

rather than anatomy by MRI (called functional diagnosis).

(v) NMR imaging has a potential application in the field of agriculture. The distribution of water, oil, the nature of binding of water, the germination process can all be investigated. The ^1H -MRI, in a specific variety of green chilli, for example, clearly demonstrates that there are at least two different types of water. Similarly, the differential distribution of water and oil in a specific variety of ground-nut seed has been investigated. The use of ^{13}C -NMR to study the germination process in a ground-nut seed has also been examined. The results indicate that the transformation of storage lipids is completed first in the radical followed by that in hypocotyle and finally in the plumule.

(vi) Magnetic resonance imaging has already been used in locating small tumors invisible to X-ray analysis, lesions, edemas and brain disorders.

Spectral Problems and Solutions

Q. 1. What property of certain atomic nuclei is involved in NMR phenomenon?
Sol. A nucleus having an odd atomic number or an odd mass number has a nuclear spin which can be observed by the NMR spectrometer. A large number of spin active nuclei such as ^1H , ^{13}C , ^{15}N , ^{19}F and ^{31}P , have permanent magnetic moments (nuclear spin = $1/2$) and can be studied by NMR spectroscopy.

Q.2. ^{13}C is NMR active while ^{12}C is not, Explain.
Sol. ^{12}C does not have a nuclear spin and cannot be used in an NMR experiment. In contrast, its isotope ^{13}C , whose natural abundance is only 1.1%, has a nuclear spin of $1/2$.

Q. 3. Halogen nuclei are practically non-magnetic where as ^{14}N and ^2H are magnetic for the purpose of high-resolution NMR spectroscopy. Explain

Sol. Although the halogen nuclei (Cl, Br and I) have large magnetic moments, the mechanism of dipole relaxation is so effective that these nuclei become practically non-magnetic for the purpose of high resolution NMR spectroscopy.

In the case of ^{14}N and ^2H , quadrupole relaxation is less effective so that their resonance lines can be observed more easily.

Q. 4. The observed chemical shift of a proton is 300 Hz from TMS and the operative frequency of the spectrometer is 100 MHz. Calculate the chemical shift in terms of δ (ppm).

Sol. Chemical shift (δ) = $300/100 = 3.0$ ppm

Q. 5. How many Hertz does 1 ppm correspond to for an PMR spectrometer operating at a radiofrequency of (a) 60 MHz (b) 100 MHz?

Sol. (a) 60 Hz (b) 100 Hz

Q. 6. How will you determine the relative number of nuclei in the higher and lower energy states?

Sol. The relative population of nuclei in the higher and lower energy states can be calculated at the thermal equilibrium from the Boltzman distribution law, as per the equation:

$$\frac{N_{\alpha}}{N_{\beta}} = e^{\Delta E/kT} \quad \text{or} \quad \exp(\Delta E/kT)$$

$$\approx 1 + \frac{\Delta E}{kT} \approx 1 + \frac{2\mu H_0}{kT}$$

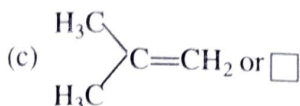
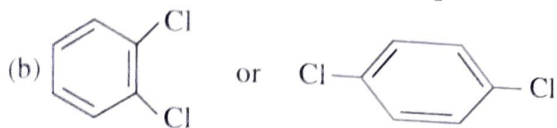
where N_{α} and N_{β} are the number of nuclei in the α (lower energy) and β (higher energy) states respectively

Q. 7. Estimate, giving appropriate reasoning, the δ value in the structural unit $-\text{O}-\text{CH}_2-\text{O}-$.

Sol. The chemical shift for the methylene protons in the grouping $-\text{O}-\text{CH}_2-\text{O}-$ is estimated to be 4.2–4.5 δ . The downfield shift is due to deshielding by the two adjacent electronegative oxygen atoms. A proton H_b is coupled to four equivalent neighbouring protons H_a . What will be the multiplicity H_b will appear as a quintet with the relative intensities of lines in the ratio 1:4:6:4:1.

Q. 8. Which member of each of the following pairs of the structural isomers would be expected to exhibit a single peak in its PMR spectrum?

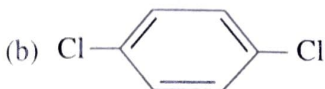
(a) CH_3-CCl_3 or $\text{ClCH}_2-\text{CHCl}_2$



(d) $\text{ClCH}_2\text{CH}_2\text{Cl}$ or $\text{CH}_2-\text{CHCl}_2$

(e) $\text{H}_2\text{C}=\text{C}=\text{CH}_2$ or $\text{CH}_3-\text{C}\equiv\text{CH}$

Sol. (a) CH_3-CCl_3



(c)

(d) $\text{ClCH}_2\text{CH}_2\text{Cl}$

(e) $\text{H}_2\text{C}=\text{C}=\text{CH}_2$

Q. 10. Which of the following compounds would be expected to show only a single peak in its PMR spectrum?

- (i) Acetone
- (ii) Dimethyl ether
- (iii) Methyl acetate
- (iv) Methyl iodide
- (v) Dibromomethane
- (vi) Chlorobromomethane
- (vii) 1,2-Dibromoethane
- (viii) 1-chloro-2-bromoethane

Sol. The following compounds will exhibit a singlet in their PMR spectra.

(i) Acetone (ii) Dimethyl ether (iv) Methyl iodide (v) Dibromomethane (vi) Chlorobromomethane (vii) 1,2-Dibromoethane.

Q. 11. Explain shielding and deshielding of a nucleus.

Sol. When the effective magnetic field experienced by the nucleus is less than that of the applied field ($H_{\text{eff}} < H_0$), the nucleus is said to be shielded. However, the electron withdrawal from a proton by a neighbouring electronegative atom causes deshielding of the proton.

Q. 12. Methyl, methylene, methine and quaternary carbons (and their attached hydrogens) come to resonance at successively lower field. Explain.

Sol. Since hydrogen is more electropositive than carbon, every replacement of hydrogen by an alkyl group causes a downfield shift in the resonance of that carbon and any remaining hydrogens on it. Thus, methylene, methine and quaternary carbons (and their attached hydrogens) come into resonance at successively lower field as shown in the following table:

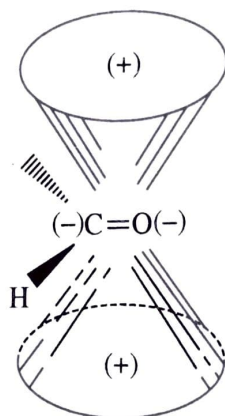
	CH_4	MeCH_3	Me_2CH_2	Me_3CH	Me_4C
δ_{C}	-2.3	8.4	15.9	25.0	27.7
δ_{H}	0.23	0.86	1.33	1.68	-

- Q. 13.** Acetylenic protons are more shielded than ethylenic protons, although the former are attached to a more electronegative sp -carbon. Explain.

Sol. An ethylene molecule in an external applied field is so oriented that the plane of its double bond lies at right angle to the applied field and consequently the induced magnetic field caused by the circulation of π -electrons is diamagnetic around the carbon atoms and paramagnetic in the region of the protons.

An acetylene molecule, on the other hand, when placed in an external magnetic field is so oriented that the plane of its triple bond lies parallel to the direction of the applied field, i.e. the molecule assumes a vertical orientation rather than the horizontal orientation and the induced magnetic field caused by the circulation of the π -electrons of the triple bond opposes the applied field in the region of the protons. Thus, the protons feel smaller field strength (shielding) and hence resonate at higher value of the applied field (lower δ value)

- Q. 14.** Explain why the aldehydic proton appears much downfield in the PMR spectrum?
Sol. The aldehydic proton is strongly deshielded (occur in the range $9-10\delta$, ppm.) because it lies in the deshielding zone of the carbonyl group.



- Q. 15.** Explain why the aromatic protons are more deshielded than the ethylenic protons although both the types of protons are attached to sp^2 hybridized carbons?

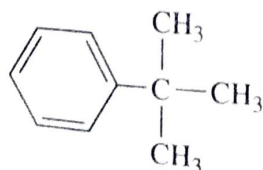
Sol. In the case of benzene ring, loops of π -electrons are delocalised cylindrically over the aromatic ring. These loops of electrons are caused to circulate in presence of the applied field producing ring currents. This induced current is diamagnetic at the centre of the ring and is paramagnetic outside the ring. Thus, the aromatic protons, around the periphery of the ring, experience a magnetic field much greater in magnitude than the applied field and consequently resonate at lower values of the applied field than the ethylenic protons.

- Q. 16.** Methyl propionate has singlet, triplet and a quartet in its PMR spectrum similar to ethyl acetate.

Sol. The singlet in the spectrum of ethyl acetate is the middle band whereas it appears farthest downfield (higher δ value) in the spectrum of methyl propionate.

- Q. 17.** A compound having the molecular formula $C_{10}H_{14}$ gave the following PMR data: (i) 0.88δ (9H, s) and 7.28δ (5H, s, aromatic protons). Assign the structural formula to the compound?

Sol. The appearance of a nine proton singlet at 0.88δ , ppm indicates a tertiary butyl group and a five proton singlet at 7.28δ confirms a phenyl ring. Since the molecular formula of the compound is $C_{10}H_{14}$, so the structural formula of the compound may be



Q. 18. How will you distinguish among primary, secondary and tertiary alcohols on the basis of PMR spectroscopy?

Sol. The three types of alcohols can be distinguished by running the PMR spectra of pure alcohols in DMSO-d₆, when the proton of the OH group appears as a triplet, doublet and a singlet respectively in the primary, secondary and tertiary alcohols?

Q. 19. Broad signals are often observed in the PMR spectra associated with OH and NH resonances. Explain.

Sol. The relaxation times of these types of protons are often shortened by chemical exchange processes and other nuclear phenomenon.

Q. 20. Why the signals due to fluorine and deuterium nuclei do not appear in the PMR spectrum of compounds containing fluorine and deuterium atoms? Explain.

Sol. Since the signals from ¹⁹F absorptions occur at considerably different magnetic field strengths than those of the protons, hence they do not appear in the PMR spectra. However, they do cause splitting of the proton signals due to spin-spin coupling between protons and ¹⁹F nuclei.

The nucleus of deuterium has a much smaller magnetic moment than that of a proton and consequently the signals from deuterium do not appear in the PMR spectra. The spin-spin couplings between deuterium and protons are small but the presence of deuterium atom can cause splitting of the proton signal. For example, the signal from two protons of 1,2-dichloro-1,1-difluoroethane is split into a triplet by fluorine atoms on the adjacent carbon.

Q. 21. How is PMR used to establish on which carbon, monochlorination of methyl ethyl ether occurs? The three possible products with their spectra are described as follows:

Sol. (a) $\overset{1}{\text{C}}\text{H}_3\overset{4}{\text{C}}\text{H}_2-\text{O}-\overset{5}{\text{C}}\text{H}_2\text{Cl}$ (a triplet, a more downfield quartet and a most downfield singlet);

(b) $\overset{4}{\text{C}}\text{H}_3\overset{1}{\text{C}}\text{HCl}-\text{O}-\overset{5}{\text{C}}\text{H}_3$ (a doublet, a downfield quartet and a singlet between them);

(c) $\text{Cl}\overset{1}{\text{C}}\text{H}_2-\overset{2}{\text{C}}\text{H}_2-\text{O}-\overset{5}{\text{C}}\text{H}_3$ (a singlet and two triplets; the downfield order is $t_1 < s < t_2$).

Q. 22. Write the structural formulae for the compounds with the following molecular formulae that show only one signal in their PMR spectra;

(a) C₅H₁₂; (b) C₃H₆ (c) C₂H₆O (d) C₃H₄ (e) C₂H₄Br₂ (f) C₄H₆ (g) C₈H₁₈

Sol. Since only one signal is observed all the protons in each molecule are equivalent.

(a) The twelve protons must be in four equivalent methyls; the structure is (CH₃)₄C.

(b) There must be three equivalent methylene groups. Hence the only possibility is (Δ).

(c) Two equivalent methyl groups are present in methyl ether, (H₃C-O-CH₃).

(d) Two equivalent methylene groups with a carbon atom bearing no hydrogen are present in H₂C=C=CH₂.

(e) Two equivalent methylene groups are present in 1,2-dibromoethane, (BrCH₂CH₂Br).

(f) Two equivalent methyl groups with two carbon atoms bearing no hydrogens, are present in H₃C-C≡C-CH₃.

(g) Four equivalent methyl groups with two other carbons are present in (CH₃)₃C-C(CH₃)₃.

Q. 23. How many different kinds of hydrogens are present in the following compounds?

(a) CH₃CH₃ (b) CH₃CH₂CH₃ (c) (CH₃)₂CHCH₂CH₃ (d) H₂C=CH₂ (e) CH₃-CH=CH₂ (f) C₆H₅NO₂

(g) C₆H₅CH₃.

Sol. (a) One (all equivalent)

(b) Two ($\overset{a}{\text{C}}\text{H}_3-\overset{b}{\text{C}}\text{H}_2-\overset{a}{\text{C}}\text{H}_3$)

(c) Four ($(\overset{a}{\text{C}}\text{H}_3)_2\overset{b}{\text{C}}\overset{c}{\text{H}}\overset{d}{\text{C}}\text{H}_2\overset{a}{\text{C}}\text{H}_3$)

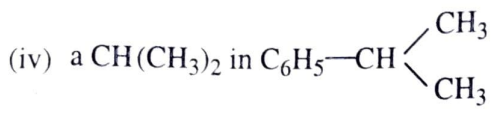
(d) One (all equivalent)

(e) Four $\begin{matrix} \overset{a}{\text{H}_3\text{C}} \\ \overset{b}{\text{H}} \end{matrix} \text{C} = \text{C} \begin{matrix} \overset{c}{\text{H}} \\ \overset{d}{\text{H}} \end{matrix}$

(f) Three (2 ortho, 2 meta and one para)

Q. 24. (g) Two (ring protons are little affected by alkyl group and are equivalent) Suggest a structure of the compound (molecular formula C_9H_{12}) showing signals at 7.1, 2.2, 1.5 and 0.9 δ ppm.
 Sol. The δ value at 7.1 shows a benzene ring and the alkyl chain comprising of the remaining three carbon atoms may be attached to the benzene ring as follows.

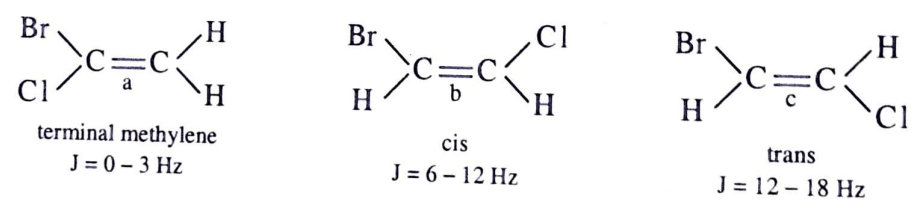
- (i) Three methyl groups in trimethylbenzene $(CH_3)_3 C_6H_3$
- (ii) $a-CH_3$ and $a-CH_2CH_3$ in $\overset{a}{H}_3CC_6\overset{b}{H}_4\overset{c}{CH}_2\overset{d}{CH}_3$
- (iii) a $CH_2-CH_2-CH_3$ group in $C_6\overset{d}{H}_5\overset{c}{CH}_2\overset{b}{CH}_2\overset{a}{CH}_3$



The compounds (i) and (iv) are not possible because they will exhibit 2 and 3 signals respectively. Compound (ii) displays four signals, H^a and H^c appearing in the range 3–2.2 δ ppm rather than a single observed signal and hence is ruled out. Hence the structure (iii) can give the four observed signals.

Q. 25. How will you distinguish between *p*-xylene and mesitylene on the basis of PMR spectroscopy?
 Sol. Both the compounds exhibit two singlets; one for the ring protons and the other for methyl protons. The relative intensities of the peaks are, however, different. In *p*-xylene, the ratio of methyl protons to ring protons is 6 : 4 or 3 : 2, while for mesitylene, it is 9 : 3 or 3 : 1.

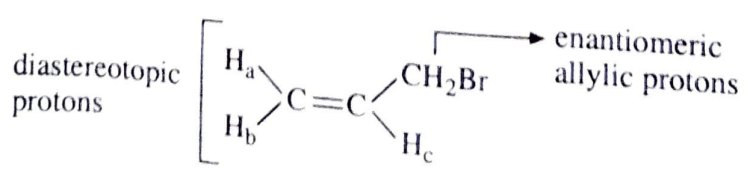
Q. 26. A compound (molecular formula C_2H_2BrCl) exhibits two doublets ($J = 16\text{Hz}$) in its PMR spectrum. Suggest a structure.
 Sol. The three possible structures pertaining to the formula C_2H_2BrCl are as follows:
 The observed value of the coupling constant ($J = 16\text{ Hz}$) agrees with the trans structure (c).



Q. 27. A compound (molecular formula $C_4H_{10}O$) gave PMR spectrum consisting of two groups of lines (multiplets) with relative intensities in the ratio of 3:2. The PMR spectrum of another compound having the same formula exhibited two lines with relative area of 9:1. Identify these substances.
 Sol. Diethylether and *t*-butyl alcohol.

Q. 28. How many different types of protons are present in allyl bromide molecule?
 Sol. Four different types of protons are present in allyl bromide as described below:

- (i) Two allylic protons are enantiomeric and thus identical.
- (ii) Two diastereotopic protons, labelled H_a and H_b , give diastereomers on imaginary replacement by a group and are therefore, different
- (iii) The remaining H_c proton.



Q. 29. The PMR spectrum of styrene oxide exhibits similarities in the chemical environment of the o, m

and *p*-protons of the aromatic ring resulting in the singlet around 7.0 δ ppm. Suggest an appropriate method to make a distinction among these protons. The spectrum of styrene oxide is given below. Distinction may be possible by using shift reagents.

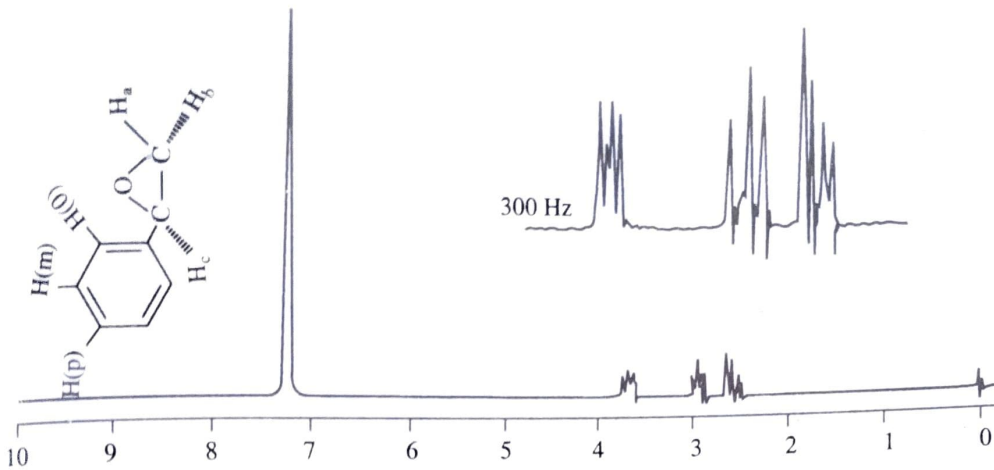
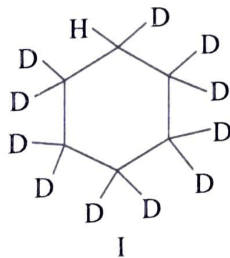


Fig. 4.108 PMR spectrum of styrene oxide.

In the presence of Pr (dpm)₃, the ortho-protons give a separate signal (3.27 δ ppm) while meta and para protons give a separate signal at 6.19 δ ppm. The three separate signals for the protons on the epoxy ring are shifted upfield past TMS.

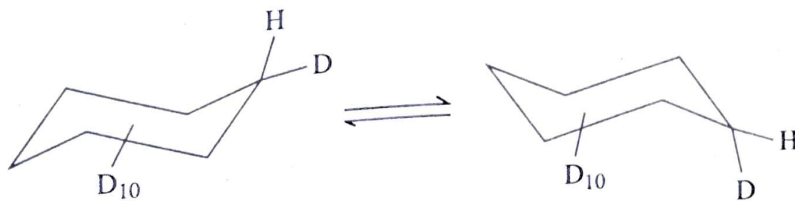
Q. 30.

What kind of PMR spectrum would you expect to obtain from undecadeuteriocyclohexane (i) at -100°C and (ii) at the room temperature?



Sol.

At -100°C , undecadeuteriocyclohexane (I) shows two signals of equal intensity. These signals correspond to the axial and equatorial hydrogen atoms of the following two chair conformations.



Interconversions between these conformations occur at this low temperature, but these happen slowly enough for the PMR spectrometer to detect the individual conformations. However, at the room temperature it gives one signal because interconversions between various chair forms occurs very rapidly.

Q. 31.

The PMR spectrum of dimethyl formamide shows two signals at 2.84 and 3.0 δ for the methyl protons at the room temperature but a single sharp line appears at higher temperature (165°).

Sol.

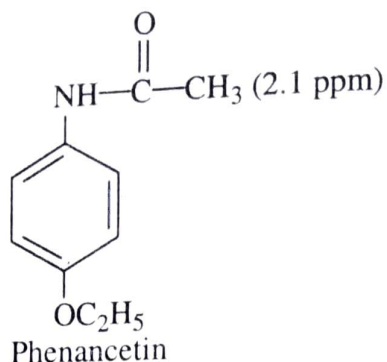
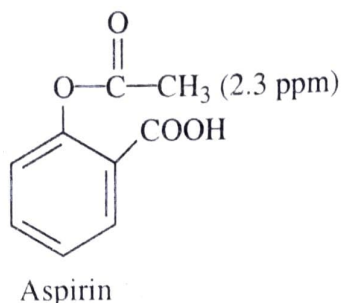
At the room temperature, the conjugation between the lone pair of electrons on the nitrogen atom and the carbonyl group increases sufficiently the double bond character of the C-N bond to restrict rotation at the room temperature and the spectrometer senses two different methyl groups (cis and trans) w.r.t lone hydrogen. At the elevated temperature, however, the rotation around the C-N bond is so rapid that each methyl group experiences the same time-averaged environment.

Q. 32.

How will you determine the relative amount of aspirin and phenacetin as a molar ratio in a mixture with the help of PMR spectroscopy?

Sol.

The relative amounts of aspirin and phenacetin as a molar ratio in a mixture can easily be determined by measuring the integration of two sharp singlets at 2.1δ , ppm and 2.3δ ppm pertaining to the acetyl methyl groups in phenacetin and aspirin respectively.

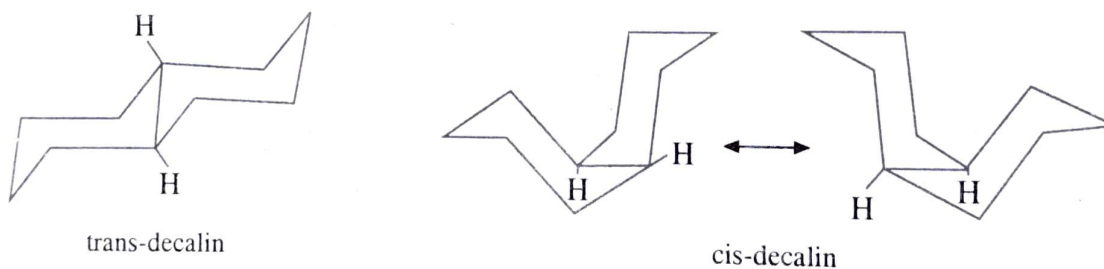


Q. 33.

cis-Decalin gives a single resonance line whereas trans-decalin displays a broad band in their PMR spectra. Explain.

Sol.

The spectra are different in appearance in the region associated with absorption due to ring protons. cis-Decalin displays a sharp resonance, whereas the trans isomer exhibits a broad band consisting of overlapping lines.



This difference arises because the trans isomer has a relatively rigid frame-work, all the hydrogen atoms being either axial or equatorial to the rings. The broad band in the trans-decalin is, thus, attributed to the presence of these two types of protons which are responsible for resonance lines at slightly different positions. cis-Decalin, on the other hand, is a more flexible system, one set of each axial hydrogen becomes equatorial and vice-versa. If this "flipping over" is sufficiently rapid, any particular proton is at any moment neither axial nor equatorial and a single narrow resonance line results.

Q. 34.

How will you distinguish between inter and intra molecular hydrogen bonding on the basis of PMR spectroscopy?

Sol.

As the hydrogen bonding involves electron cloud transfer from hydrogen atom to a neighbouring electronegative atom, the hydrogen experiences a net deshielding effect; the amount of deshielding is proportional to the strength of the hydrogen bond. The amount of hydrogen bonding is a function of concentration and temperature. The more concentrated the solution, the more molecules can come into contact with each other and form hydrogen bonding and consequently the protons will resonate at higher value of δ . However, in dilute solution (practically no hydrogen bonding), the protons will resonate upfield (lower value of δ). In other words, the intermolecular hydrogen bonding is concentration dependent.

Intramolecular hydrogen bonding, on the other hand, remains unchanged on dilution and consequently the PMR spectra pertaining to such systems usually remain unaltered by varying the concentration or temperature.

How will you distinguish between equatorial and axial protons of cyclohexane rings?

The equatorial protons in cyclohexane rings come to resonance at about 0.5 δ higher than the axial protons. This is attributed to anisotropic deshielding by the σ -electrons in the $\beta\gamma$ bonds as shown in the Fig. 4.109.

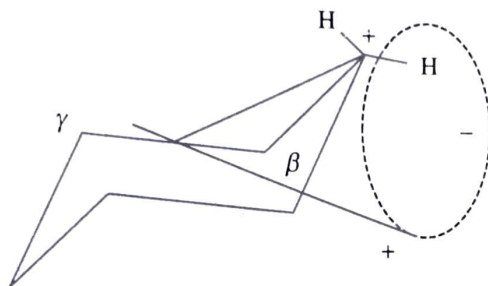
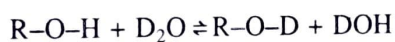


Fig. 4.109 Anisotropic shielding and deshielding in cyclohexane ring.

Q. 36. How will you verify that a particular signal arises from the proton of the following groups: $-\text{OH}$, $-\text{NH}$ or SH ?

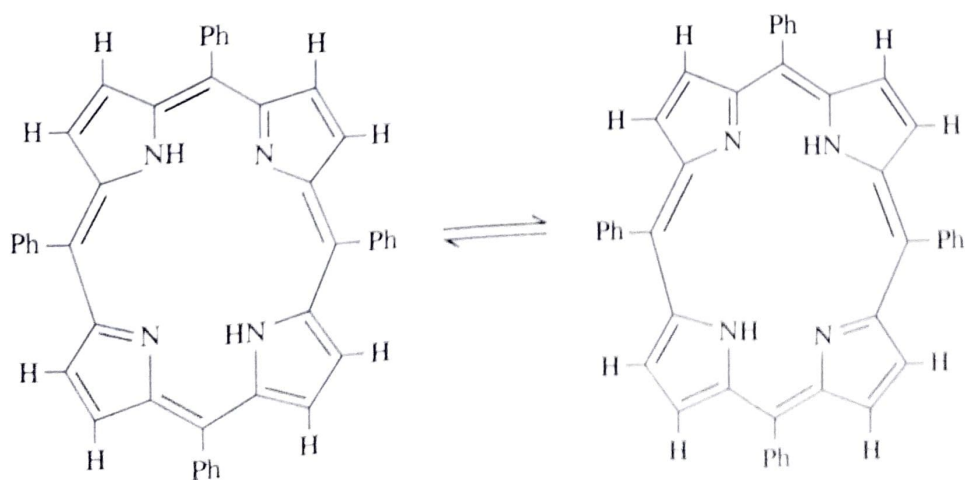
Sol. Add excess D_2O , shake the tube and rerun the spectrum. The protons in these groups are replaced by deuterium.



Since deuterium does not resonate under conditions used for ^1H -NMR, the original peak for $\text{O}-\text{H}$ proton disappears in the spectrum rerun in D_2O and a new signal for DOH appears.

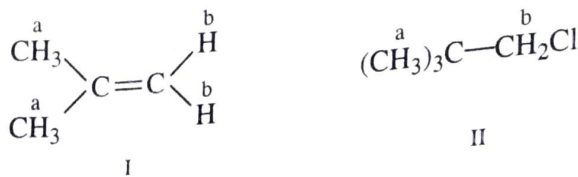
Q. 37. meso-Tetraphenylporphyrin (TPP) shows only one signal for the β -hydrogens at the room temperature but on cooling to -60° , the signal is split into a doublet ($J = 17 \text{ Hz}$). Explain.

Sol. The equilibrium structures shown in the Fig. illustrate that in meso-tetraphenylporphyrin, there are two types of β -hydrogens attached to two different types of five-membered heterocyclic rings. However, at the room temperature, there is a fast exchange (time averaged situation) which is slowed down by cooling to afford a doublet for the β -hydrogens. Proton exchange equilibrium in meso-tetraphenylporphyrin is illustrated as follows:



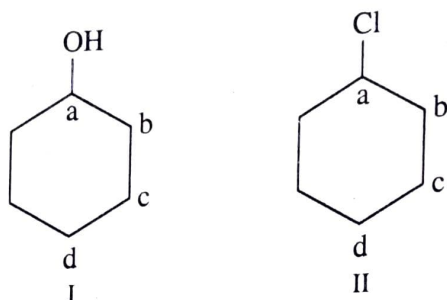
Proton exchange equilibrium in meso-tetraphenylporphyrin

Q. 38. Why is splitting observed in 2-methylpropene (I) but not in neopentyl chloride (II). Explain?

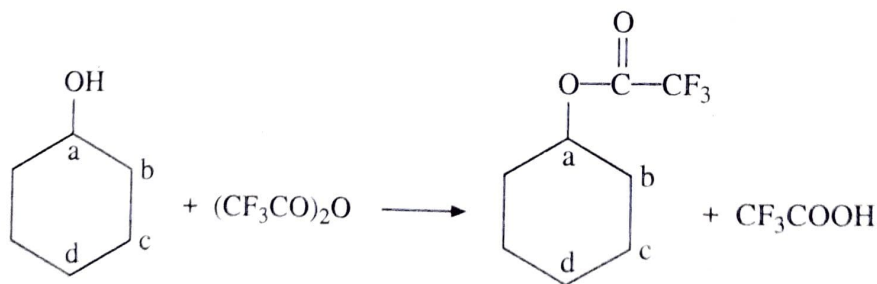


Sol. Although H^a and H^b in I are not on adjacent carbon atoms, they are close enough to couple because of shorter C=C bond. In II, H^a and H^b , on nonadjacent carbons, are too far away to couple, the carbon atoms being joined by longer single bonds.

Q. 39. How would you distinguish cyclohexanol from chlorocyclohexane on the basis of PMR spectroscopy.



Sol. The chemical shift of proton 'a' would be similar in both I and II. Secondly, the $-OH$ proton itself, is obscured in cyclohexanol by the rest alkyl signals. Integration of the alkyl multiplet before and after deuteration will not necessarily be very reliable, since there may be a small amount of some other alkyl impurity under the multiplet. Furthermore the multiplet is broad, and therefore, any integral drift will make the measurement less accurate than usual, and looking for one proton in a multiplet of ten or eleven, will give a relative small change in integral intensity (trace of water in $CDCl_3$ or residual water in the compound will also absorb in this region) compared with the inherent accuracy of integration by continuous-wave spectrometers. However, the two compounds may be distinguished by carrying out trifluoroacetylation of cyclohexanol by shaking it for a few seconds with a few drops of trifluoroacetic anhydride. The following reaction occurs:



The resulted spectrum is clearly very different from the alcohol, as the trifluoroacetic ester function is far more deshielding with respect to proton 'a' than is the $-OH$ group—well over 1 ppm downfield shift has occurred. This clearly distinguishes the alcohol from the analogous chloro-compound which would of course give no reaction.

Q. 40. Why is coupling between bonded ^{13}C 's not a factor in ^{13}C -NMR spectroscopy?

Sol. ^{13}C -Spectra are generally much simpler than the corresponding 1H spectra because of the very low natural abundance of ^{13}C . It is improbable that a particular ^{13}C -nucleus in a molecule will have a second ^{13}C -nucleus as an immediate neighbour. Therefore, splitting of a ^{13}C -resonance by coupling with a neighbouring ^{13}C -nucleus is unlikely.

Q.41. A compound with the molecular formula C_3H_7Cl exhibits in its PMR spectrum the following signals:

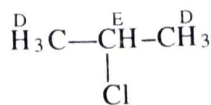
- (i) a triplet A at δ 0.9 ppm.
- (ii) another triplet B, more downfield and less intense (2/3 the intensity) than A.
- (iii) a complex multiplet 'C' in between the two triplets.

Is this compound *n*-propylchloride or iso-propylchloride.

The possible structures are;



I



II

In the compound I, H_A and H_B protons are split into individual triplets by the two H_C protons. The intensity ratio of B:A is 2:3 and H_B is more downfield. H_C -protons are split by H_A and H_B protons to give complex multiplet.

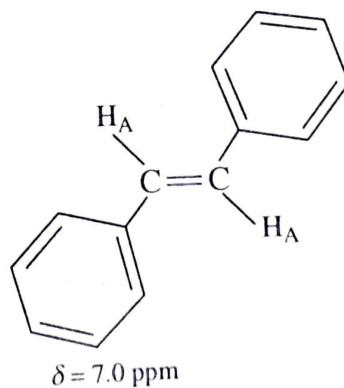
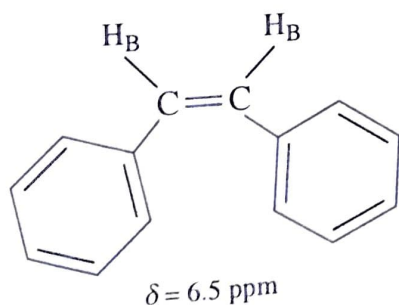
In the compound II, six H_D protons of the two methyl groups are split into an upfield doublet and H_E is split into a more downfield septet.

Hence the compound is $CH_3CH_2CH_2Cl$.

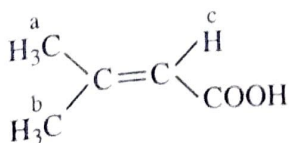
Q. 42. The PMR spectrum of a compound with molecular formula $C_3H_5ClF_2$ displays two non-coupled triplets. The triplet A is more intense (1.5 times) than the more downfield triplet B. Suggest a suitable structure.

Sol. Since A is 1.5 times more intense than B and the molecular formula contains five hydrogen atoms, A indicates a methyl triplet and B a methylene triplet. The formation of triplets must be due to the coupling of methyl and methylene protons independently with two fluorine atoms. B is more downfield than A indicates a $-CH_2Cl$ group. Hence the structure of the compound is $ClCH_2-CF_2-CH_3$.

Q. 43. How will you distinguish between *cis* and *trans*-stilbenes on the basis of PMR spectroscopy? *cis* and *trans*-Stilbenes can be distinguished from their respective chemical shift values.



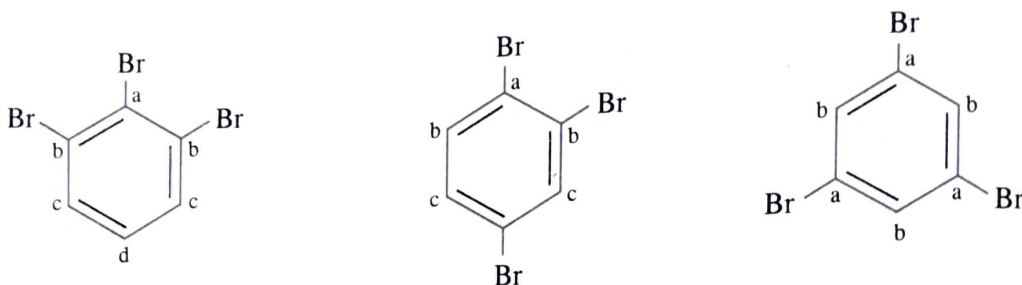
In *trans*-stilbene, a planar structure, each of the two olefinic protons (H_A) is deshielded by both the aromatic rings while in the *cis*-stilbene each hydrogen (H_B) is deshielded by only one adjacent aromatic ring. H_A 's, therefore, appear at a low field than H_B 's (7.0 δ and 6.50 δ ppm respectively). How will you determine the stereochemical relations in molecules on the basis of NOE effect? The technique of Nuclear Overhauser Effect is very useful to determine the stereochemical relationships in molecules as illustrated by the following example:



Q.44.
Sol.

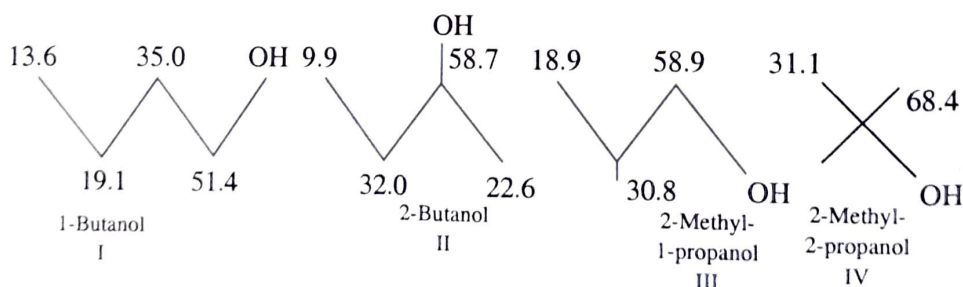
The irradiation of cis-methyl group (a) shows a 17% increase in the integral intensity of H (c). Irradiation of the more remote trans methyl group (b) causes no change in the integral intensity of H (c).

- Q. 45.** Peak area measurements (integration) are not usually obtained in routine ^{13}C -spectra. The loss of correlation between the integrated peak area and the number of carbon nuclei comprising the peak is mainly due to the differential saturation effects from variable spin-lattice relaxation times and variable Nuclear Overhauser Enhancement.
- Q. 46.** The proton-decoupled ^{13}C -NMR spectrum of a tribromobenzene ($\text{C}_6\text{H}_3\text{Br}_3$) consists of two signals only. Which tribromobenzene is it?
- Sol.* There are three possible tribromobenzenes:



The presence of two signals indicates that only two different types of carbon atoms are present in the compound. Only 1,3,5-tribromobenzene has a degree of symmetry such that it would give only two signals and, therefore, it is the correct structure.

- Q. 47.** 1,2,3-Tribromobenzene would give four ^{13}C -signals and 1,2,4-tribromobenzene would give six. Why quaternary carbons exhibit small Nuclear Overhauser enhancements. Explain?
- Sol.* Since the magnitude of the observed NOE will depend upon its distance from the nearest hydrogen, the quaternary carbons, being deeply buried inside the complex structures, will exhibit less NOE than those on the outside of the molecule.
- Q. 48.** How will you distinguish among the four isomeric alcohols represented by the molecular formula $\text{C}_4\text{H}_{10}\text{O}$.
- Sol.* The four isomeric butanols with their respective ^{13}C -chemical shift values are given below:



I-Butanol (I) and 2-butanol (II) will exhibit four signals each. They can easily be distinguished from their respective ^{13}C -chemical shift values.

t-Butyl alcohol (IV) (2-methyl-2-propanol), due to the equivalence of three methyl groups, will exhibit two signals whereas 2-methyl-1-propanol (III) will give rise to three signals in its ^{13}C -NMR spectrum.

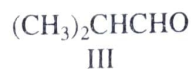
- Q. 49.** How will you distinguish between cis- and trans-2-butenes on the basis of ^{13}C -NMR spectroscopy?



Sol. The stereochemical influence of γ -effects in alkenes is extremely useful in assigning configuration for the trans, i.e. γ -effect for cis is stronger by 5.4 ppm and consequently the cis and trans-2-butenes can easily be distinguished from the chemical shifts of methyl carbons, i.e. 11.4 ppm in cis and 16.8 ppm in trans.

Q. 50. How will you distinguish among the carbonyl isomers pertaining to the molecular formula C_4H_8O on the basis of ^{13}C NMR spectroscopy?

Sol. The three possible carbonyl isomers are:



- (i) The ketone (I) exhibits a strongly downfield singlet whereas both the aldehydes (II and III) display a strongly downfield doublet.
- (ii) The aldehyde II shows two triplets and one quartet whereas the aldehyde III exhibits a second doublet and a quartet.

Nuclear Magnetic Resonance Spectroscopy

Study Problems

1. Explain briefly the basic theory of NMR spectroscopy.
2. The PMR spectrum of a dibromopropane shows a quintet and downfield triplet of about twice the intensity. Is the isomer 1,1-; 1, 2-; 1, 3-; or 2, 2-dibromopropane? Support your answer by suitable reasoning.
3. The NMR spectrum of [18] annulene exhibits only two absorptions, one at δ 9.28 and the other at -2.99 . The relative integration of the two absorptions is 2 : 1 for δ 9.28 to -2.99 . Account for this large shielding and deshielding of protons.
4. Discuss the phenomenon of chemical exchange and how would you overcome this difficulty in the interpretation of NMR spectra.
5. How many NMR signals would you expect from cyclohexane at -60°C . Explain
6. Explain briefly the following:
 - (a) AX and AB splitting patterns
 - (b) Vicinal coupling and Karplus equation curve.
7. Discuss the factors on which the magnitude of vicinal coupling constant depends.
8. What is INDOR? How does it help in the simplification of NMR spectra.
9. Sketch and explain COSY spectrum of m-dinitrobenzene.
10. (a) What do you understand by relaxation process in NMR? Explain its significance
(b) Explain the importance of integration line in PMR spectrum.
11. (a) A downfield shift for the proton of chloroform is observed in ^1H NMR spectrum when diluted with triethylamine. Explain.
(b) What happens to the OH resonance signal for phenol, in ^1H NMR spectrum, when the temperature is increased.
(c) In which of the compounds given below, the coupling constant (J_{AB}) is expected to be larger? Explain.

