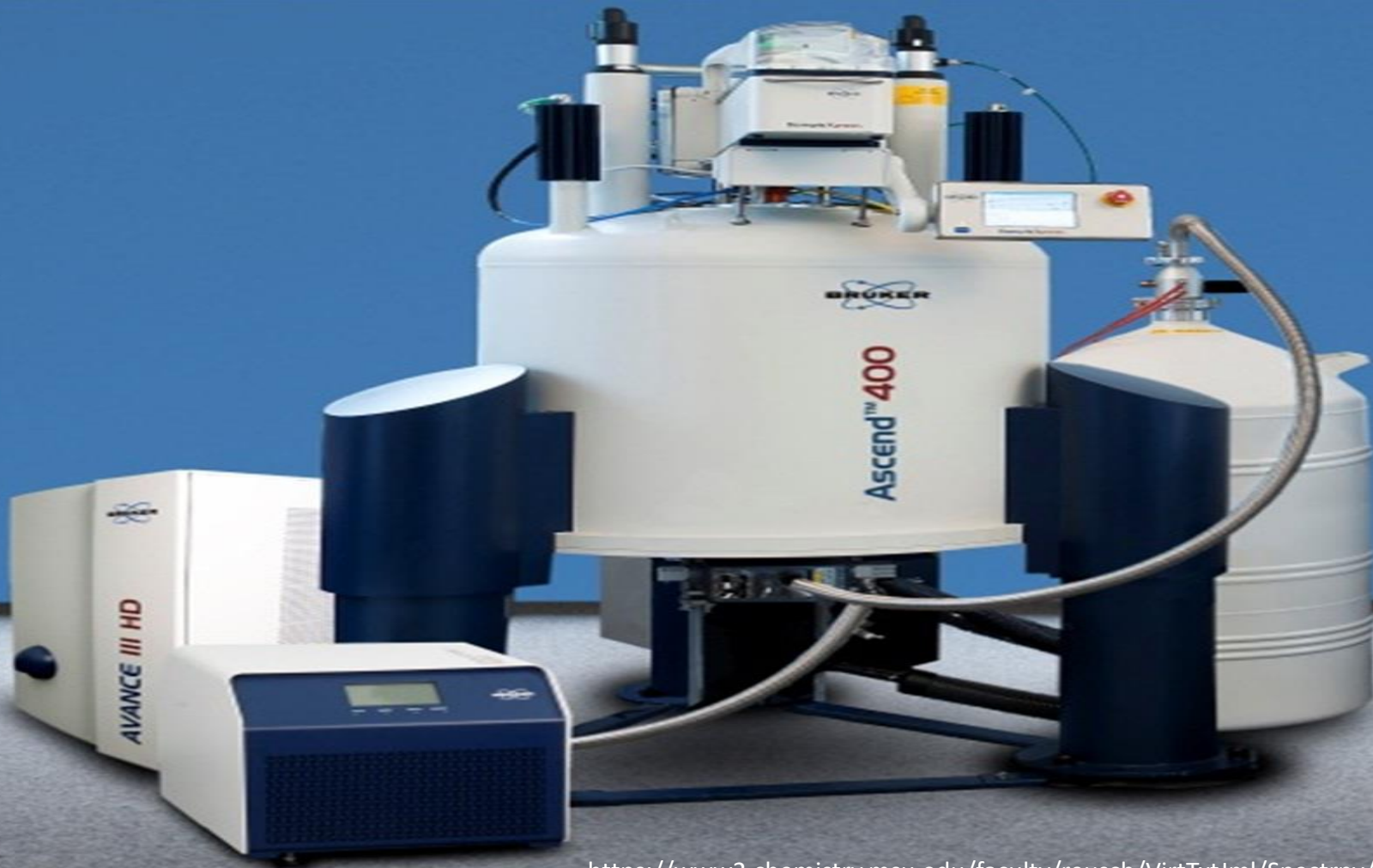


Nuclear Magnetic Resonance Spectroscopy



<https://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/Spectrpy/nmr/nmr1.htm>

nmr spectroscopy

Concerned with magnetic nuclei & their environment

Not Concerned with the type of bonds(IR) and loosely held electrons as in (UV)

Like electrons nuclear particles also spin

If spins of all the nuclear particles are not paired, then the nucleus will have resultant spin(I)

As nucleus is charged, the spinning nucleus will produce magnetic field. It will give magnetic moment along the axis of spin



nmr spectroscopy

Nuclei having resultant spin


MASS NUMBER	ATOMIC NUMBER	Resultant spin	EXAMPLES
Odd	Even or odd	1/2	${}^1_1\text{H}^1, {}^{13}_6\text{C}^{13}, {}^{19}_9\text{F}^{19}$
Even	Even	0	${}^4_2\text{He}^4, {}^{12}_6\text{C}^{12},$
Even	Odd	1	${}^2_1\text{H}^2, {}^{14}_7\text{N}^{14}$

If the number of neutrons and the number of protons are both even, then the nucleus has NO spin.

If the number of neutrons plus the number of protons is odd, then the nucleus has a half-integer spin (i.e. 1/2, 3/2, 5/2)

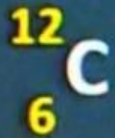
If the number of neutrons and the number of protons are both odd, then the nucleus has an integer spin (i.e. 1, 2, 3)

nmr spectroscopy

Nucleus  Protons + neutrons

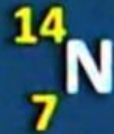
Both even

$$I = 0$$



Both odd

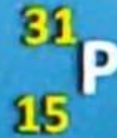
$$I = 1$$




One is odd & another even

$$I = \frac{1}{2}, \frac{3}{2}, \frac{5}{2} \dots$$

$$I = \frac{1}{2}$$



nmr spectroscopy

Why $I = \frac{1}{2}$?  $I = \text{Spin quantum number}$ ⁱ

Magnetic moment number (m)

It is the number of spin states of a nuclei in magnetic field

$$m = 2(I) + 1$$

nmr spectroscopy

Case 1

$$l = 0$$

$$m = 2(0) + 1$$

$$= 1$$

Only 1 state

0

Case 2

$$l = \frac{1}{2}$$

$$m = 2\left(\frac{1}{2}\right) + 1$$

$$= 2$$

2 states

$-\frac{1}{2}$

$+\frac{1}{2}$

Case 3

$$l = 1$$

$$m = 2(1) + 1$$

$$= 3$$

3 states

-1

0

+1

nmr spectroscopy

Case 1

$$l = 0, m = 0$$

— 0

*Both states are equivalent
with opposite signs*

Case 2

$$l = \frac{1}{2}, m = 2$$



Case 3

$$l = 1, m = 3$$



*All states are not
equivalent*

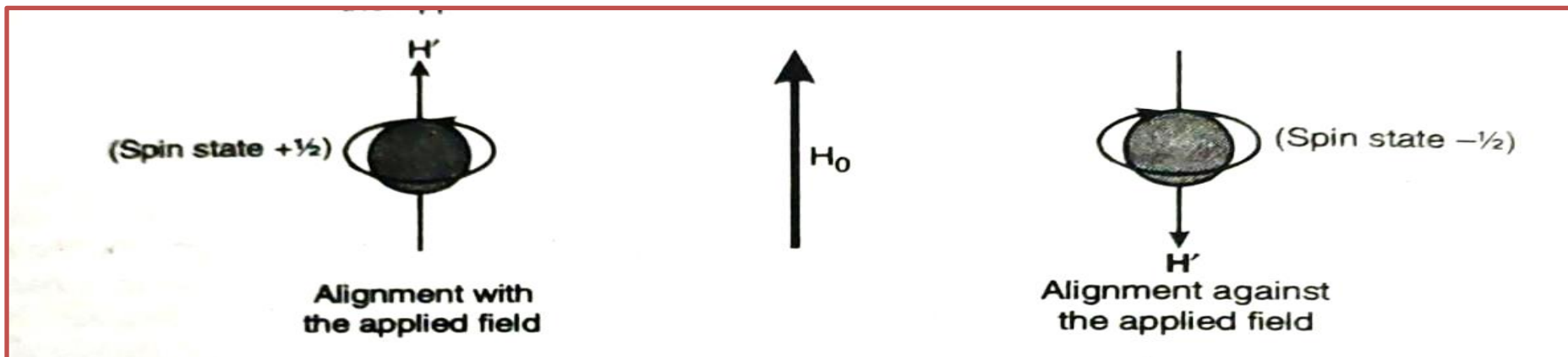
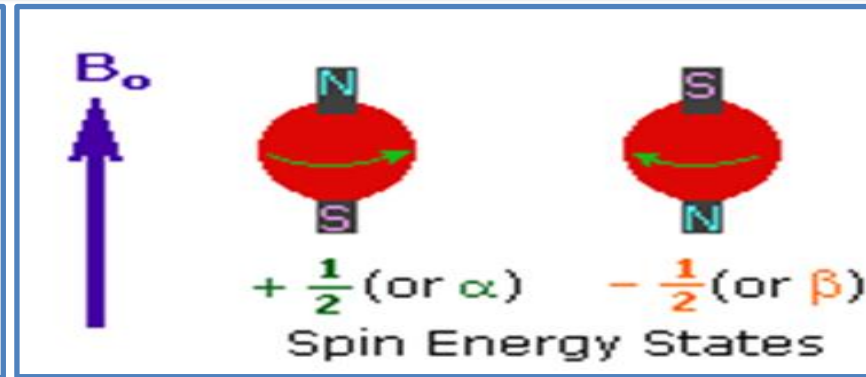
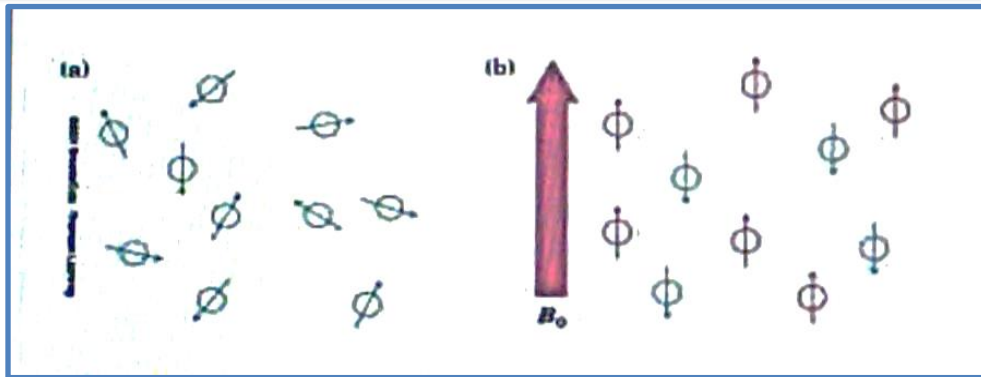
nmr spectroscopy

NUCLEAR SPIN STATES

The number of orientations taken up by nucleus in the presence of magnetic field = $(2I+1)$
for a proton $I=1/2$ so number of orientations = 2

In the absence of strong magnetic field, the nuclear spins are randomly oriented

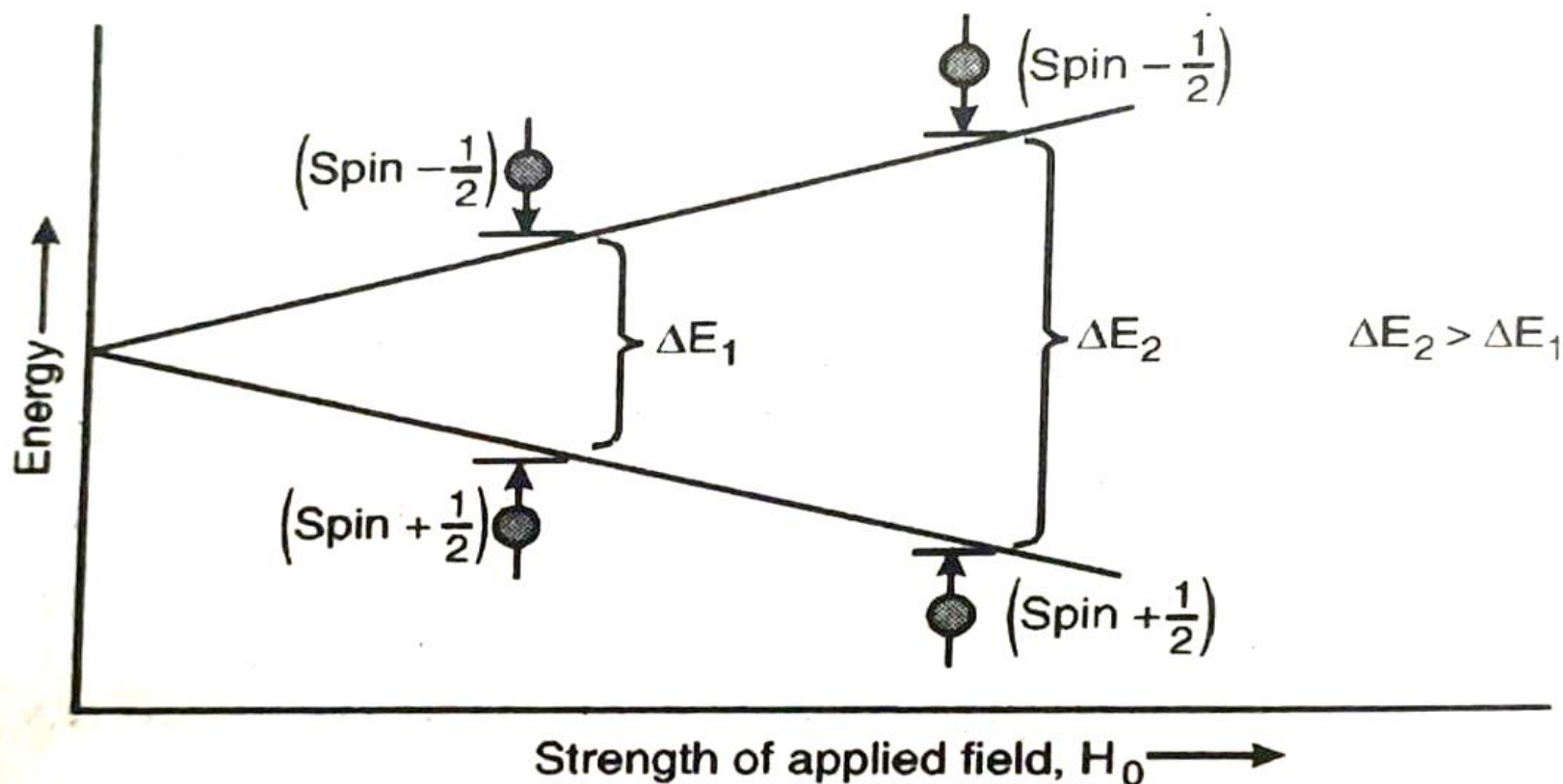
In the presence of magnetic field, two possible orientations (spin states) are possible



nmr spectroscopy

NUCLEAR SPIN STATES contd.

- Difference in energy of spin states depends upon the strength of applied magnetic field

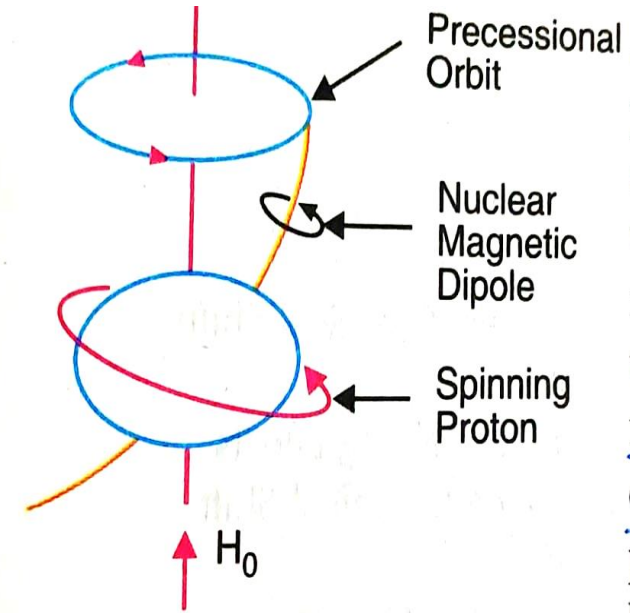


PRINCIPLE OF NUCLEAR MAGNETIC RESONANCE

❖ Precessional Frequency or Larmor frequency

- Spinning nuclear magnet undergoes precessional motion (just like spinning top) around the axis of external magnetic field
- The frequency with which the magnetic moment vector of the nucleus revolves around the external field is called as precessional frequency

- When precessional frequency is equal to the frequency of em radiations, the spinning nucleus & radiations are said to be in resonance
- Under these conditions the nuclei absorb energy & flip over from low energy state to high energy spin state
- **This is called as flipping of protons**



PRINCIPLE OF NUCLEAR MAGNETIC RESONANCE contd.

❖ The relation between energy required for flipping of protons ΔE , frequency of e.m. radiations, and strength of applied magnetic field

H_0 is $\Delta E = h\nu$ and $\nu = \gamma H_0 / 2\pi$

$$\Delta E = h\gamma H_0 / 2\pi$$

γ is gyromagnetic ratio which is a nuclear constant and its value for proton is 26750

➤ Higher is H_0 higher is frequency so higher is energy needed for flipping over of proton

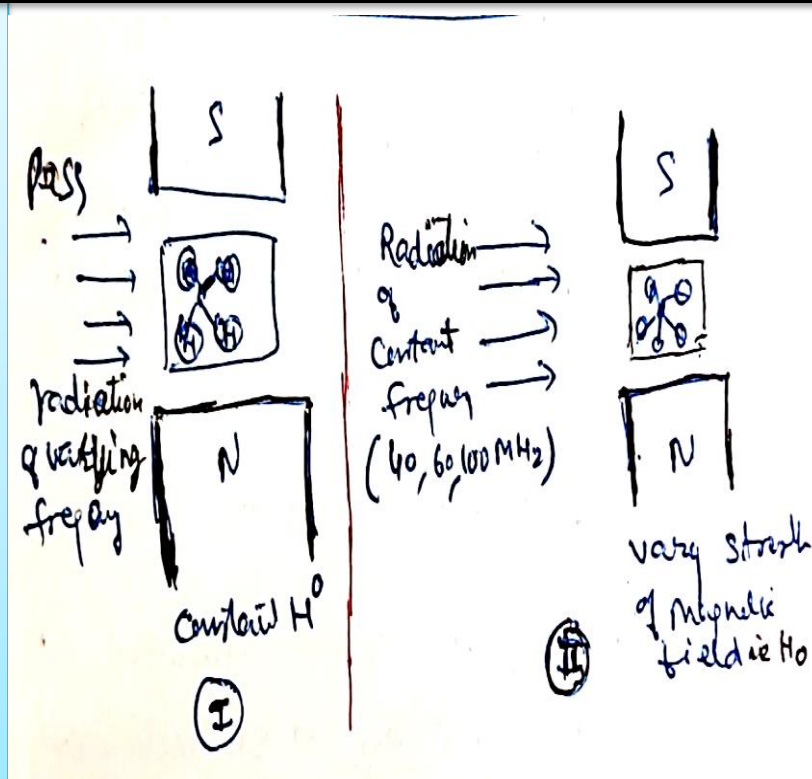
➤ If H_0 is 14092 Gauss, then frequency needed is 60 MHz which corresponds to **radio waves**

1H-NMR or PMR spectroscopy

PMR or 1H-NMR spectrum: Origin of signals

Two ways of obtaining spectrum

1. Irradiate the sample with em radiations of varying frequencies at constant applied magnetic field
 2. Irradiate the sample with em radiations of constant frequency and vary the strength of applied magnetic field (this way is commonly used)
- At a certain field strength, the energy of em radiation is sufficient to cause flipping and absorption of radiation occurs, giving rise to NMR signal



- The magnetic field experienced by the protons is not same as the applied field strength
- The field felt by the proton depends upon its local environments like electron density around it and the number of other protons in the neighbourhood.
- Protons with different local environments will feel different fields and will absorb at different applied field strengths. Thus different nmr signals are seen.

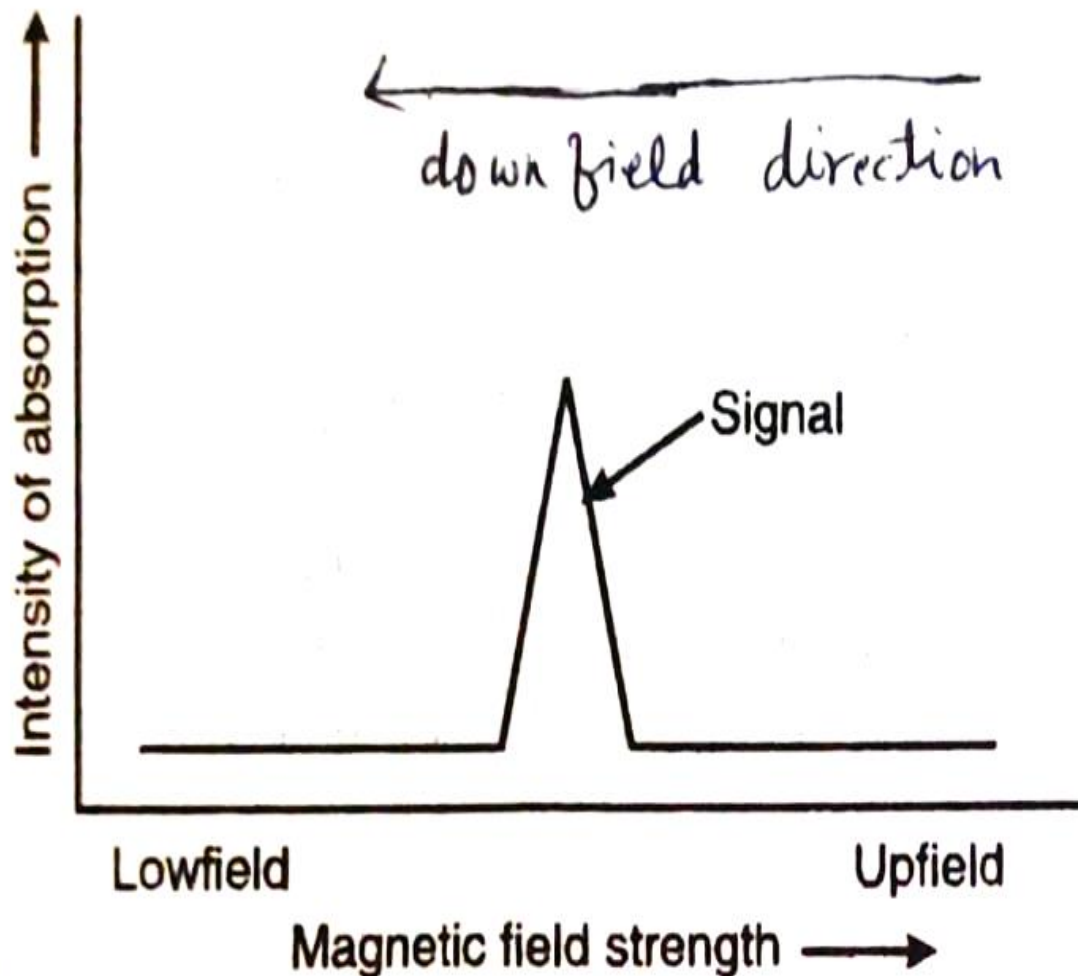
1H-NMR or PMR spectroscopy

PMR or 1H-NMR spectrum: Origin of signals

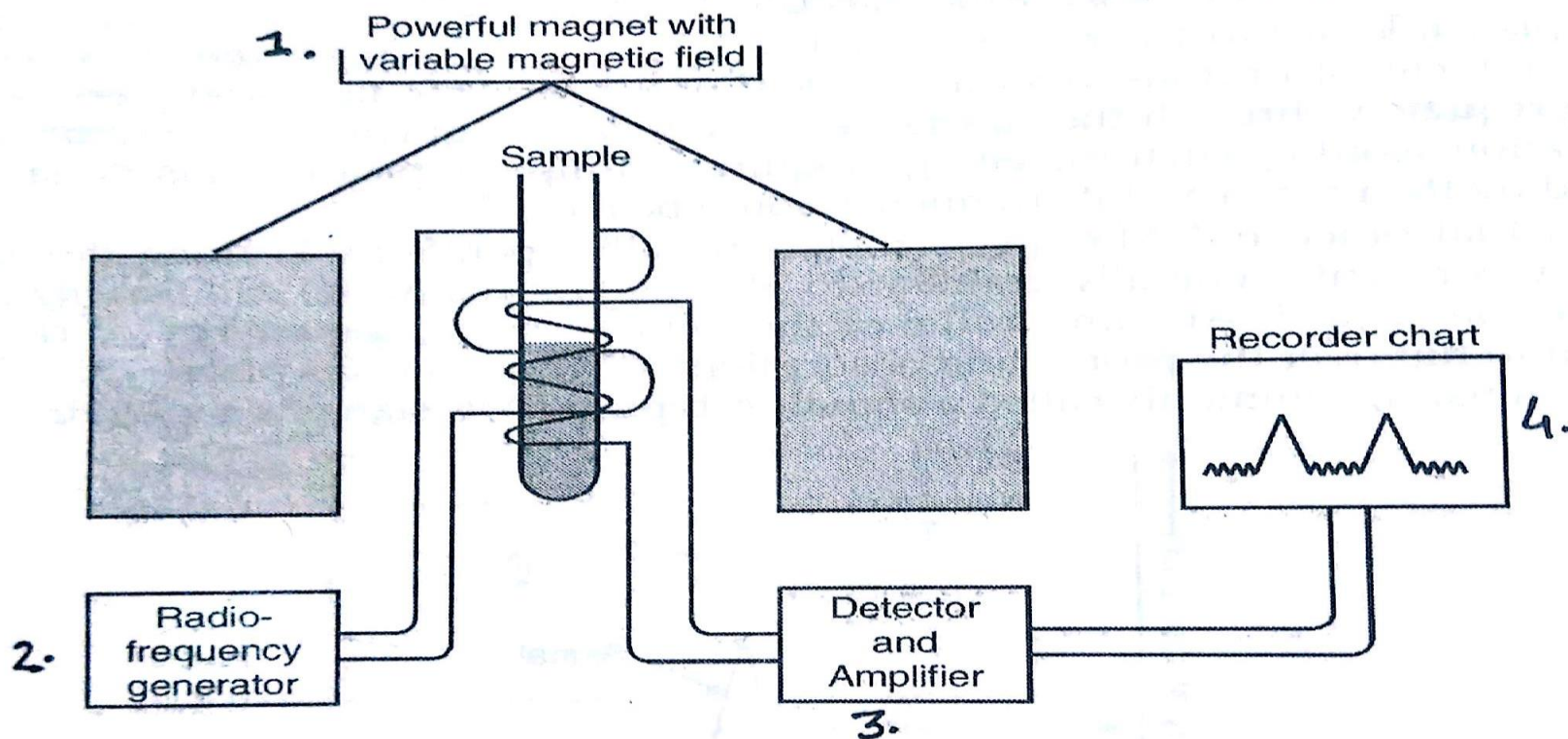
❖ NMR

spectrum

- It is the plot of intensity of absorption versus strength of applied magnetic field



NMR SPECTROMETER(SWEEP or CONTINUOUS WAVE)



- CW spectrometer takes 2 to 5 minutes to record the spectrum
- Fourier Transform(FT) NMR spectrometers take only 5 seconds to record the spectrum
- In FT technique, radiofrequency is varied at a constant applied magnetic field strength

NUMBER OF SIGNALS

EQUIVALENT AND NONEQUIVALENT PROTONS

Set of protons having identical environments absorb at same applied field

Give one signal

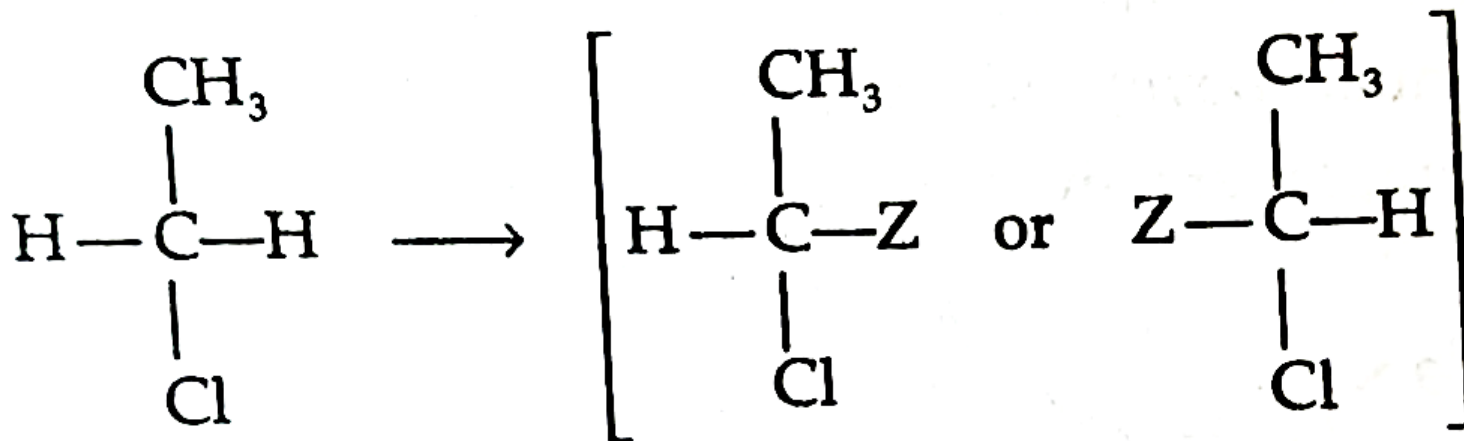
Set of protons having different environments absorb at different applied field strength

Give different signals

Number of signals tells us as to how many different kind of protons are there

NUMBER OF SIGNALS contd.

- Protons of methylene group are enantiotropic because replacement of any proton with Z gives a pair of enantiomers.
- **Enantiotropic protons are equivalent** because PMR does not distinguish between mirror images and can be interconverted by reflection through a plane



NUMBER OF SIGNALS contd.

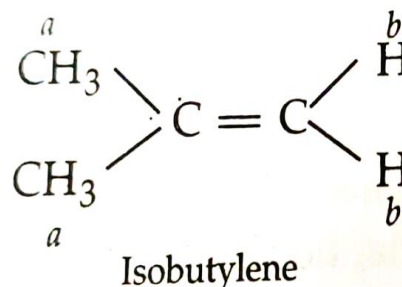
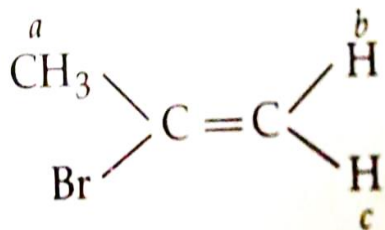
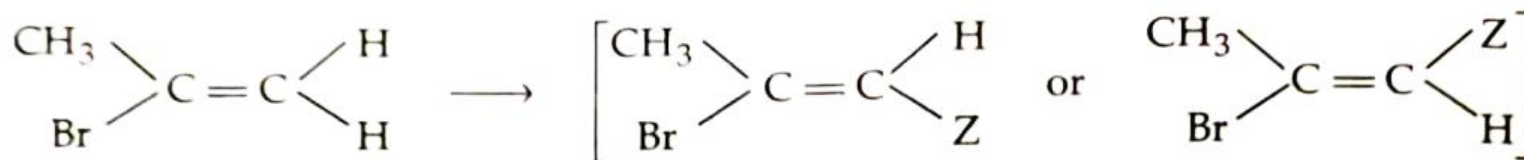
To be chemically equivalent, protons must be Stereo chemically equivalent also

Diastereotopic protons

Can not be interconverted by rotation or reflection

For example in 2-Bromopropene vinylic protons are diastereotopic protons

Diastereotopic protons are stereo chemically different

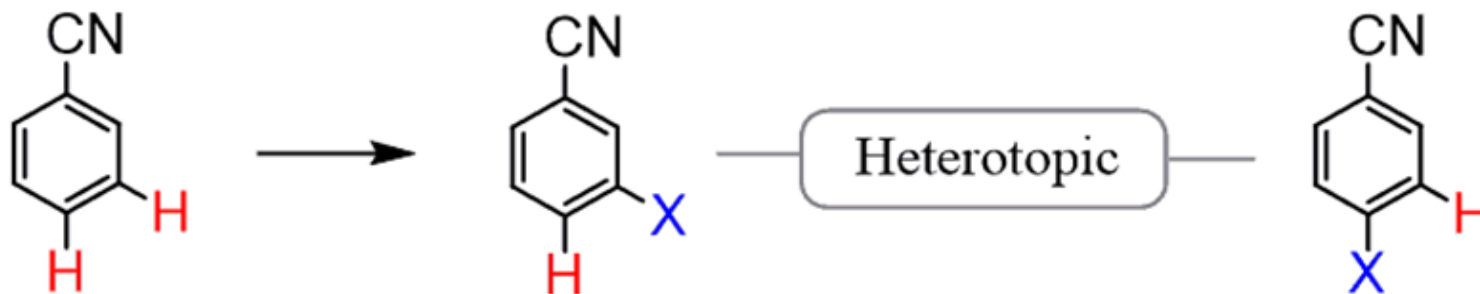


Diastereotopic protons are stereo chemically different

NUMBER OF SIGNALS contd.

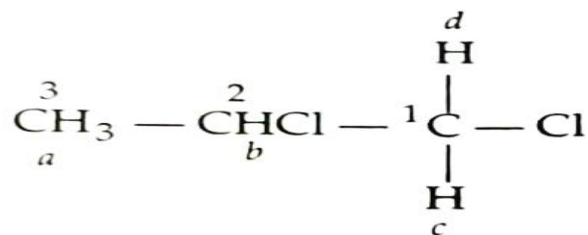
❖ Heterotopic protons

- Replacement of these protons with Z gives two different constitutional isomers
- Heterotopic protons are stereo chemically different

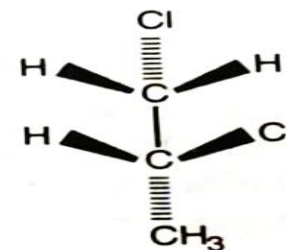


- To summarize, homotopic and enantiotopic protons are chemically equivalent and give one signal. Locate them with a symmetry axis or a plane of symmetry respectively.
- Diastereotopic and heterotopic protons are chemically nonequivalent and give two signals.

NUMBER OF SIGNALS contd.



1, 2-Dichloropropane ;

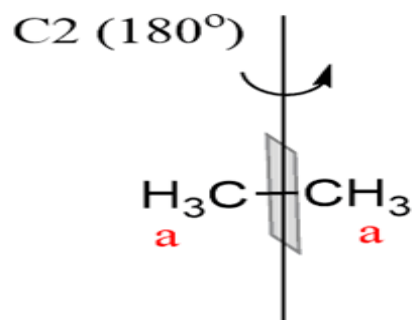


Stereochemical formula

Symmetry element - one signal, equivalent protons.

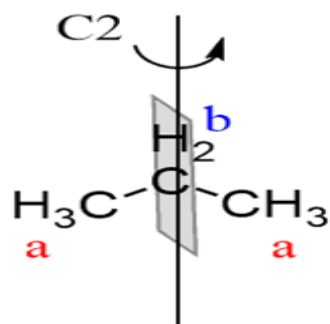
No symmetry element - different signals, not equivalent protons.

These protons are exchangeable by both a symmetry plane and an axis:



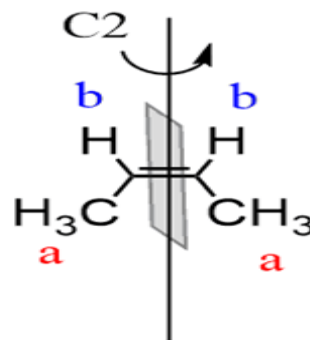
6 protons but

1 signal



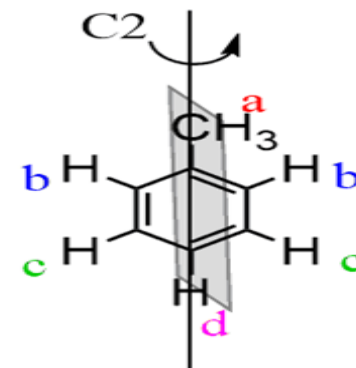
8 protons but

2 signals



8 protons but

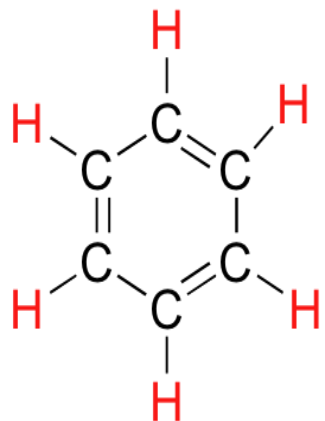
2 signals



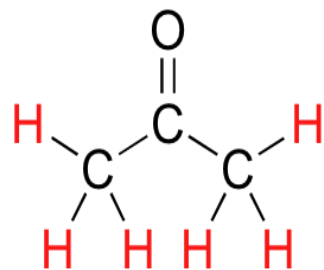
8 protons but

4 signals

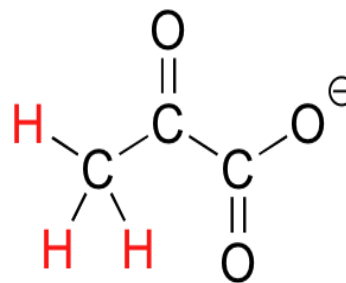
NUMBER OF SIGNALS contd.



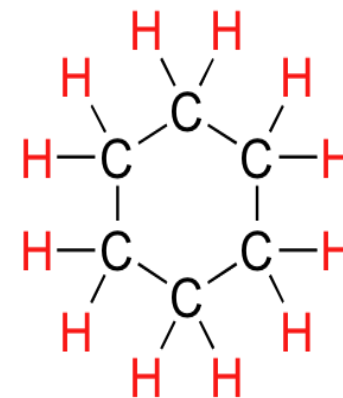
benzene



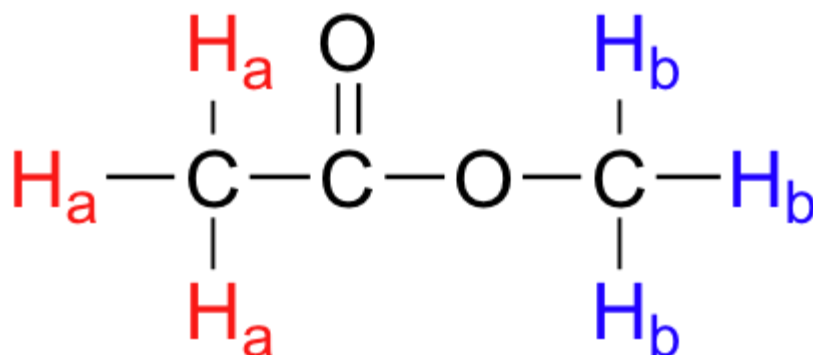
acetone



pyruvate

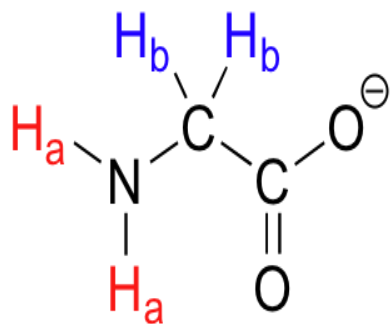


cyclohexane

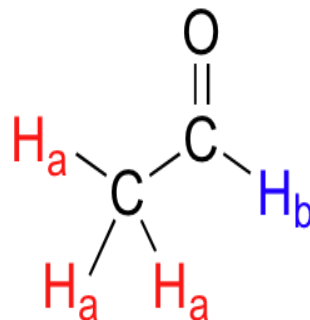


Methyl acetate

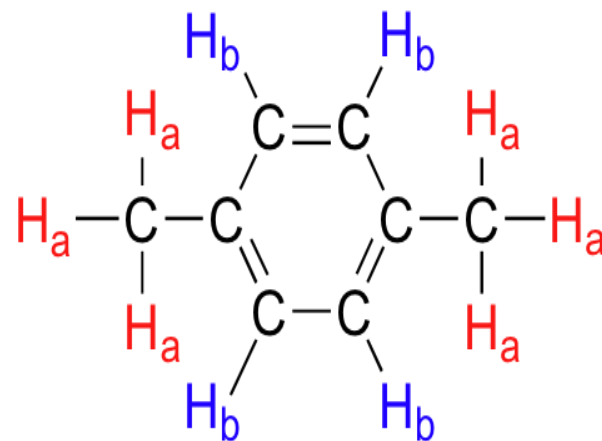
NUMBER OF SIGNALS contd.



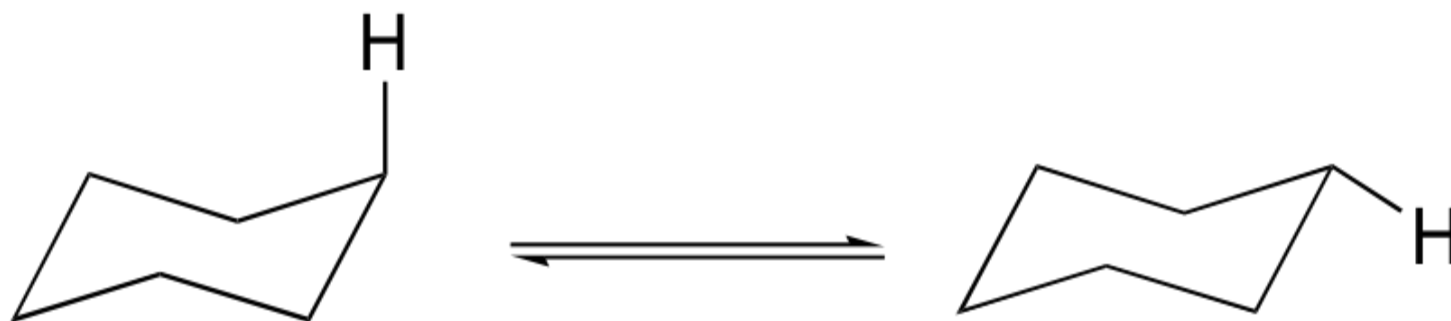
glycine



acetaldehyde



para-xylene



ring-flip process is *fast* compared to the NMR time-scale

NUMBER OF SIGNALS contd.

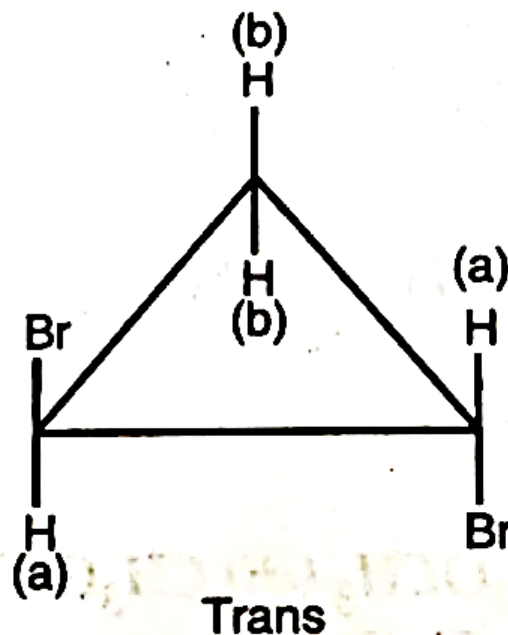
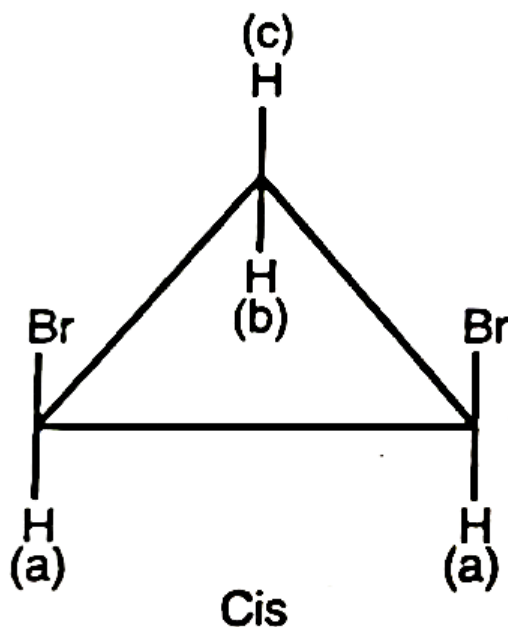
Cis- 1,2-dibromocyclopropane

Trans- 1,2-dibromocyclopropane

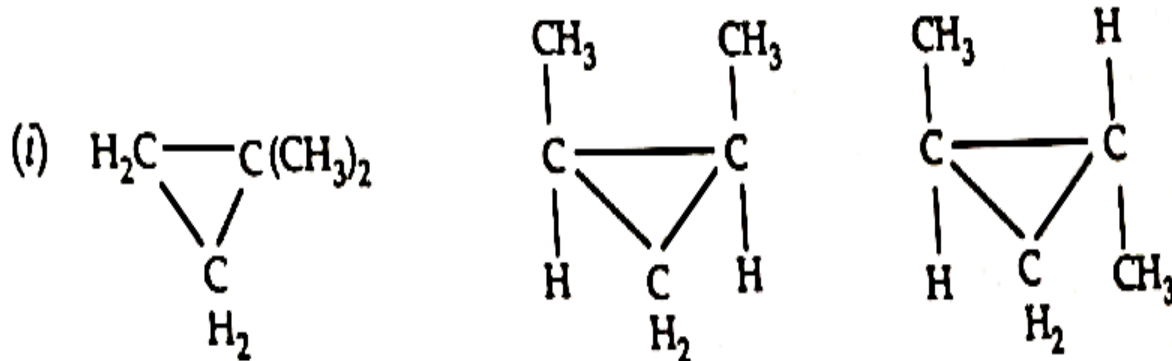
Three signals

How?

Two signals



NUMBER OF SIGNALS contd.



Three Isomeric Dimethyl cyclopropanes

Propose structural formula as per given number of nmr signals

1. C_2H_6O (1 nmr signal)
2. C_2H_6O (3 nmr signal)
3. $C_2H_4Cl_2$ (1 nmr signal)
4. $C_2H_4Cl_2$ (2 nmr signal)
5. C_6H_{12} (1 nmr signal)

Position of Signals

SHIELDING & DESHIELDING OF PROTONS

Induced magnetic field

In the presence of magnetic field, the electrons of molecule circulate which also produce secondary magnetic field.

This either oppose or reinforce the applied magnetic field at proton

SHIELDING:

When induced magnetic field opposes the applied magnetic field

Shielded proton absorbs upfield

Effect is called Shielding effect eg Acetylenic proton

DESHIELDING:

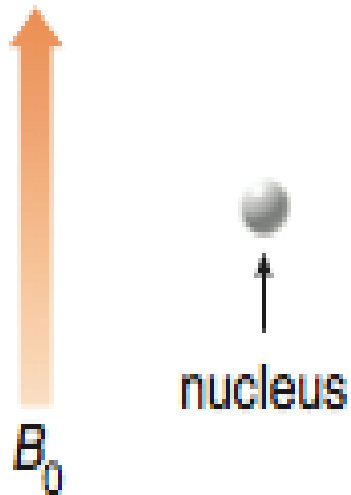
When induced magnetic field reinforces the applied magnetic field

Deshielded proton absorbs downfield

Effect is called as deshielding effect eg aromatic proton

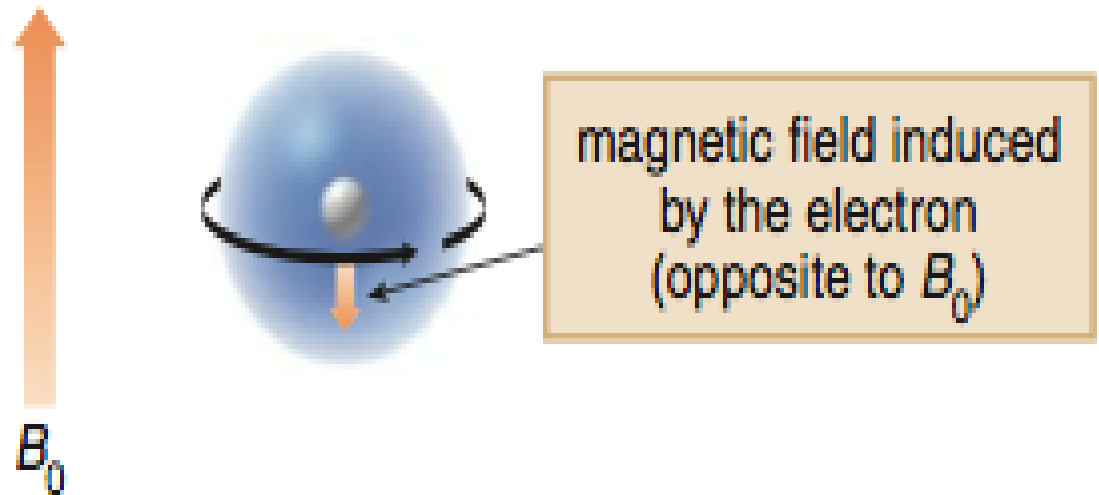
SHIELDING & DESHIELDING OF PROTONS

An isolated proton



The nucleus "feels" B_0 only.

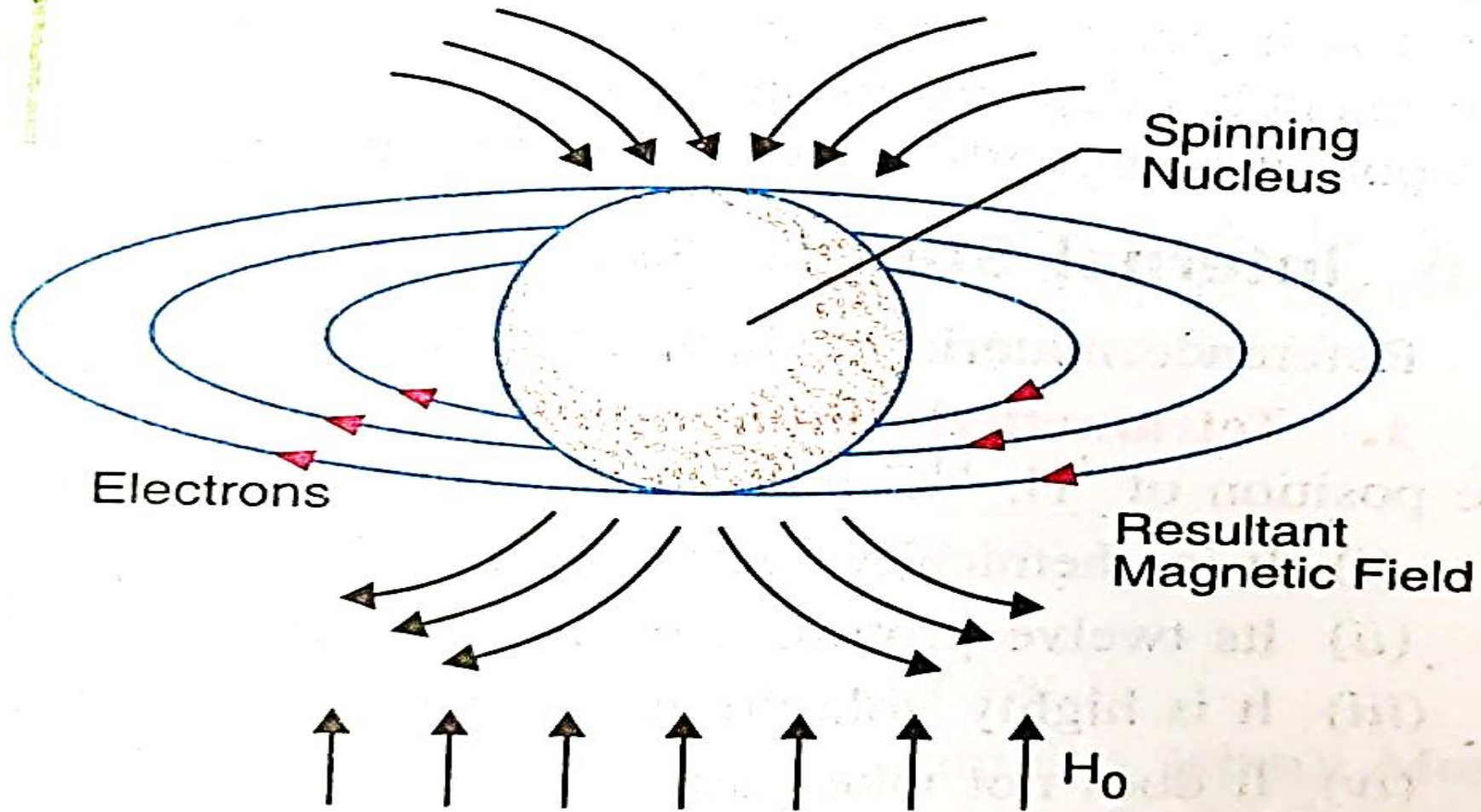
A proton surrounded by electron density



The induced field *decreases* the strength of the magnetic field "felt" by the nucleus.

This nucleus is shielded.

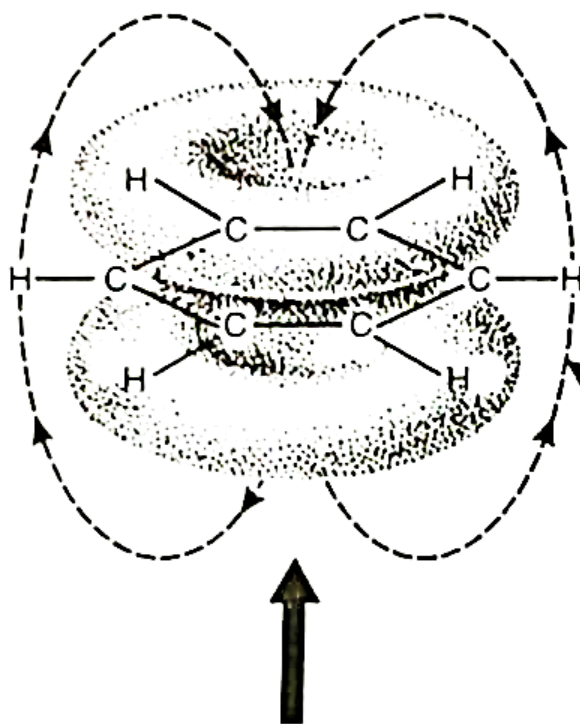
SHIELDING & DESHIELDING OF PROTONS



Diamagnetic shielding about the nucleus

SHIELDING & DESHIELDING OF PROTONS

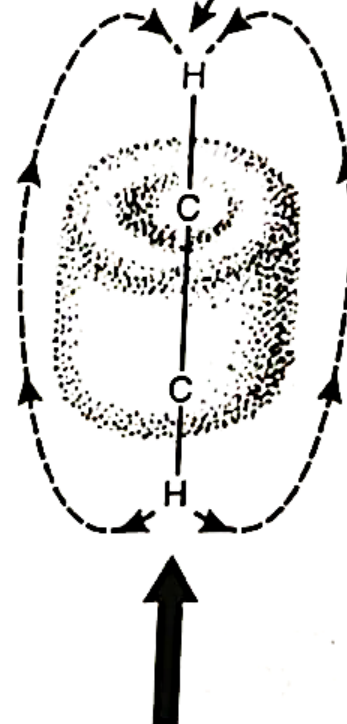
Electrons of pi bonds start circulating at right angle to the direction of applied magnetic field which produce secondary magnetic field



APPLIED FIELD, H₀

(a) Benzene : Deshielding of aromatic protons

paramagnetic shielding



APPLIED FIELD, H₀

(b) Acetylene ; Shielding of acetylenic protons

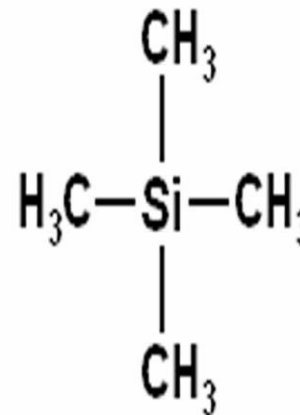
Diamagnetic shielding

CHEMICAL SHIFT

- The Due to shielding or deshielding of protons there is shift in the position of PMR or NMR signals of different Protons.
- For measurement of the shift, the nmr signal of TMS(Tetramethyl silane) is taken as a reference
- The difference in the absorption position of the protons with respect to TMS signal is called as chemical shift.

➤ Why TMS (Tetra methyl silane) is taken as reference compound?

1. Has 12 equivalent protons so give strong signal
2. Silicon is less electronegative than carbon. So all the 12 protons are highly shielded. The nmr signal of all other protons are downfield to it.
3. It is inert & volatile.
4. It is miscible with almost all compounds.



Expressing chemical shift

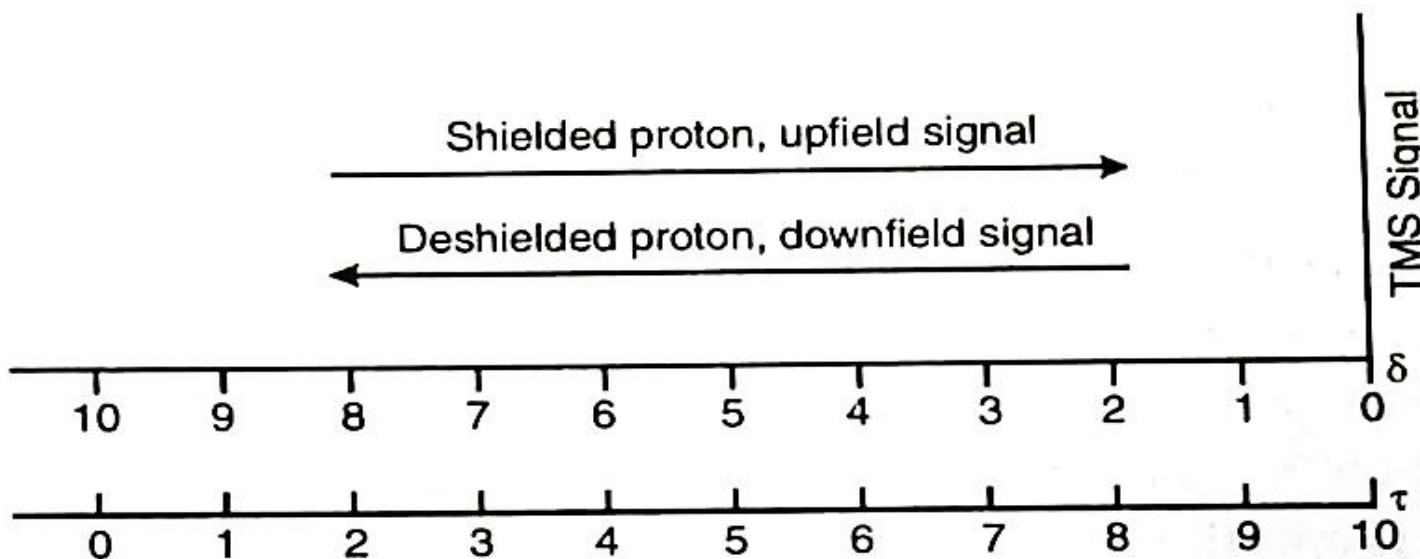
➤ Measured in units of Frequency and Expressed in PPM

➤ Two scales to express

1. Delta (δ) scale

2. Tau (τ) scale

$$\text{Delta } (\delta)\text{ scale} = \frac{\Delta\gamma \text{ in Hz}}{\text{Operating frequency in Hz}} \times 10^6$$



➤ Relation between two scales

$$\tau = 10 - \delta$$

Factors Affecting Chemical Shift

1. Inductive Effect

- ❖ **-I effect** causes deshielding because it reduces the electron density around the proton.

Examples

➤ Compare $\text{CH}_3\text{-O-CH}_3$ and $\text{CH}_3\text{-CH}_3$

➤ Compare $\text{CH}_3\text{-F}$, CH_3Cl , CH_3Br

Tau values 5.75 6.90 7.36

➤ Compare methyl and methylene protons of $\text{CH}_3\text{CH}_2\text{Cl}$

- ❖ **+I effect** causes shielding of protons because it increases electron density around the proton so absorption occurs upfield.

2. Vander Wall's deshielding

- If proton occupies sterically hindered position, bulky groups tend to repel electron crowd surrounding the proton. So such a proton will be slightly deshielded

Factors Affecting Chemical Shift contd.

2. Anisotropic effect (Space effect)

induced magnetic field is produced due to circulation of electrons which operates through the space and causes shielding & deshielding of the protons

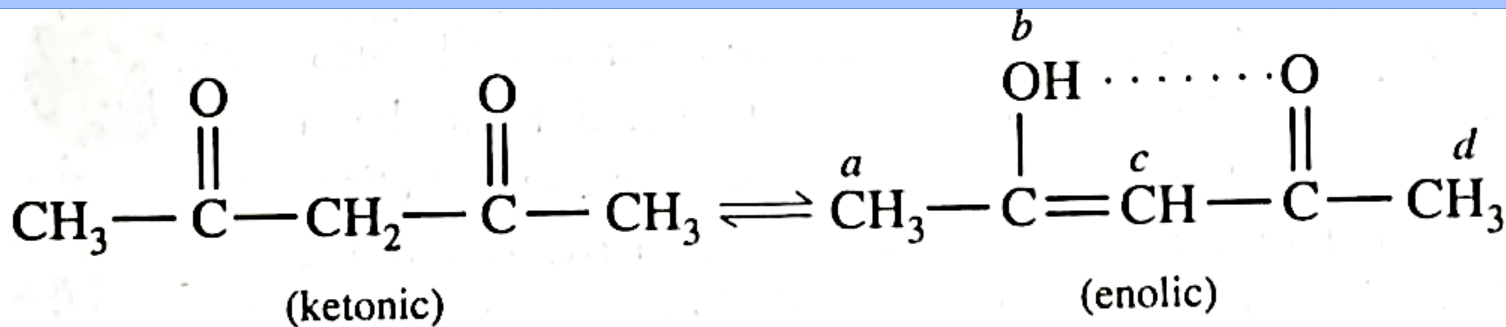
Examples

- Shielding of Acetylenic proton
- Deshielding of aromatic, aldehydic and ethylenic protons

3. Hydrogen bonding

Hydrogen bonded proton is highly deshielded
e.g. Enolic form of acetylacetone

Tau values are for $a= 8.02$, $b= -4.9$, $c= 4.5$, $d= 8.02$



Factors Affecting Chemical Shift contd.

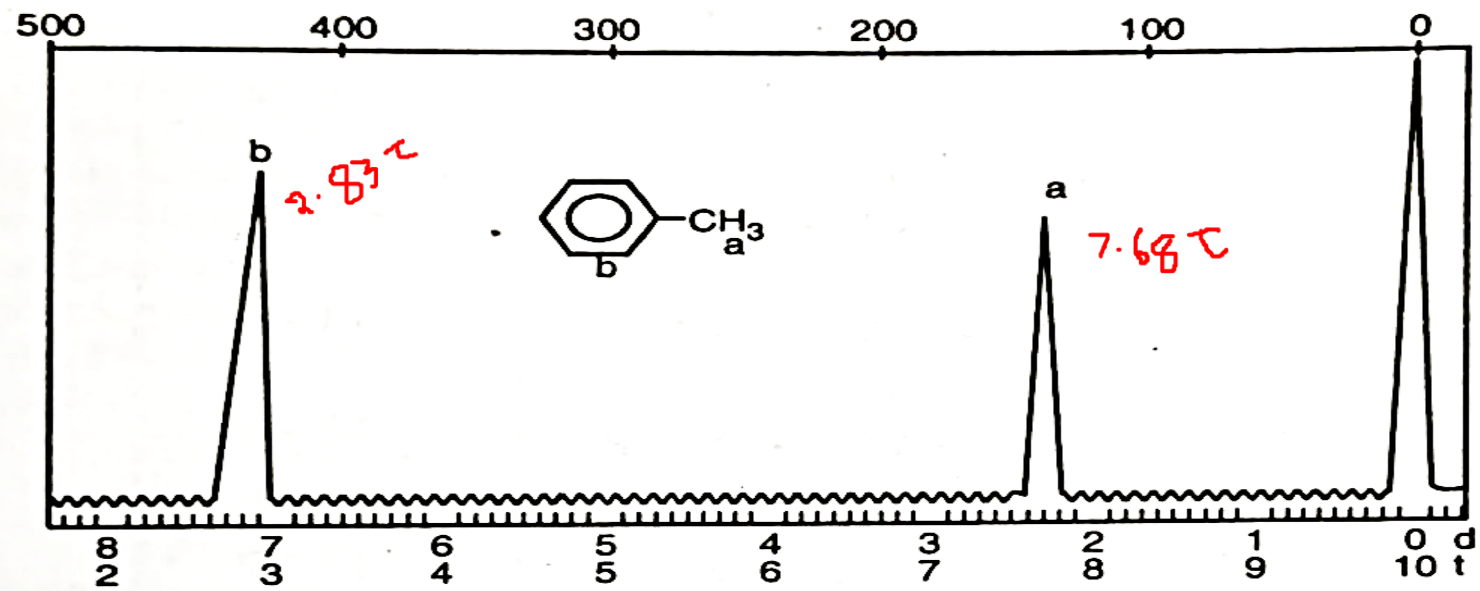
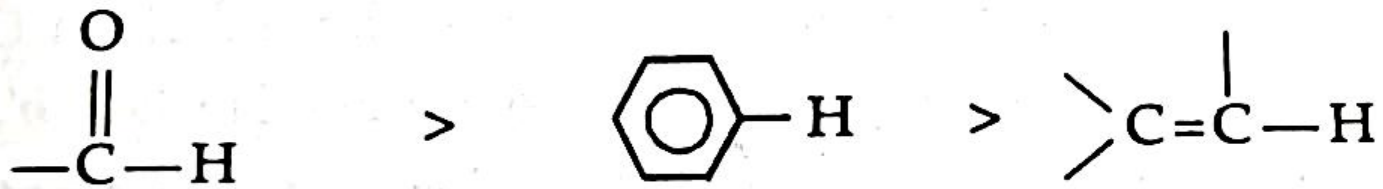


Fig. 6.6. PMR spectrum of toluene, Cc1ccccc1

CHEMICAL SHIFT

Types of proton		Chemical shift, ppm	
		δ	τ
Primary (Saturated)	$R-CH_3$	0.9	9.1
Secondary (Saturated)	R_2CH_2	1.3	8.7
Tertiary (Saturated)	R_3CH	1.5	8.5
Vinylic	$\begin{array}{c} \quad \\ -C=C-H \\ \quad \end{array}$	4.6 — 5.9	4.1 — 5.4
Acetylenic	$-C \equiv C-H$	2 — 3	7 — 8
Aromatic	$Ar-H$	6 — 8.5	1.5 — 4
Benzylic	$\begin{array}{c} \\ Ar-C-H \\ \end{array}$	2.2 — 3	7 — 7.8
Allylic	$\begin{array}{c} \quad \quad \\ -C=C-C-H \\ \quad \end{array}$	1.7	8.3

CHEMICAL SHIFT

Types of proton	Chemical shift, ppm	
	δ	τ
Alkyl fluoride $\begin{array}{c} \\ - \text{CH} - \text{F} \end{array}$	4 - 4.5	5.5 - 6
Alkyl chloride $\begin{array}{c} \\ - \text{CH} - \text{Cl} \end{array}$	3 - 4	6 - 7
Alkyl bromide $\begin{array}{c} \\ - \text{CH} - \text{Br} \end{array}$	2.5 - 4	6 - 7.5
Alkyl iodide $\begin{array}{c} \\ - \text{CH} - \text{I} \end{array}$	2 - 4	6 - 8
Alcohol $\begin{array}{c} \\ - \text{CH} - \text{OH} \end{array}$	3.4 - 4	6 - 6.6
Ethers $\begin{array}{c} \\ - \text{CH} - \text{O} - \text{R} \end{array}$	3.3 - 4	6 - 6.7
Carbonyl compounds $\begin{array}{c} \quad \quad \quad \text{O} \\ - \text{CH} - \text{C} - \\ \quad \quad \quad \quad \end{array}$	2 - 2.7	7.3 - 8
Acids $\begin{array}{c} \\ - \text{CH} - \text{COOH} \end{array}$	2 - 2.6	7.4 - 8
Hydroxyl $\text{R} - \text{O} - \text{H}$	1 - 5.5	4.5 - 9
Phenolic $\text{Ar} - \text{O} - \text{H}$	4 - 12	(-2) - 6
Enolic $\begin{array}{c} \quad \quad \\ - \text{C} = \text{C} - \text{OH} \end{array}$	9 - 10	0 - 1
Aldehydic $\begin{array}{c} \text{O} \\ \\ \text{R} - \text{C} - \text{H} \end{array}$	9 - 10	0 - 1
Carboxylic $\text{R} - \text{COOH}$	10.5 - 12	(-2) - (-0.5)
Amino $\text{R} - \text{NH}_2$	1 - 5	5 - 9

Solvents used in nmr

Solvents should fulfil the following conditions

1. It should not contain H atoms
 2. It should dissolve the sample compound readily
 3. It should be chemically inert
- CCl_4 , CS_2 , CDCl_3 , Hexachloroacetone.
 - Trifluoroacetic acid can also be used.
 - ($\delta = 11.2$) most protons absorb in the range 0-10

Peak area & proton counting

- The area under the nmr peak is directly proportional to the number of equivalent protons giving that signal
- The area is measured by automatic integrator and is indicated by an integral curve

Examples

Toluene ($\tau = 7.68, 3\text{H}$ and $\tau = 2.83, 5\text{H}$)

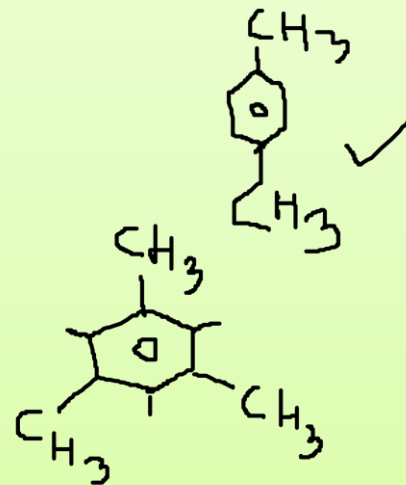
ratio of area under peaks 3:5

P-Xylene ($\tau = 7.6, 6\text{H}$ and $\tau = 3, 4\text{H}$)

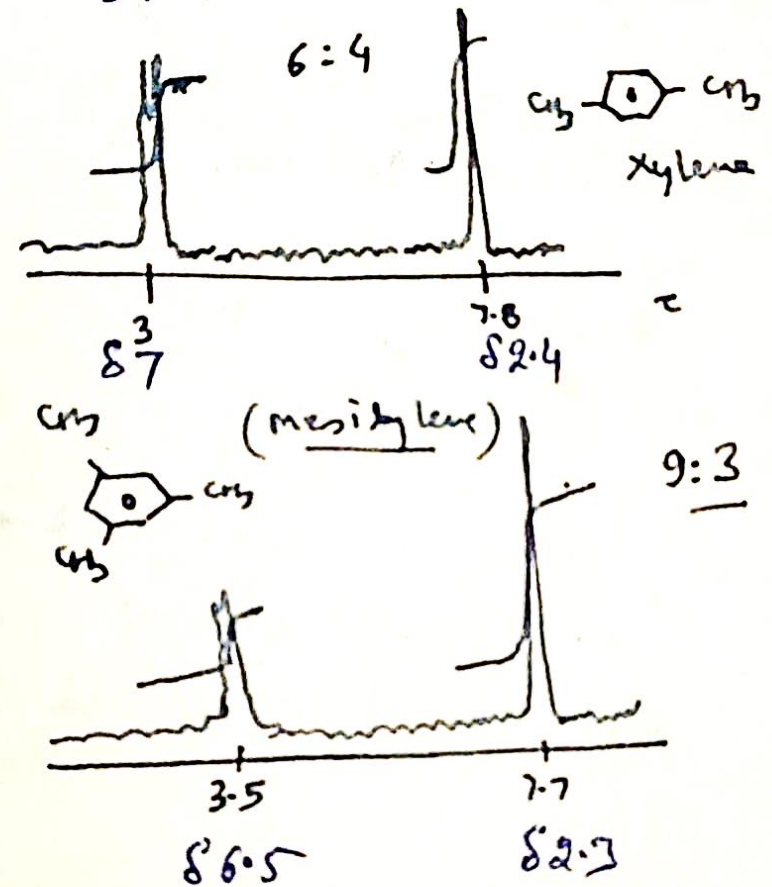
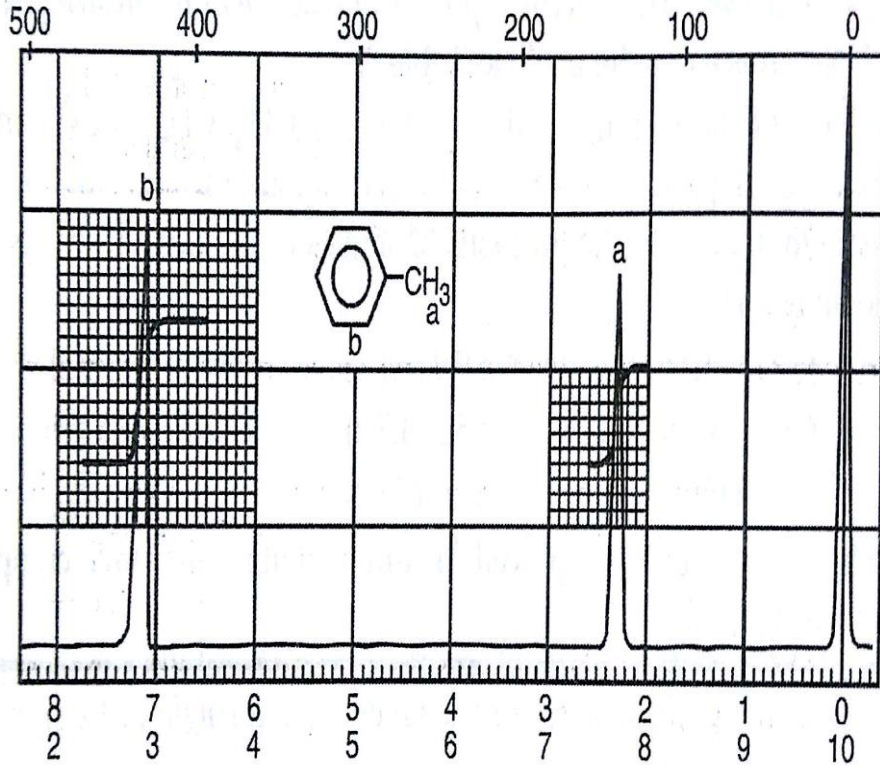
ratio of area under peaks 6:4

Mesitylene ($\tau = 7.7, 9\text{H}$ and $\tau = 3.5, 3\text{H}$)

ratio of area under peaks 9:3



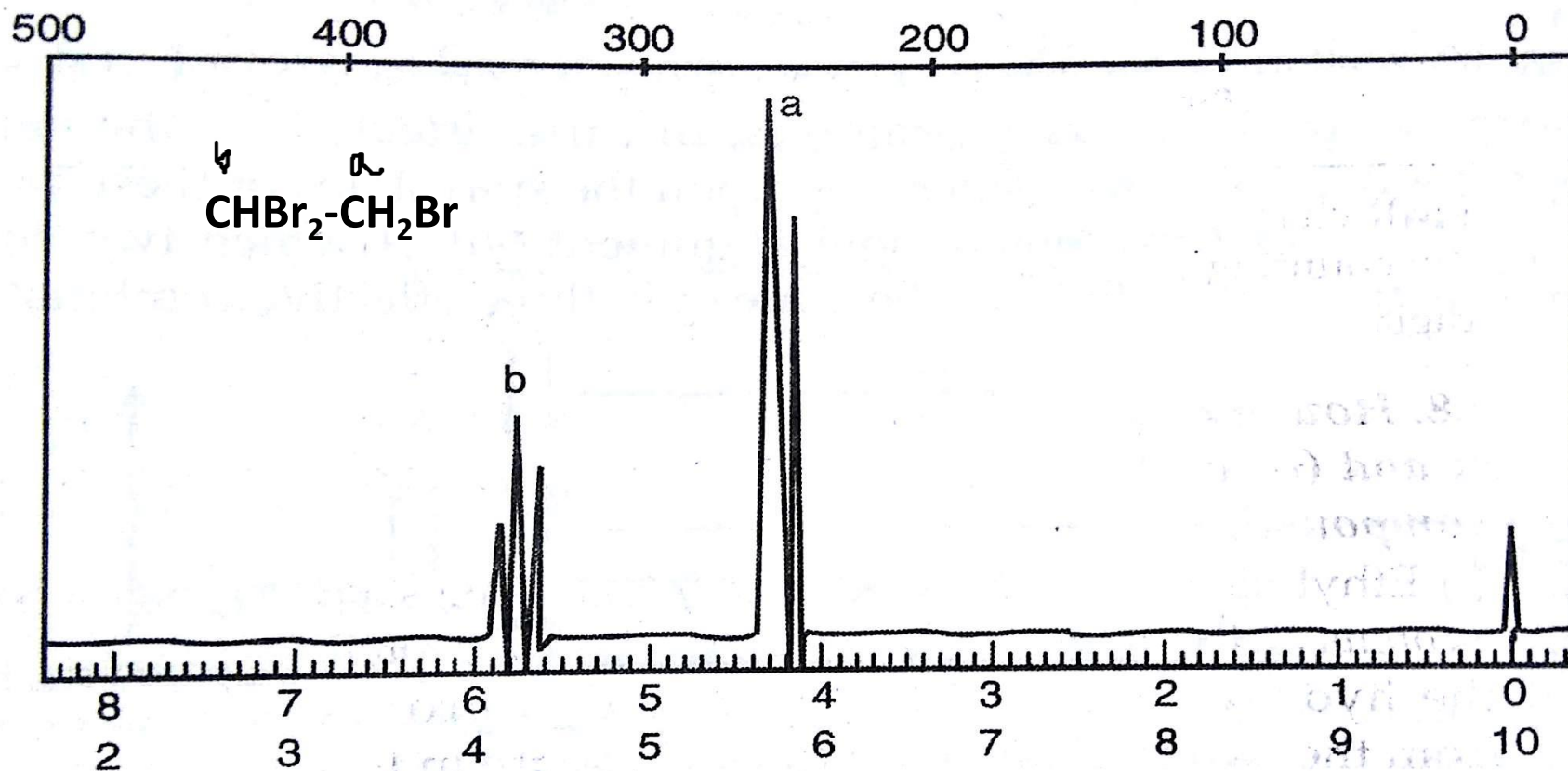
Peak area & proton counting contd



Splitting of signals(Spin - Spin Coupling)

An nmr signal is splitted due to Protons present on adjacent carbons

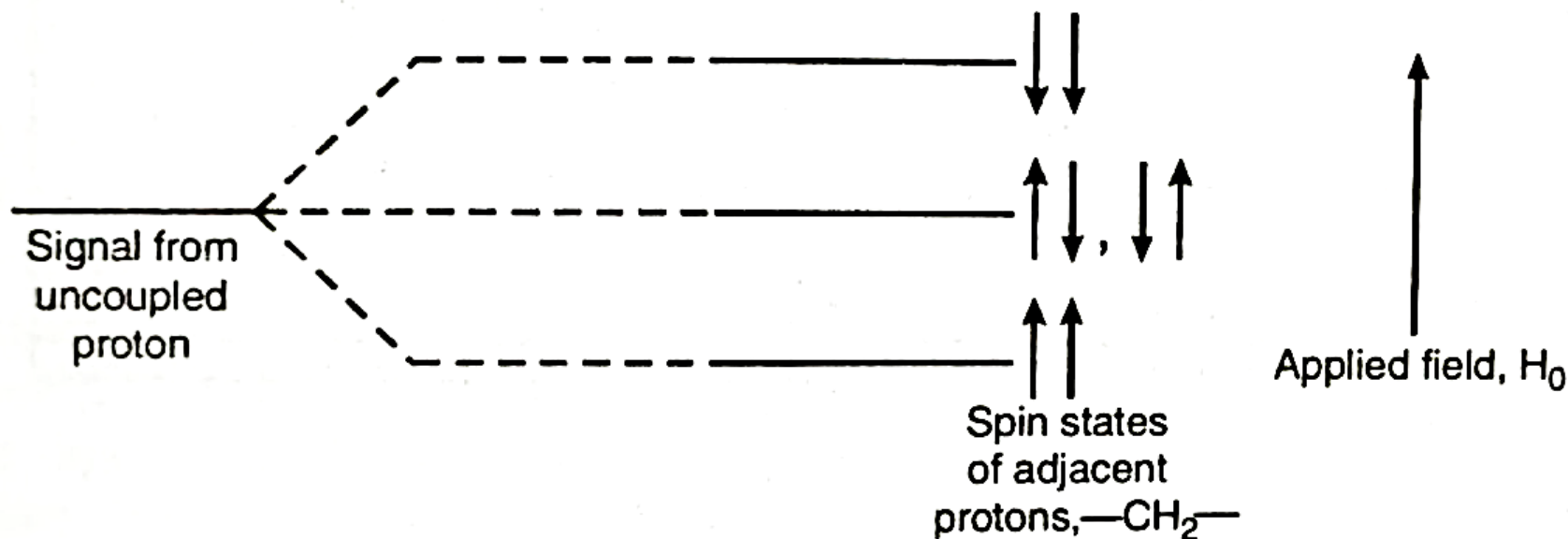
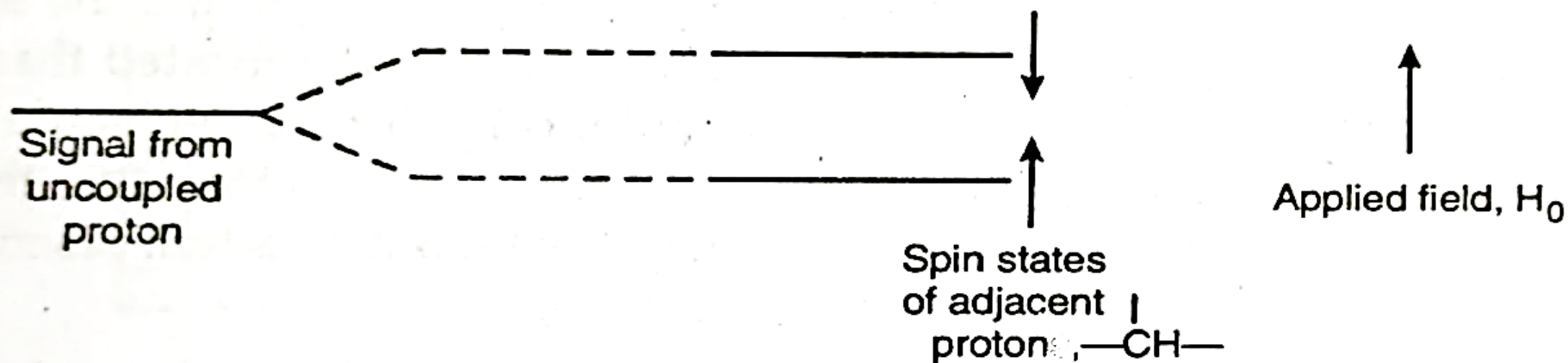
- **Cause:-**
- It is due to spin-spin coupling of absorbing protons and protons present on adjacent carbons



Splitting of signals(Spin - Spin Coupling) contd

Examples:-

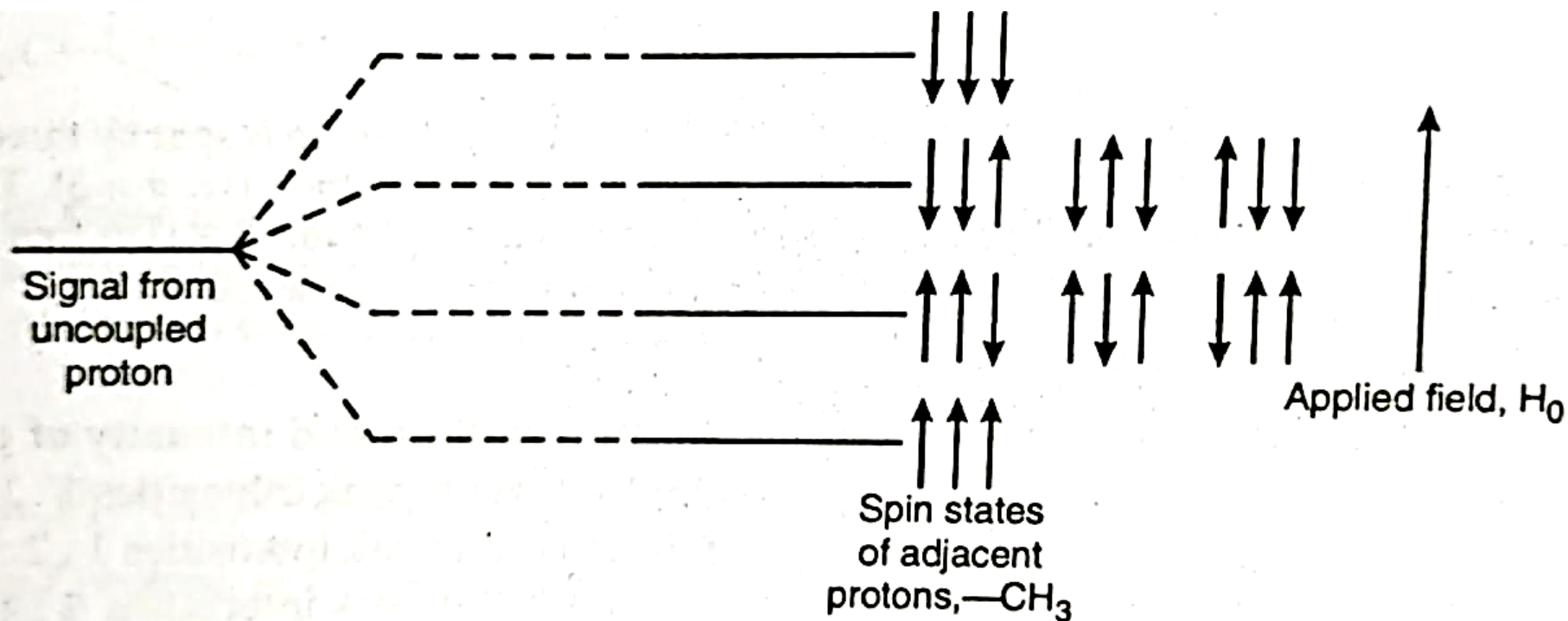
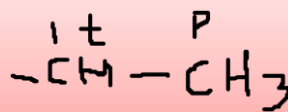
1. 3^0 & 2^0 protons



Splitting of signals(Spin - Spin Coupling) contd

Examples:-

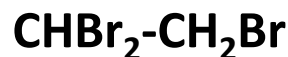
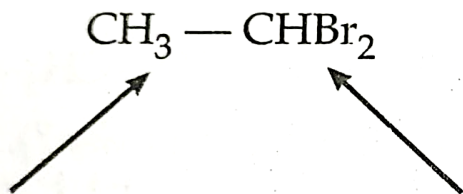
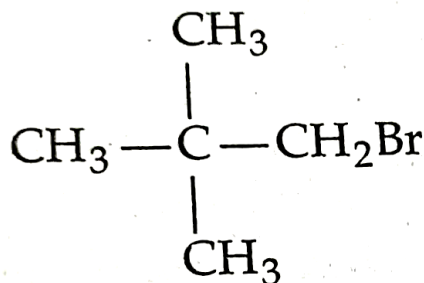
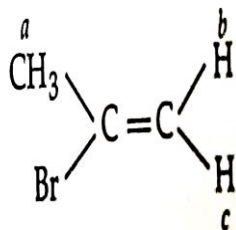
2. 3^0 & 1^0 protons



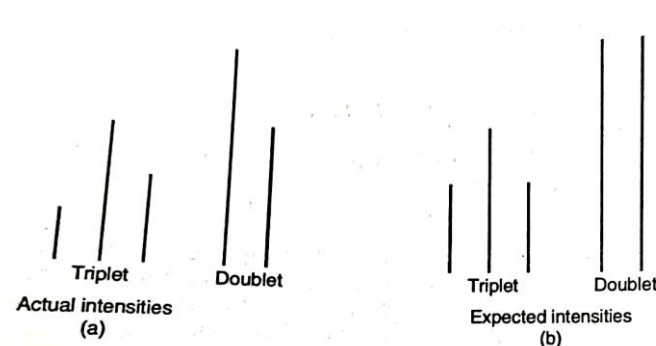
Splitting of signals(Spin-Spin Coupling) contd.

RULES FOR SPLITTING:-

1. Only vicinal non equivalent protons cause splitting
2. Geminal protons if non equivalent also cause splitting
3. Protons separated by more than two atoms do not cause splitting
4. $N = n+1$
5. Peak area ratios
6. Inner peaks of a multiplet are larger than the outer peaks



Peak area ratio	Signal
1	Singlet
1 : 1	Doublet
1 : 2 : 1	Triplet
1 : 3 : 3 : 1	Quartet
1 : 4 : 6 : 4 : 1	Quintet
1 : 5 : 10 : 10 : 5 : 1	Sextet



COUPLING CONSTANT

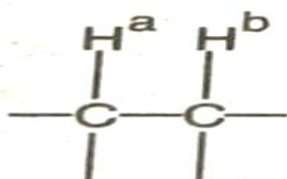
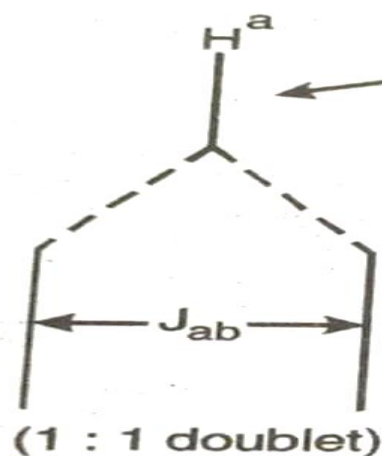
Distance between the centres of two adjacent peaks of a Multiplet.

Denoted by J

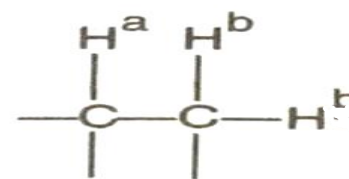
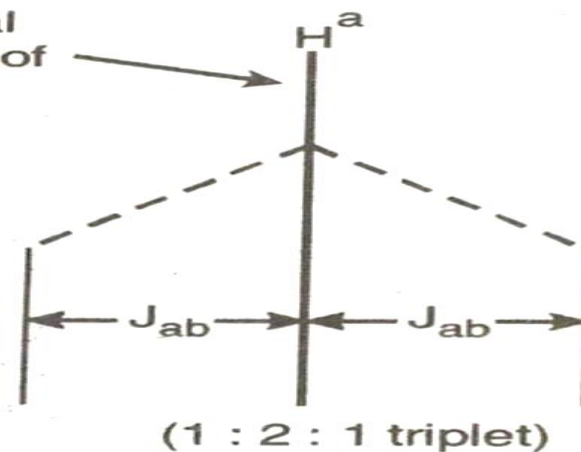
Expressed in Hz.

FEATURES:-

1. Value is constant and independent of external field
2. Value depends upon the number of covalent bonds through which protons interact
3. Value also depends upon the structural relationship between the coupled protons



Expected signal
in the absence of
 H^b



COUPLING CONSTANT contd.

TYPES:-

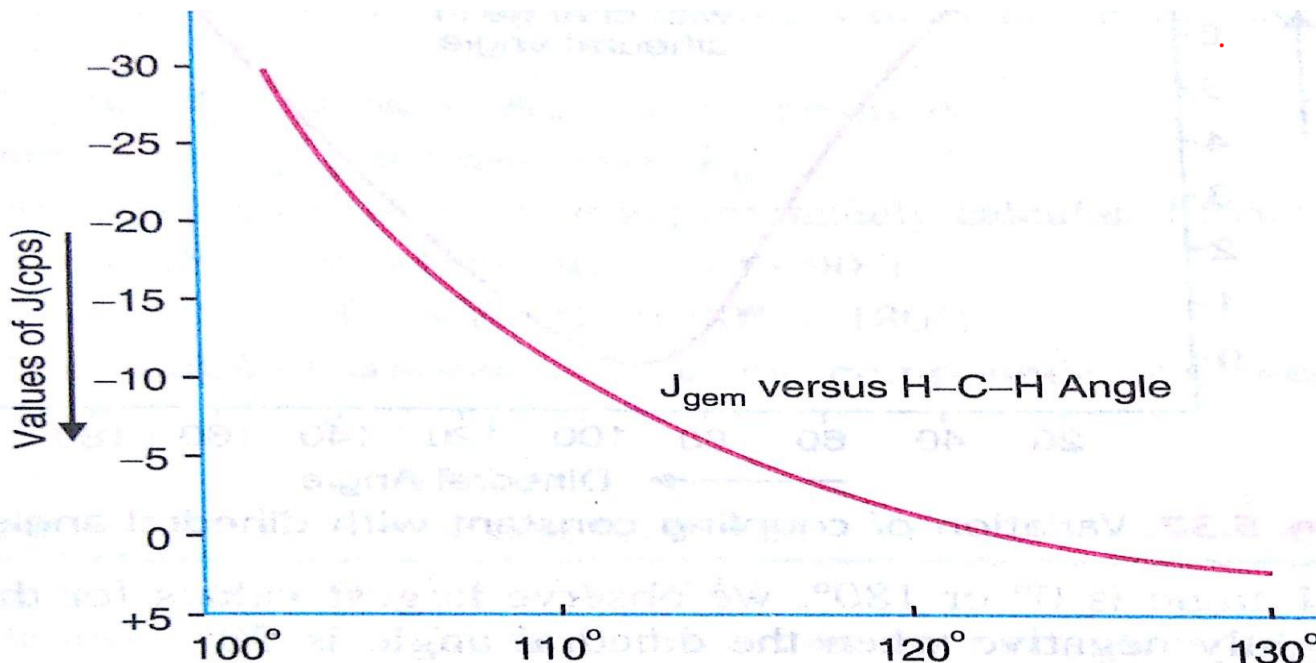
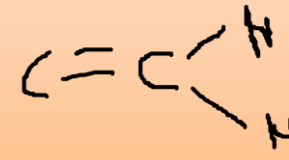
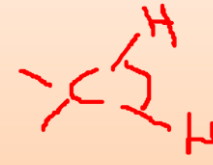
1. Geminal Coupling (J depends upon bond angle)

a) Value increases with bond angle

CH_4 (-12.4 Hz) Ethene(+2.5 Hz)

b) Value increases with increase in electronegativity

CH_3F (-9.4 Hz), CH_3Cl (-10.8 Hz)



COUPLING CONSTANT contd.

TYPES:-

2. Vicinal Coupling

J varies with dihedral bond angle

- a) When dihedral angle is 0° or 180° , J has large value
- b) When dihedral angle is 90° , J has slightly negative value



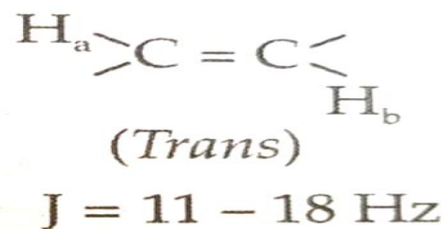
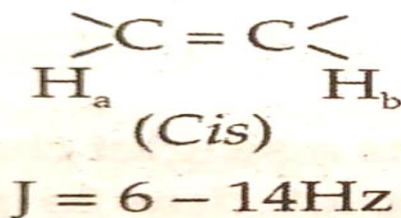
Examples

- 1. Protons in Gauche Conformation $J = 2-4$ Hz & protons in anti conformation $J = 5-12$ Hz



2. Vinylic protons

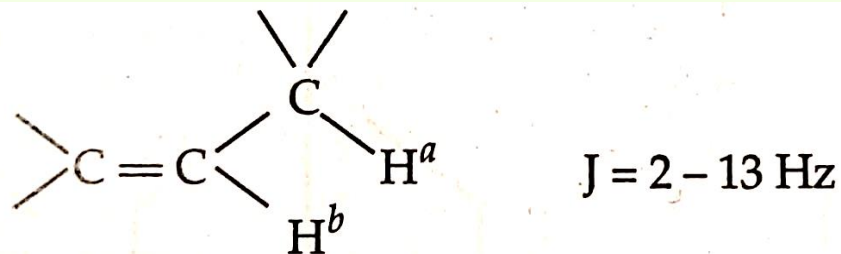
J_{cis} (6-14 Hz) is less than J_{trans} (11-18 Hz)



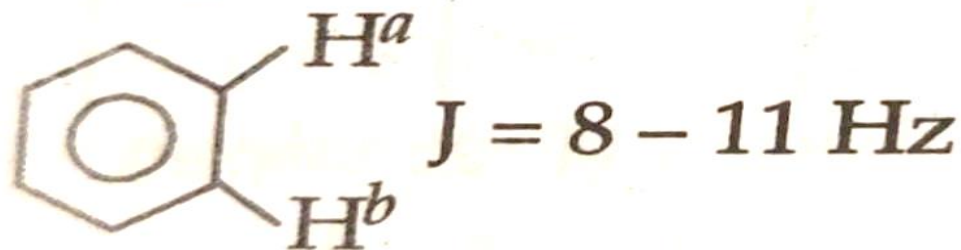
COUPLING CONSTANT contd.

Examples

3. Allylic protons $J = 2-13$ Hz



4. Aromatic protons $J = 8-11$ Hz



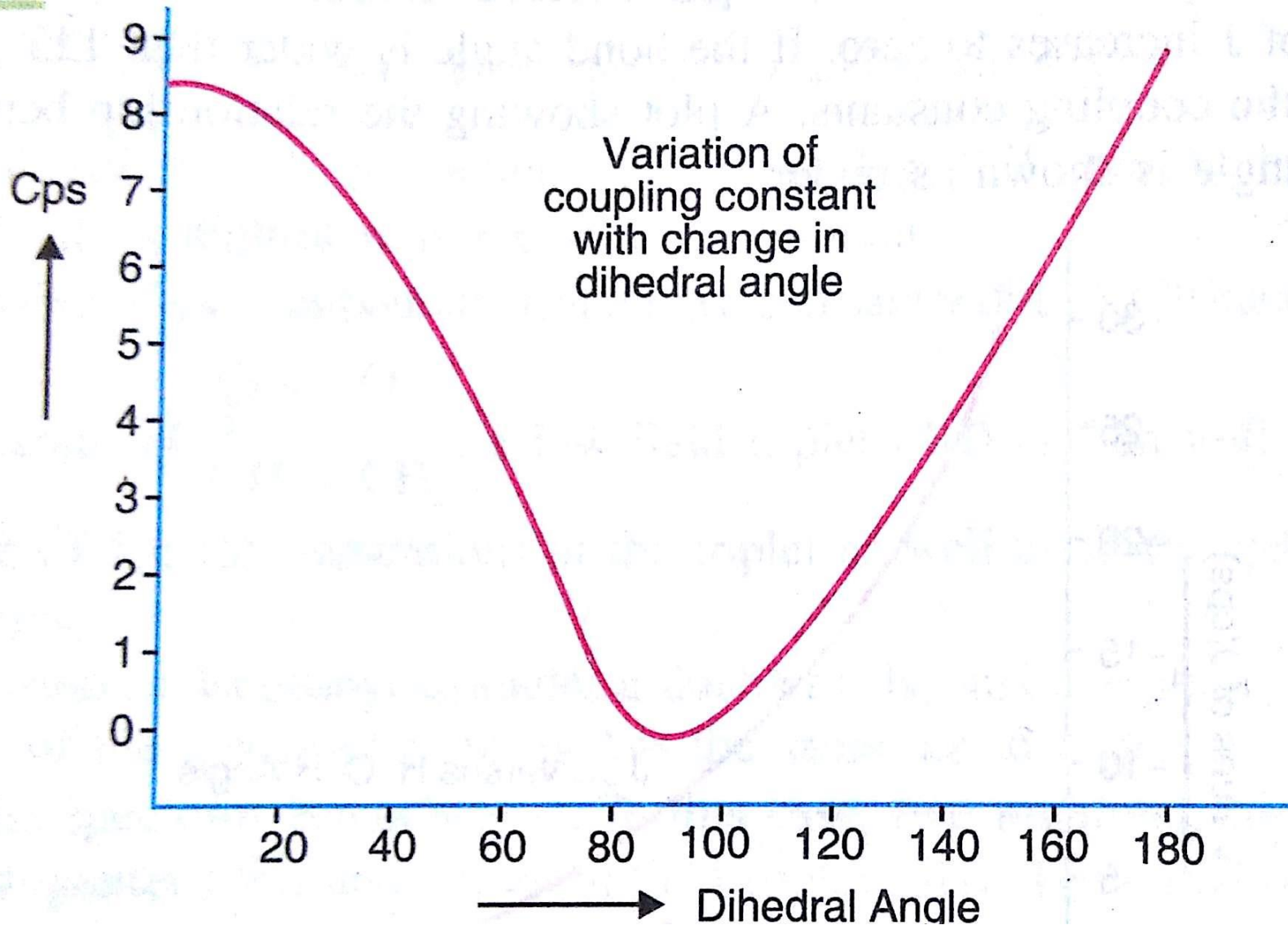
5. We can distinguish equatorial protons and axial protons from J_{vic} values.

axial- axial $J=8$ cps

axial-equatorial $J=2$ cps



COUPLING CONSTANT contd.



MAGNETIC EQUIVALENCE OF PROTONS

Due to rapid changes in the molecule

(i.e. rotation about C-C bond or proton exchange)

It is not possible to distinguish between non equivalent protons. Then protons become Magnetically equivalent.

SPOKES OF A WHEEL , FAN

Examples

A) Conformational Changes

1. Ethyl bromide

(Anti & Gauche protons can not be distinguished)

2. Cyclohexane

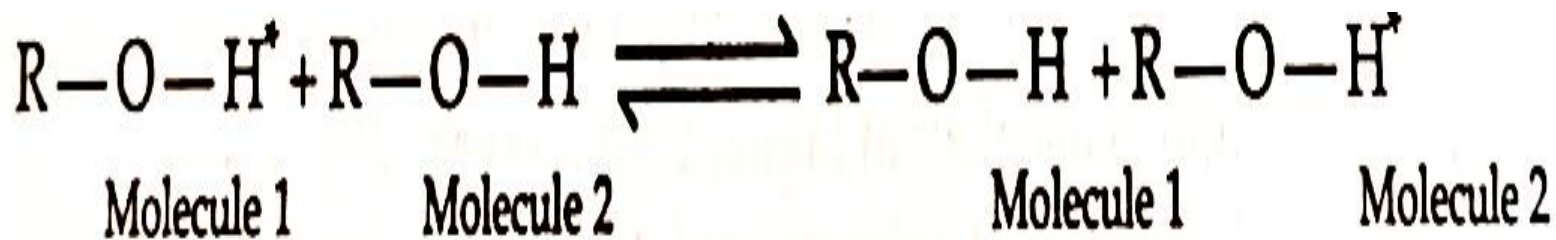
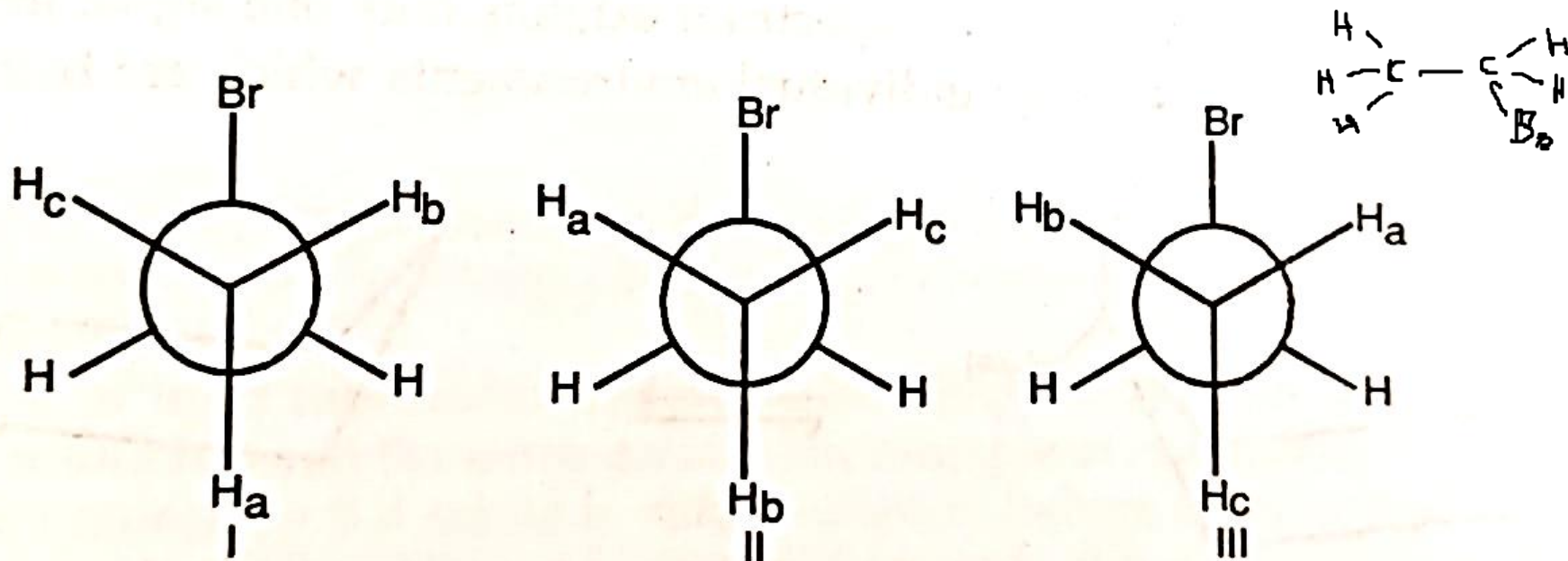
(Equatorial & axial protons can not be distinguished)

B) Proton exchange processes

1. In ultra pure ethanol(anhydrous)

2. In alcohols(in presence of little water)

MAGNETIC EQUIVALENCE OF PROTONS contd.



MAGNETIC EQUIVALENCE OF PROTONS contd.

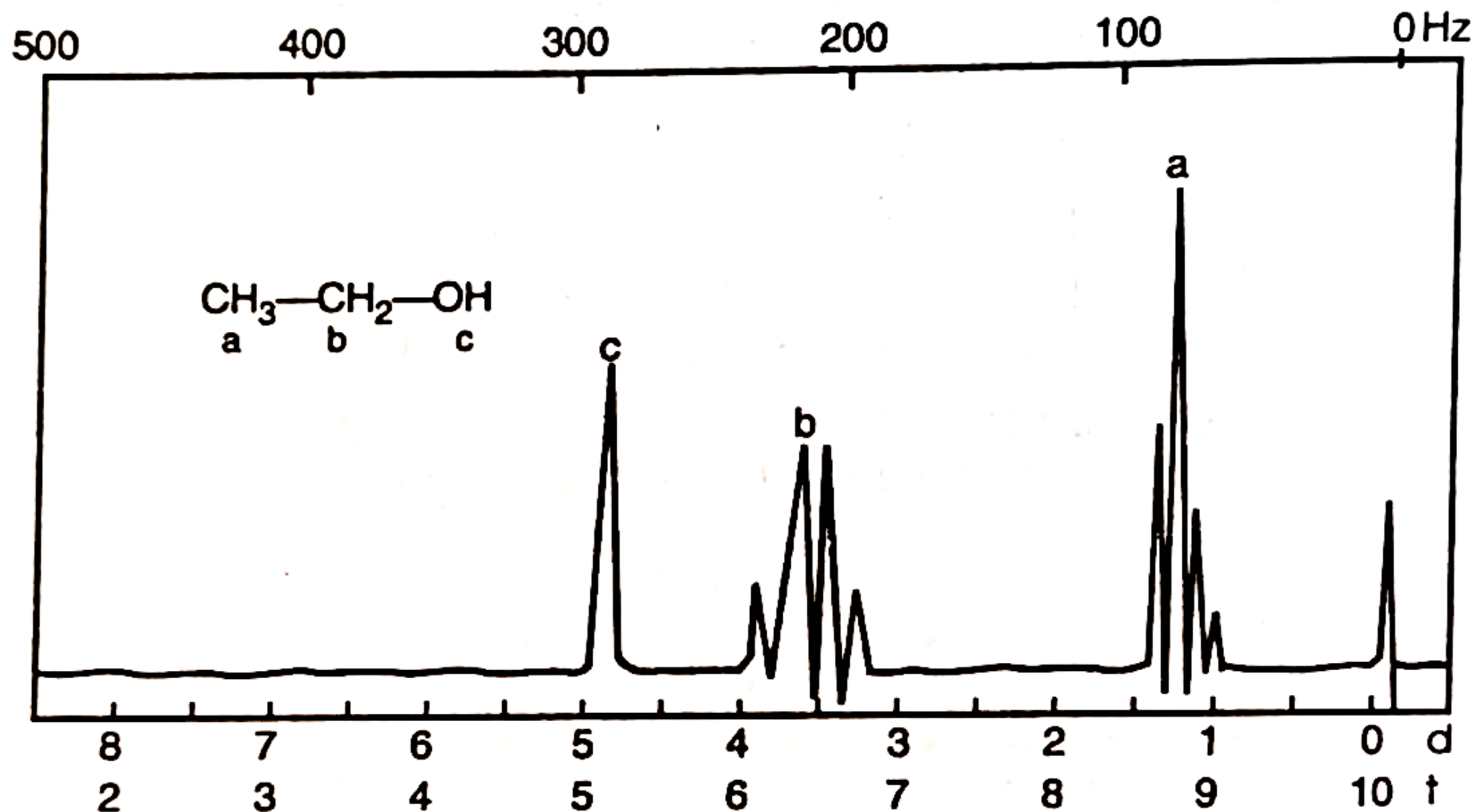
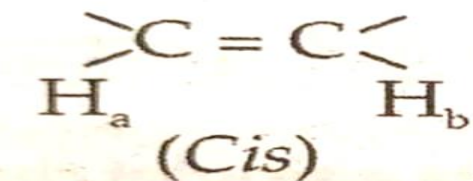


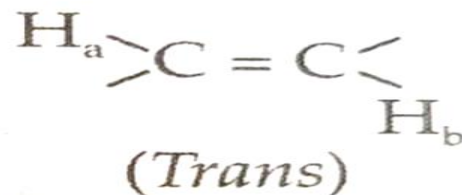
Fig. 6.15. PMR spectrum of an ordinary sample of ethanol.

APPLICATIONS OF NMR SPECTROSCOPY

1. Distinction between geometrical isomers (from J_{vic} values)



$$J = 6 - 14 \text{ Hz}$$

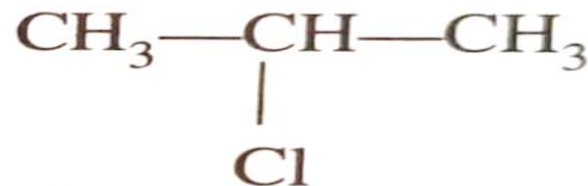


$$J = 11 - 18 \text{ Hz}$$

2. Identification of structural isomers



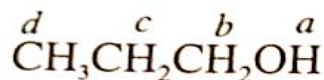
(a)



(b)

APPLICATIONS OF NMR SPECTROSCOPY contd.

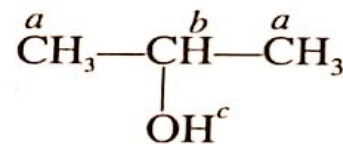
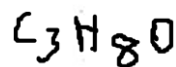
3. Identification of structural isomers



Propanol-1

Four signals

- (i) *a*-Singlet (1H)
- (ii) *b*-Triplet (2H)
- (iii) *c*-Sextet (2H)
- (iv) *d*-Triplet (3H)



Propanol-2

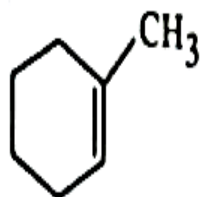
Three signals

- (i) *a*-doublet (6H)
- (ii) *b*-Septet (1H)
- (iii) *c*-Singlet (1H)

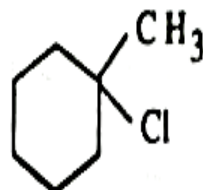
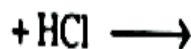
Tau
value
increases

Tau
value
decreases

4. Identification of reaction products

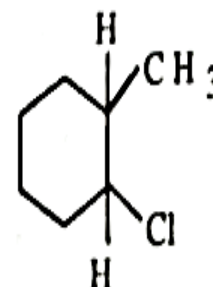


1-Methylcyclohexene



1-Chloro-1-methylcyclohexane

or



1-Chloro-2-methylcyclohexane

APPLICATIONS OF NMR SPECTROSCOPY contd.

5. Detection & Extent of Hydrogen bonding

H-bonded proton gives nmr signal downfield i.e. negative tau values. In highly concentrated solution, proton of $-OH$ group gives signal at -4 to -5 tau. Greater is the degree of hydrogen bonding, greater is the downfield shift.

6. Distinction between intra & intermolecular H-Bonding

Intermolecular and intramolecular H-bonding can be distinguished. Downfield shift decreases with dilution in case of intermolecular H-bonding.

In intramolecular H-bonding, the shift does not depend upon concentration.

7. Detection of proton exchange reactions

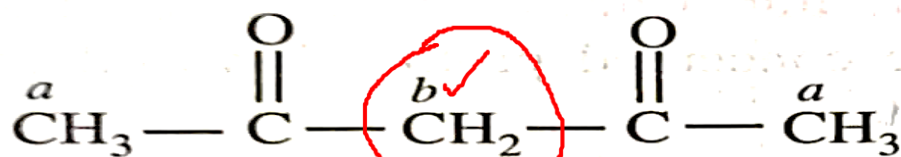
With the help of nmr studies, we can predict whether proton exchange is taking place between the molecules of alcohol and amines.

APPLICATIONS OF NMR SPECTROSCOPY contd.

8. Identification of compounds

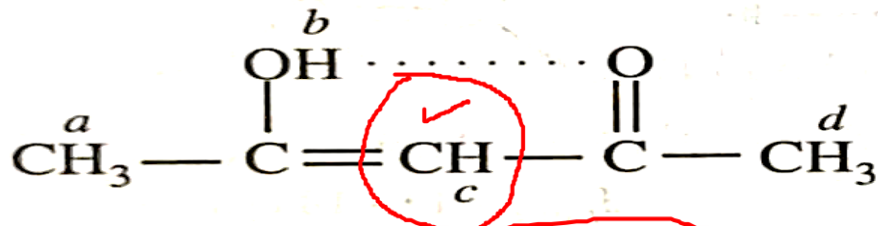
The unknown compound can be identified by comparing its nmr spectrum with that of known compound

9. Determination of relative amounts of tautomers



Ketonic

$$a = 7.86\tau \quad [\text{ketonic}]$$
$$b = 6.35\tau$$



$$a = 8.03\tau$$
$$b = -4.3\tau$$
$$c = 4.4\tau$$
$$d = 7.87\tau$$

[enolic]

$$\frac{2}{1} \times \frac{\text{No of mol keto}}{\text{No of mol enolic}} = \frac{\text{intensity of } \text{CH}_2}{\text{intensity of } =\text{CH}} = \frac{1}{2}$$
$$= \frac{1}{2} \times \frac{1}{2} = \frac{1}{4} \checkmark$$

INTERPRETATION OF NMR SPECTRA

1. Number of signals

Kinds of protons

2. Position of signals(Chemical shift)

Electronic environment

3. Intensity of signals(Area)

Relative number of protons of different kinds

4. Splitting of signals

Number of protons on adjacent carbons

TIPS FOR INTERPRETATION OF NMR SPECTRA

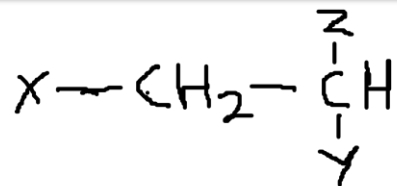
All trends in tau values

1. **Methyl > Methylene > Methyne**
2. If electronegative atom is attached to C atom
Then higher is electronegativity lower is tau value
3. **Type of carbon holding proton**
 $SP^3 > SP^2 > SP$
4. **For aromatic protons**
 $\tau =$ always lower than 4 (1.5 to 4)
5. **Aldehydic proton**
 $\tau = 1.0$ or lower
6. **Proton of acid group**
 $\tau = -0.5$ to -2.0
7. **Acetylenic proton**
 $\tau = 7$ to 8
8. **Vinylic proton** $\tau = 4.4$ to 5.6
9. **Hydroxyl proton** $\tau = 4.5$ to 9

TIPS FOR INTERPRETATION OF NMR SPECTRA

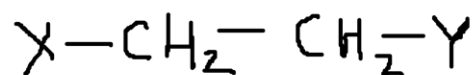
If nmr spectrum contains one doublet & one triplet

What does it represent?



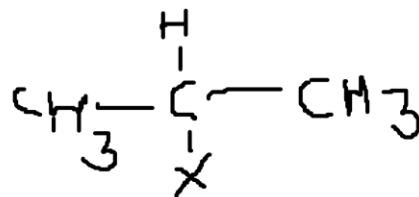
If nmr spectrum contains two triplets

What does it represent?



If nmr spectrum contains a septet & a doublet

What does it represent?



Limitations OF NMR SPECTROSCOPY

- 1. NMR spectra are complicated & difficult to interpret**
- 2. We have to prepare solution of compound**
- 3. Sensitivity is low**
- 4. It does not tell about molecular mass.
Tells only about relative number of protons**

Solved questions

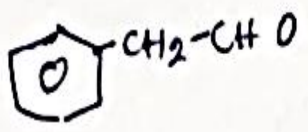
1. A compound with molecular formula C_8H_8O gives the following PMR spectrum
(i) Multiplet τ 2.72, 5H (ii) Doublet τ 7.2, 2H (iii) Triplet τ 0.22, 1H
Give structural formula of the compound.

⇒ Three nmr signals indicates three sets of equivalent protons

(i) Five proton multiplet at 2.72τ is due to benzene ring
i.e. C_6H_5

(ii) Two proton doublet and one proton-triplet shows that
there is $-CH_2-CH-$ fragment in the molecule.

(iii) A signal at very low field i.e. 0.22τ shows the presence of
 $-CHO$ gp.

So the structure of the compound should be 

Solved questions

2. A compound with molecular formula $C_6H_{12}O_2$ shows four signals

(i) Singlet 8.9 τ , 6H (ii) Singlet 7.9 τ , 3H (iii) singlet 7.4 τ , 2H

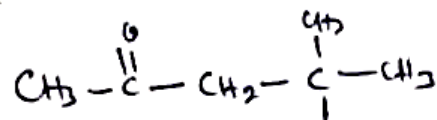
(iv) singlet 6.1 τ 1H. Propose structure for the compound.

\Rightarrow In this compound, all the four signals are singlets. It means there is no splitting and there are no vicinal ^{non equivalent} protons.

(i) 6H signal at high field 8.9 τ must be due to $\begin{array}{c} \text{CH}_3 \\ | \\ \text{C} \\ | \\ \text{CH}_3 \end{array}$ sp.

(ii) 3H signal at 7.9 τ must be due to $-\text{CH}_3$ sp which may be attached to >C=O sp. So the expected unit is $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-$

(iii) 2H singlet at 7.4 τ must be due to $-\text{CH}_2-$ sp. Since there is no splitting so $-\text{CH}_2-$ must be between above two units i.e.



(iv) 1H singlet at low field i.e. ~~6.1~~ 6.1 τ must be due to H attached to oxygen.

From above points it is clear that the compound is $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{OH}}{|}{\text{C}}}-\text{CH}_3$

Solved questions

3. A compound with molecular formula $C_9H_{11}Br$ shows following signals in PMR data

(i) Multiplet 7.75 τ (2H) (ii) Triplet 7.25 τ (2H) (iii) Triplet 6.62 τ (2H)

(iv) Singlet 2.78 τ (5H).

Assign structure of the compound giving reasons

⇒ Since compound is highly unsaturated and there is ^{5H} Singlet at 2.78 τ so
the compound must contain a benzene ring

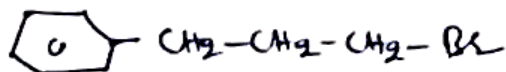
2H multiplet must be due to $-CH_2-\overset{*}{CH_2}-CH_2-$ linkage, ~~proton~~

Protons on starred carbon are under the influence of four protons on vicinal carbons so signal is splitted into a quartet which is indicated as multiplet in the data.

2H triplet at 6.62 τ (downfield) must be due to $-CH_2$ group attached to Br.

2H triplet at 7.25 τ must be due to $-CH_2$ sp. attached to benzene ring

So the expected structure of compound is



Solved questions

4. Predict the structure of an organic compound with molecular mass 88 whose PMR data is given below

(i) Triplet 8.77 τ (3H) (ii) Singlet 8.03 τ (3H) (iii) Quartet 5.94 τ (2H)

\Rightarrow formation of ^3H triplet at 8.77 τ and ^2H quartet at 5.94 τ shows that the molecule contains $\text{CH}_3\text{-CH}_2\text{-}$ as part of structure.

Three proton singlet at upfield shows -CH_3 sp.

Now all the hydrogens have been accounted for and the molecular mass of the above two units is $29 + 15 = 44$

2H quartet is downfield so $\text{-CH}_2\text{-}$ of $\text{CH}_3\text{-CH}_2\text{-}$ must be attached to some electronegative atom like oxygen.

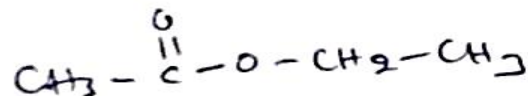
If we take 'O' then molecular mass accounted for becomes

$$44 + 16 = 60$$

The remain molecular mass i.e. $88 - 60 = 28$ must be due to

>C=O sp

Hence most probably the structure of the compound must be



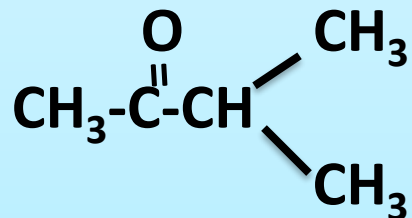
Questions

1. Arrange in the increasing order of shielding of protons $(\text{CH}_3)_3\text{N}$, CH_3CH_3 , CH_3F , CH_3OCH_3
2. Explain why the different protons of a molecule $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ donot give signal at the same position
3. Indicate what PMR would you expect for
A) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ B) 1,2,2-Trichloropropane
4. A compound having molecular formula C_9H_{12} gave following PMR data
a) δ 1.25(6H,d) b) δ 2.8(1H,m) c) δ 7.2(5H,s)
Assign structure to the compound
5. A compound having molecular formula $\text{C}_3\text{H}_3\text{Cl}_5$ gave following PMR data
a) A triplet at δ 5.48(1H) b) A doublet at δ 3.93(2H)
Assign structure to the compound
6. How will you distinguish inter and intramolecular hydrogen bonding on the basis of PMR spectroscopy?

Questions

7. A compound having molecular formula C_7H_8 gave following PMR data
a) A singlet at δ 2.32(3H) b) A singlet at δ 7.2(5H)
Assign structure to the compound

8. Predict number of signals and the splitting pattern of each signal



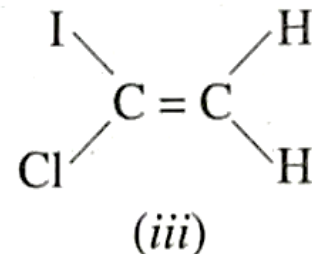
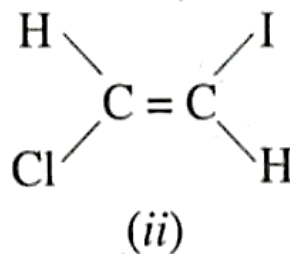
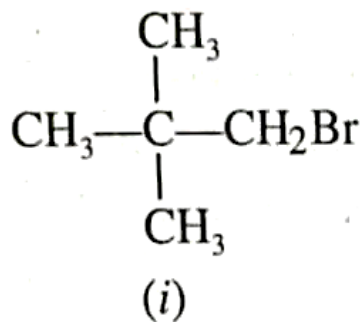
9. Predict the structural formula for the compounds with the following formulae showing only one signal
a) C_8H_{18} b) C_2H_6O c) C_5H_{12}

Questions

Predict the number of signals in PMR spectroscopy of each of the following :

- (i) 1, 1-Dimethyl cyclopropane (ii) cis-1, 2-Dimethyl cyclopropane
(iii) trans-1, 2-Dimethyl cyclopropane (iv) 1, 2-Dichloropropane.

What will be the multiplicity of each kind of proton in the following molecules.



Calculate the chemical shift in ppm (δ) for a proton that has resonance at 126 Hz downfield from TMS on spectrophotometer that operates at 60 MHz.