_B \cdot \frac{N_B}{N_A} \frac{A_A}{A_B} \frac{M_A}{M_B}$$

where N is the number of protons responsible for the signals chosen. A is the area under the signals and M_A and M_B are the molecular weights of A and B, respectively.

4.9 ELECTRON COUPLED SPIN-SPIN SPLITTING THEORY

Consider two vicinal protons similar to the alkene protons of cinnamic acid, H_A and H_X.
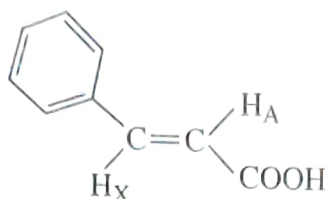
The protons, having different chemical and magnetic environments, come to resonance at different positions, thus giving rise to two doublets in the NMR spectrum. The spacing between the lines of each doublet is constant and is called the coupling constant J.

The resonance position of H_A depends upon its total magnetic environment: a part of which is contributed by the nearby proton H_X. The proton H_X can either have its nuclear magnetic field aligned with or against the proton H_A. Thus, the proton H_X can either increase (if aligned) or decrease (if opposed) the net magnetic field experienced by H_A. These two spin orientations of H_X, therefore, create two different magnetic fields around H_A and consequently the proton H_A comes to resonance not once but twice and thus splits into doublet.

The mutual magnetic interaction between the protons H_A and H_X is not transmitted through space but through the electrons in the intervening bonds. The nuclear spin of H_A couples with the electron spin of C–H_A bonding electrons; these in turn couple with the C–C bonding electrons and then with the C–H_X bonding electrons.

This electron coupled spin-spin interaction operates strongly through one or two bonds, less strongly through three bonds and rather weakly through four or more bonds.

4.9.1 Designation of nuclei in a spin system (nomenclature)

Spin system
The term spin system is used to describe a group of nuclei that are spin-spin coupled among each other but not with any other nucleus outside the spin system. It is not necessary, however, for all the nuclei within the spin system to be coupled to all the other nuclei. In many cases, the spin system embraces the complete molecule, e.g., $CH_3CH=CH_2$ is a spin system. On the other hand, a molecule may consist of two (or more) parts insulated from each other and thereby giving rise to two or more independent spin systems, e.g., $CH_3CH_2–O–CH_2CH_2CH_3$. This contains two spin systems; the five-spin ethyl group and the seven-spin *n*-propyl group.

Nomenclature
A simple nomenclature to designate a spin system is based on the relative chemical shifts and the size of the chemical shift difference with respect to the coupling constant. J. The symbols used to designate individual nuclei and spin systems are given below:

(i) A group of protons for which chemical shift difference is comparable to the spin-spin coupling are denoted by letters A, B, C etc. (in the order of increasing shielding).

(ii) A group of protons having resonance positions well separated from A or B etc. are denoted by the letters X, Y, Z etc.

(iii) The number of protons in each group is denoted by a subscript. The ethyl group in ethyl acetate

can thus be described as A_2X_3 system but an ethyl group at the end of a long aliphatic chain, for example in n-hexyl bromide, is designated as A_2B_3 system.

(iv) The primed symbols are used to designate chemically equivalent but magnetically non-equivalent protons. In 1, 3-butadiene (I), for example, the system AA' indicates hydrogens H_A and H'_A with the same chemical shift but different coupling constants w.r.t. other nuclei. Similarly, the hydrogens, H_B and H'_B and H_C and H'_C are chemically equivalent but magnetically non-equivalent as the spin-spin interactions of H'_C with H'_A and H'_B are different from those of H'_C with H_A and H_B.

I
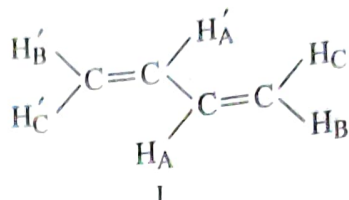
4.9.2   First order and non-first order splitting

First order splitting

The simple splitting pattern resulting from the coupling of protons having large chemical shift difference (Δv) as compared to the coupling constant J ($\Delta v/J > 6$) is called first order splitting.

The PMR spectra of dichloroacetaldehyde and 1,1-dibromoethane (Fig. 4.15) are the examples of first order splitting (AX pattern) because the coupled system consists of two protons of widely different chemical shifts (indicated by the widely separated letters of the alphabet). By convention, the proton resonating at a lower field is denoted by the earlier letter of the alphabet.
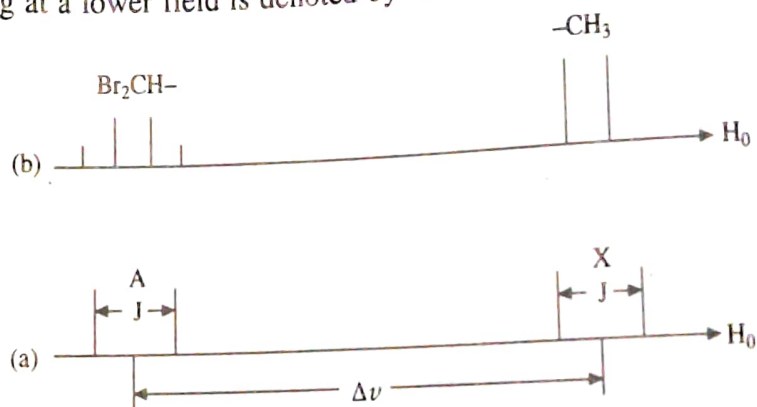

Fig. 4.15   (a) Simplified PMR spectrum of dichloroacetaldehyde (b) simplified PMR spectrum of 1,1-dibromoethane.

The values of the chemical shifts and the coupling constants may be measured directly from the spectrum.

Rules and Conditions for first order splitting

Rules for first order splitting

The first order splitting is governed by the following rules:

1. The multiplicity of a signal arising from an adjacent group of equivalent nuclei of nuclear sp I is given by $2nI + 1$, where n is the number of equivalent nuclei, causing the splitting. For proton $I = 1/2$ so that the multiplicity is $n + 1$.

2. The intensity distribution in the multiplet is given by the co-efficients of the binomial expression $(1 + x)^n$ or by the use of the pascal's triangle.

3. The centre of the multiplet gives the resonance position of the nucleus and hence the chemical shift.

4. In the case of only two interacting groups of nuclei, the separation between the components of multiplet is equal and correspond to the coupling constant.

Conditions for first order splitting rules

The first order splitting rules are applicable only if the following conditions are met.

(a) The chemical shift difference between the interacting nuclei must be large compared with the coupling constant ($\Delta v/J > 6$).

(b) Each nucleus of one group must interact equally with each and every nucleus of the second group.

Non-first order splitting

When the chemical shift difference (Δv) between the interacting nuclei becomes comparable with the coupling constant (J) between them, the first order splitting rules are no longer applicable. The pattern of splitting in the multiplet becomes distorted and the bands are no longer symmetrical. With this pattern of splitting (called non-first order splitting) it is not possible to extract chemical shift and coupling constant values without the use of calculations.

Non-first order splitting can be explained by taking into consideration the effect of changes in $\Delta v/J$ ratio on the PMR spectrum of a two proton AX system (Fig. 4.16).
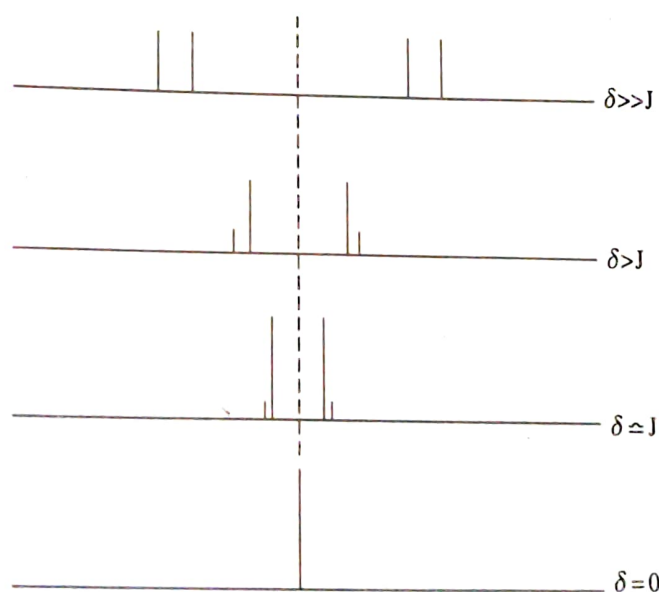

Fig. 4.16   Effect of changes in $\Delta v/J$ ratio on PMR spectrum of two protons of AX group.

The inner lines of each doublet increase in intensity at the expense of the outer ones and in the extreme case the outer lines may become too weak to be observed and consequently the AB quartet may be wrongly interpretted as a doublet. Thus, the chemical shift position of each proton is no longer at the mid-point of the doublet and can be calculated by the use of the following relations:

$$\Delta v_{AB} = \sqrt{(v_1 - v_4)(v_2 - v_3)}$$

$$\delta_A = v_1 - \frac{(v_1 - v_4) - \Delta v_{AB}}{2}$$

where v_1, v_2, v_3 and v_4 are the frequencies of the peaks.

Suppose an AB system displays a pattern of four peaks at 300, 290, 289, 279 Hz, then the chemical shifts δA and δB can be calculated as follows:

$$\delta_A - \delta_B = \sqrt{(v_1 - v_4)(v_2 - v_3)}$$

$$= \sqrt{(300 - 279)(290 - 289)}$$

$$= \sqrt{21} = 4.6 \text{ Hz}$$

$$\delta_A = v_1 - \frac{(v_1 - v_4) - \Delta v_{AB}}{2}$$

$$= 300 - \frac{21 - 4.6}{2} = 300 - 8.2 = 291.8$$

$$\delta_B = 291.8 - 4.6 = 287.2 \text{ Hz}$$

A simple AB pattern is exhibited by the spectrum of 2-bromo-5-chlorothiophene (Fig. 4.17).

$$\Delta v_{AB} = 4.70 \pm 0.2 \text{ Hz}$$

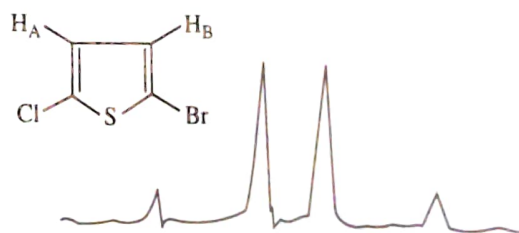$$J_{AB} = 3.9 \pm 0.2 \text{ Hz} \quad \Delta v/J = 1.205$$

Fig. 4.17   PMR spectrum of 2-bromo-5-chlorothiophene

4.9.3   Systems containing two interacting nuclei (A$_2$, AX and AB systems)

(i) A$_2$ system

A system containing two equivalent nuclei is designated as A$_2$ system. The resonance of an A$_2$ system is always a singlet despite any intraset coupling between the nuclei. A good example of an A$_2$ system is 1,1,2,2-tetrachloroethane.

In general, the protons of a methylene group in an aliphatic chain and bearing no protons on adjacent carbon atoms are equivalent and constitute an A$_2$ system.

(ii) AX system

Any molecule possessing two hydrogen atoms that are of widely different chemical shifts, and that couple together to give rise to a pair of doublets with all the four lines of equal intensity. Such a

system is called an AX system. For example, dichloroacetaldehyde exhibits two doublets of equal intensity in its PMR spectrum and represents an AX system (Fig. 4.15).

The spectrum indicates that the coupled system involves two protons of widely different chemical shifts (widely separated letters of the alphabet). By convention, the proton absorbing at a lower field is given the earlier letter of the alphabet.

In such a system, the chemical shift difference between the protons A and X is measured from the centers of doublets.

(iii) AB system

An AB system consists of two mutually coupled nuclei A and B, which are not coupled to any other protons and have the chemical shift difference $(\delta_A - \delta_B)$ comparable in magnitude to the coupling constant J_{AB}.

As the chemical shift difference between interacting nuclei (Δv) approaches in magnitude to the value of the coupling constant between them, the simple splitting rules already considered no longer apply. The pattern of splitting in the multiplet becomes distorted, extra lines appear in the spectrum and the bands are no longer symmetrical. Thus, it is not possible to deduce chemical shift and coupling constant values by inspection. They may, however, be obtained readily by using the following prescriptions.

(i) Numbering the bands serially from 1 to 4, in order of increasing shielding, the coupling constant is given by

$$J_{AB} = v_1 - v_2 = v_3 - v_4$$

(ii) The chemical shift is readily obtained as

$$\delta_A - \delta_B(\delta_{AB}) = \sqrt{(v_1 - v_4)(v_2 - v_3)}$$

If I_x = intensity of line x, then
(iii) The intensities are in the ratio

$$\frac{I_3}{I_4} = \frac{I_2}{I_1} = \frac{(v_1 - v_4)}{(v_2 - v_3)}$$

Nuclei exhibiting these characteristics are said to be strongly coupled and are designated by adjacent letters in the alphabet. Two such nuclei constitute an AB system.

A typical example of an AB system is furnished by the PMR spectrum of 3-bromo-2-t-butoxythiophene (Fig. 4.18). The parameters obtained for the thiophene ring protons in this compound are $\delta_{AB} = 0.17$ ppm (100 MHz) and $J = 6.0$ Hz.

4.9.4 Systems containing three interacting nuclei

(A_3, AX_2 or A_2X, AMX, ABX, ABC and AB_2 or A_2B systems)

(i) A_3 system

The resonance of an A_3 system is always a singlet. The common examples are methyl iodide and 1, 1, 1-trichloroethane. Methyl acetate would be said to contain two A_3 systems at different chemical shifts whereas p-xylene to consist of two A_3 systems at the same chemical shift.

In general, the resonance of an A_n system is always a singlet, despite any intraset coupling among n members within the set.
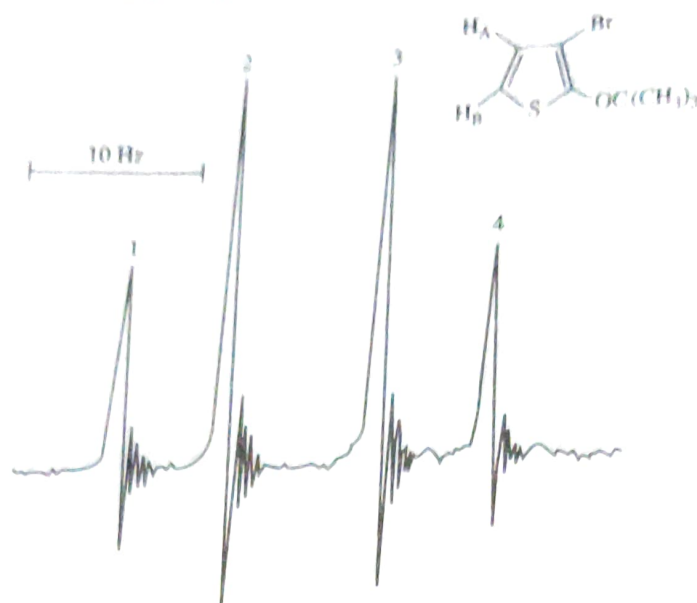
Fig. 4.18   The 100 MHz PMR spectrum of 3-bromo-2-t-butoxythiophene in a mixture of C_6D_6 and $CDCl_3$.

(ii) AX_2 or A_2X system

In this system, the two magnetically equivalent nuclei are coupled to the third nucleus which is far removed in its chemical shift as compared to the other two. The spectrum of 1,1,2-trichloroethane (Fig. 4.19) is an example of AX_2 system.
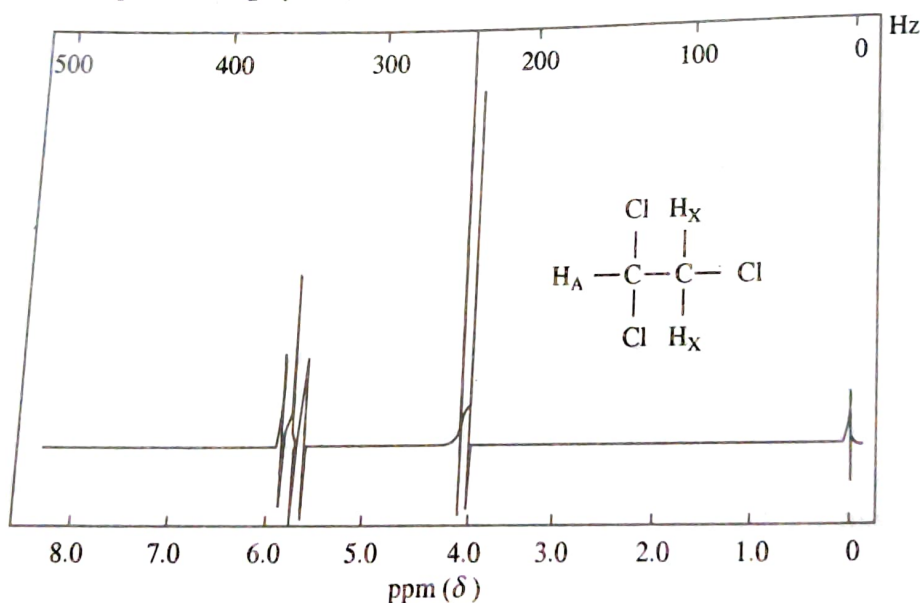

Fig. 4.19   PMR spectrum of 1,1,2-trichloroethane in CCl_4.

The higher field methylene group is a doublet because the two equivalent protons are influenced by the one-adjacent methine proton. The absorption due to the latter, however, appears as a 1 : 2 : 1 triplet since there are three different ways of arranging the spins of the protons of the methylene group. The protons of 1, 1, 2-trichloroethane can be described as an AX_2 spin system.

This notation means that there is one magnetically active nucleus at chemical shift A and two magnetically equivalent nuclei are at a very different chemical shift X. In addition, it also implies that each of the two possible interset coupling constants, J_{AX}, are exactly the same.

Another example of an AX_2 (or A_2X) spin system is 1,1,2,3,3-pentachloropropane.

The PMR spectrum (Fig. 4.20) exhibits a 1 : 1 doublet for the two X protons and a 1 : 2 : 1 triplet for the A proton. The interpretation of this compound is exactly analogous to that for the spectrum of 1,1,2-trichloroethane.
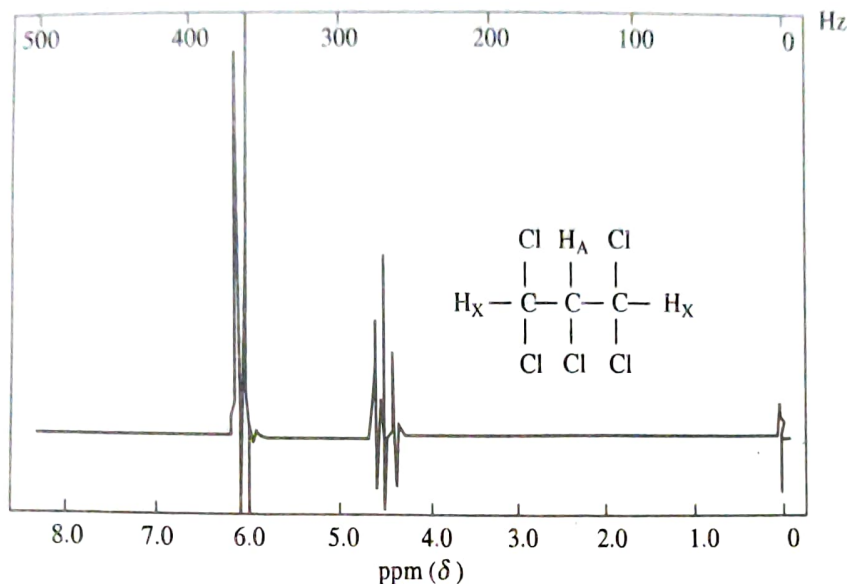

Fig. 4.20   PMR spectrum of 1,1,2,3,3,-pentachloropropane in CCl_4 solution.

(iii) AMX systems

In an AMX system, the three protons are non-equivalent with large $\delta v/J$ ratios ($\delta v > 6J$). They are equally coupled, thus, giving rise to three chemical shifts and three coupling constants, J_{AM}, J_{MX} and J_{AX}.

The spectrum of an AMX system exhibits 12 lines of almost equal intensity arranged in three pairs of doublets, from which the chemical shifts and coupling constants can easily be extracted by inspection. The vinyl protons of vinyl acetate, for example, constitute an AMX system (Fig. 4.21).
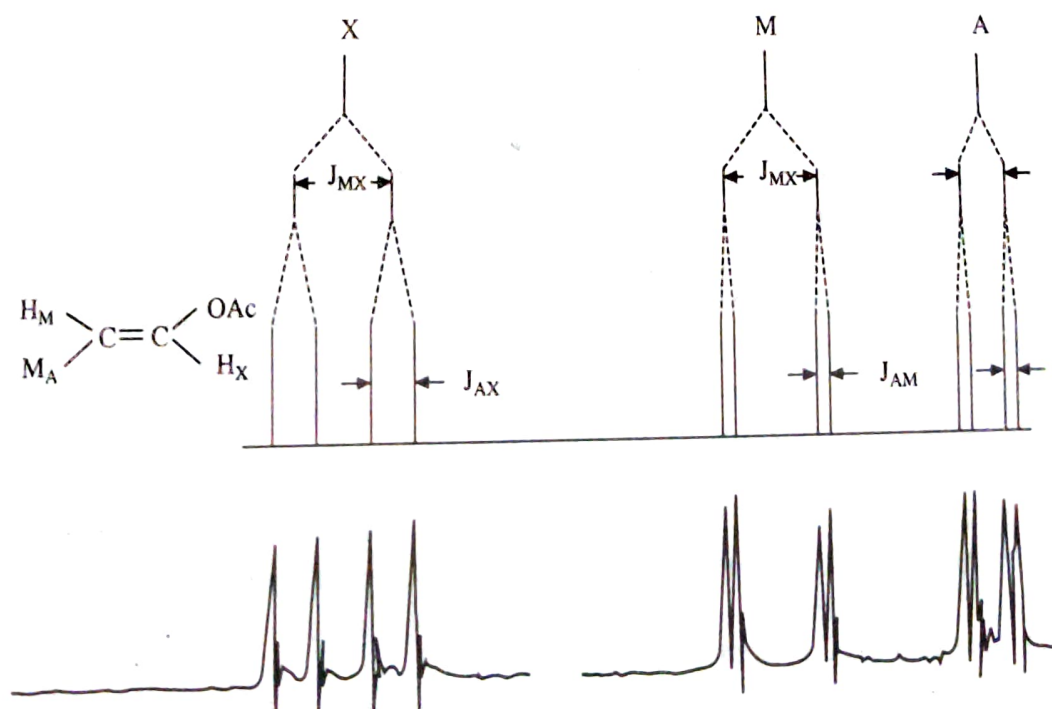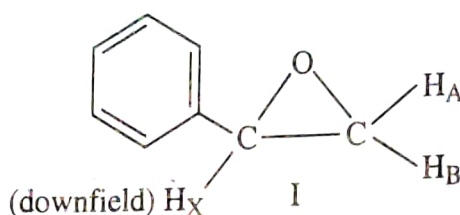

Fig. 4.21   The PMR spectrum of the olefinic protons in vinyl acetate at 100 MHz (An AMX system).

The interpretation of the splitting pattern is that the resonance of X proton is split into a doublet by coupling with the M proton and then further split into a pair of doublets by coupling with the A proton. Similarly, the resonance of M proton is split into a doublet by coupling with the X proton and then further split into a pair of doublets by coupling with the A proton. The appearance of the resonance of A proton is similarly accounted for in terms of successive splitting by the X and M protons. The three coupling constants can be measured from the spacings of the multiplets.

(iv) ABX system

In an ABX system, the chemical shift difference (Δv) and the coupling constant (J) between two of the three interacting nuclei are of comparable magnitude and both are coupled to the third nucleus well removed in chemical shift. In the epoxide I, for example, the two hydrogens H_A and H_B are non-

(downfield) H_X I

equivalent due to the restricted rotation of the epoxide system. The third hydrogen H_X is in a very different electronic environment and appears considerably downfield as compared to H_A or H_B. The system is thus an ABX system. Other examples of this type of system include 2-chloro-3-aminopyridine and 2,3-dichloropyridine.

2-Chloro-3-aminopyridine   2,3-Dichloropyridine
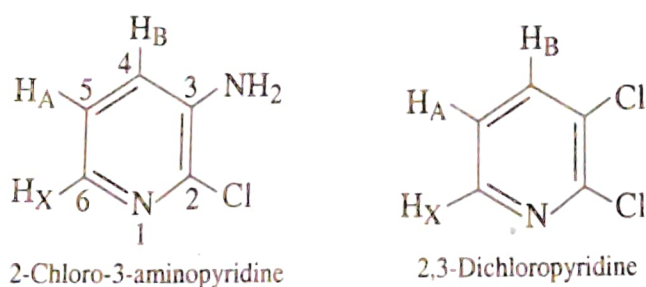
The spectrum for such a system often exhibits 12 lines. Fifteen are customarily listed, one of these being of zero intensity and two others are usually too weak to be observed, since they represent combination transitions to the simultaneous excitation of two nuclei.

The AB portion of the spectrum consists of eight lines, but in some cases an overlap of lines may occur reducing this number. The X portion of the spectrum, which is symmetrical about the origin of proton X, may consist of four to six lines.

(v) ABC system .

In an ABC system, the chemical shift differences among the three protons are not large relative to the corresponding coupling constants. The spectrum of such a system is complex with no element of symmetry and exhibits a total of fifteen lines. Acrylonitrile represents a typical ABC system (Fig. 4.22).

Common example of an ABC system are:

(i) Monosubstituted olefins such as styrene, ethyl acrylate and vinyl chloride.

(ii) Trisubstituted benzenes, such as 3-nitro-o-xylene (Fig. 4.23 a), 2, 4-dinitrochlorobenzene and 3-nitrosalicylic acid.
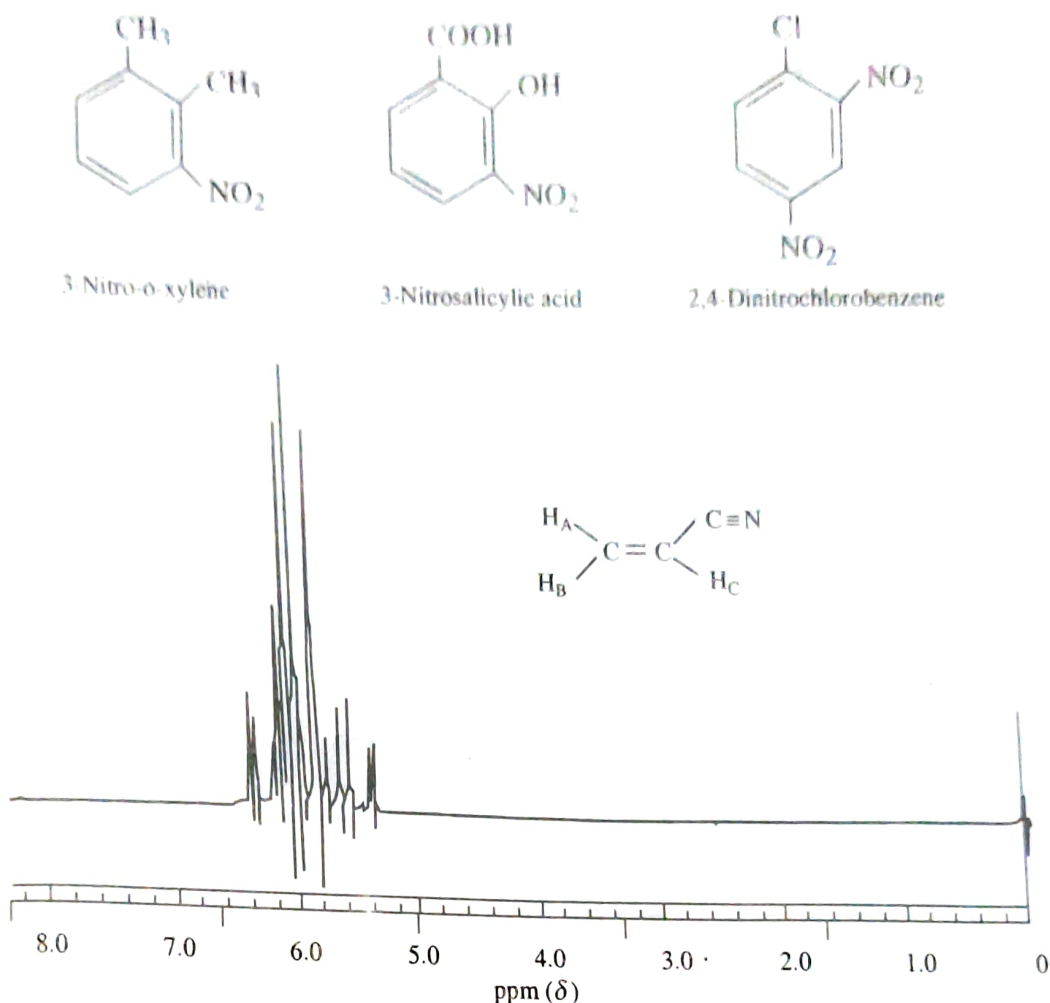
3-Nitro-o-xylene   3-Nitrosalicylic acid   2,4-Dinitrochlorobenzene

Fig. 4.22   PMR spectrum of acrylonitrile in CCl$_4$ solution.

(vi) AB$_2$ or A$_2$B system

In an AB$_2$ system, two magnetically equivalent nuclei are coupled to a third nucleus which is not far removed in its chemical shift. AB$_2$ spectra are observed for compounds that possess a two fold symmetry.

An AX$_2$ system, as already mentioned, consists of five lines (a doublet for X protons and a triplet for A proton); the chemical shift and coupling constant values can be measured directly from the spectrum. However, as the ratio of chemical shift to coupling constant becomes small, each line of the doublet splits into two and so also the centerline of the triplet splits into two, thus, producing a total of eight lines in the spectrum. In addition, the simultaneous change of spin states of all the three nuclei produces a weak signal which is detectable only if $\Delta v/J$ is extremely small. Thus, in an AB$_2$ system, nine lines are possible. The actual appearance of the spectrum depends upon the ratio of the chemical shift to the coupling constant. A typical AB$_2$ spectrum is given by 2,6-lutidine (Fig. 4.23 b).

Compounds such as 5-nitro-*m*-xylene, 1,2,4-trichlorobenzene, 2,5-dichloronitrobenzene, pyrogallol and 2,6-dichloropyridine are known to exhibit AB$_2$ or A$_2$B spectral pattern.

4.9.5   The symmetrical four spin systems

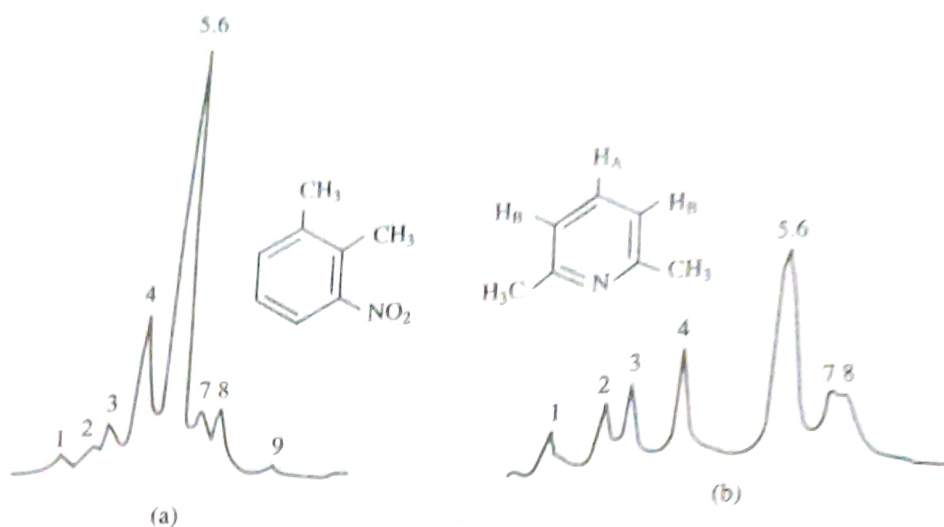(A$_2$X$_2$, A$_2$B$_2$, AA′XX′ and AA′BB′ systems)

Fig. 4.23   Aromatic protons in the PMR spectra of (a) 3-nitro-o-xylene (ABC) and (b) 2,6-Lutidine (AB_2).

(a) A_2X_2 system

An A_2X_2 system is simplest but least common. Difluoromethane, for example, contains two sets of chemically equivalent nuclei: (H, H) and (F, F). Each hydrogen is coupled equally to each fluorine and the system is consequently A_2X_2. Both the proton and fluorine spectra thus exhibit a triplet.

The PMR spectrum of phenylethyl acetate [Fig. 4.24(i)] provides a good example of an A_2X_2 system in which the two methylene triplets are well separated ($\Delta v/J > 10$).

(b) A_2B_2 system

The compounds containing the grouping $-CH_2-CH_2-$ bearing substituents of similar electronegativity at both the ends will present an A_2B_2 spectrum provided the rotation about the carbon-carbon single bond is sufficiently rapid to make the hydrogens chemically and magnetically equivalent.

The splitting patterns of a four-proton system $-CH_2-CH_2-$ for various ratios of $\Delta v/J$ are shown in the (Fig. 4.25). The two systems shown in the Fig. are then A_2B_2 ($\Delta v/J < 10$) and A_2X_2 ($\Delta v/J > 10$).

Some common examples of A_2B_2 system are represented by the PMR spectra of β-chlorophenetole (ii) 2-chloroethanol (iii) 2-phenoxyethanol (iv) (Fig. 4.25).

(c) AA′XX′ and AA′BB′ systems.

The spectrum of 1, 1-difluoroethylene (Fig. 4.26) is considerably more complex due to the fact that the two protons are chemically equivalent but magnetically non-equivalent.

F_1 is coupled to H_1 to a smaller extent than H_2 (trans couplings are always larger than cis couplings) and therefore the system is probably designated as AA′XX′.

Aromatic compounds—substituted benzene rings

The ring protons of an unsubstituted aromatic system, in general, resonate near δ 7.27. However, electron withdrawing ring substituents (e.g. nitro, cyano, carboxyl or carbonyl) will move the resonance of these protons downfield (1,3, 5-trinitrobenzene: δ 9.5) and electron donating ring substituents (e.g., methoxy or amino) will move the resonance of these protons upfield (p-ethoxyaniline: δ 6.7).

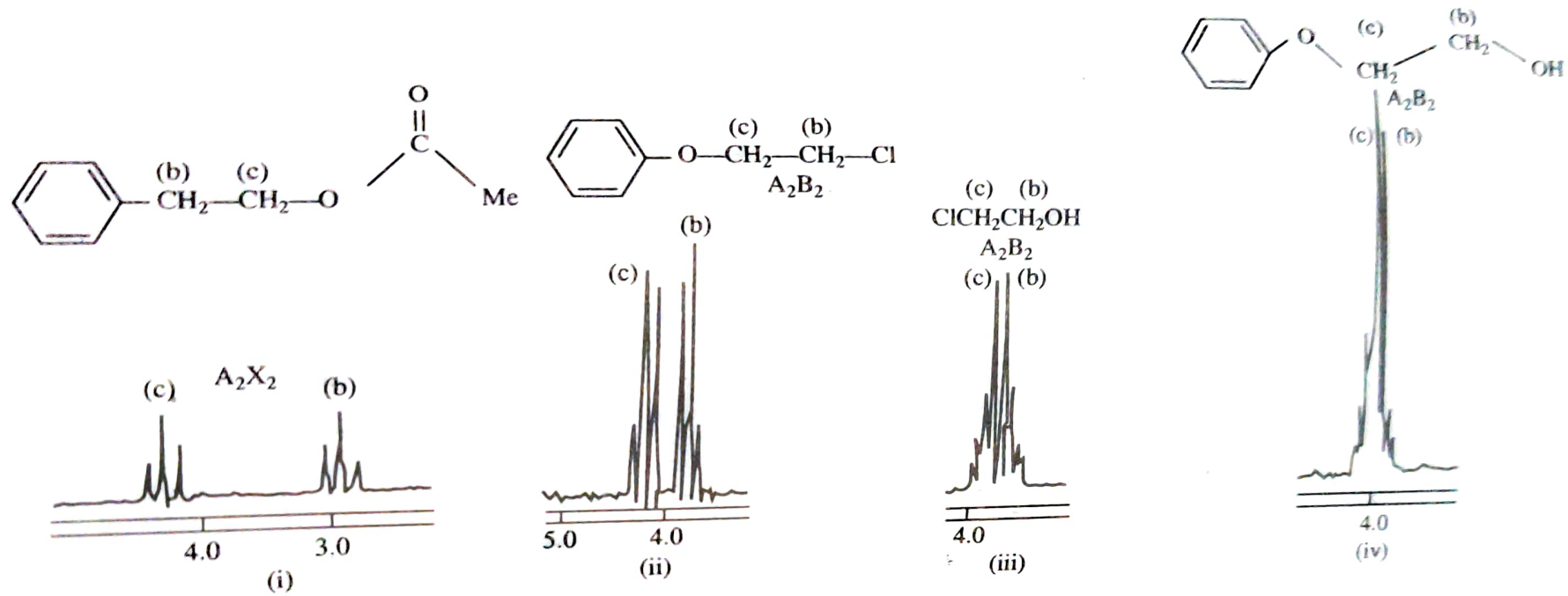A brief description of the resonance positions of various protons in substituted benzene rings is as follows.

Fig. 4.24 Progressive distortion as AA′ XX′ changes to AA′ BB′ in –CH₂–CH₂–system bearing different substituents at 60 MHz.
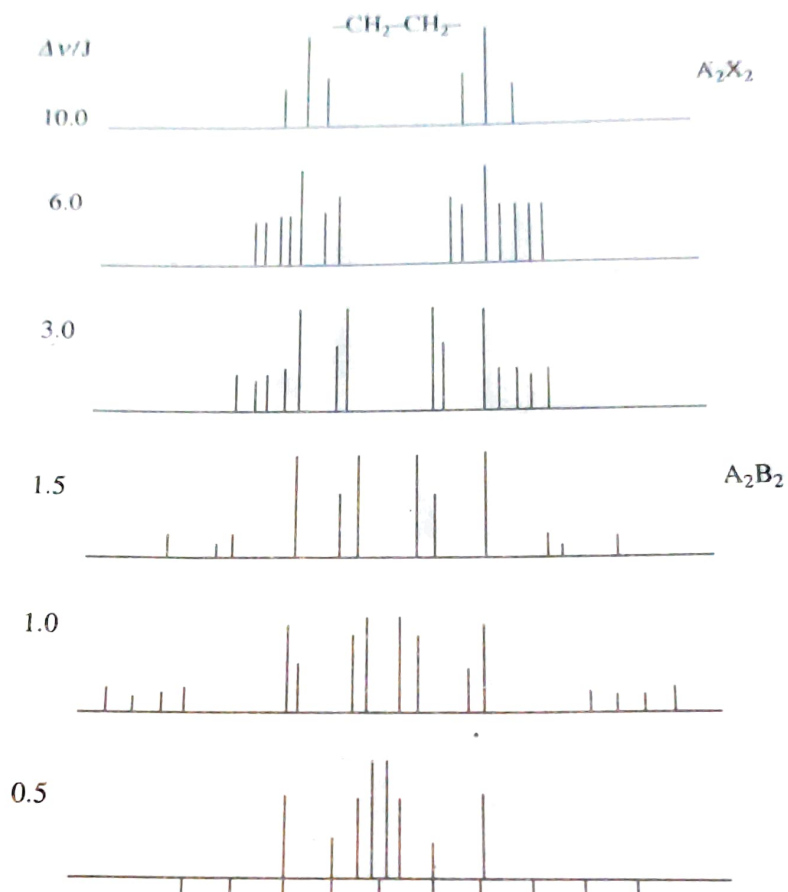
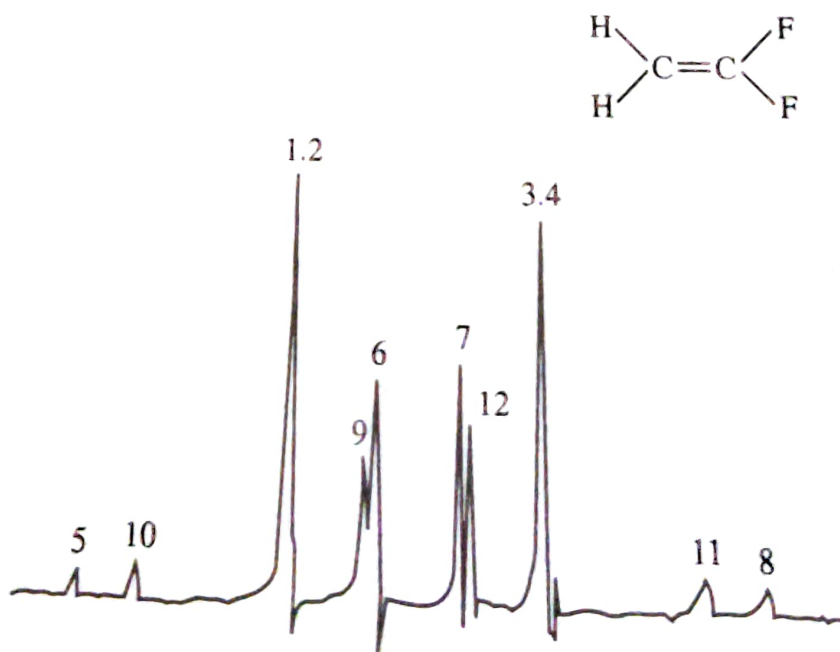Fig. 4.25 Splitting Patterns of –CH$_2$–CH$_2$–System for various ratios of $\Delta v/J$.

Fig. 4.26 The 60 MHz spectrum of 1, 1-difluoroethylene