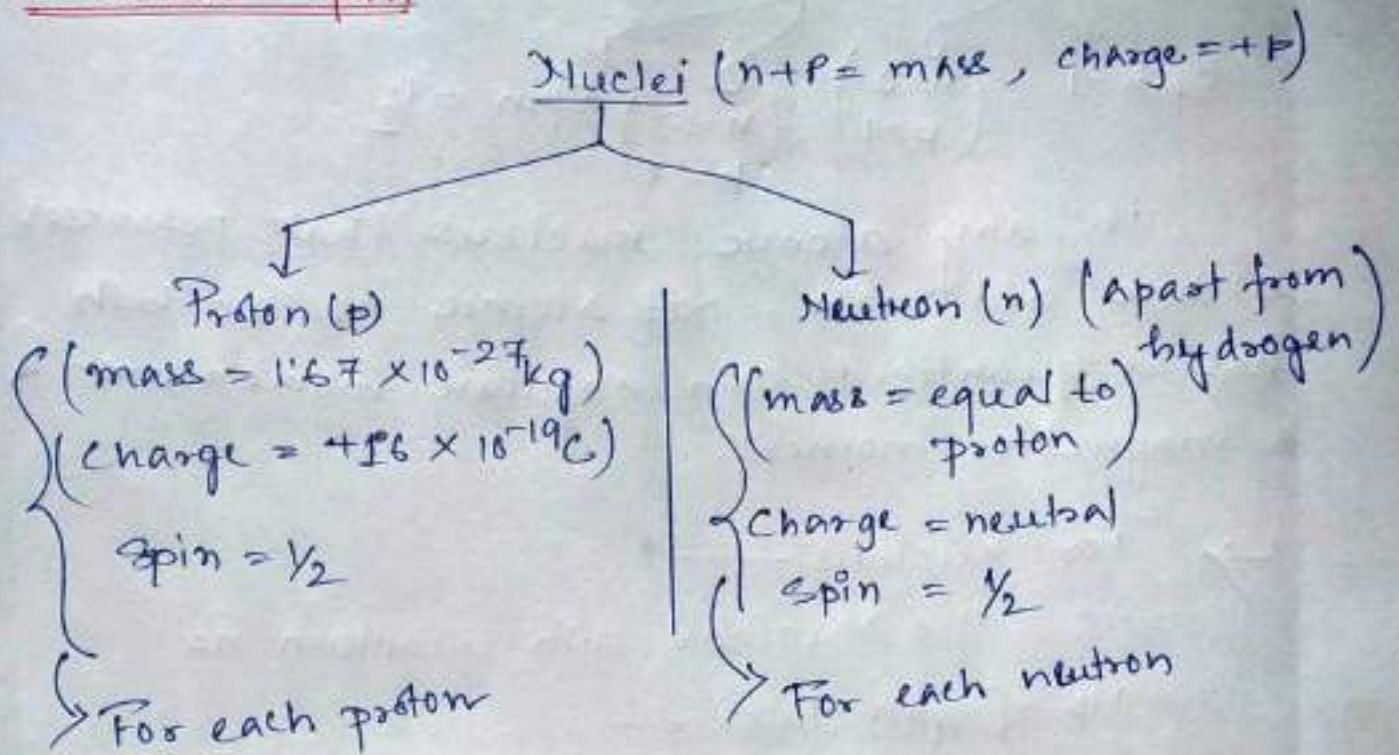


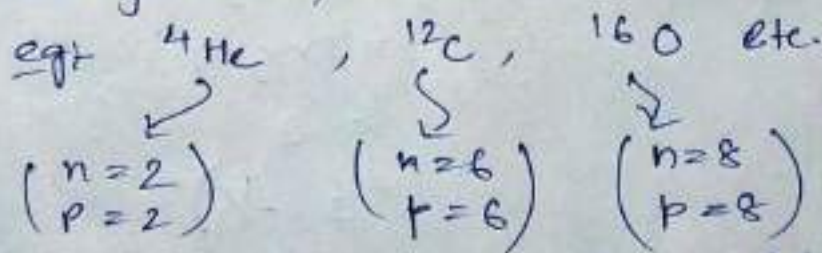
SPIN RESONANCE SPECTROSCOPY

Nuclear spin

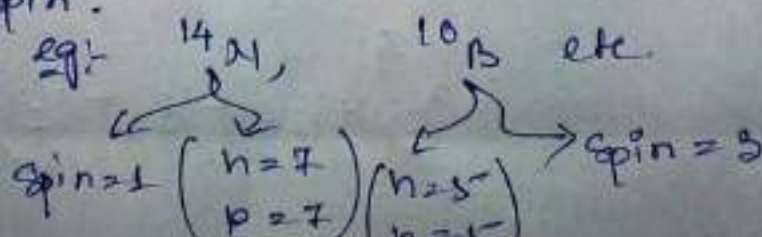


↳ Therefore, spin of nuclei, $I = \text{Total spin of } p + \text{Total spin of } n$

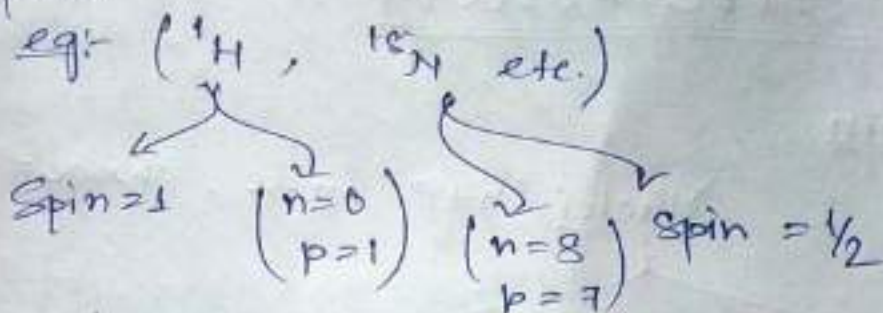
↳ i) Nuclei with both p & n even (both mass & charge even) have zero spin.



ii) Nuclei with both p & n odd (charge = odd & mass = $n+p = \text{even}$) have integral spin.



iii) Nuclei with odd mass have half-integral spins.



i.e., any atomic nucleus that possesses either odd mass, odd atomic no. or both has a quantized spin angular momentum & a magnetic moment.

→ For nucleus —

I = Nuclear spin quantum no.

∴ No. of spin states —
= $2I + 1$

∴ Allowed spin states —
 $+I, (I-1), \dots, (-I+1), -I$

eg: i) $I = 1/2$

No. of spin states = $2I + 1$
= $2 \times 1/2 + 1$
= 2
 $(+1/2, -1/2)$

ii) $I = 3/2$

No. of spin states = $2I + 1$
= $2 \times 3/2 + 1$
= 4
 $(+3/2, +1/2, -1/2, -3/2)$

Element	${}^1_1\text{H}$	${}^2_1\text{H}$	${}^{12}_6\text{C}$	${}^{13}_6\text{C}$	${}^{14}_7\text{N}$	${}^{16}_8\text{O}$	${}^{17}_8\text{O}$
Nuclear spin quantum no. (I)	$\frac{1}{2}$	1	0	$\frac{1}{2}$	1	0	$\frac{5}{2}$
No. of spin states (2I+1)	2	3	1	2	3	1	6

Angular momentum of a nuclei —

$$I = \sqrt{I(I+1)} \left(\frac{h}{2\pi} \right)$$

$$= \sqrt{I(I+1)} \text{ units}$$

(I = spin quantum no. of nuclei)

Along a particular direction \hat{z} —

I have components —

$$I_z = (2I+1) \text{ No.}$$

$$\text{i.e., } I_z = +I, (I-1), \dots, (-I+1), -I$$

Nuclear magnetic moments (Interaction between spin & a magnetic field) $\frac{0}{0}$

↳ In an applied magnetic field, spin states are not of equivalent energy.

Because, nucleus is a charged particle & it spins around its axis. So any moving charged particle generates a magnetic field of its own. Thus nucleus ~~has~~ has a magnetic moment, μ , generated by its charge & spin.

For a nucleus —

$$\mu = \frac{q}{2m} I$$

$$\left[\begin{array}{l} q = \text{charge of nucleus} \\ m = \text{mass of nucleus} \end{array} \right]$$

$$= \frac{q}{2m} \left(\sqrt{I(I+1)} \frac{h}{2\pi} \right)$$

$$\mu = \frac{q h}{4\pi m} \sqrt{I(I+1)} \text{ Am}^2$$

$$\text{or } \mu = \frac{q h}{4\pi m} \left(\sqrt{I(I+1)} \right) \text{ JT}^{-1}$$

Since, nucleus is a point charge —

$$\mu = \frac{g q h}{4\pi m} \left(\sqrt{I(I+1)} \right) \text{ JT}^{-1}$$

g = Nuclear factor.

$\therefore \beta_N = \text{Nuclear magneton}$

$$= \frac{q\hbar}{4m\pi} = 5.05 \times 10^{-27} \text{ J T}^{-1}$$

$$\therefore \mu = g\beta_N \sqrt{I(I+1)} \text{ J T}^{-1}$$

In an applied magnetic field, the spin states of nuclei either align or oppose the applied magnetic field.

eg:- For Proton - (Hydrogen atom)

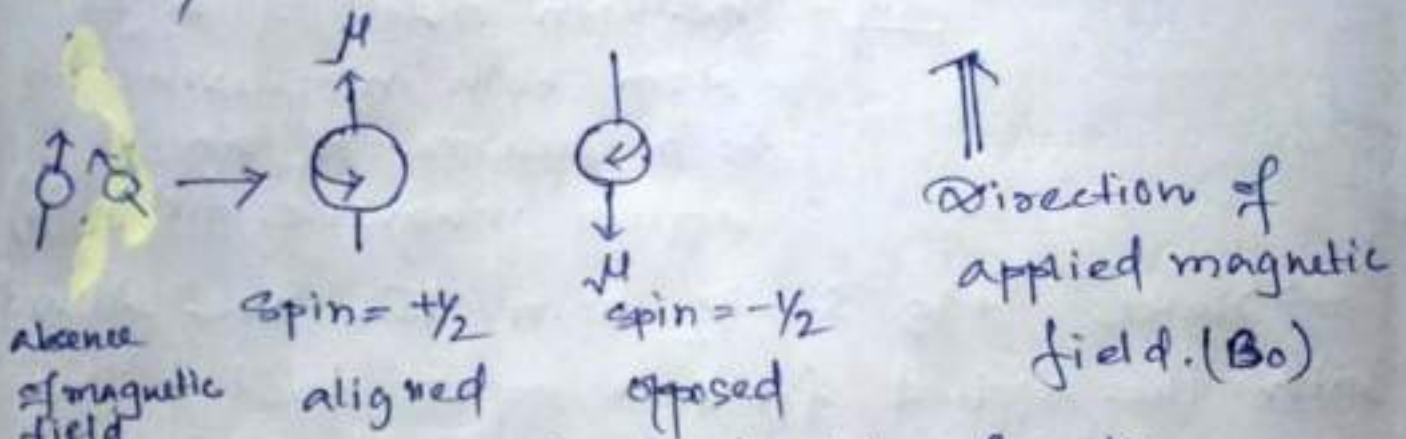


Fig:- The two allowed spin states of proton

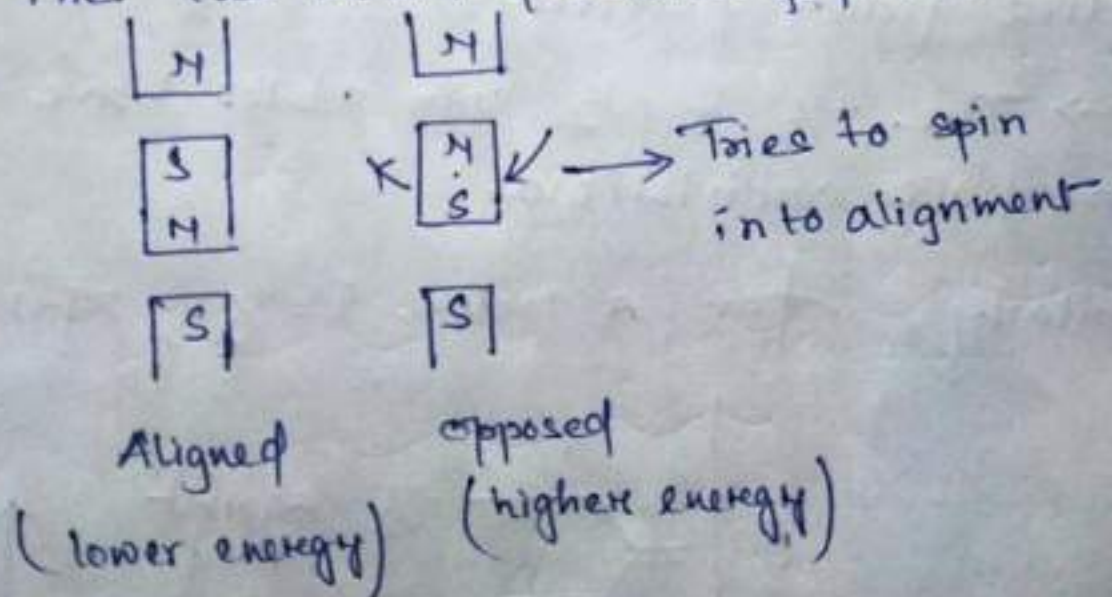


Fig:- Aligned & opposed arrangements of bar magnets.

Hence, in an external magnetic field the degenerate spin states of proton split into two states of unequal energy —

e.g. For ^{35}Cl , $I = 3/2$, $2I+1 = 2 \times 3/2 + 1 = 4$

∴ No. of spin states (or energy levels) = 4

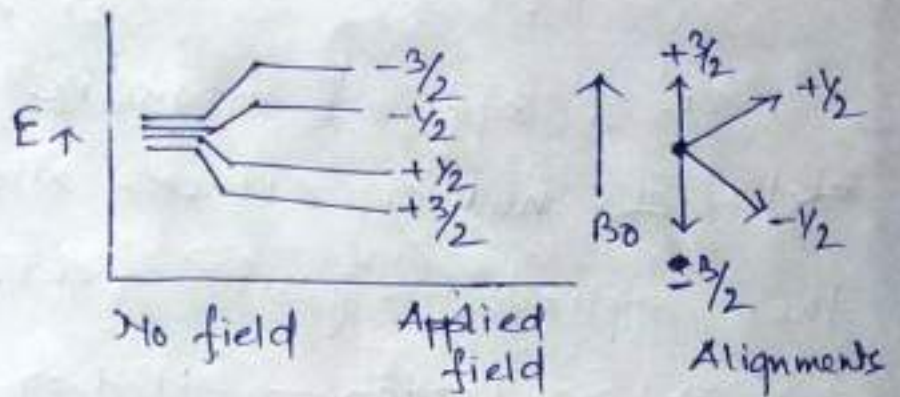
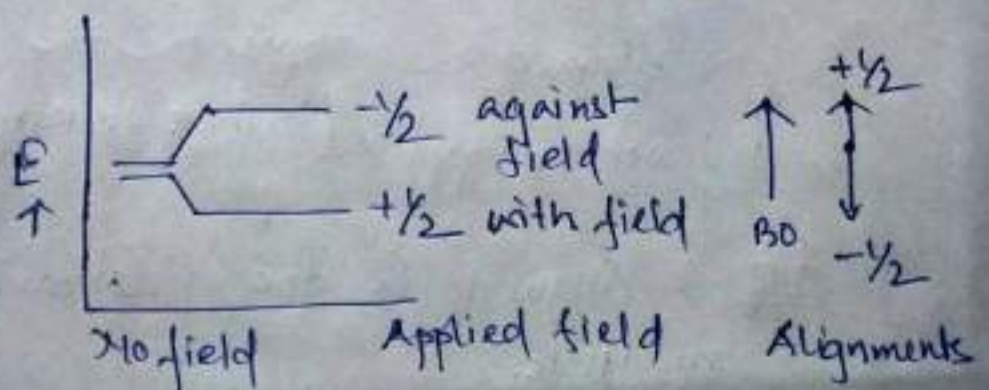


Fig:- The spin states of a Cl-atom both in presence & in absence of an applied magnetic field (B_0)

→ Here, $+3/2$ & $-3/2$ spin states are aligned with the applied field & opposed to the applied field respectively.

→ The $+1/2$ & $-1/2$ spin states have intermediate orientations.

Similarly, for a proton, $I = 1/2$, $2I+1 = 2$



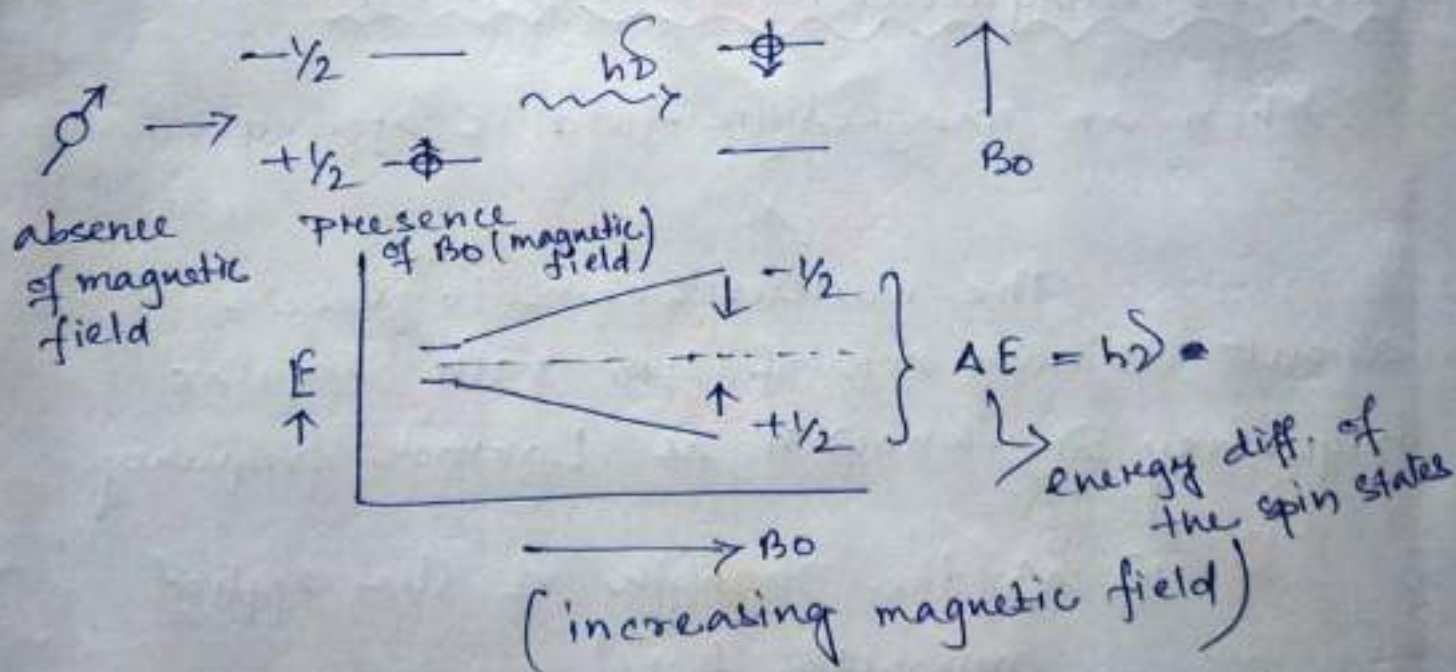
Absorption of energy -

The energy absorption is a quantized process & the energy absorbed must be equal to the energy difference between the two states involved. eg:- For proton —

$$E_{\text{absorbed}} = (E_{-\frac{1}{2} \text{ state}} - E_{+\frac{1}{2} \text{ state}}) = h\nu$$

When nuclei aligned with an applied magnetic field are induced to absorb energy their spin orientation changes with respect to the applied field —

For a hydrogen nucleus —



$$\Delta E = f(B_0)$$

i.e., The stronger the applied magnetic field (B_0) the greater the energy difference

between the possible spin states.

$$\therefore \Delta E = \hbar (\gamma B_0) = h\nu$$

↳ magnetogyric ratio /
gyromagnetic ratio
(const. for each nucleus)

Since angular momentum of nucleus is
quantized in units of $\frac{h}{2\pi}$

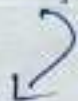
$$\Rightarrow \Delta E = \gamma \left(\frac{h}{2\pi} \right) B_0 = h\nu$$

$$\Rightarrow \nu = \left(\frac{\gamma}{2\pi} \right) B_0$$

↳ frequency of the absorbed
energy.

Nuclear magnetic resonance (NMR)

When an magnetic field is applied



The nucleus begins to precess
about its own axis of spin with angular
frequency ω , known as Larmor frequency.

ω is (the strength of the applied
magnetic field)

eg:- For Proton —

$$\text{If } B_0 = 1.41 \text{ T}$$

$$\text{then, } \omega = 60 \text{ MHz}$$

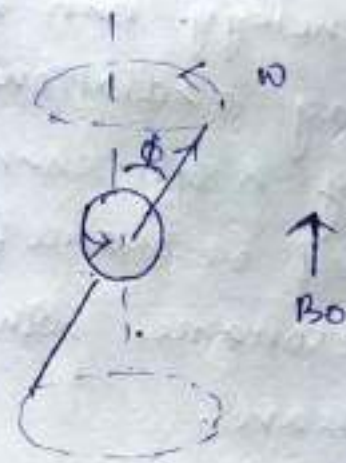


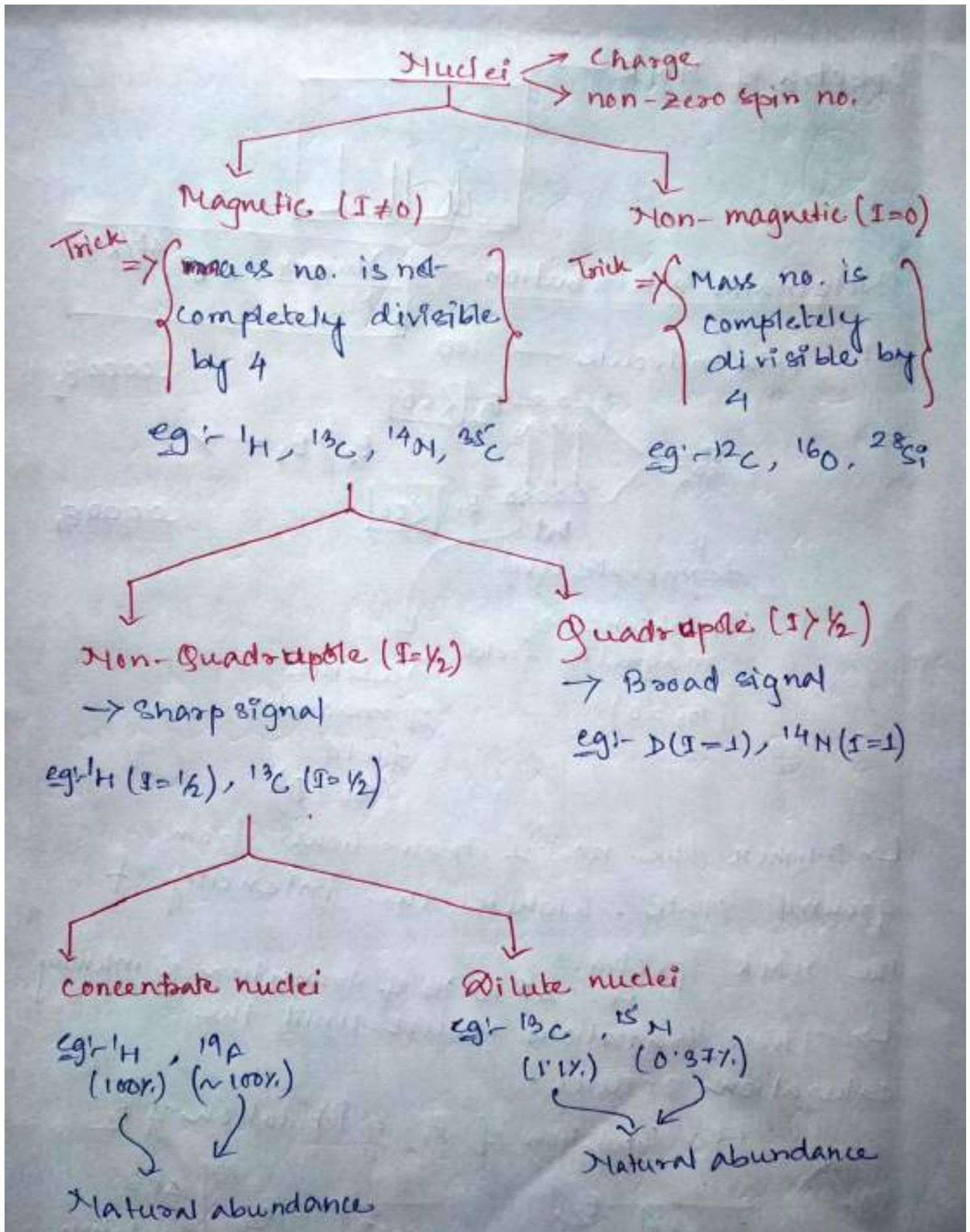
Fig:- The precession of a spinning nucleus resulting from the influence of an applied magnetic field, B_0 .

Since, nucleus has a charge.

do the precession generates an oscillating electric field of ^{same} frequency, ω

If radiofrequency waves of this frequency are supplied to the precessing proton, the energy can be absorbed.

That is when the frequency of the oscillating electric field component of the incoming radiation just matches the frequency ω of the electric field generated by the precessing nucleus, the two fields can



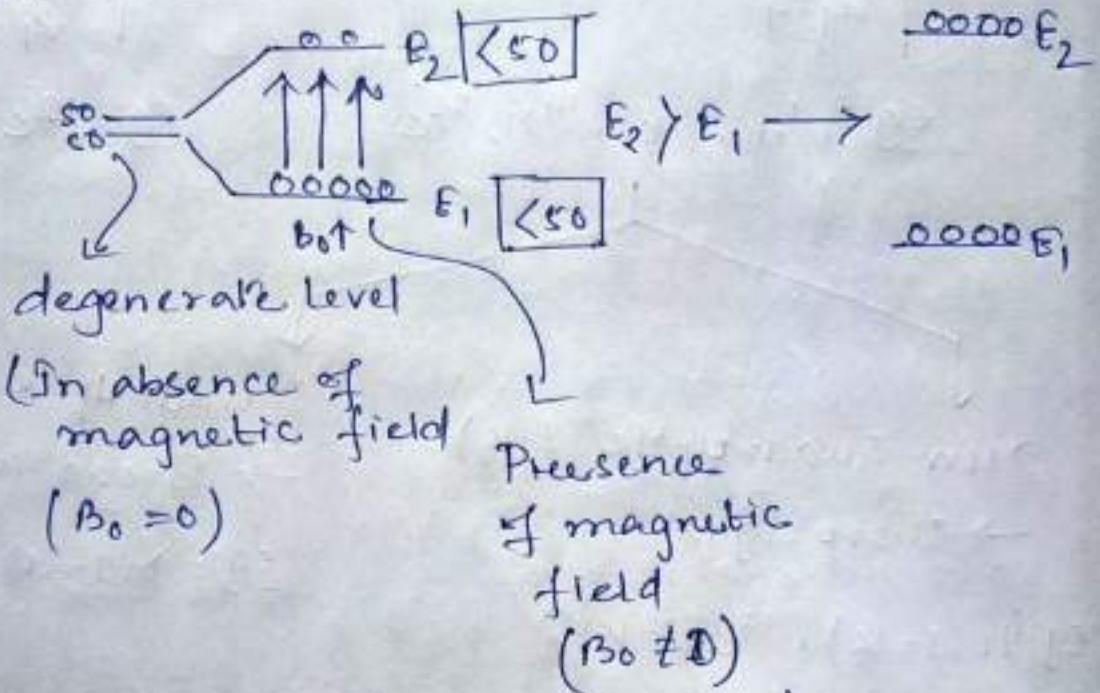
Spectra of NMR —



Boltzmann Distribution

$$\frac{N_{upper}}{N_{lower}} = e^{-\Delta E/KT}$$

Let, Total molecule — 100



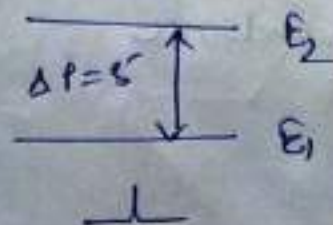
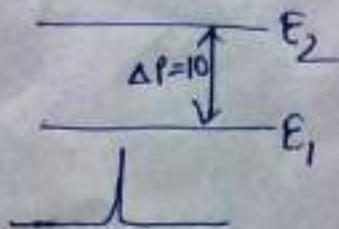
↳ Higher the no. of transitions from ground state, higher the intensity of the NMR spectra.

i.e. $\Delta P \propto$ No. of transition & intensity

↳ These transitions occurs until the saturation occurs —

i.e., Population of $E_1 =$ Population of E_2

eg:-



$\Delta P =$
Population difference.

Sensitivity — Depends on —

① Nuclei

- ↳ Natural abundance
- ↳ gyromagnetic ratio

$$^1\text{H}, \quad \gamma_{\text{H}} = 42.57 \text{ MHz/T}$$

$$^{13}\text{C}, \quad \gamma_{\text{C}} = 10.705 \text{ MHz/T}$$

↳ low natural abundance

② Instrument

$$\nu = 200 \text{ MHz} \quad \nu = 600 \text{ MHz}$$

more sensitive

$$\nu \propto B_0$$

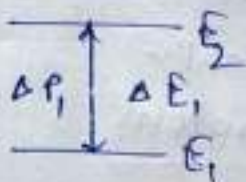
$$\therefore \nu = \frac{\gamma}{2\pi} B_0$$

$$\& B_0 \propto \Delta E$$

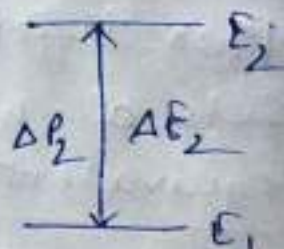
$$\Delta E = h\nu$$

$$\therefore \Delta E \propto \nu$$

$$\& \nu \propto \gamma$$



$$\Delta P_1 < \Delta P_2$$



$$\Delta E_1 < \Delta E_2$$

more sensitive

H-NMR

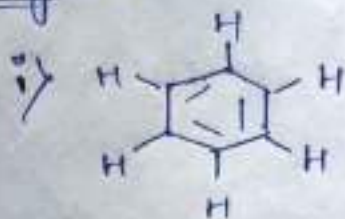
Chemical equivalence —

↳ All the protons found in chemically identical environments within a molecule are chemically equivalent.

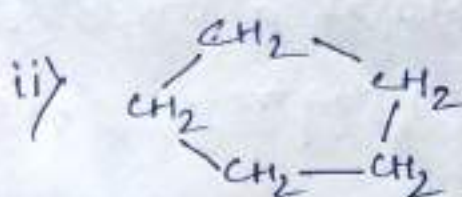
↳ A molecule that has set of protons that

Are chemically distinct from one another
 Are known as chemically non-equivalent.

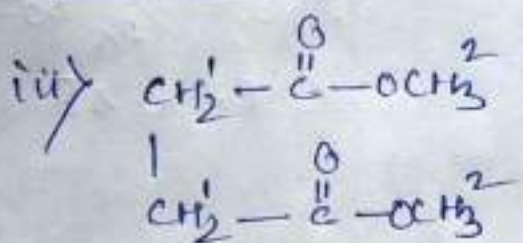
eg:-



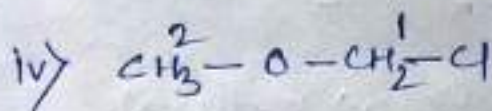
All protons
 are chemically
equivalent



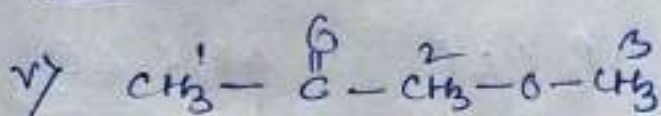
All protons are
chemically equivalent



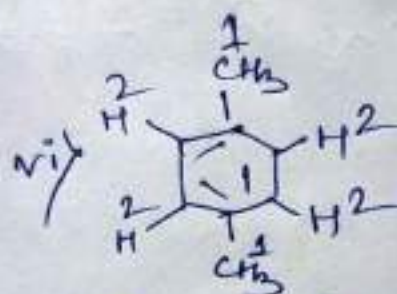
Two different
 sets of chemically
equivalent protons



Two different
 sets of chemically
equivalent protons



Three different
 sets of chemically equivalent
protons



Two different
 sets of chemically
equivalent protons

↳ Chemically equivalent protons show the
 one absorption peak in NMR.

↳ Chemically non-equivalent protons show
 the different absorption peaks in NMR

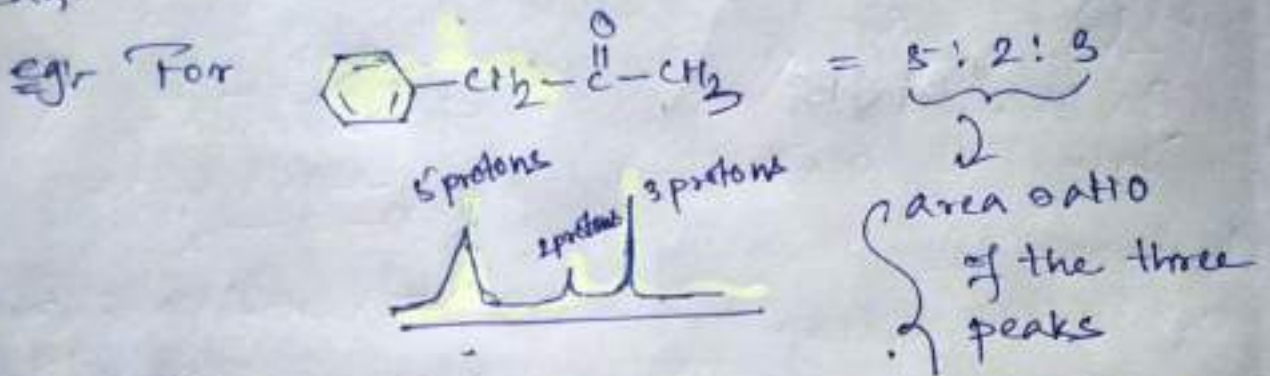
↳ For a molecule —

No. of peaks as No. of ^{different sets of chemically} non-equivalent protons.

∴ NMR spectrum distinguishes how many different types of protons a molecule has.

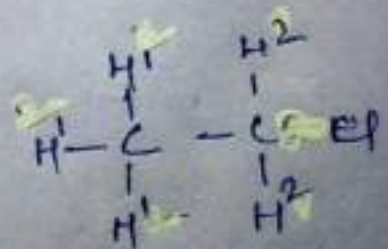
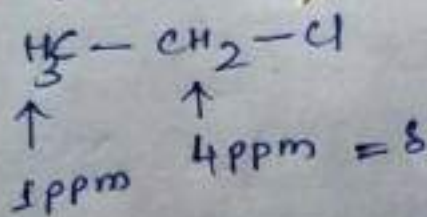
Integrate & integration

↳ The area under the peaks is proportional to the no. of hydrogens generating that peak.



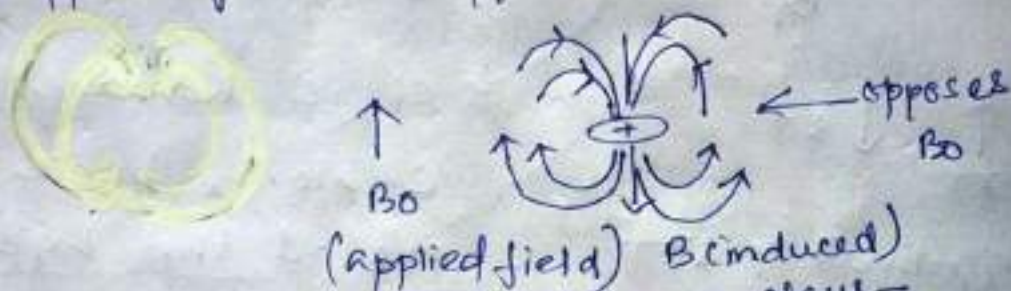
The NMR-spectrometer has the capability to electronically integrate the area under each peak. It does by tracing over each peak a vertically rising line called integral, which rises in height by an amount proportional to the area under the peak.

Chemical shift — (δ)



$\delta = \frac{\delta}{2\pi} B_0$, $\delta \propto B_0$

→ In the presence of an applied magnetic field, the surrounding e^- clouds tend to circulate in such a direction as to produce a field opposing that applied field, B_0



∴ Total field experienced by nucleus -

$$B_{\text{effective}} = B_0 - B_{\text{induced}}$$

Since induced field is directly proportional to B_0 —

$$B_{\text{induced}} \propto B_0$$

$$\Rightarrow B_{\text{induced}} = \sigma B_0$$

↳ const. (shielding const.)

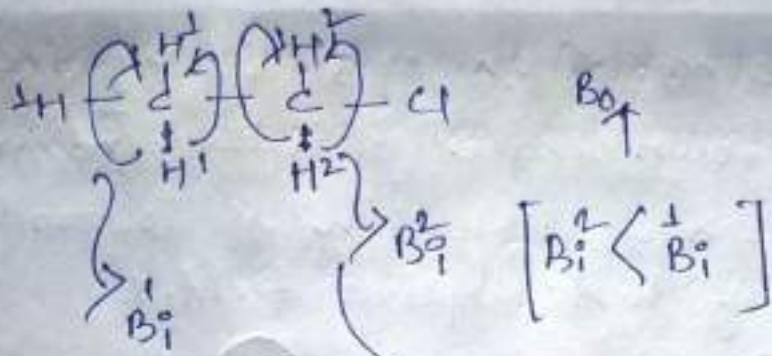
$$\therefore B_{\text{effective}} = B_0(1 - \sigma)$$

Thus the nucleus is shielded from the applied field by diamagnetic electronic circulation.

$$\sigma \propto B_{\text{effective}}$$

$$\left[\begin{array}{l} \sigma = \frac{\delta}{2\pi} B_0 \\ \therefore \sigma \propto B_0 \end{array} \right]$$

↳ is the field experienced by a particular nucleus.



$$\uparrow \quad \downarrow \text{ST}$$

$$\uparrow \text{FT}$$

$$\text{effective} = (7-s)T$$

Cl is electronegative than C-atom, hence e^- density around the hydrogen atom in C-H² bonds should be considerably lower than C-H¹ bonds.

$$\therefore \sigma_{C-H^1} > \sigma_{C-H^2}$$

$$\therefore B_{\text{effective}}(CH^1) < B_{\text{effective}}(C-H^2)$$

Thus, the field experienced by the hydrogen nucleus in C-H² bonds is greater than that of C-H¹ bonds.

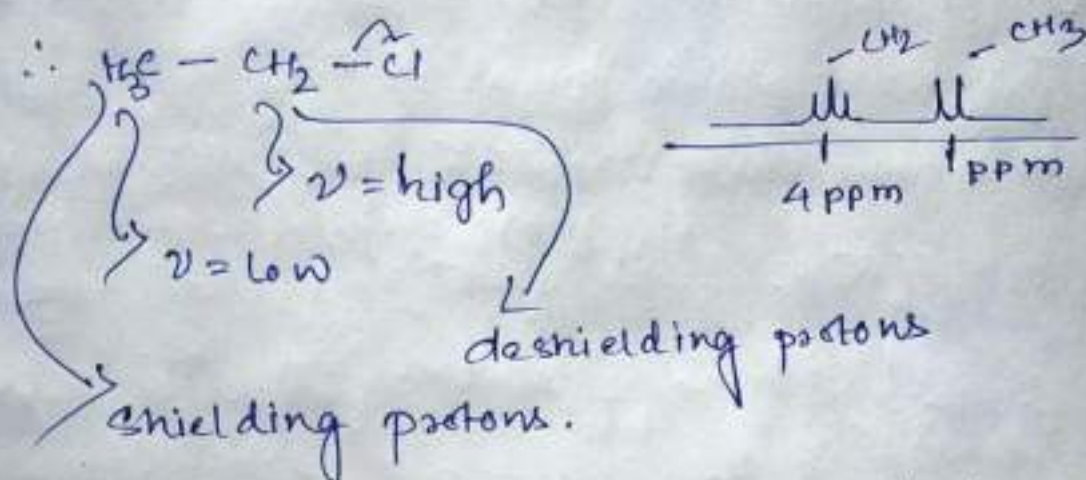
So, In an applied magnetic field, the C-H¹ hydrogen nucleus will precess with a smaller frequency (Larmor frequency) than that of C-H².

Therefore in order to come to resonance with radiation of a particular frequency, a C-H¹ hydrogen requires a

greater field. applied field. Therefore, signal due to these protons will come at upfield region. Since,

$$B_{\text{effective}}(\text{C-H}^1) < B_{\text{effective}}(\text{C-H}^2)$$

$$\nu(\text{C-H}^1) < \nu(\text{C-H}^2) \quad [\because \nu \propto B_{\text{effective}}]$$



↳ Identical nuclei (i.e., H-nuclei) give rise to different absorption positions when in different chemical surroundings. For this reason, the ~~the~~ separation between absorption peak is referred to as chemical shift.

↳ The area of an absorption peak is proportional to the no. of equivalent nuclei (i.e., nuclei with the same chemical shift position) giving rise to the absorption.

The chemical shift & shielding

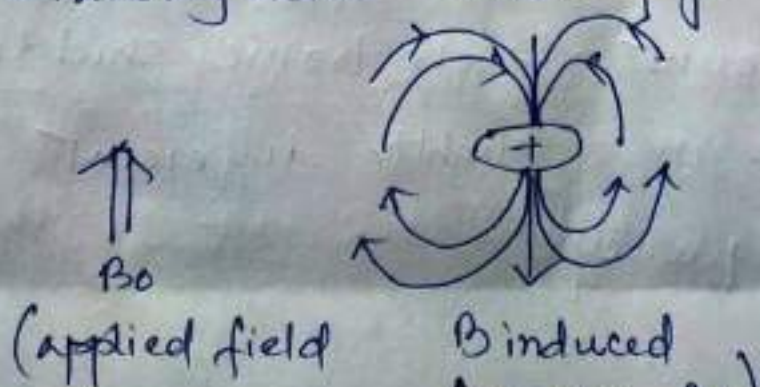
↳ The valence-shell e^- densities vary from proton to another.

↳ The protons in a molecule are surrounded by e^- s & exist in slightly different electronic environments from one another. So, all protons in a molecule ^{do not} have resonance at the same frequency.

↳ The protons are shielded by the e^- that surround them.

↳ In an applied magnetic field, the valence e^- of the protons are caused to circulate & this circulation is called local diamagnetic current, that generates a counter magnetic field which opposes the applied magnetic field.

This effect is called diamagnetic shielding or diamagnetic anisotropy.



↳ Diamagnetic Anisotropy of a nucleus

↳ As a result of diamagnetic anisotropy, each proton in a molecule is shielded from the applied magnetic field to an extent that depends on the e^- density surrounding it.

↳ The greater the e^- density around a ~~nucleus~~ nucleus, the greater the induced counter field that opposes the applied field.

↳ The counter field that induced due to the circulation of e^- s shields a nucleus & diminishes the net applied magnetic field that the nucleus experience.

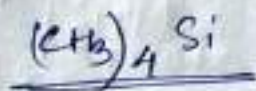
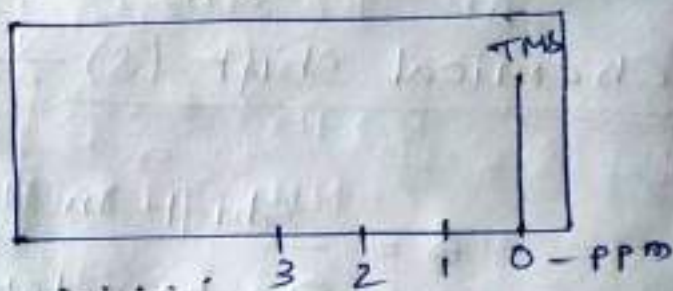
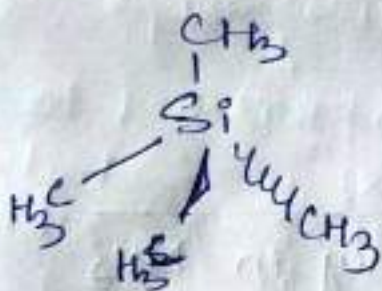
↳ As a result, the nucleus precesses at a lower frequency. This means that it also absorbs lower of radiofrequency radiation at this lower frequency.

↳ Therefore, in a molecule, protons which are in a slightly different chemical environment from each other, have slightly different amount of electronic shielding which results in a slightly different resonance frequency.

The Standard reference substance

↳ A reference compound is placed in the solution of the substance to be measured, & resonance frequency of each proton in the sample is measured relative to the δ resonance frequency of the protons of the reference substance.

↳ TMS (Tetramethyl silane) is used as a reference in ^1H & ^{13}C -NMR.



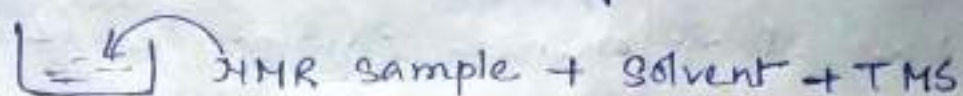
* Internal standard → Does not react with sample, eg:- TMS

* External " → React with sample
eg:- H₃PO₄, used in ^{31}P -NMR.

Advantages of TMS over other substances

↳ 1) Volatile, b.p. = 27°C

So, sample can be easily recovered.

 NMR sample + solvent + TMS

ii) All the 12 protons are chemically equivalent & more shielded than those of most other known compounds. Shows $\delta = 0$ ppm, & gives very sharp peak, so easily distinguishable from other peaks.

iii) Chemically inert, & does not react with the sample.

Chemical shift (δ) —

$$\delta = \frac{\text{Shift in Hz}}{\text{Spectrometer frequency in MHz}}$$

Chemical shift in δ units express the amount by which a proton resonance is shifted from TMS in parts per million (ppm) of the spectrometer's basic operating frequency.

eg:- δ for a proton —

If at 60 MHz, the shift of the

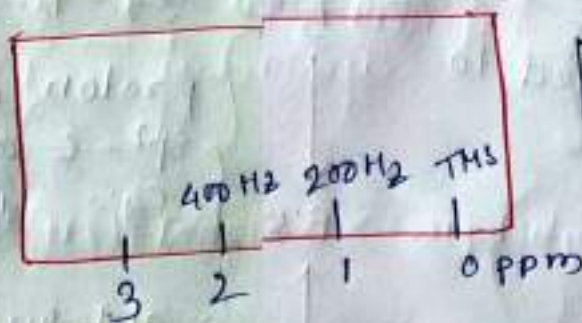
is 162 Hz from TMS

$$\delta = \frac{162 \text{ Hz}}{60 \text{ MHz}} = 2.70 \text{ ppm.}$$

↳ The value of 'δ' for a given proton are always the same irrespective of whether the measurement was made at 60 MHz, 100 MHz, 200 MHz etc.

eg:- At 60 MHz, shift of a given proton = 162 Hz
At 100 MHz, shift of a given proton = 270 Hz

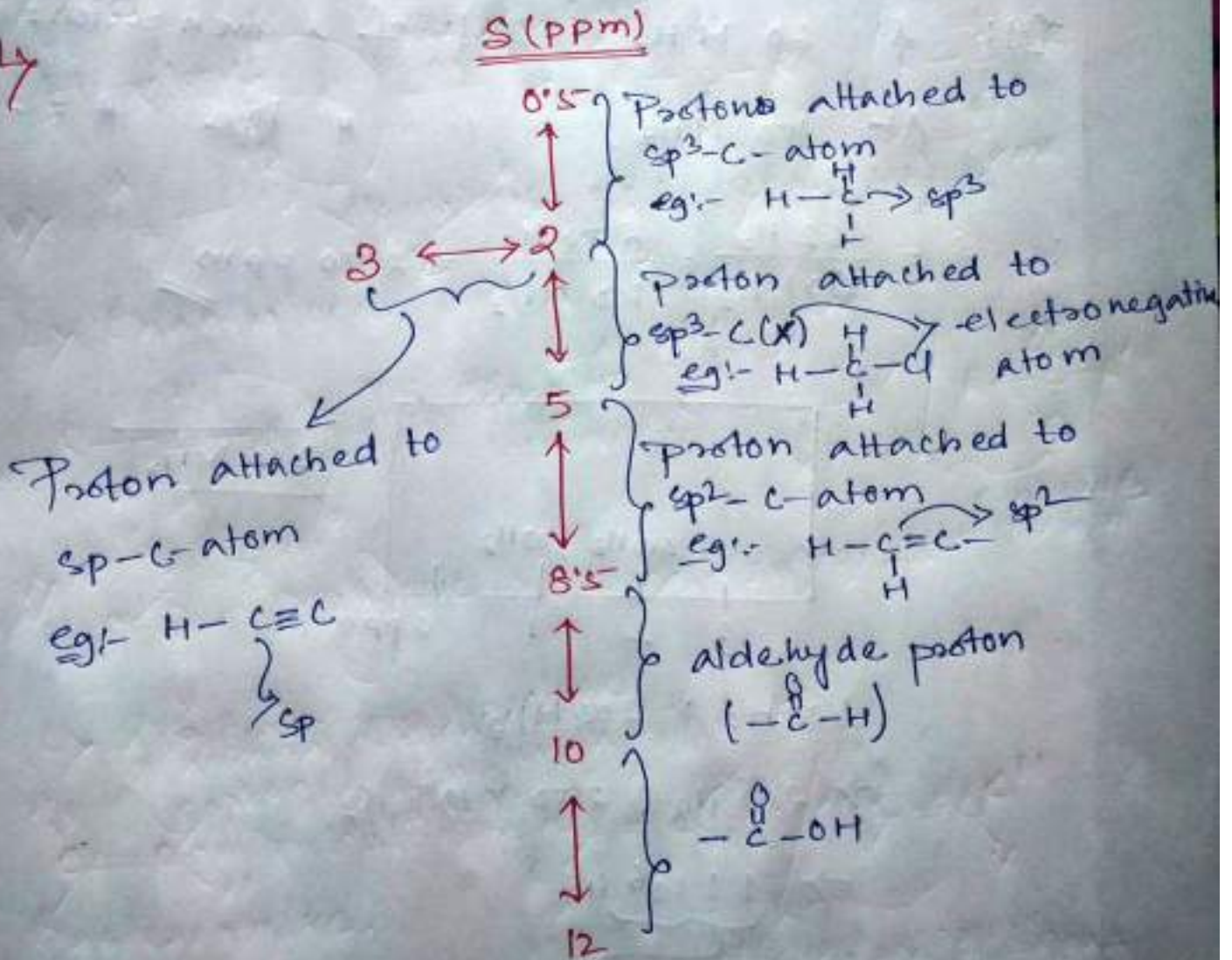
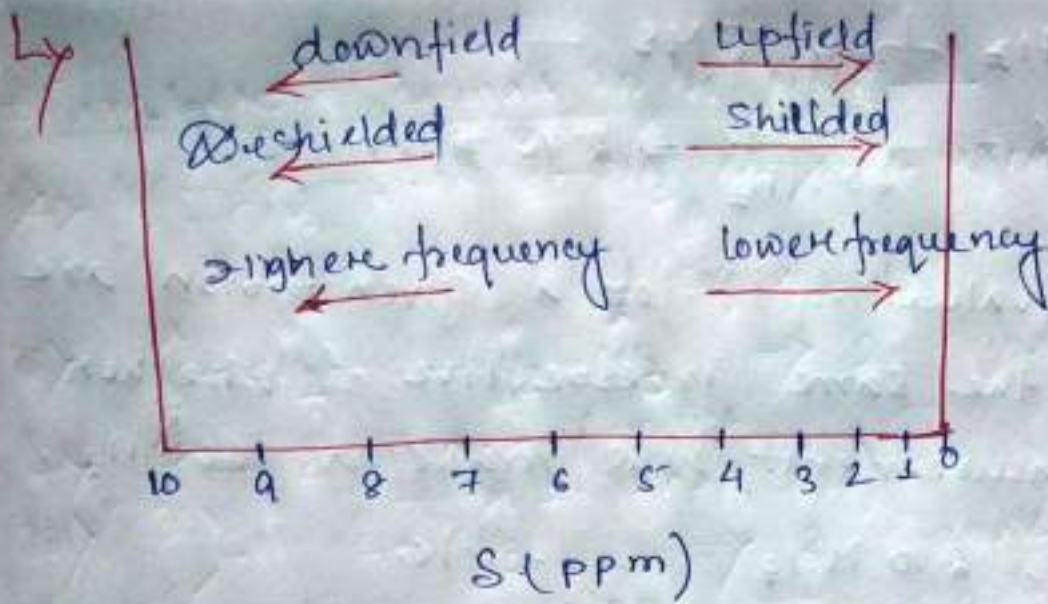
$$\therefore \delta = \frac{162 \text{ Hz}}{60 \text{ MHz}} = \frac{270 \text{ Hz}}{100 \text{ MHz}} = 2.70 \text{ ppm}$$



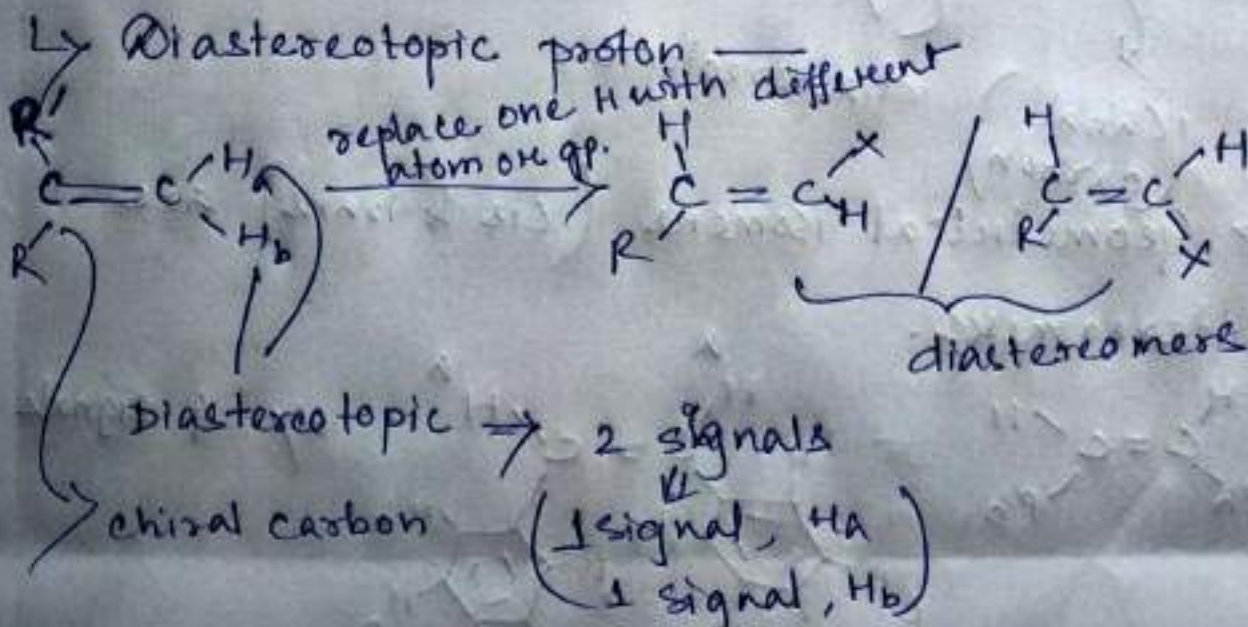
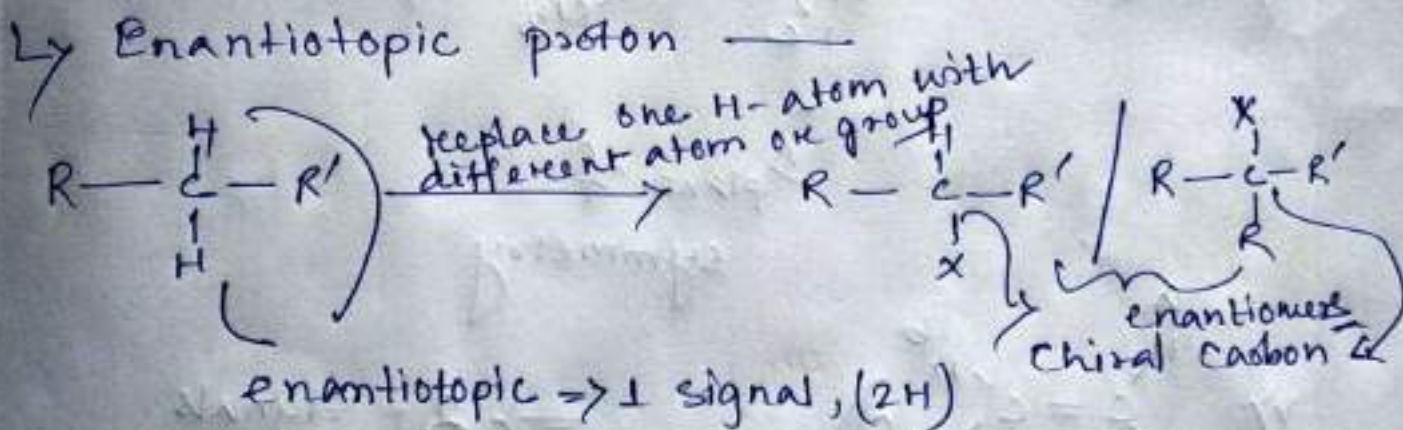
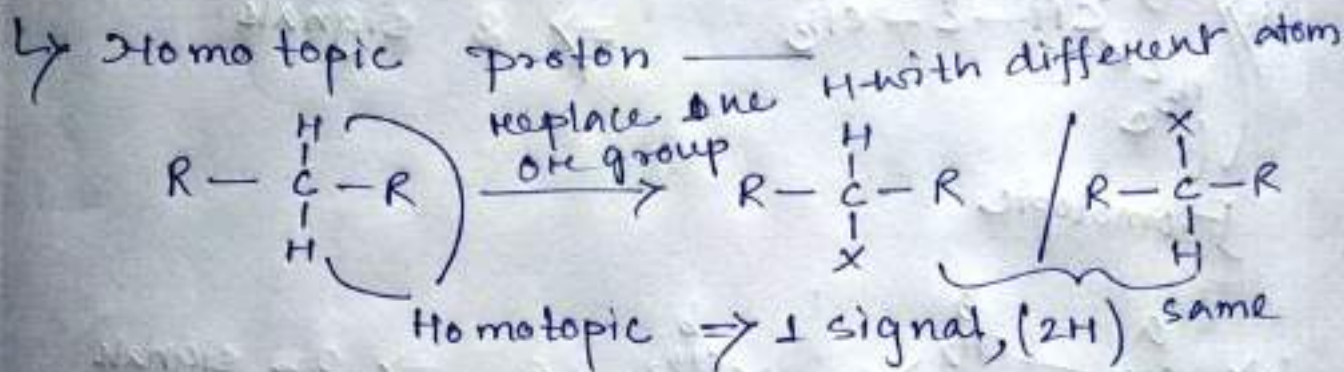
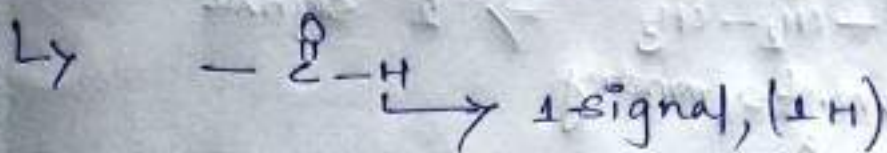
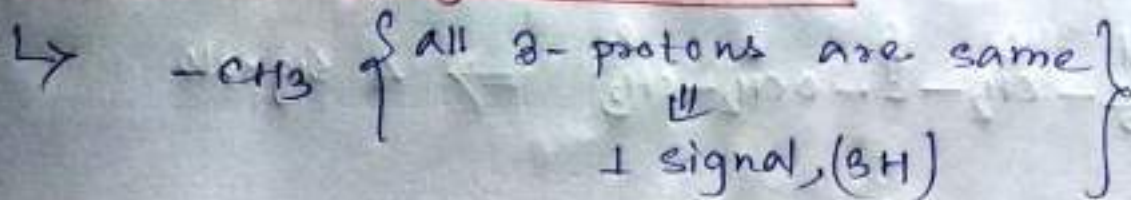
$$200 \text{ Hz} : 200 \text{ MHz}$$

$$\Rightarrow 200 \text{ Hz} : 200 \times 10^6 \text{ Hz}$$

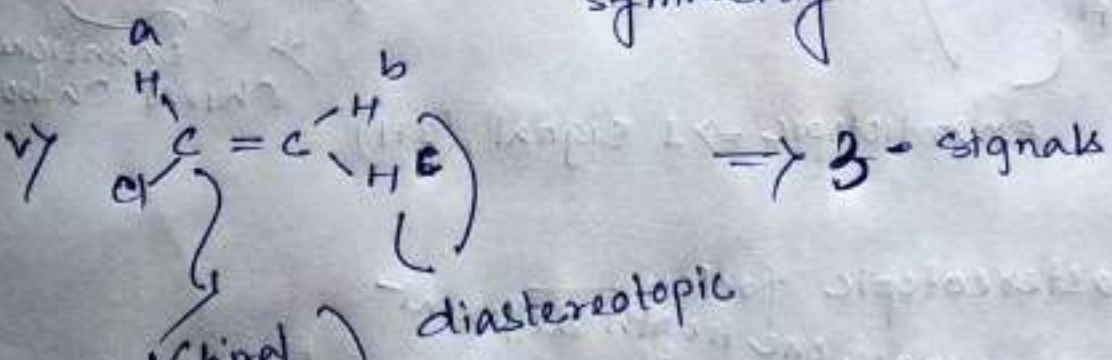
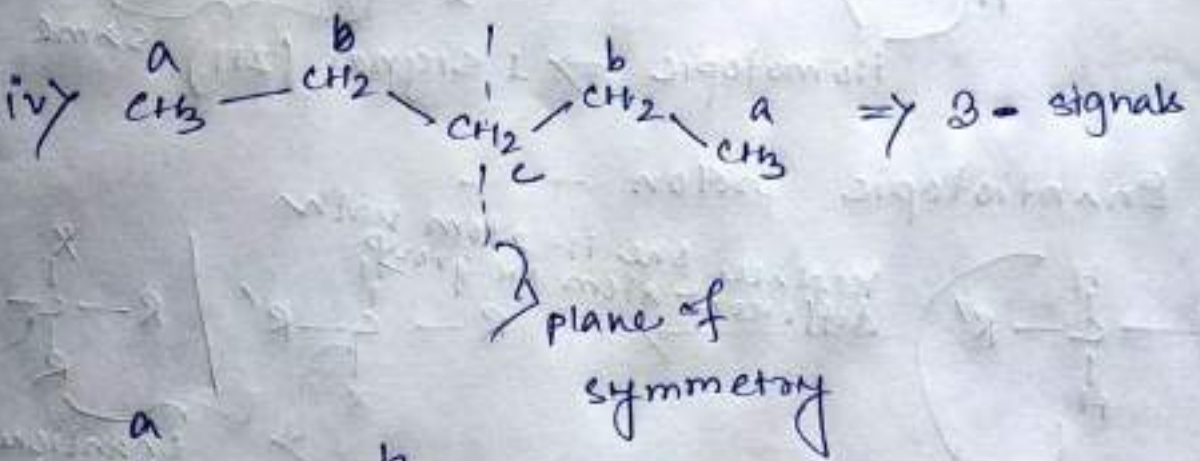
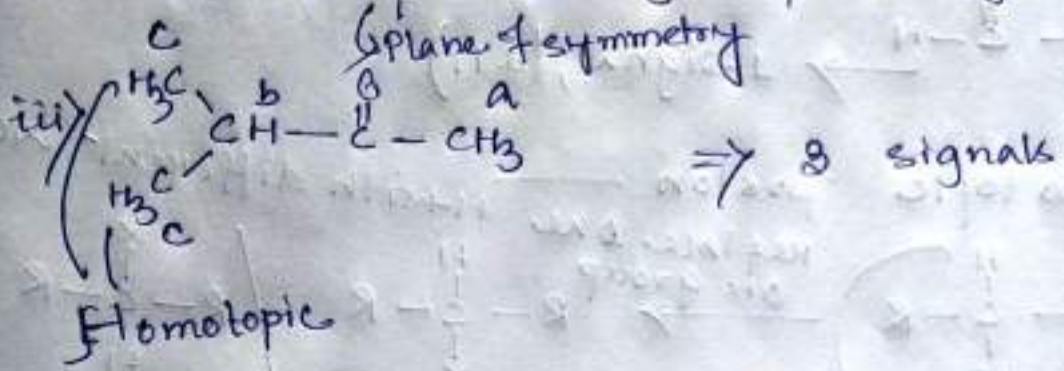
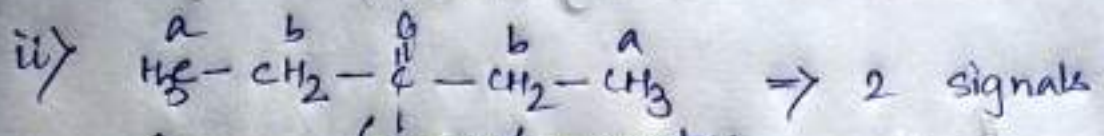
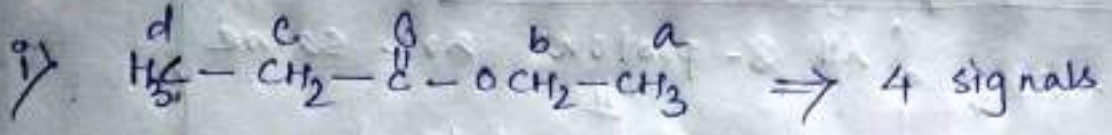
$$\Rightarrow \underbrace{1 : 10^6 \text{ Hz}}_{\text{ppm}}$$



Number of signals in $^1\text{H-NMR}$ —

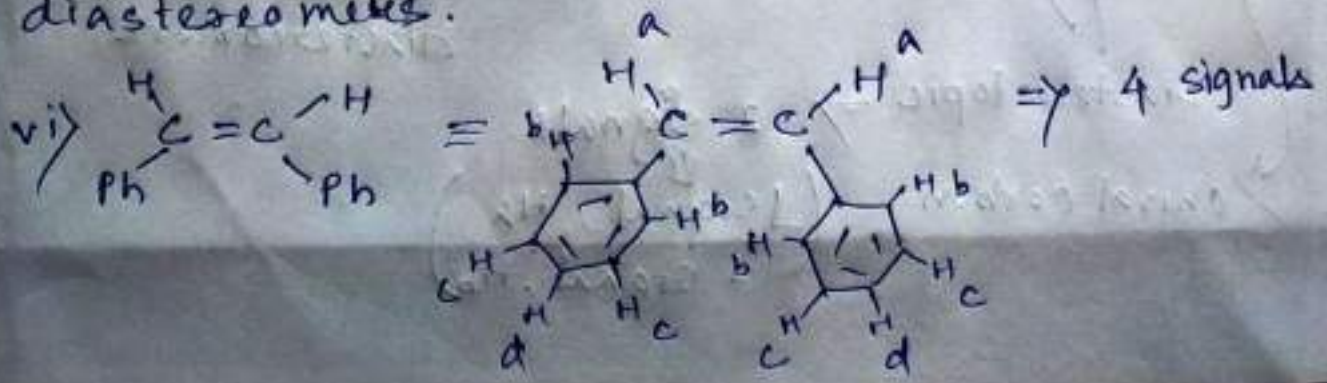


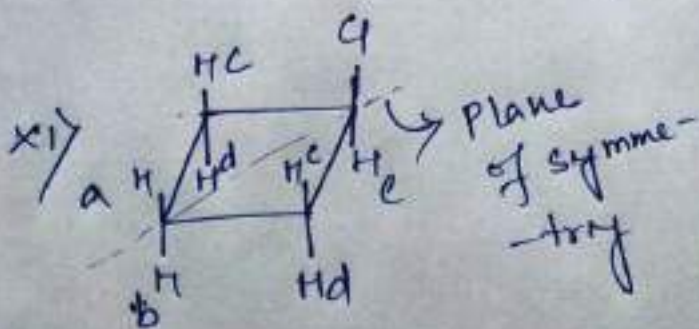
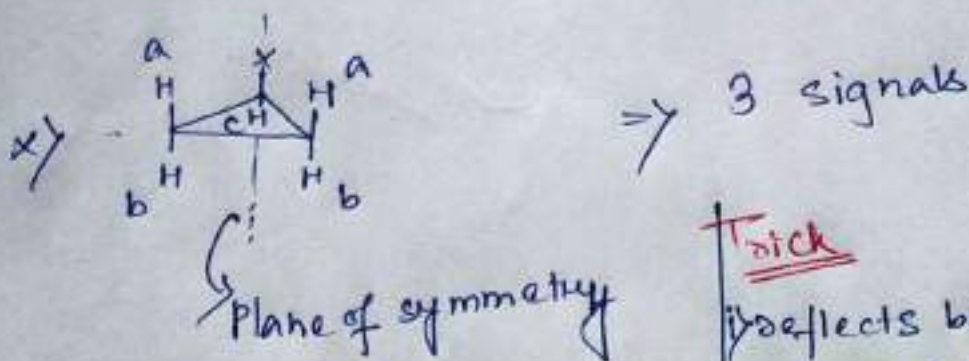
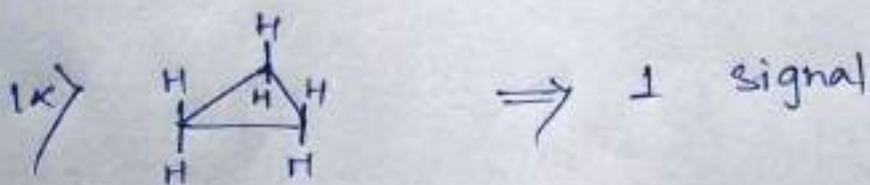
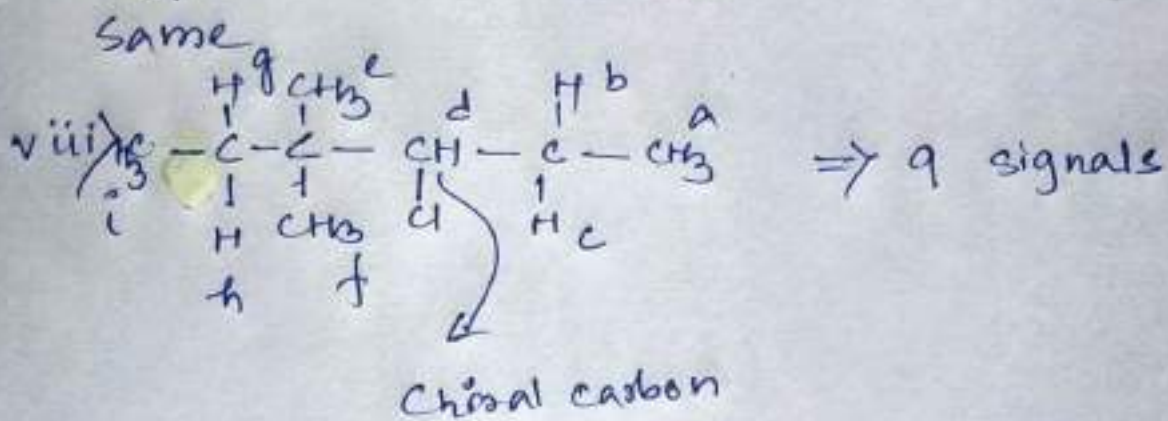
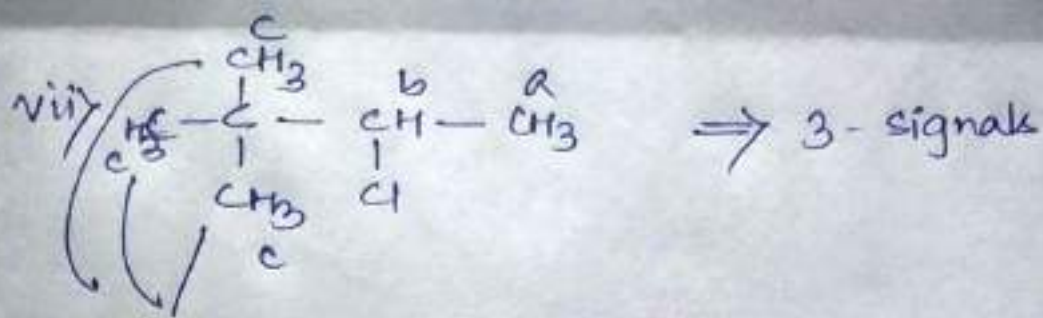
eg:-



Geometrical isomers (cis & trans) are

diastereomers.





Trick

i) Bisects by plane of symmetry = enantiotopic protons

ii) Bisects by plane of symmetry = diastereotopic protons

\Downarrow
5 signals

① Electronegativity effects on chemical shift

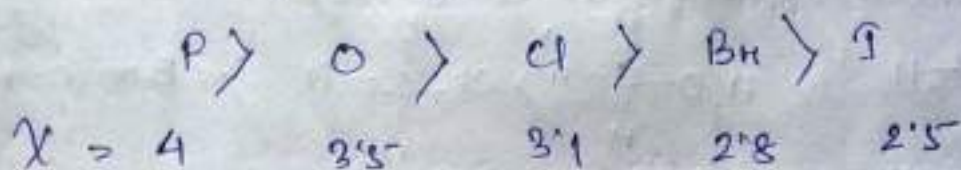
↳ The chemical shift simply increases as the electronegativity of the attached elements increases.

↳ Electronegative substituents attached to a carbon atom, because of their e^- -withdrawing effects, reduce the valence e^- density around the protons attached to that carbon.

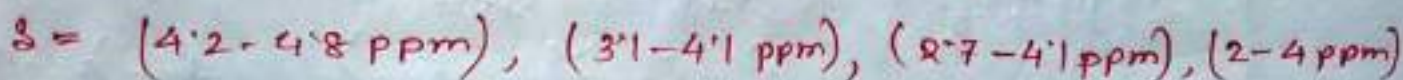
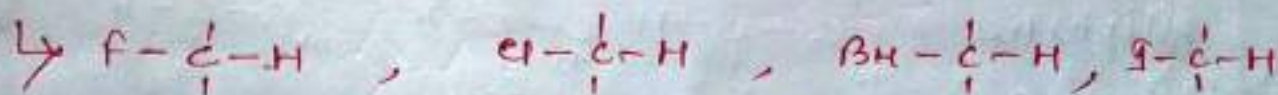
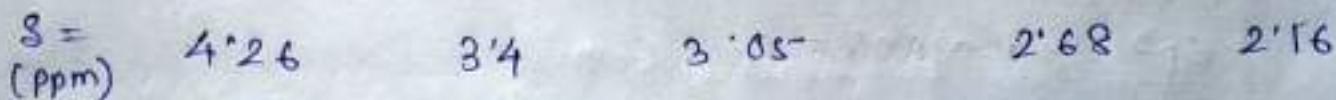
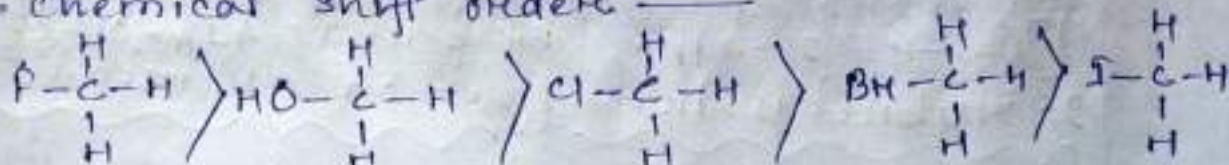
↳ Electronegative substituents on carbon reduce the local diamagnetic shielding in the vicinity of the attached protons because they reduce the e^- -density around those protons. — substituents which have this type of effect are said to deshield the proton.

↳ The greater the electronegativity of the substituent, the more it deshields the proton & hence the greater is the chemical shift of those protons.

Electronegativity order —

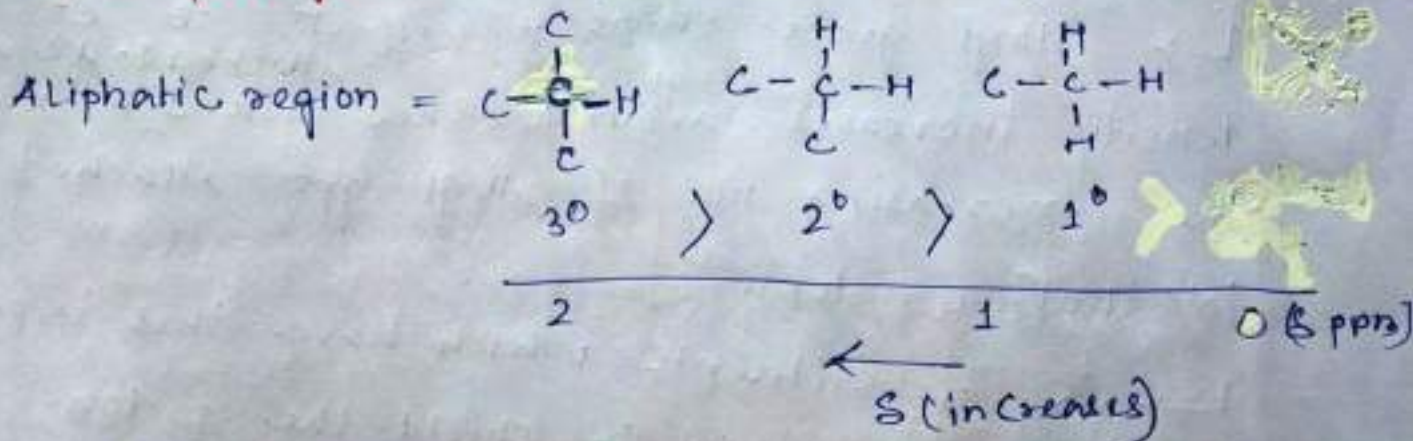


The chemical shift order —



2) Hybridization effect on chemical shift —

sp^3 - Hydrogens — (for saturated hydrocarbon)

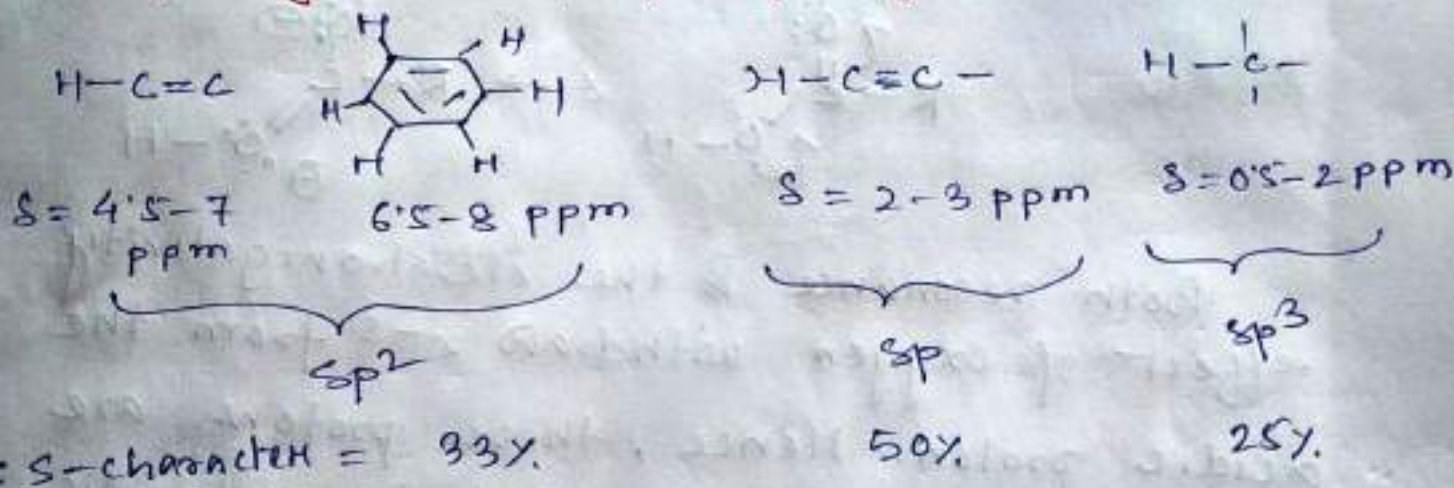


Bulkiness around the proton increases as we move from 1° to 2° & 2° to 3° -C atoms. So due to the steric hindrance, bulky groups

push away the protons that attached to sp^2 -C atom. Hence e^- -density around the nucleus decreases & the protons becomes deshield.

↳ The greater the bulkiness of the substituents on the sp^3 -C, the more deshield the protons attached to sp^3 -C & finally, the chemical shift values of protons become greater.

sp^2 -hydrogens — & sp -hydrogens —



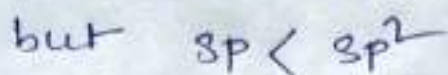
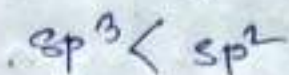
Order of s-character —
 $sp^3 < sp^2 < sp$

Electronegativity order —
 $sp^3 < sp^2 < sp$ [∵ electronegative]

Since,
 electronegativity ∝ s-character

Therefore —

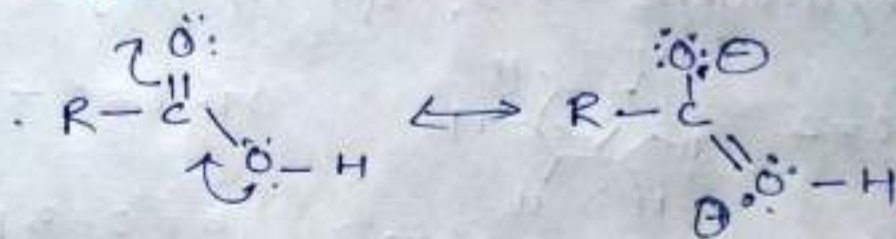
chemical shift order —



⇓ diamagnetic anisotropy.

9) Acidic & Exchangeable Protons, H-bonding effects on chemical shift —

Acidic Hydrogens —



Both resonance & the electronegativity effect of oxygen withdraw e^- s from the acidic proton. Hence, these protons are least shielded or deshielded in carboxylic acids. So, these protons have their resonance at 10–12 ppm.

H-bonding & exchangeable Hydrogens —

↳ Protons that can exhibit hydrogen bonding (eg: hydroxyl or amino protons) exhibit extremely variable absorption positions over a

wide range.

↳ The more hydrogen-bonding that ~~takes~~ ^{takes} place, the more deshielded a proton becomes.

eg:-

		<u>δ-value</u>
Phenols	ArOH	4-7 ppm
Alcohols	ROH	0.5-5 ppm
Amines	RNH ₂	0.5-5 ppm

↳ The amount of H-bonding depends on concentration & temperature.

The more concentrated the solution, the more molecules can come into contact with each other & the more H-bonding will be possible.

eg:- At high dilute solution —

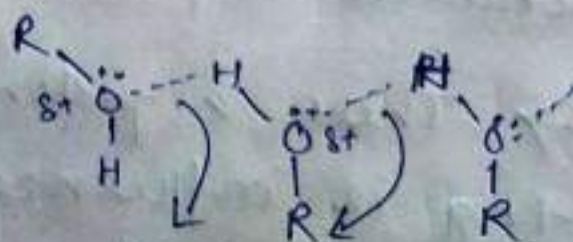
No. H-bonding, so hydroxyl protons absorb near 0.5-1.0 ppm.

In concentrated solution —

The absorption is closer to 4-5 ppm



Free hydroxyl proton
(dilute solution)



H-bond
(concentrated solution)

↳ Hydrogens which can exchange either with the solvent medium or with one another also tend to be variable in their absorption positions — so chemical shift value varies within a wide range.
eg:-



Magnetic Anisotropy —

↳ In the presence of a magnetic field the π e^- s in the aromatic ring system are induced to circulate around the ring. This circulation is called ring current.

↳ The moving e^- s generate a magnetic field much like that generated in a loop of wire through which a current is induced to flow.

↳ Thus a proton attached to a benzene ring is influenced by δ -magnetic fields —

1) The applied magnetic field of the NMR spectrometer

2) Induced magnetic field due to the valence e^- s around the proton. The direction of this field is opposite to the applied magnetic field.

3) The secondary magnetic field generated by the π - e^- s of the ring system. This field is also called secondary anisotropic field.

These anisotropic effects that gives the benzene ring protons a chemical shift that is greater than expected.

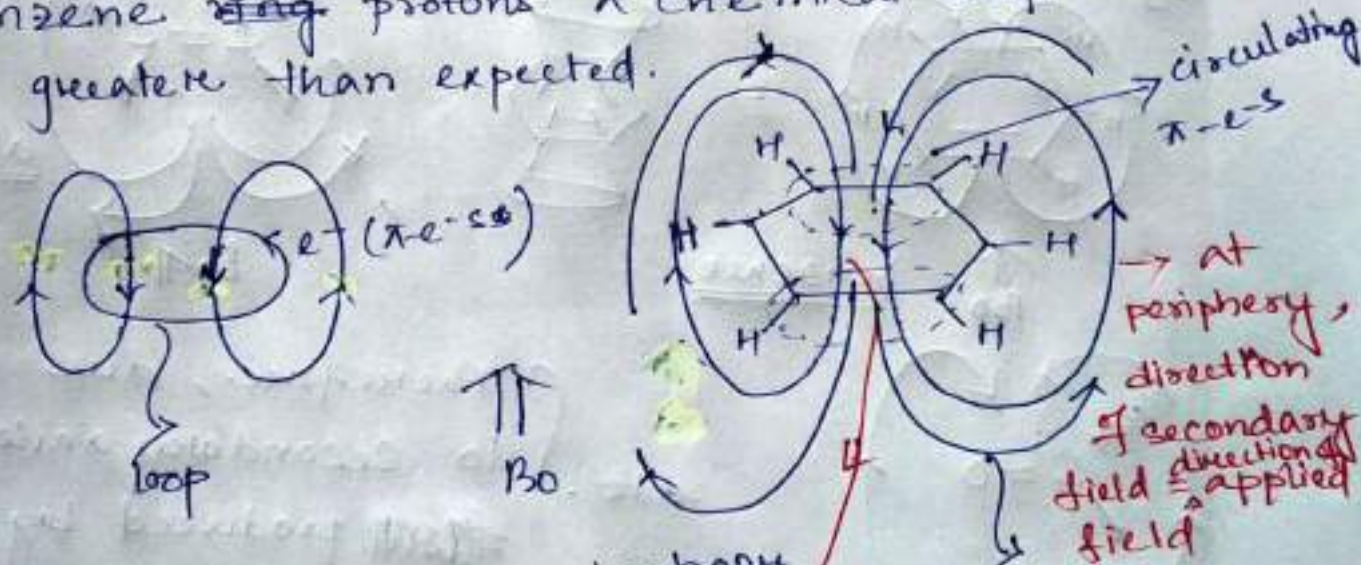


Fig- Diamagnetic anisotropy in benzene

Since the secondary field's direction is same as applied field

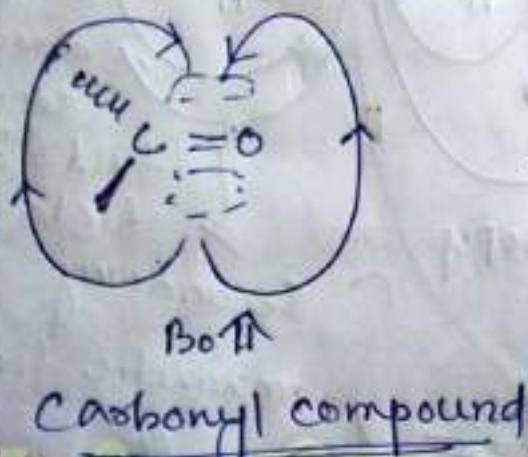
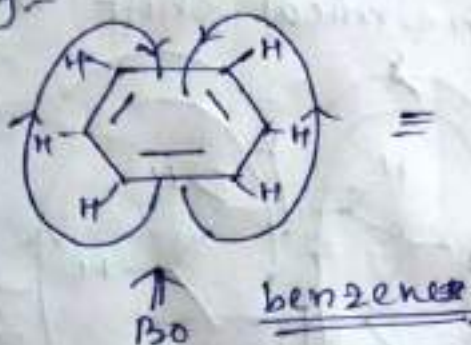
Deshields the aromatic protons.

At the centre secondary field opposes the applied field.

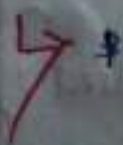
↳ Thus, if a proton were placed in the center of the ring rather than periphery it would ~~have~~ be found to be shielded, since the field lines there would have the opposite direction from those at the periphery.

↳ All groups in a molecule that have π -e^{-s} generate secondary anisotropic field.

eg:-



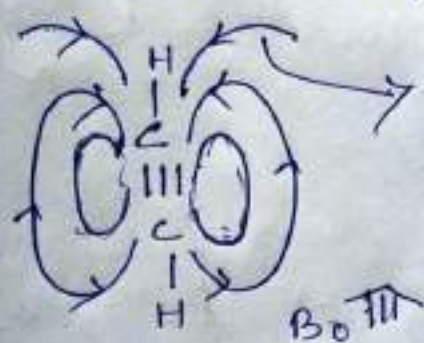
Therefore, due to secondary anisotropic ~~field~~ produced by the circulation of π -e^{-s} deshield the protons, & hence these protons shows high chemical shift value or ~~high~~ resonance frequencies. (values vary from 6.5-8 ppm)



↳ But in acetylene, the ^{secondary} magnetic field generated by induced circulation of the π -e⁻s has a geometry such that, the acetylene hydrogens are shielded.

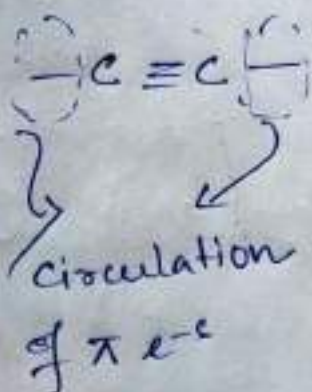
→ Hence, acetylenic hydrogens (i.e., ~~sp~~ hydrogens attached to sp-C atom) have resonance at higher ^{magnetic} field than expected.

i.e., $\delta = 2-3$ ppm



secondary magnetic field
 ↓
 opposes the applied magnetic field

↓
 Thus shielded the protons

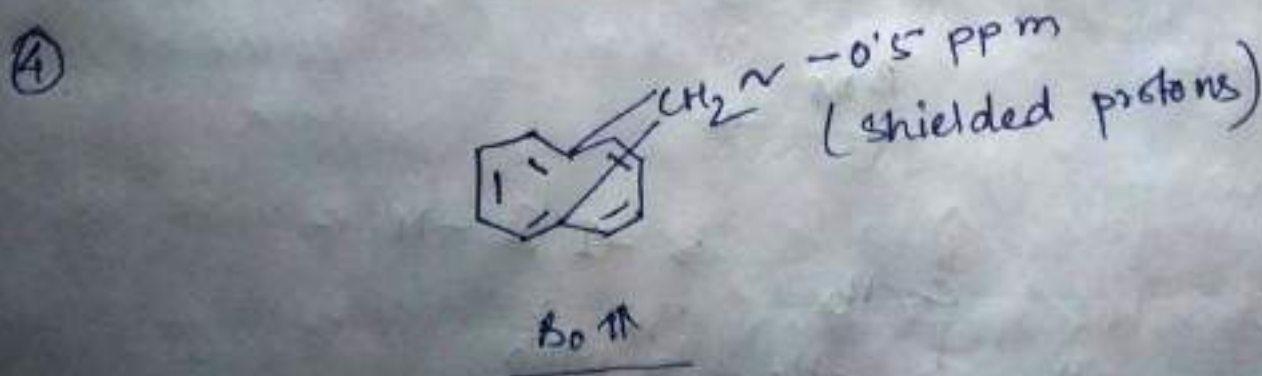
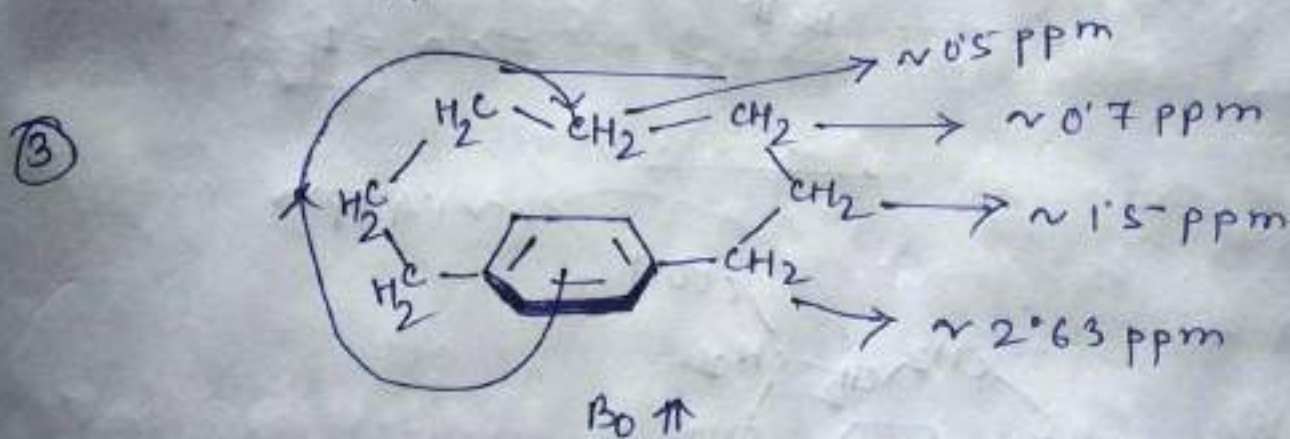
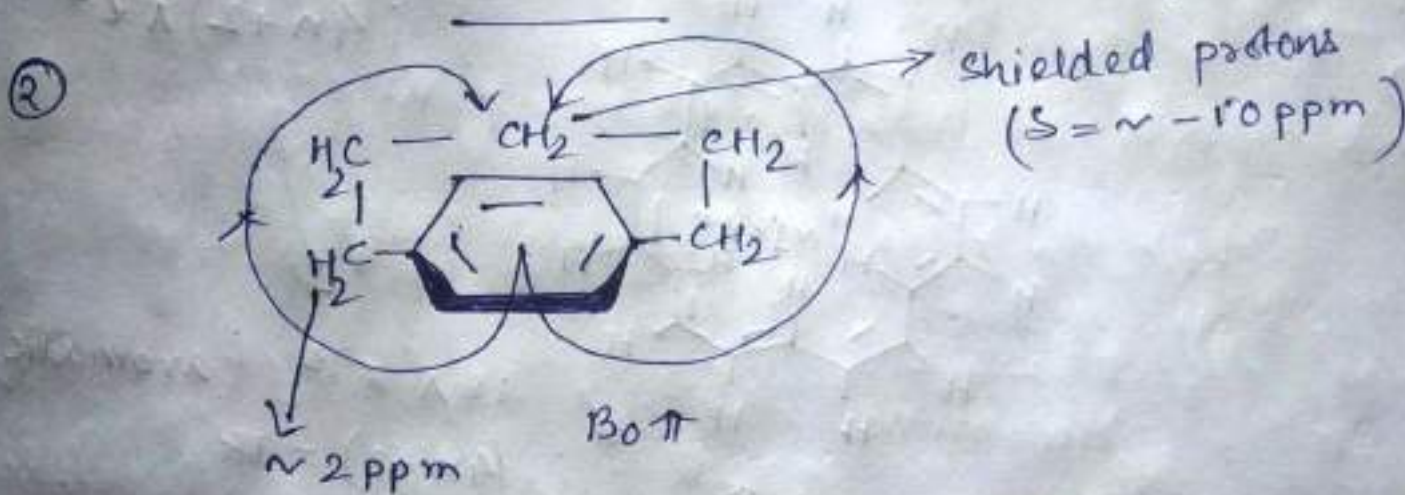
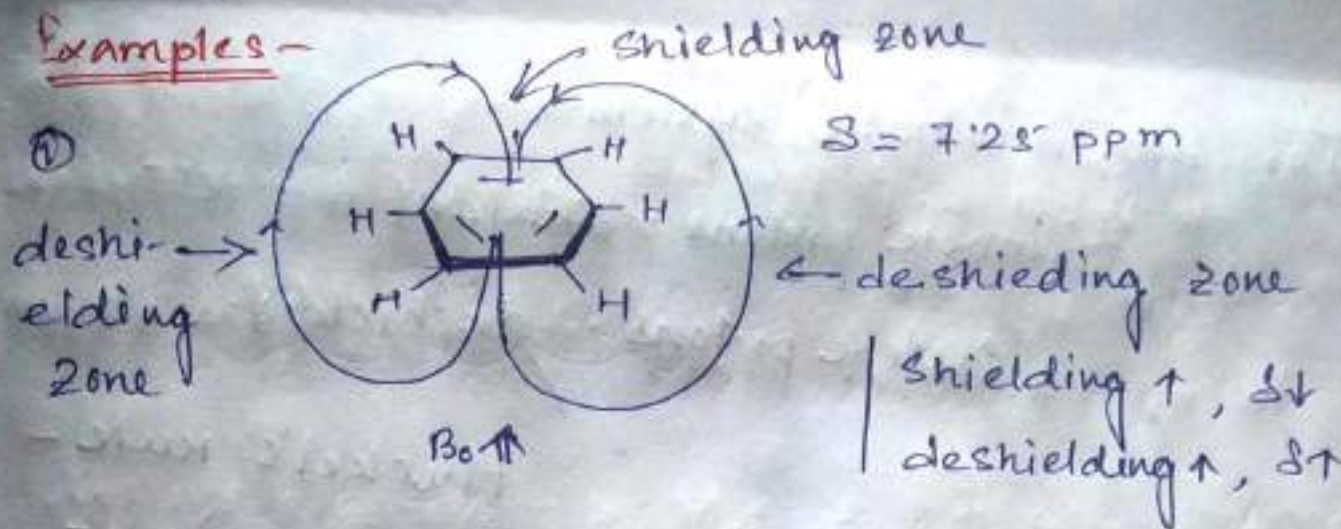


Circulation of π e⁻

Hence, acetylenic protons shows low chemical shift value, or low resonance frequency values.
 i.e., $\delta = 2-3$ ppm

Fig - Diamagnetic anisotropy in acetylene

Examples -



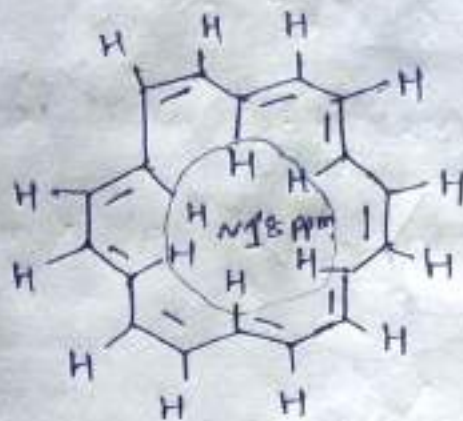
↳ For ~~the~~ aromatic system —

Innere protons = shielded

Outere protons = deshielded

eg:-

(5)



Both

Huckel's rule —

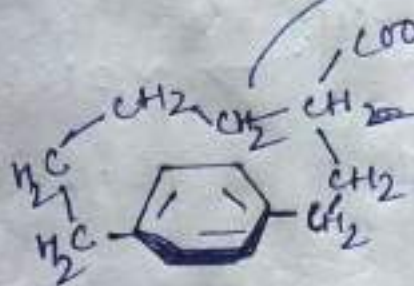
$$(4n+2)\pi e^-$$

$18\pi e^-$ (aromatic)

$$\therefore (4n+2) = 18$$

$$\Rightarrow n = 4$$

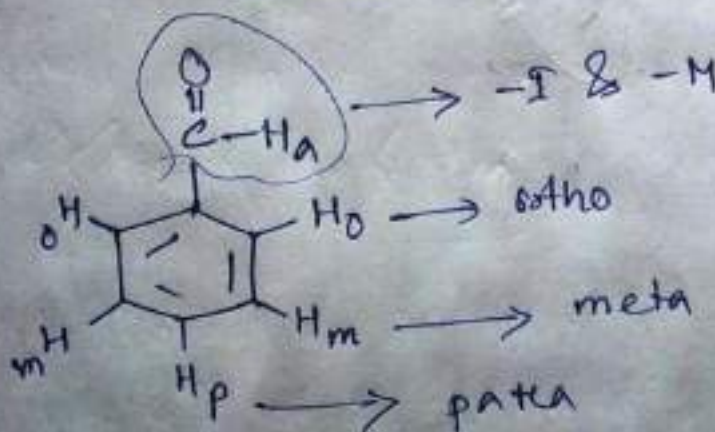
(6)



Both

$\sim 1.4 \text{ ppm}$

(7)



↳ Note - For benzene system - (The chemical shift values for benzene protons)

→ If electron withdrawing group is present,

then, chemical shift > 7.25 ppm

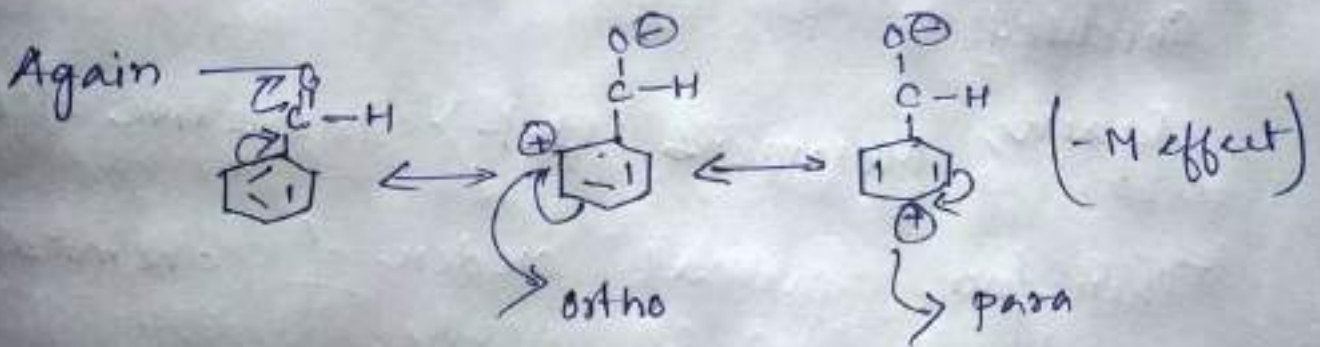
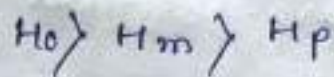
→ If electron donating group is present,

then, chemical shift < 7.25 ppm

↳ $-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$ group has, $-I$ as well as $-M$ effect & Mesomeric effect \rightarrow Inductive effect:

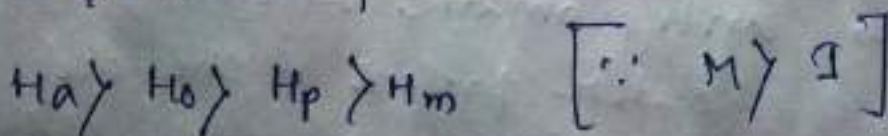
Since, inductive effect is distance dependent,

hence, chemical shift order -

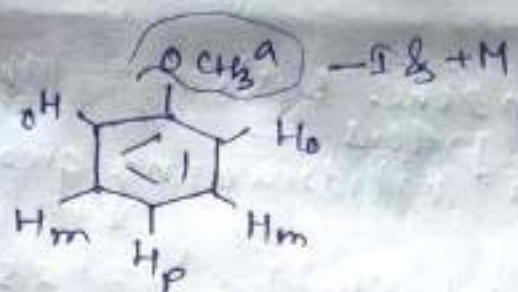


Therefore, ortho & para-positions will be more deshielded than meta-position

Therefore, overall order of chemical shift



②



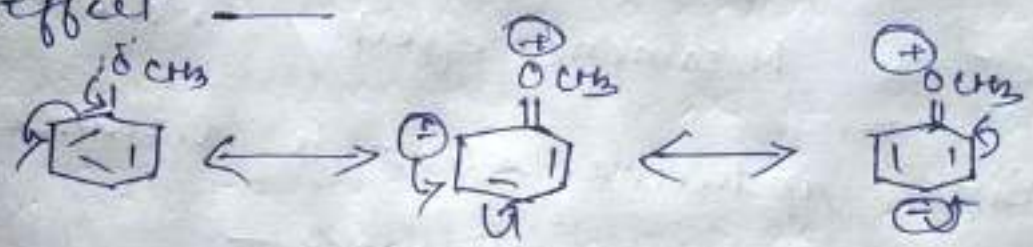
- OCH₃ = 3.5 - 4 ppm
- OCH₂ = 4 - 4.5 ppm
- OCH = 4.5 - 4.8 ppm

↳ -OCH₃ group has +M & -I effect

-I effect (distance dependent)

Ha > Hb > Hc (chemical shift)

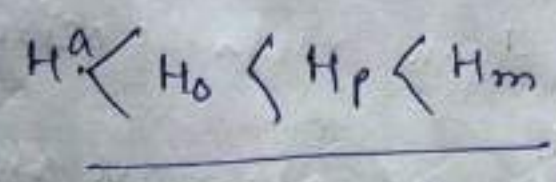
+M effect



So, ortho & para-positions are highly shielded

Again, Mesomeric effect > Inductive effect

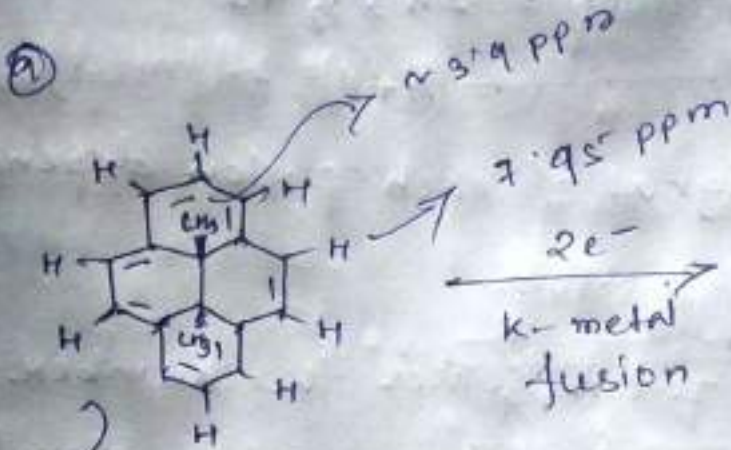
Therefore, overall order of chemical shift value will be



↳ For antiaromatic system —
outer protons = shielded
inner protons = deshielded

Huckel's rule —

$4n\pi e^-$ system = Aromatic
 $4n\pi e^-$ system = Anti aromatic



$14\pi e^-$ system

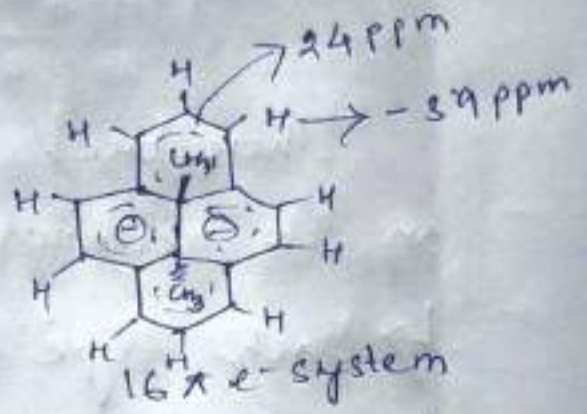
Aromatic

Outer protons = $\sim 7.95 \text{ ppm}$

Inner " = $\sim 3.9 \text{ ppm}$

Outer protons = $\sim 3.9 \text{ ppm}$

Inner protons = 24 ppm



Anti aromatic

Secondary anisotropic magnetic field's direction become opposite, while the molecule changes from aromatic to anti-aromatic system.

Spin-spin splitting (n+1) Rule —

Signal multiplicity = $(2nI + 1)$

Where, n = no. of neighbouring protons/nuclei

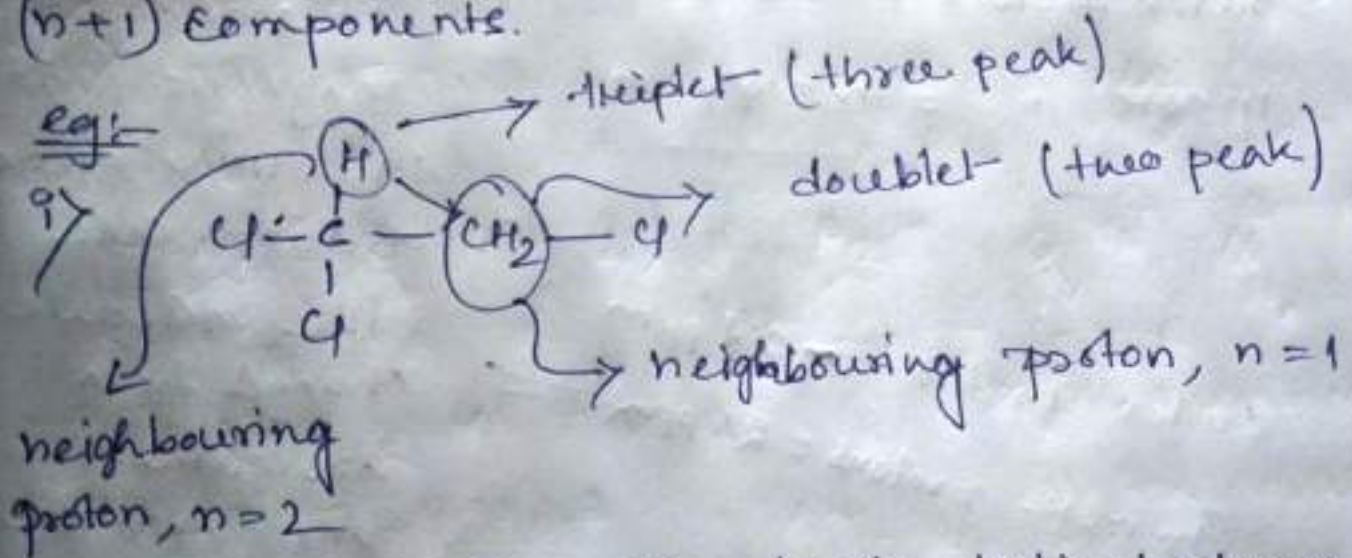
I = spin no. of proton/nucleus

For a proton, $I = \frac{1}{2}$

$$\therefore \text{Signal multiplicity} = 2n \times \frac{1}{2} + 1 \\ = (n+1)$$

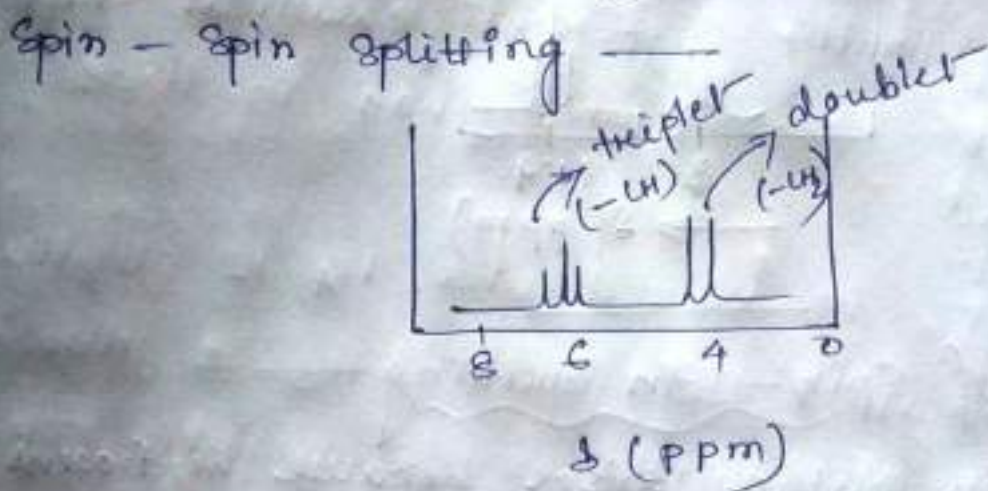
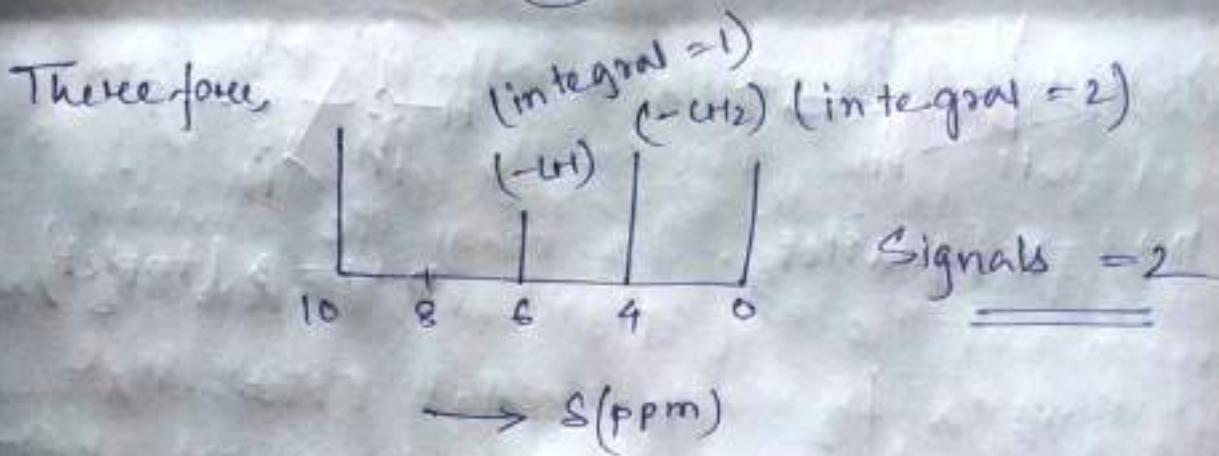
Therefore, signal of each proton depends on its neighbouring protons.

↳ Each type of proton senses the number of equivalent protons (n) on the carbon atom/atoms next to the one to which it is bonded & its resonance peak is split into $(n+1)$ components.

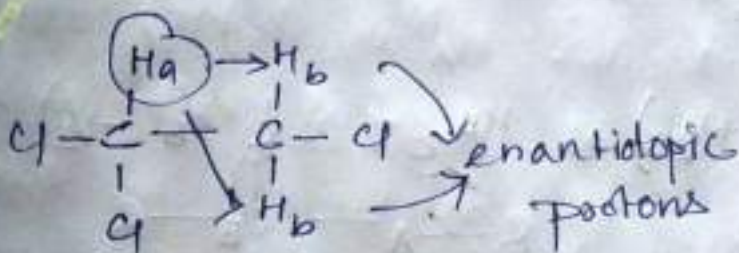


⇒ Two chemically distinct types of protons present.

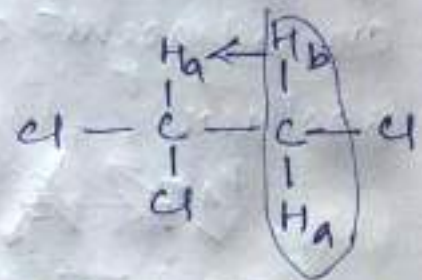
⇒ equivalent protons behave as a group.



Since

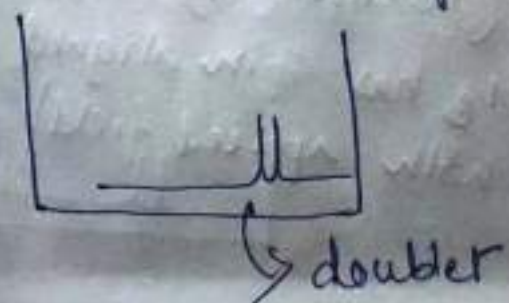


→ Two neighbors give a triplet, $n+1=3$



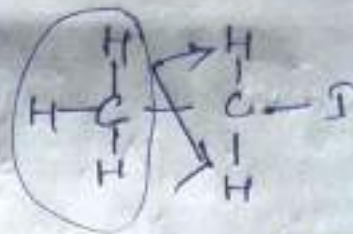
→ One neighbor gives a doublet
 $n+1=2$

→ equivalent protons behave as a group

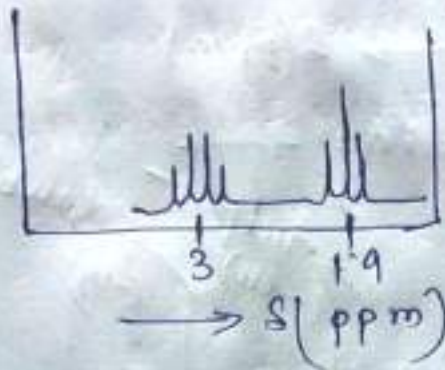




$n+1=4$ (quartet)

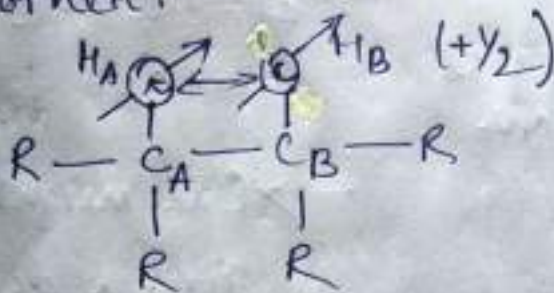


$n+1=3$ (triplet)

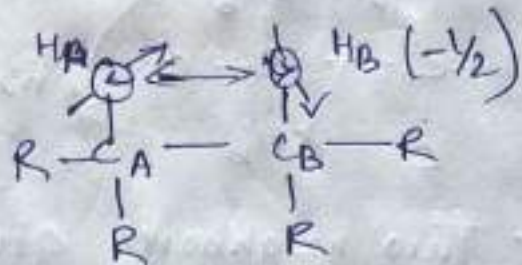


The origin of Spin-spin splitting

Spin-spin splitting arises because hydrogens on adjacent carbon atoms can 'sense' one another.

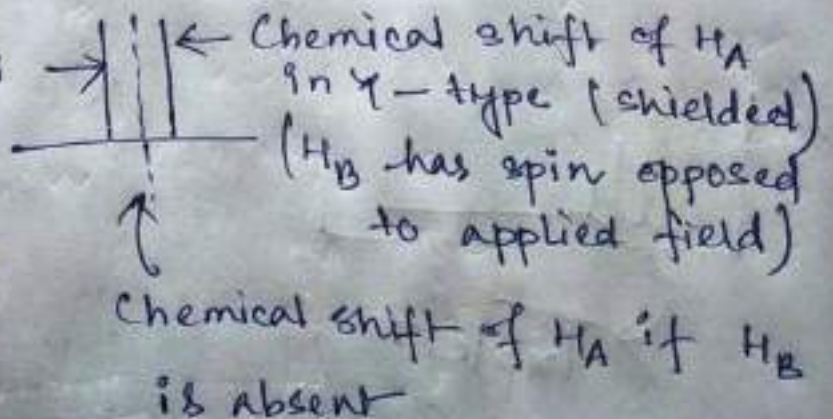


X-type molecules



Y-type molecules

Chemical shift of H_A in X-type (deshielded) (H_B has spin aligned with applied field)

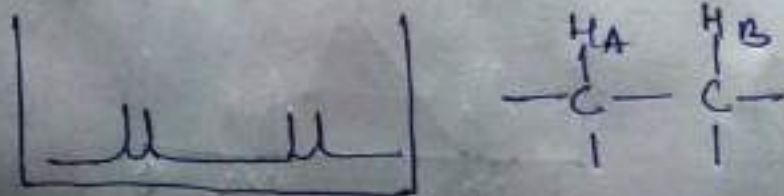


\hookrightarrow Chemical shift of H_A is influenced by the direction of the spin in H_B . H_A is said to be coupled to H_B . Its magnetic environment is affected by whether H_B has a $+\frac{1}{2}$ or a $-\frac{1}{2}$ spin state. Thus, H_A absorbs a slightly different chemical shift value in type X-molecules than in type Y-molecules.

\hookrightarrow In fact, in X-molecules, H_A is slightly deshielded because the field of H_B is aligned with the applied field & its magnetic moment adds to the applied field.

\hookrightarrow In Y-type molecules, H_A is slightly shielded with respect to what its chemical shift would be in the absence of coupling. In this case, the field of H_B diminishes the effect of the applied field on H_A .

\hookrightarrow H_A also splits H_B , since H_A can adopt two spin states as well. The final spectrum for this situation consists of two doublets.



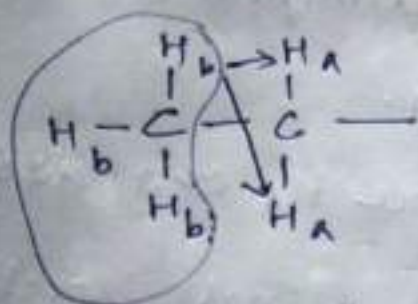
Splitting Patterns

↳ The intensity ~~of~~ ratios of multiplets derived from the $n+1$ rule follow the entries in the mathematical mnemonic device called Pascal's triangle.

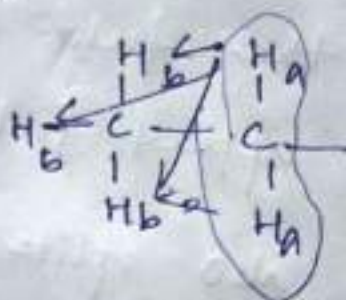
Singlet				1				
doublet			1	1				
Triplet		1	2	1				
Quartet		1	3	3	1			
Quintet	1	4	6	4	1			
Sextet	1	5	10	10	5	1		

Fig Pascal's triangle.

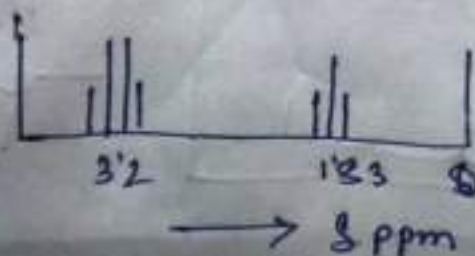
eg CH_3CH_2- (ethyl group)



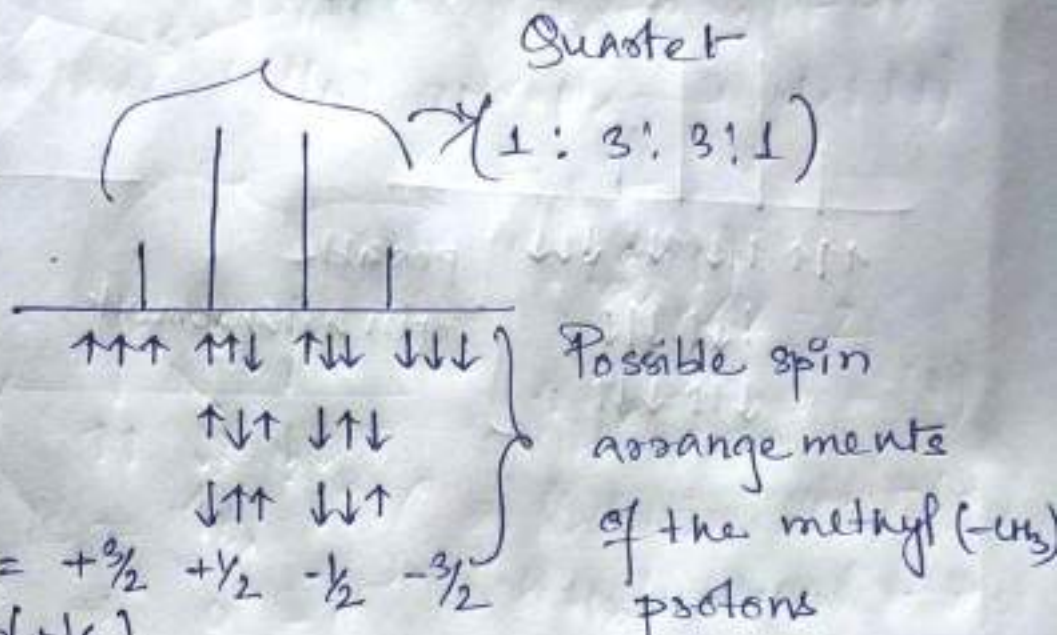
$n+1 = 3$ (triplet)



$n+1 = 4$ (quartet)



↳ Splitting pattern of $-CH_2$ protons due to the presence of an adjacent methyl ($-CH_3$) group —



Net spin = $+3/2$
 where, $\uparrow = \text{spin}(+1/2)$
 $\downarrow = \text{spin}(-1/2)$

Since, for proton, $I = 1/2$ & $(+1/2 \text{ or } -1/2)$ spin

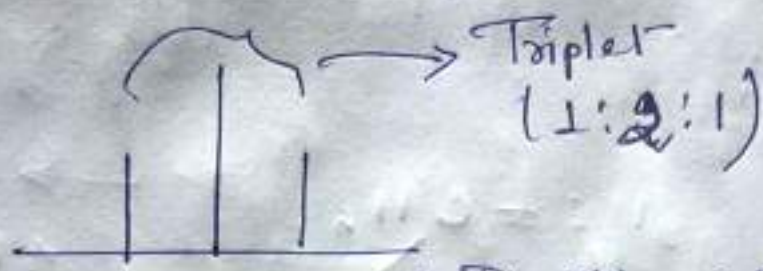
For, $-CH_2$ group, adjacent protons, $n = 3$

$$\therefore \text{Net } I = 1/2 \times 3 = 3/2$$

\therefore Possible spin states —

$$\begin{aligned}
 & 2I + 1 \\
 &= 2 \times 3/2 + 1 \\
 &= 3 + 1 = 4 \quad \left(+3/2, +1/2, -1/2, -3/2 \right)
 \end{aligned}$$

→ The splitting pattern of methyl protons (CH_3) protons due to the presence of an adjacent methylene ($-\text{CH}_2$) group —



Net spin = $+1$ 0 -1

Possible spin arrangements of the methyl ($-\text{CH}_3$) protons.

Since, For, $-\text{CH}_3$ group, adjacent protons, $n=2$

$$\therefore \text{Net } I = 2 \times \frac{1}{2} = 1$$

\therefore possible spin states —

$$= 2I + 1 = 2 \times 1 + 1 = 3 \quad (+1, 0, -1)$$

eg:

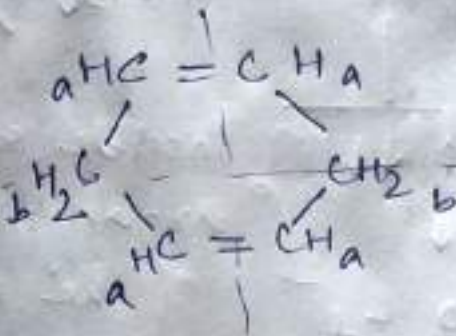


→ Signals = 2

4 H_A = triplet (t)

4 H_B = triplet (t)

ii)



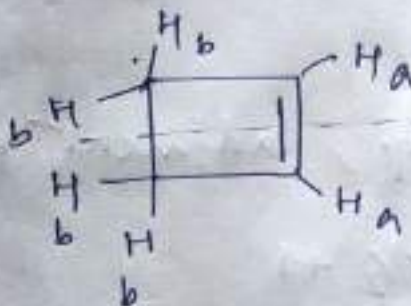
→ signals = 2

4 H_A = triplet (t)

~~4 H_B = doublet (d)~~

4 H_B = triplet (t)

iii)

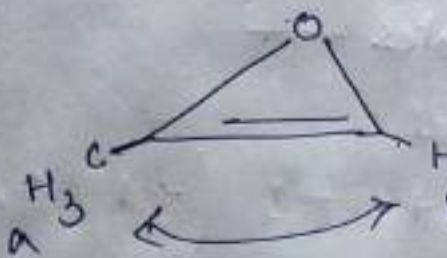


→ signals = 2

4 H_B = doublet (d)

2 H_A = triplet (t)

iv)



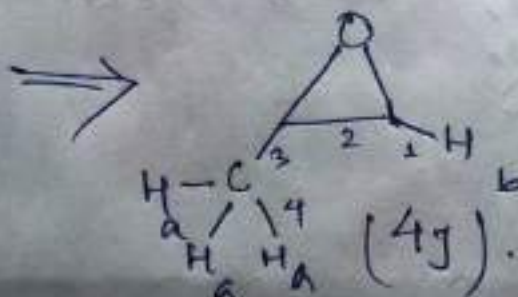
→ signals = 2

3 H_A = singlet (s)

1 H_B = singlet (s)

4J coupling ← } no coupling possible

is not allowed



[4J \propto OH₂]

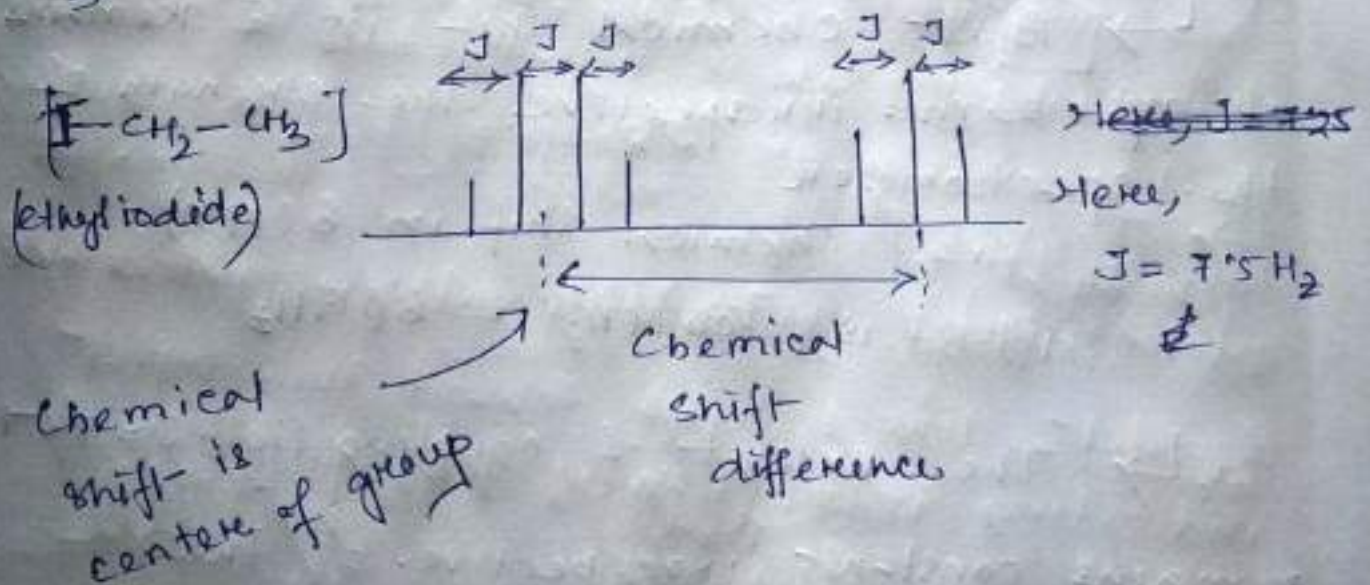
Coupling constant — (J)

↳ The distance between the peaks in a simple multiplet is called the coupling constant, J .

↳ The coupling constant is a measure of how strongly a nucleus is affected by the spin states of its neighbor.

↳ Coupling constant is always expressed in Hertz (Hz).

↳ The amount of coupling is constant, hence J can be called a coupling constant.



↳ The amount of coupling between two particular sets of protons remains constant irrespective of the spectrometer frequency at

which the spectrum was determined.

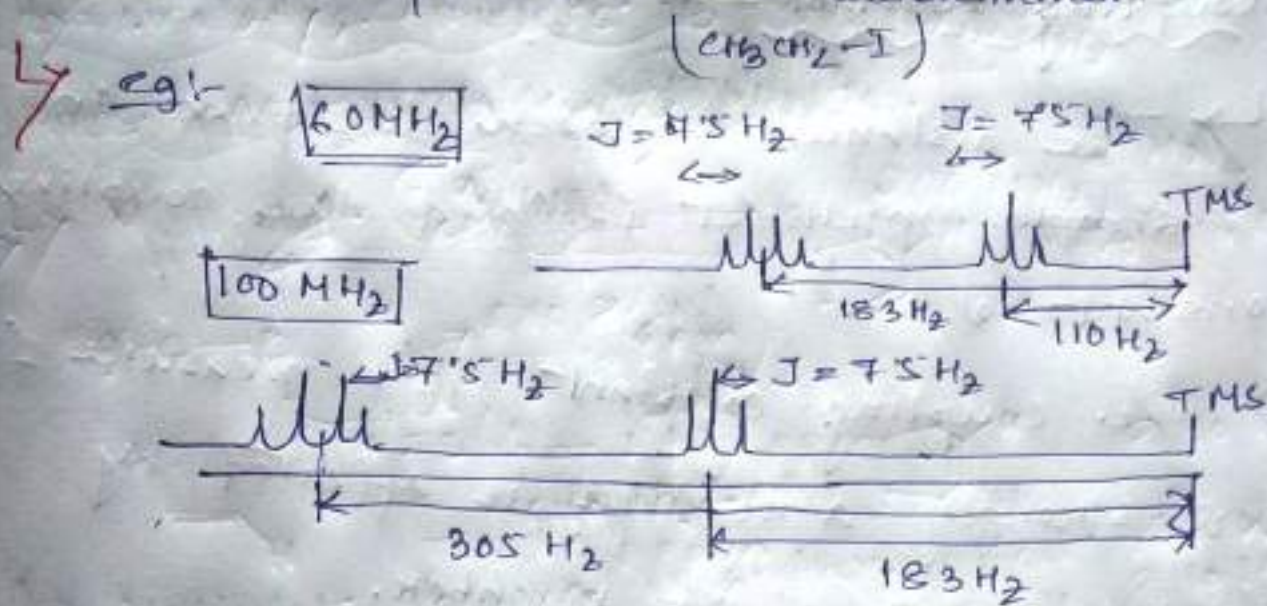


Fig:- Relationship between the chemical shift & the coupling constant.

↳ Chemical shift in H_2 is much larger for $-\text{CH}_3$ & $-\text{CH}_2$ protons in 100MHz

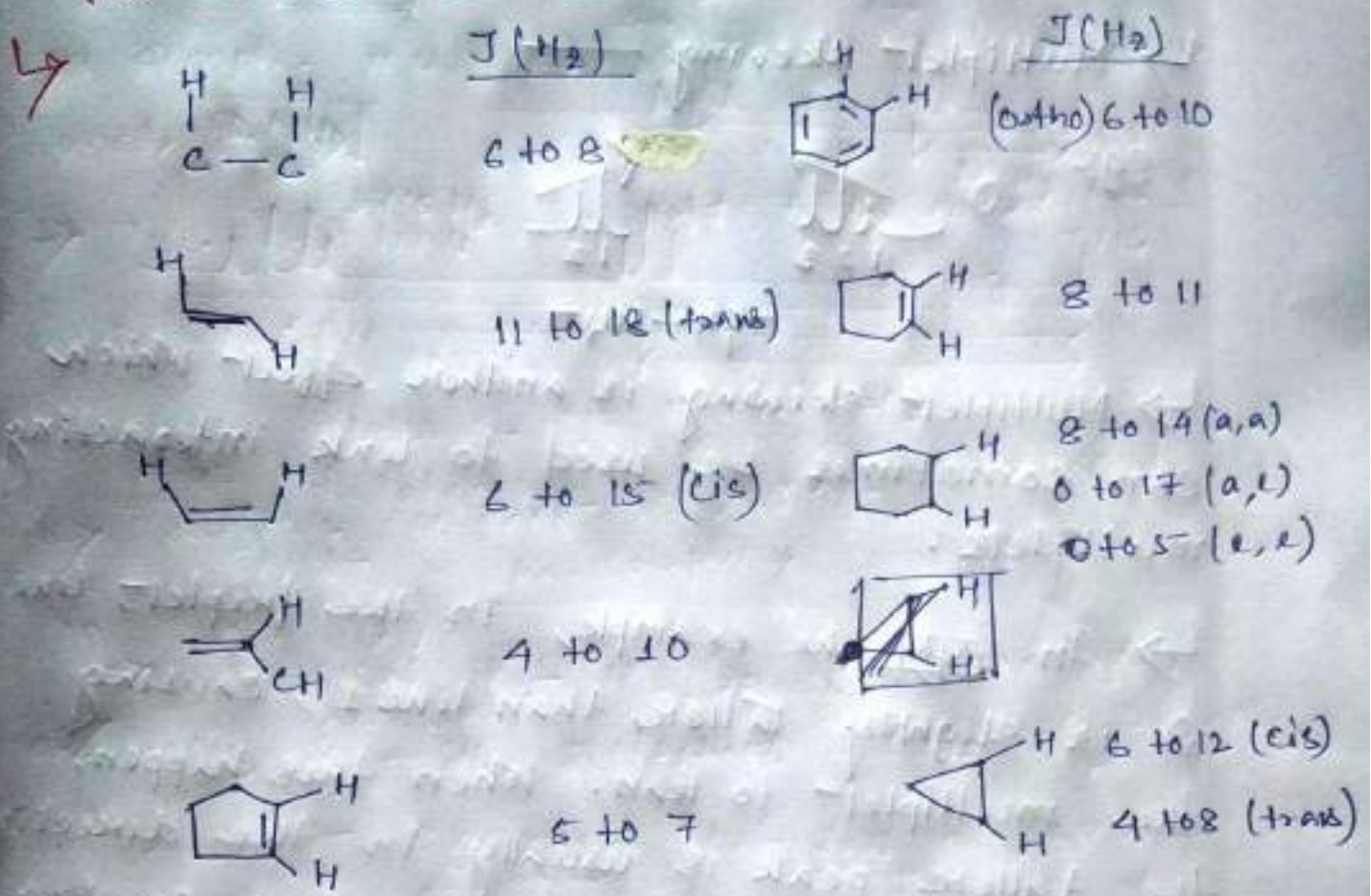
↳ But chemical shift in δ remains always same irrespective the strength of the spectrometer

i.e., chemical shift in δ (ppm) -

$$\text{is, } 100\text{MHz} = 60\text{MHz}$$

↳ The extent of coupling (i.e., $J = 7.5\text{Hz}$) remains constant irrespective of the spectrometer frequency.

Some representative coupling constants & their approximate values (H_2)



\rightarrow The coupling constants of the groups of protons that split one another must be identical

eg:-

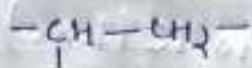


\rightarrow quartet A ($J = 7 H_2$) is associated with triplet C ($J = 7 H_2$) & not with triplet B or D ($J = 5 H_2$).

↳ Similarly, triplets B ($J=5 \text{ Hz}$) & D ($J=5 \text{ Hz}$) are related to each other.

↳ Multiplet skewing —

eg:-

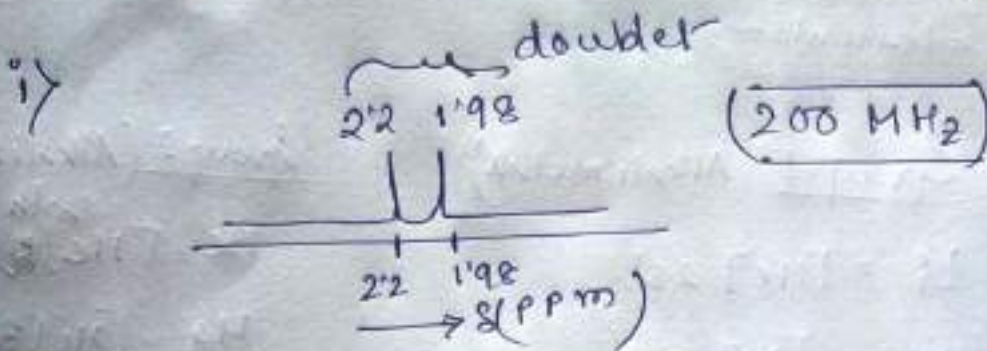


↳ Multiplet skewing is another effect which can sometimes be used to link interacting multiplets.

↳ In ~~eg~~ the example, in the triplet, line 3 is slightly taller than line 1, causing the multiplet to lean. When this happens, the taller peak is usually in the direction of the protons or group of protons causing the splitting.

↳ Similarly, the second group of protons is a doublet, line 1 leans toward the triplet indicating interacting proton or group of protons.

eg: $J = H_2, \quad \delta(\text{ppm}) = \frac{H_2 (2)}{200 \text{ MHz}}$



$$\therefore J = (2.2 - 1.98) \text{ ppm}$$

$$= 0.04 \text{ ppm}$$

$$\therefore 0.04 (\text{ppm}) = \frac{H_2}{200}$$

$$\Rightarrow 0.04 = \frac{H_2}{200}$$

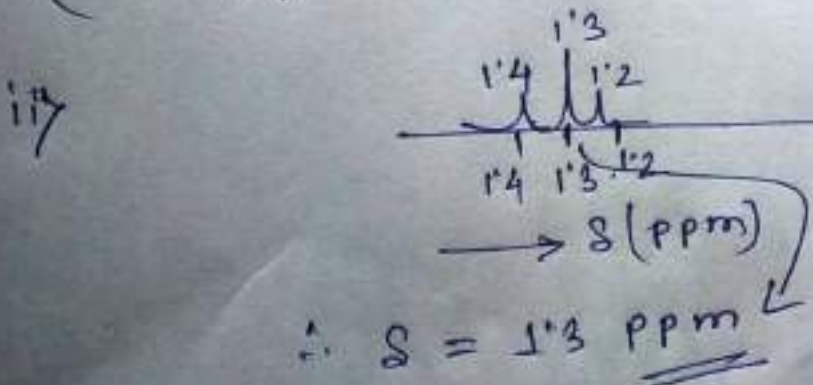
$$\Rightarrow H_2 = 200 \times 0.04$$

$$\therefore J = \underline{\underline{8 \text{ Hz}}}$$

Similarly — $\delta = \frac{(2.2 + 1.98)}{2} \text{ ppm}$

(chemical shift)

$$= \underline{\underline{2.09 \text{ ppm}}}$$



iv)

$1.4 \quad 1.3 \quad 1.2 \quad 1.1$

δ

$$\therefore \delta = \frac{1.4 + 1.3 + 1.2 + 1.1}{4}$$

$$= 1.25 \text{ ppm}$$

→ Coupling between two nuclei of the same type is called homonuclear coupling.

→ Coupling between two different types of nuclei is called heteronuclear coupling.

→ Magnitude of coupling constant depends on the number of bonds intervening between the two atoms or groups of atoms that interact.

→ In general, one-bond couplings are larger than two-bond couplings, which in turn are larger than three-bond couplings.

i.e., ${}^1J > {}^2J > {}^3J$

[Add a superscript to the symbol 'J' to indicate the number of bonds through which the interaction occurs.]

→ For ${}^1\text{H-NMR}$, 1J value is very small

Mechanism of coupling — (Direct vector model)

→ The electrons in the intervening bonds between the two nuclei transfer spin information from one nucleus to another by means of interaction between the nucleus & electronic spins.

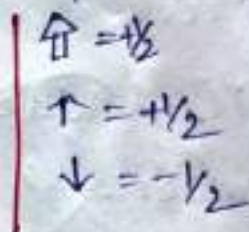
↳ An electron near the nucleus is assumed to have the lowest energy of interaction with the nucleus when the spin of the electron has its spin direction opposed to (or paired with) that of the nucleus.



Spins of nucleus & e-
paired or opposed
(lower energy)



Spins of nucleus & e-
parallel (higher energy)



where,

Spin of nucleus = heavy arrow

Spin of electron = small arrow

↳ Theory shows that couplings involving an odd number of intervening bonds (1J , 3J , ...) are expected to be positive.

↳ While those involving an even number of intervening bonds (2J , 4J , ...) are expected to be negative.

Short Range Couplings — (1J , 2J & 3J)

↳ One bond, two bond & three bond couplings are known as short range couplings.

One-Bond coupling (1J) —

↳ A one-bond coupling occurs when a single bond links two spin-active nuclei.



Two-Bond coupling (2J) — (geminal coupling)

↳ 2J coupling is also called geminal coupling, because two nuclei that interact are attached to the same central atom.

↳ Two bond coupling constants are abbreviated as ' 2J '

↳ Two-bond coupling constants are typically (although not always) smaller in magnitude than one-bond coupling.



The 2J coupling constants increase as the angle ' α ' decrease. As the angle ' α ' decreases, the two orbitals & the e^- spin correlations become

greater.



$\uparrow = +1/2$
 $\downarrow = -1/2$
 $\uparrow = +1/2$
 $\downarrow = -1/2$

Preferred alignment

Where,
 Small arrow = spin of e^-
 heavy " = " " nuclei

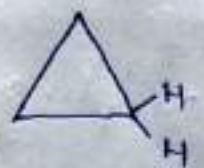
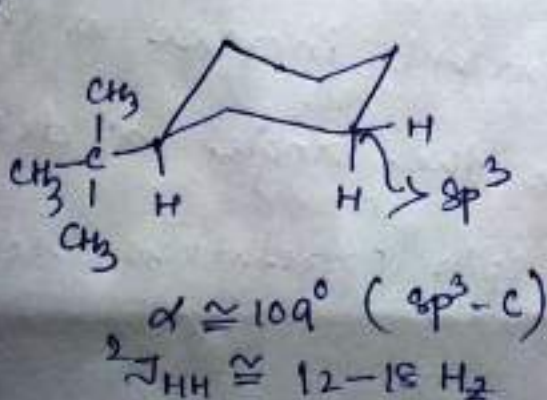
Fig Mechanism of geminal coupling.

Since common type of 2J coupling is frequently negative.

Note:- When two spin-active nuclei prefer an opposed alignment (have opposite spins), the coupling constant, J is usually positive
 → If the nuclei are parallel or aligned (have same spins), J is usually negative

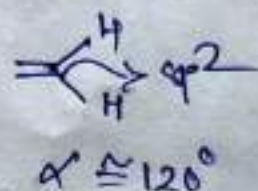
↳ The coupling constants become smaller, as predicted, when HCH angle becomes larger,

eg:-



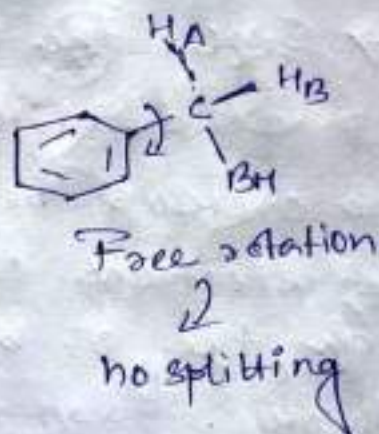
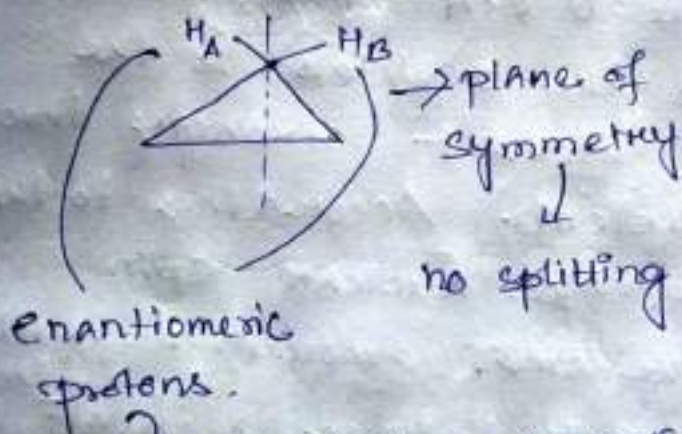
$^2J_{HH} \approx 5 \text{ Hz}$

due to ring strain



$^2J_{HH} \approx 0-3 \text{ Hz}$

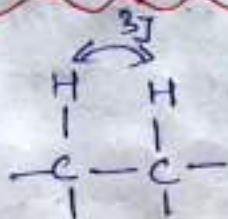
↳ In many cases, no geminal HCH coupling (no spin-spin splitting) is observed, either because the geminal protons are equivalent by symmetry or because free rotation renders them equivalent.



↳ chemically equivalent.

Three-Bond Couplings (3J) — (vicinal couplings)

↳



These H-C-C-H couplings are sometimes called vicinal couplings because the hydrogens are on neighboring carbon atoms.

↳ Vicinal couplings are three-bond couplings & have a coupling constant designated as 3J .

↳ In a typical hydrocarbon, the spin of a hydrogen nuclei in one C-H bond is coupled to the spins of these hydrogens in adjacent C-H bonds.

↳ Since the σ C-C bond is nearly orthogonal (perpendicular) to the σ C-H bonds, there is no overlap between the orbitals, & the σ electrons cannot interact strongly through the σ -bond system. According to the theory, they transfer the nuclear spin information via the small amount of parallel orbital overlap that exists between adjacent C-H bond orbitals.

↳ The spin interaction between the electrons in the two adjacent C-H bonds is the major factor determining the size of the coupling constant.



The orbitals actually have some sideways overlap. This overlap transfers spin information from one C-H bond to the other.

The C-C bond is orthogonal to the C-H bonds

↳ Three-bond H-C-C-H couplings are expected to be positive, hence, the interacting nuclei are spin paired in the favoured arrangement:

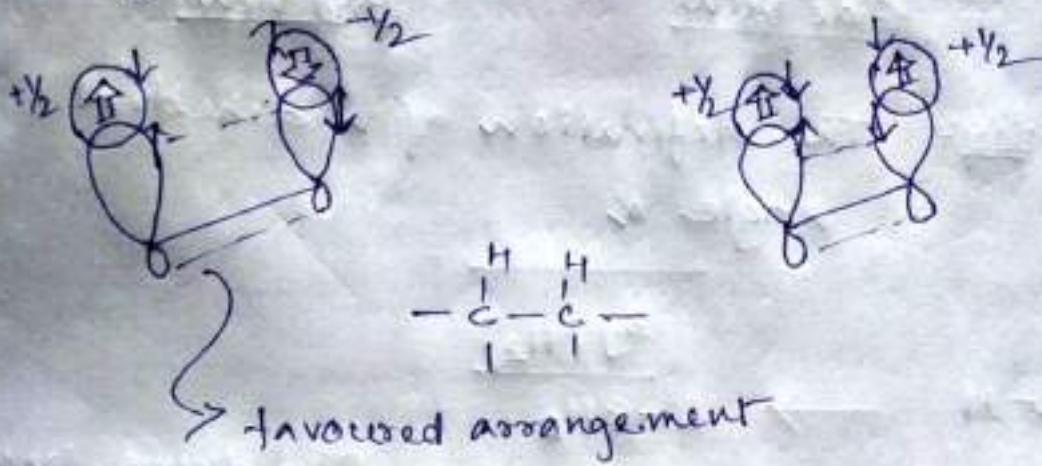
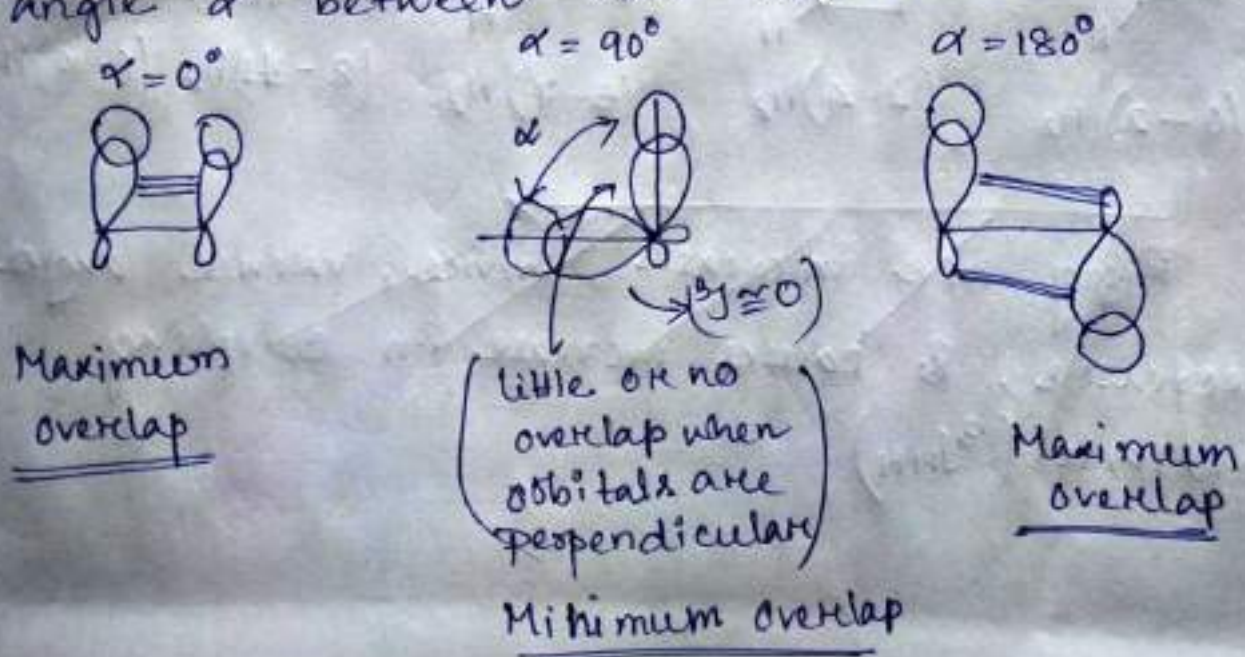


fig - The method of transferring spin information between two adjacent C-H bonds.

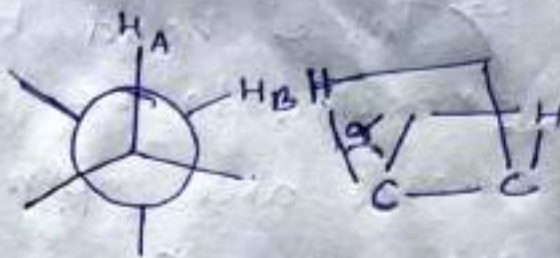
↳ The actual magnitude of the coupling constant between two adjacent C-H bonds can be shown to depend directly on the dihedral angle ' α ' between these two bonds —



Note -



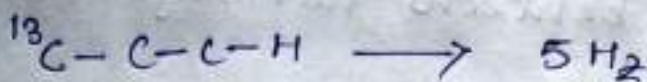
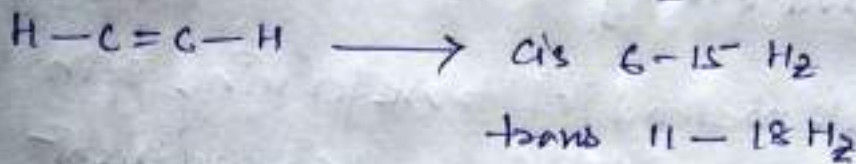
Side view



End view

Defn The definition of a dihedral angle α

↳

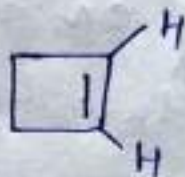


In alkenes, trans coupling constant is always larger than the cis-coupling constant

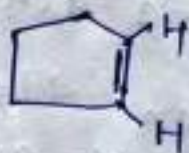
↳ Variation of $^3J_{HH}$ with valence angles in cyclic alkenes (H_2) -



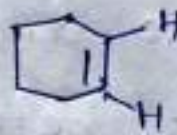
(0-2) H_2



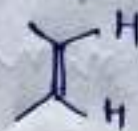
(2-4) H_2



(5-7) H_2



(8-11) H_2



(6-15) H_2

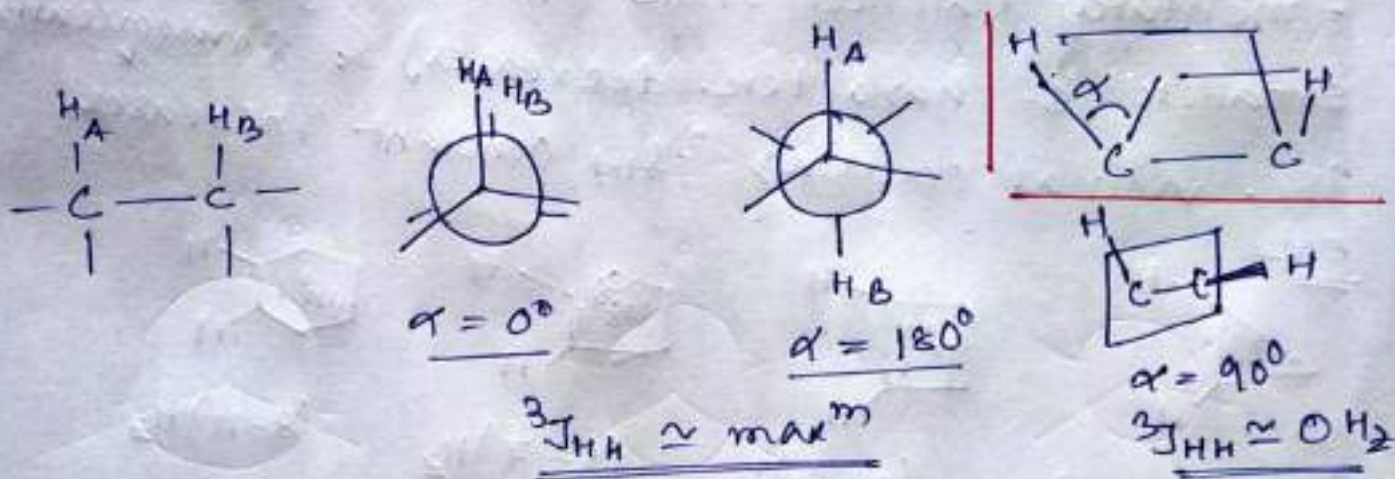
↳ As ring size decreases, the absolute value of the coupling constant ${}^3J_{HH}$ also decreases.

Factors influencing the magnitude of ${}^3J_{HH}$

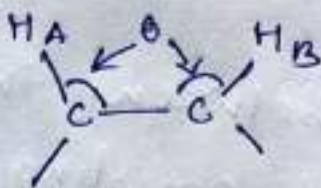
1) Dihedral angle (α) —

↳ When, $\alpha = 90^\circ$, ${}^3J_{HH} \cong 0$

$\alpha = 0^\circ$ & 180° , ${}^3J_{HH} = 8 - 10 \text{ Hz}$



2) Valence angle (θ) —



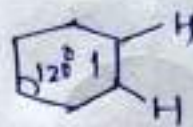
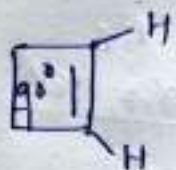
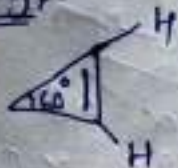
↳ Valence angle is related to ring size.

↳ Typically, when the valence angle decreases the coupling constant ${}^3J_{HH}$ decreases.

↳ Valence angle decreases with increasing ring size.

\hookrightarrow As the angle $\text{C}-\text{C}-\text{C}$ in the ring becomes larger (as p-character decreases), the complementary valence angle (H-C-H angle) becomes smaller (s-character decreases) & consequently the vicinal coupling $^3J_{\text{HH}}$ constant increases.

eg-



$$\therefore ^3J_{\text{HH}} = (0-2) \text{ Hz}$$

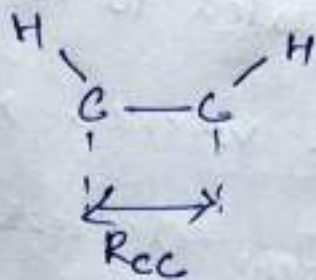
$$(2-4) \text{ Hz}$$

$$(5-7) \text{ Hz}$$

$$(8-11) \text{ Hz}$$

\Rightarrow Bond length —

\hookrightarrow The distance between the C-atoms gives influences to vicinal coupling constant. The

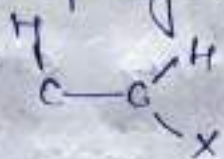


coupling constant increases with the decrease of bond length.

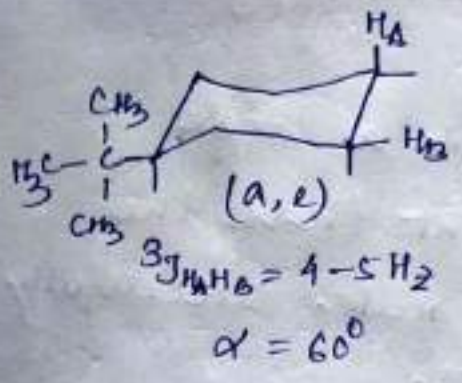
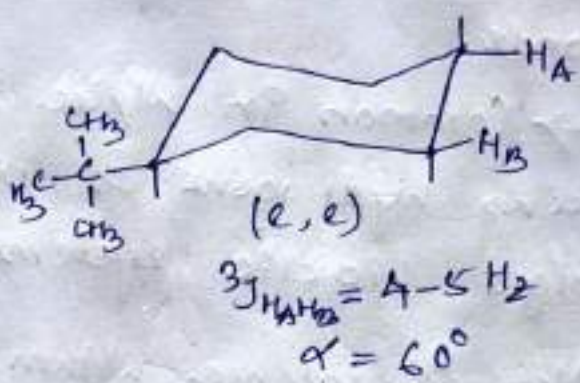
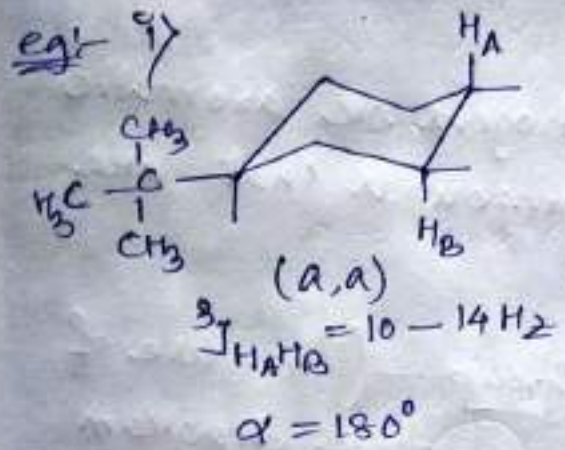
\Rightarrow Electronegative substituent —

\hookrightarrow Electronegative atoms affect vicinal coupling

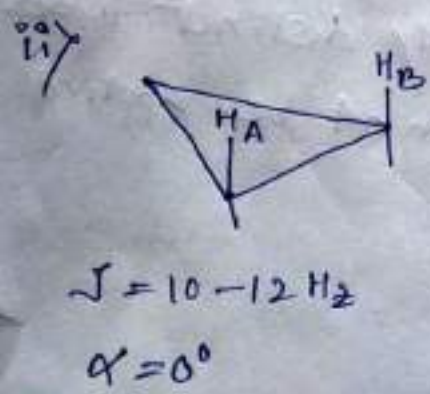
constants so that electronegative atoms decrease the vicinal coupling constants.



X = electronegative substituent.



The ring is locked in the indicated conformation because the bulky tert-butyl groups must be placed equatorially. So, free rotation is not possible here.



Cyclopropane is derivative also provide another conformationally rigid example

* Here also, $J_{cis}(\alpha=0^\circ)$ is a larger coupling constant than $J_{trans}(\alpha=120^\circ)$, opposite to alkenes

↳ Coupling between two nuclei of the same type is called homonuclear coupling.

↳ Coupling between two different types of nuclei is called heteronuclear coupling.

↳ Magnitude of coupling constant depends on the number of bonds intervening between the two atoms or groups of atoms that interact.

↳ In general, one-bond couplings are larger than two-bond couplings, which in turn are larger than three-bond couplings.

i.e., $^1J > ^2J > ^3J$

[Add a superscript to the symbol 'J' to indicate the number of bonds through which the interaction occurs.]

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paired or opposed
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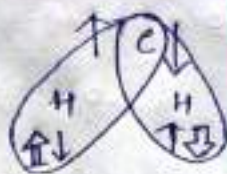


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Preferred alignment



Where,
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heavy " = " " nuclei

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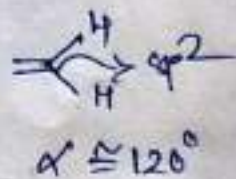
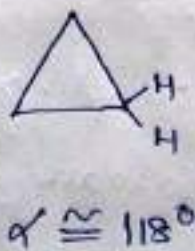
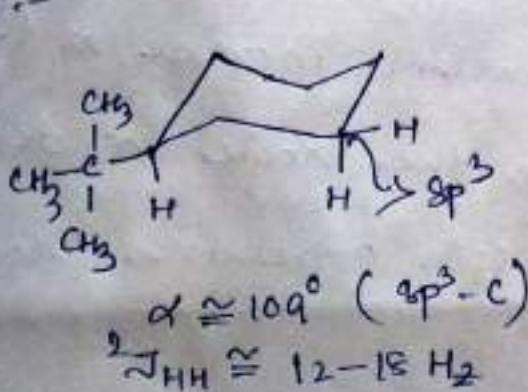
Fig Mechanism of geminal coupling.

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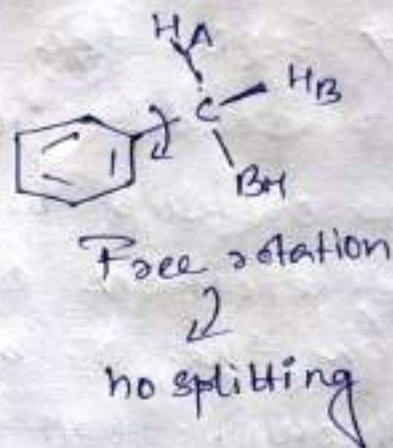
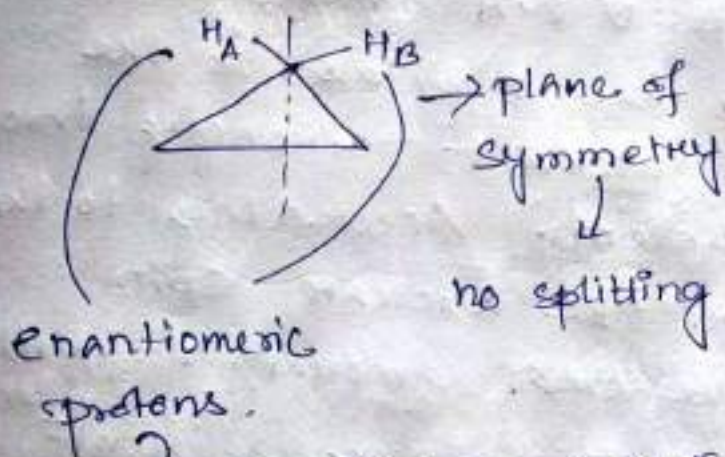
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due to ring strain

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→ Vicinal couplings are three-bond couplings & have a coupling constant designated as 3J .

↳ In a typical hydrocarbon, the spin of a hydrogen nuclei in one C-H bond is coupled to the spins of those hydrogens in adjacent C-H bonds.

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↳ The spin interaction between the electrons in the two adjacent C-H bonds is the major factor determining the size of the coupling constant.



The orbitals actually have some sideways overlap. This overlap transfers spin information from one C-H bond to the other.

The C-C bond is orthogonal to the C-H bonds

Three-bond H-C-C-H couplings are expected to be positive, hence, the interacting nuclei are spin paired in the favored arrangement.

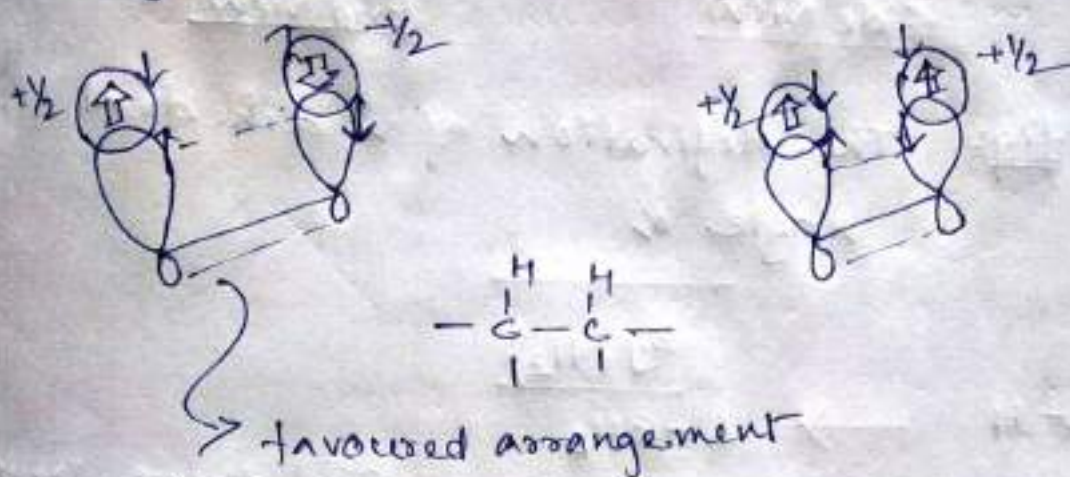
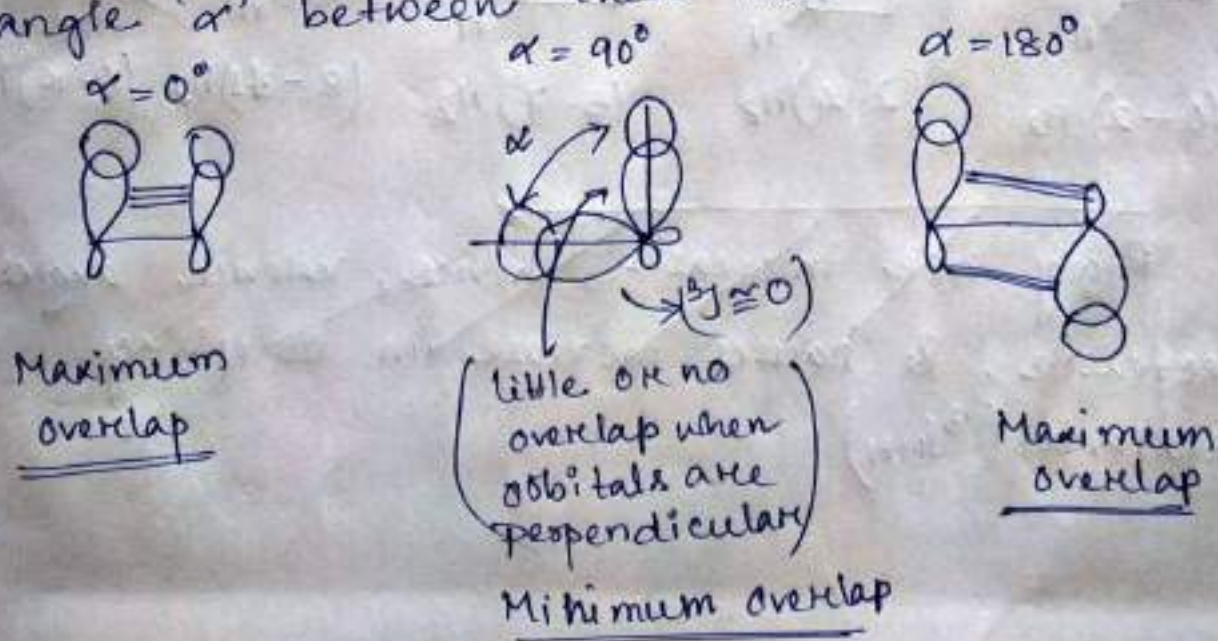
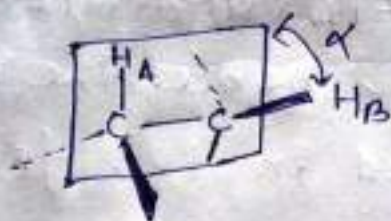


Fig- The method of transferring spin information between two adjacent C-H bonds.

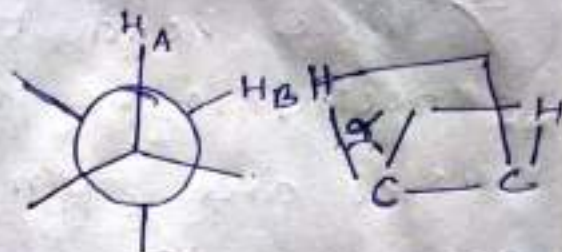
The actual magnitude of the coupling constant between two adjacent C-H bonds can be shown to depend directly on the dihedral angle ' α ' between these two bonds—



Note -

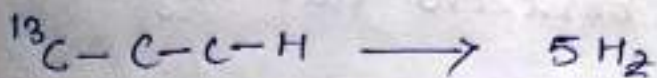


Side view



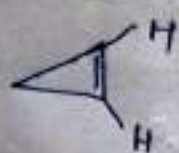
End view

Defn The definition of a dihedral angle α

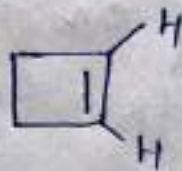


In alkene, trans coupling constant is always larger than the cis-coupling constant

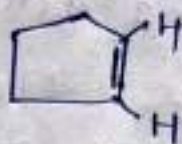
\rightarrow Variation of $^3J_{HH}$ with valence angles in cyclic alkenes (H_2) -



$(0-2) H_2$



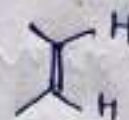
$(2-4) H_2$



$(5-7) H_2$



$(8-11) H_2$



$(6-15) H_2$

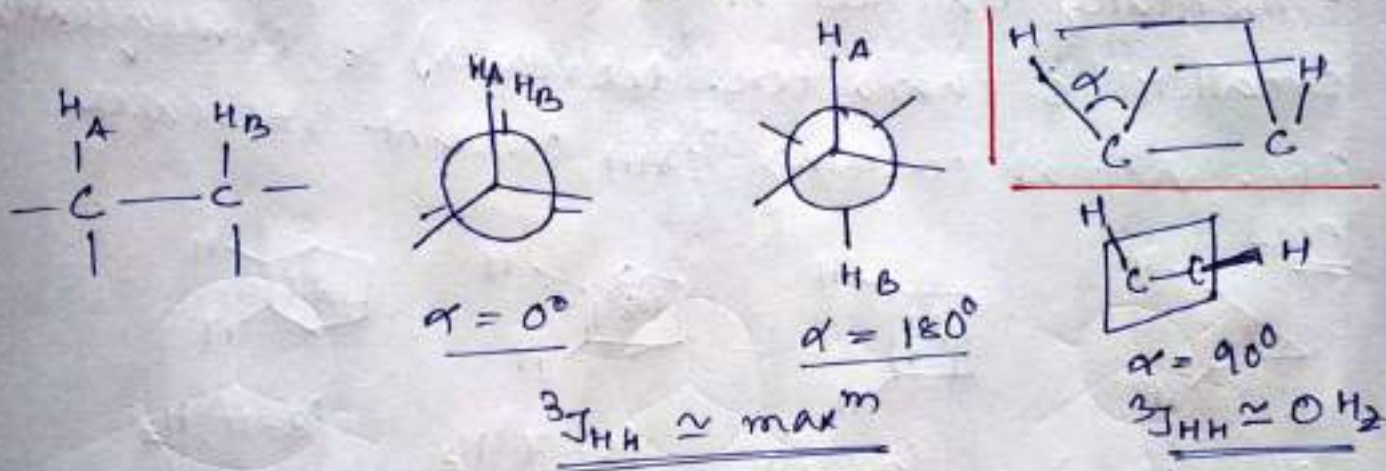
↳ As ring size decreases, the absolute value of the coupling constant $^3J_{HH}$ also decreases.

Factors influencing the magnitude of $^3J_{HH}$ —

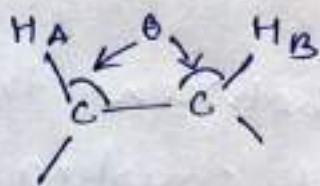
1) Dihedral angle (α) —

↳ When, $\alpha = 90^\circ$, $^3J_{HH} \approx 0$

$\alpha = 0^\circ$ & 180° , $^3J_{HH} = 8 - 10 \text{ Hz}$



2) Valence angle (θ) —



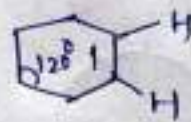
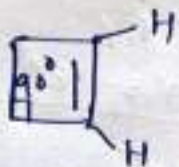
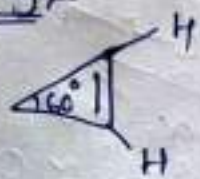
↳ Valence angle is related to ring size.

↳ Typically, when the valence angle decreases the coupling constant $^3J_{HH}$ decreases.

↳ Valence angle decreases with increasing ring size.

↳ As the angle C-C-C in the ring becomes larger (as p-character decreases), the complementary valence angle (H-C-H angle) becomes smaller (s-character decreases) & consequently the vicinal coupling $^3J_{HH}$ constant increases.

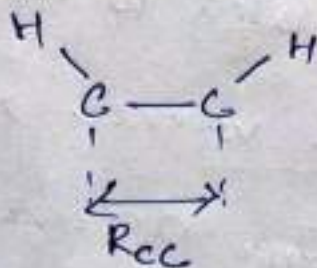
eg:



$$\therefore ^3J_{HH} = (0-2)H_2 \quad (2-4)H_2 \quad (5-7)H_2 \quad (8-11)H_2$$

3) Bond length —

↳ The distance between the C-atoms gives influences to vicinal coupling constant. The



coupling constant increases with the decrease of bond length.

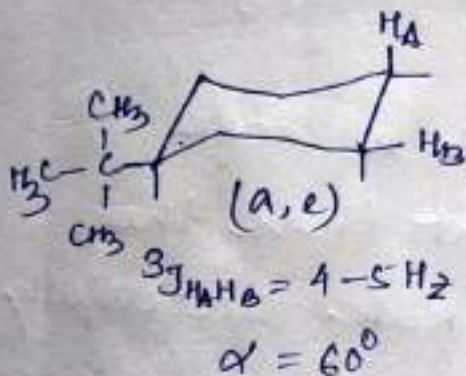
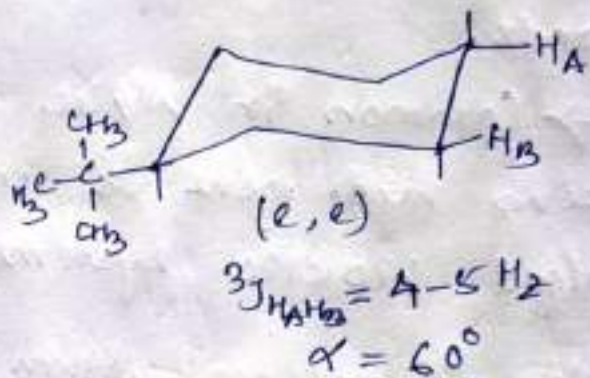
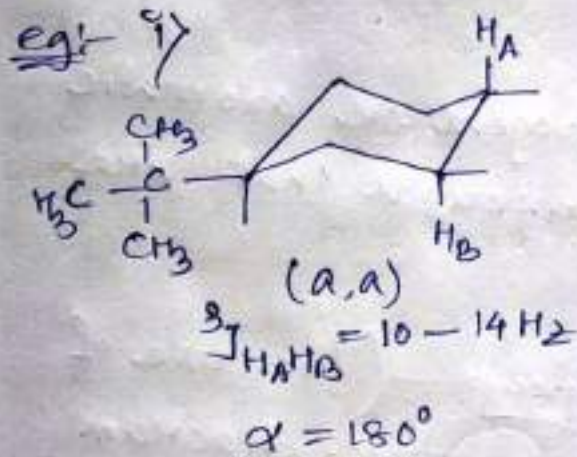
↳ Electronegative substituent —

↳ Electronegative atoms affect vicinal coupling

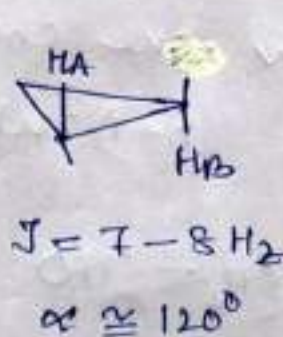
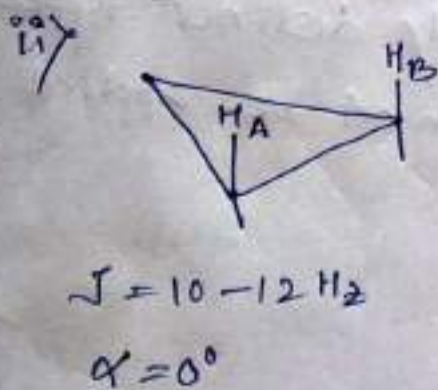
constants so that electronegative atoms decrease the vicinal coupling constants.



X = electronegative substituent.



The ring is locked in the indicated conformation because the bulky tert-butyl groups must be placed equatorially. So, free rotation is not possible here.



Cyclopropane is derivative also provide another conformationally rigid example.

* Here ~~the~~, $J_{cis}(\alpha=0^\circ)$ is ~~the~~ larger coupling constant than $J_{trans}(\alpha=120^\circ)$, opposite to alkenes.

Long Range Couplings — ($4J - {}^nJ$)

↳ Long range couplings are four bond coupling, five bond coupling etc.

↳ These couplings involve more than three bonds.

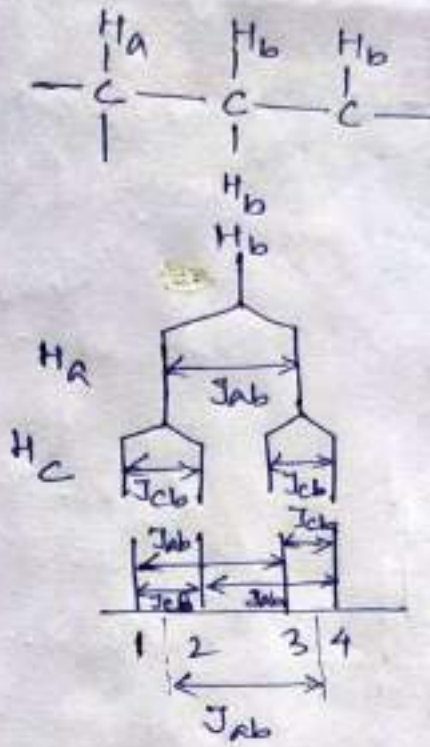
↳ Common in allylic hydrogens or aromatic ring hydrogens & in compounds that are rigid bicyclic systems.

Non equivalence within a group — (The use of tree diagram when the $(n+1)$ rule fails)

↳ When the protons attached to a single carbon are chemically equivalent (have the same chemical shift), the $n+1$ rule successfully predicts the splitting patterns.

↳ In contrast, when the neighbouring protons ^{are} have more than one chemically distinct types of protons than $(n+1)$ rule cannot be applied

eg:-



Four hydrogens, (H_b)
 First, two possible spins of H_a split H_b (³J_{ab}) into a doublet, second H_c splits each of the doublet peaks (³J_{cb}) into another doublet.

↳ To obtain J_{ab} —

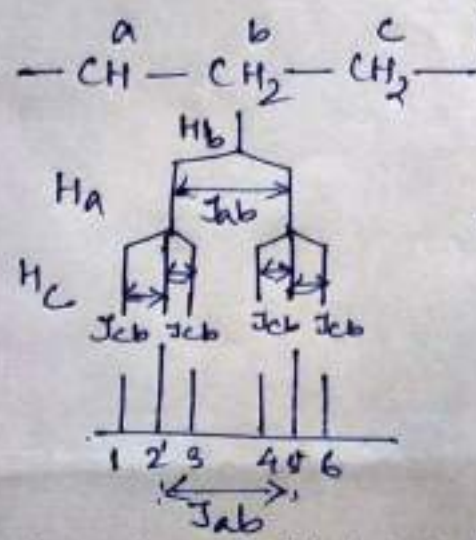
Measure difference between lines 1 & 3 OR 2 & 4 in H₂

↳ To obtain J_{cb} —

Measure difference between lines 1 & 2 OR 3 & 4 in H₂

↳ The resulting pattern of two doublets is called doublet of doublets (dd)

ii) →

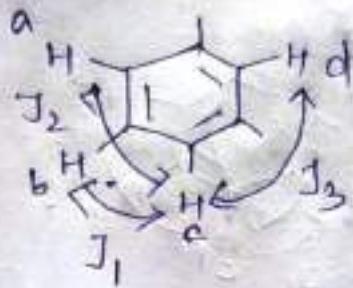


↳ To obtain J_{ab}, measure the difference between the most intense lines (2 & 5) in H₂

↳ To obtain J_{cb}, measure the spacing between lines 1 & 2, OR 2 & 3 OR 4 & 5 OR 5 & 6 in H₂

Doublet of triplets (dt)

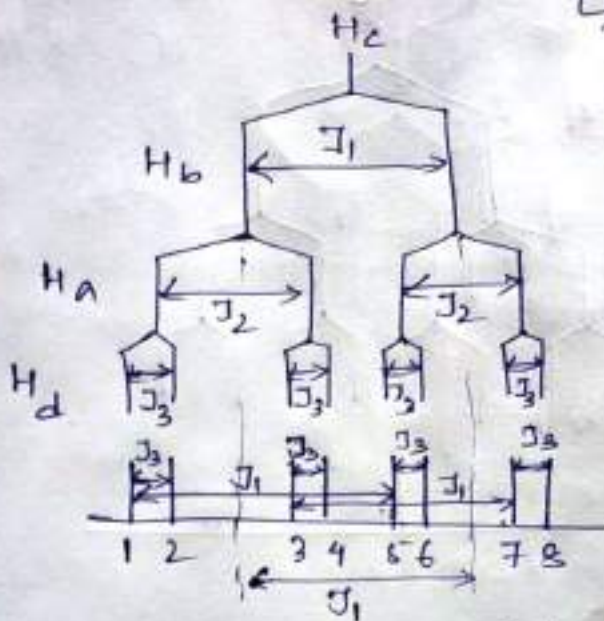
iii)



↳ To obtain J_1 measure difference between lines 1 & 5, or 3 & 7, or 2 & 6, or 4 & 8 in H_2

↳ To obtain J_2 measure difference between lines 1 & 3 or 2 & 4 or 3 & 5, or 4 & 6, or 5 & 7, or 6 & 8 in H_2

↳ To obtain J_3 measure difference between lines 1 & 2, or 3 & 4, or 5 & 6, or 7 & 8 in H_2



doublet of doublet of doublets (ddd)

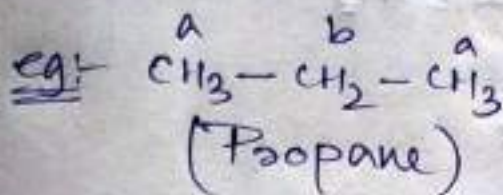
1H NMR absorptions by type of compounds

1) Alkanes

↳ Alkanes have three different types of hydrogens — methyl, methylene & methyne.

	δ (ppm) (chemical shifts)
↳ $R-CH_3$	$\rightarrow 0.7 - 1.3$ ppm
$R-CH_2-R$	$\rightarrow 1.2 - 1.4$ ppm
R_3CH	$\rightarrow 1.4 - 1.7$ ppm.

↳ Coupling behavior —



$$6H_a = (n+1)$$

$$= 2+1$$

$$= 3 \text{ (triplet) (6H)}$$

$$2H_b = (n+1)$$

$$= 3+1$$

$$= 4 \text{ (quartet) (2H)}$$

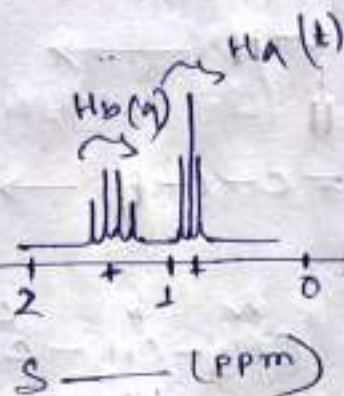


fig - ¹H-spectrum of propane

⇒ Alkene —

↳ Alkenes have two types of hydrogens —

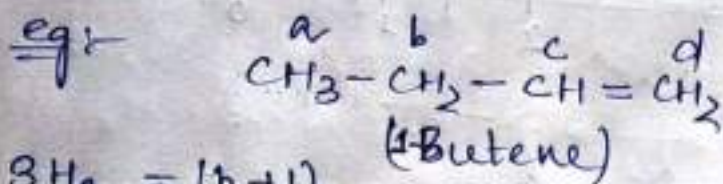
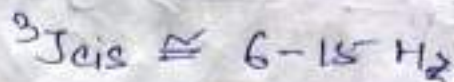
i) vinyl (those attached directly to the double bond) &

ii) allylic (those attached to a α -carbon atom, the carbon atom attached to the double bond)

chemical shift



→ Coupling behavior —

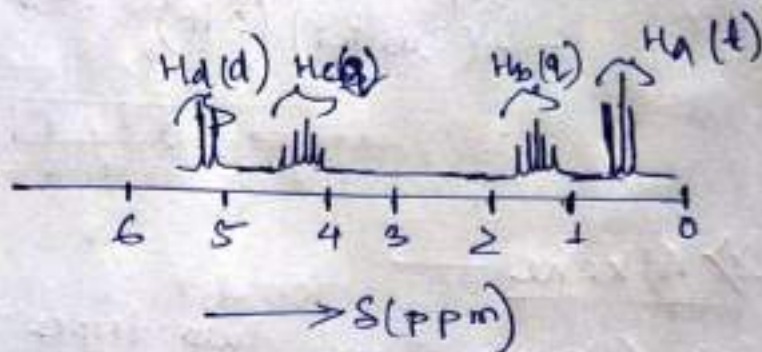


$$3H_a = (n+1) \\ = 3 \text{ (triplet)}$$

$$2H_b = (n+1) \\ = 5 \text{ (quintet)}$$

$$1H_c = (n+1) \\ = 5 \text{ (quintet)}$$

$$2H_d = (n+1) \\ = 2 \text{ (doublet)}$$



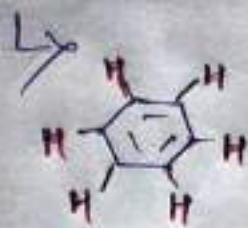
3) Aromatic Compounds —

↳ Aromatic compounds have two characteristic types of hydrogens —

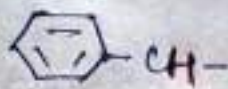
i) Aromatic ring hydrogens (benzene ring hydrogens) &

ii) benzylic hydrogens (those attached to an adjacent carbon atom)

Chemical shifts

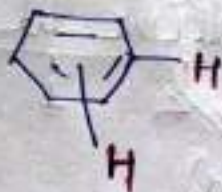


→ 6.5 - 8 ppm



→ 2.3 - 2.7 ppm

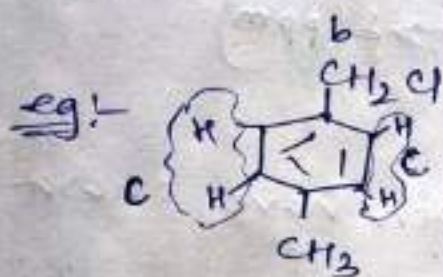
↳ Coupling behavior —



$^3J_{ortho} \approx 7-10 \text{ Hz}$

$^4J_{meta} \approx 2-3 \text{ Hz}$

$^5J_{para} \approx 0-1 \text{ Hz}$

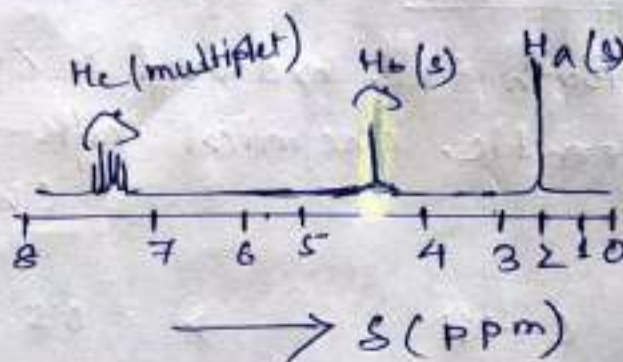


(α -chloro-p-xylene)

$2 H_b = (n+1), n=0$
 $= 1$ (Singlet)

$3 H_a = (n+1), n=0$
 $= 1$ Singlet

$4 H_c = (n+1)$
 $=$ multiplet



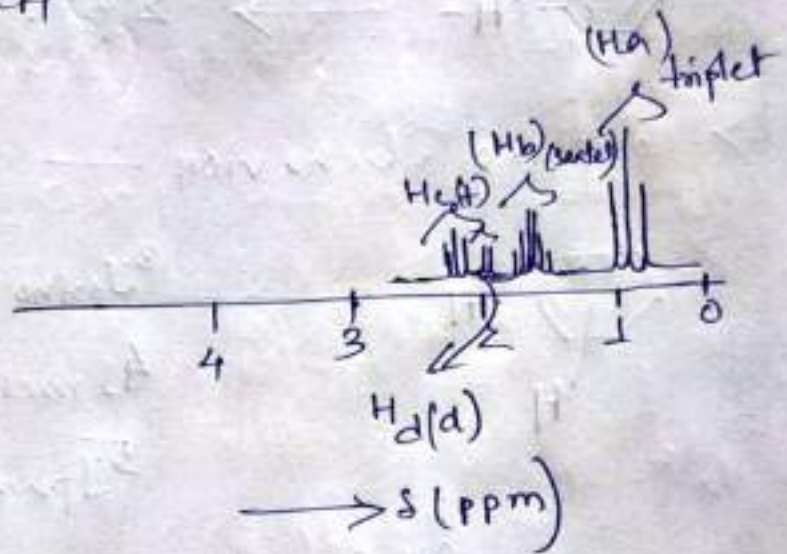
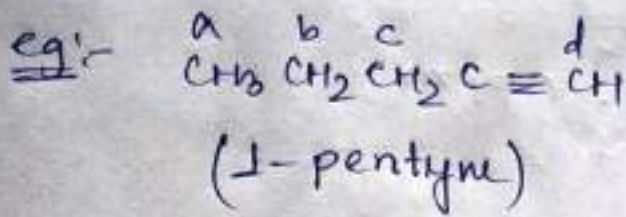
4) Alkynes —

Chemical shifts

$C \equiv C-H$ → 1.7 - 2.7 ppm
(terminal Alkyne)

$C \equiv C-CH-$ → 1.6 - 2.6 ppm
(α -hydrogen)

↳ Coupling behavior —



5) Alcohols —

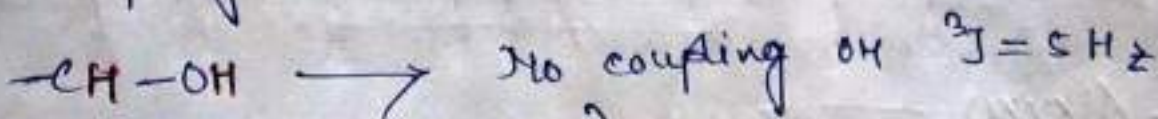
↳ Both the hydroxyl & α -hydrogen have characteristic chemical shifts —

Chemical shifts



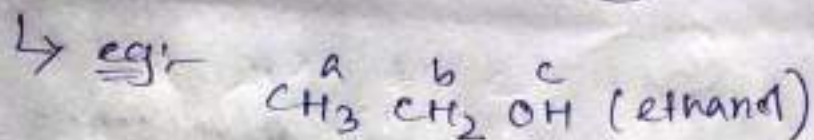
(α -hydrogen)

↳ Coupling behavior —

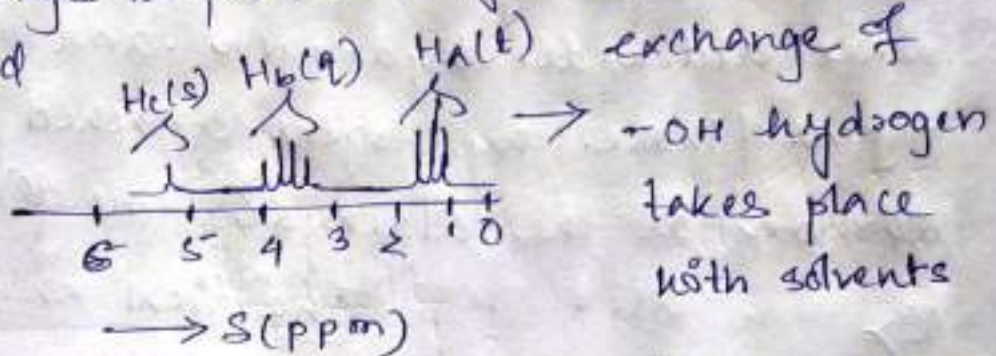


↳ Rapid chemical exchange of the $-OH$ proton in many solutions, coupling is not usually observed.



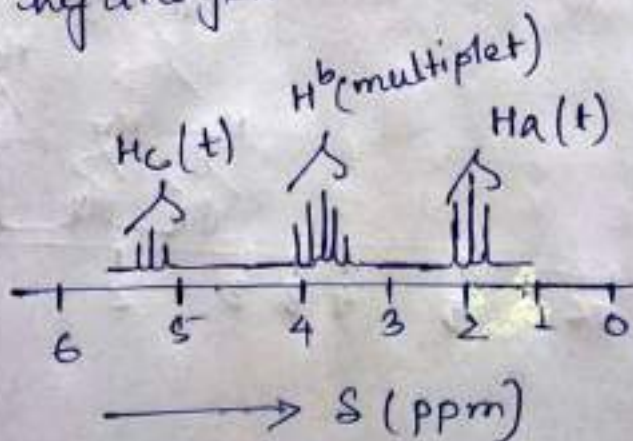


↳ The exchange is promoted by temperature, small amounts of acid impurities or the presence of water in the solution.



↳ If exchange is taking place, $-\overset{b}{\text{CH}_2}-$ hydrogens will not show any coupling with the $-\text{OH}$ hydrogen, but it may show coupling to any hydrogens on the adjacent carbon located further along the carbon chain.

↳ If the exchange is not occurring (in case of pure ethanol) the pattern of $-\overset{b}{\text{CH}_2}-$ hydrogens may be complicated as it may show coupling with $-\text{OH}$ hydrogen.



↳ Rate of exchange increases with the temperature.

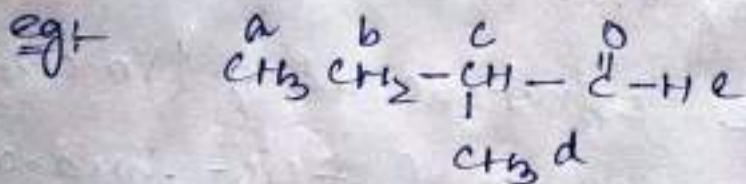
6) Aldehydes —

↳ Two hydrogens are found in aldehydes, the aldehyde hydrogen and the α -hydrogens (those hydrogens attached to the same carbon as the aldehyde group).

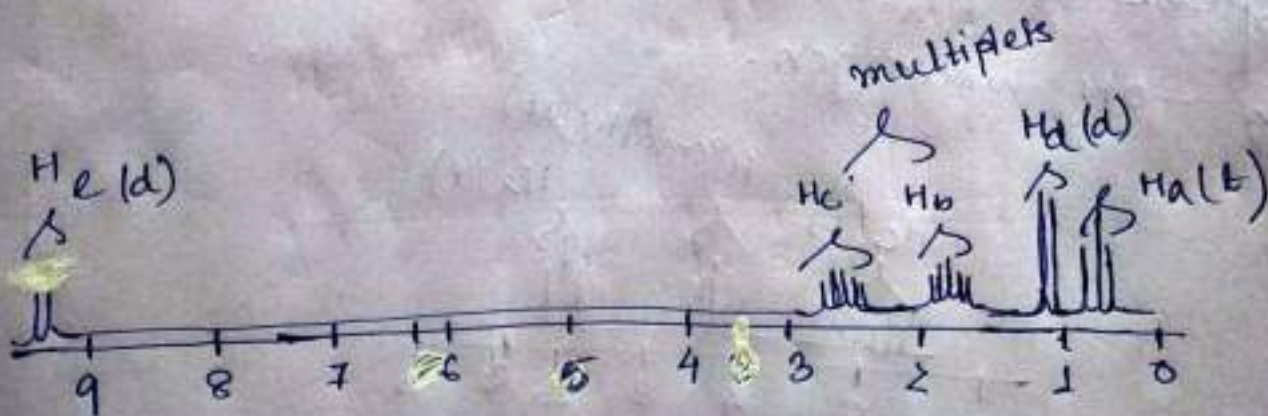
↳ Chemical shifts



↳ Coupling behaviour —



(2-methylbutyraldehyde)



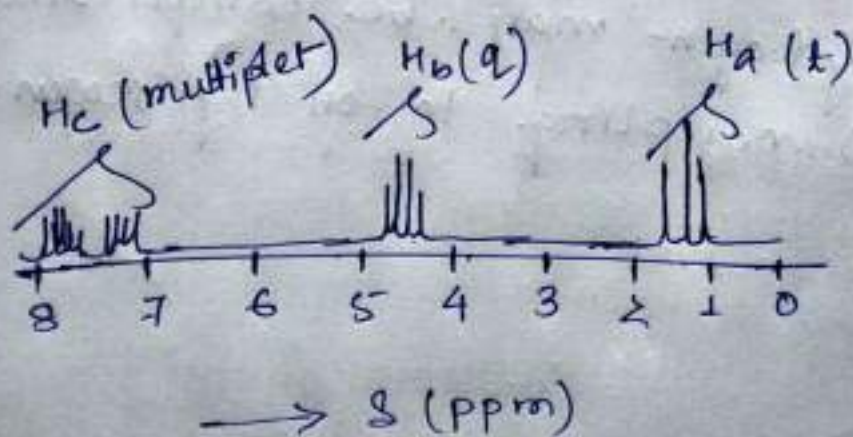
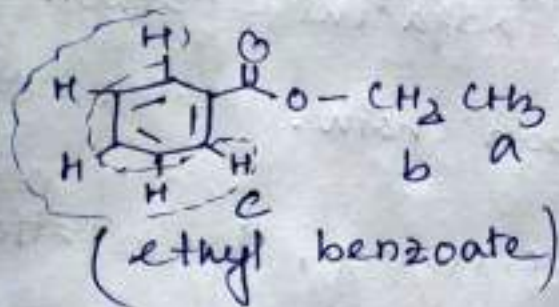
7) Esters

↳ Two distinct types of hydrogens are found in esters — those on the carbon atom attached to the oxygen atom in the alcohol part of the ester & those on the α -carbon in the acid part of the ester (that is those attached to the carbon next to $C=O$ group).

Chemical shifts



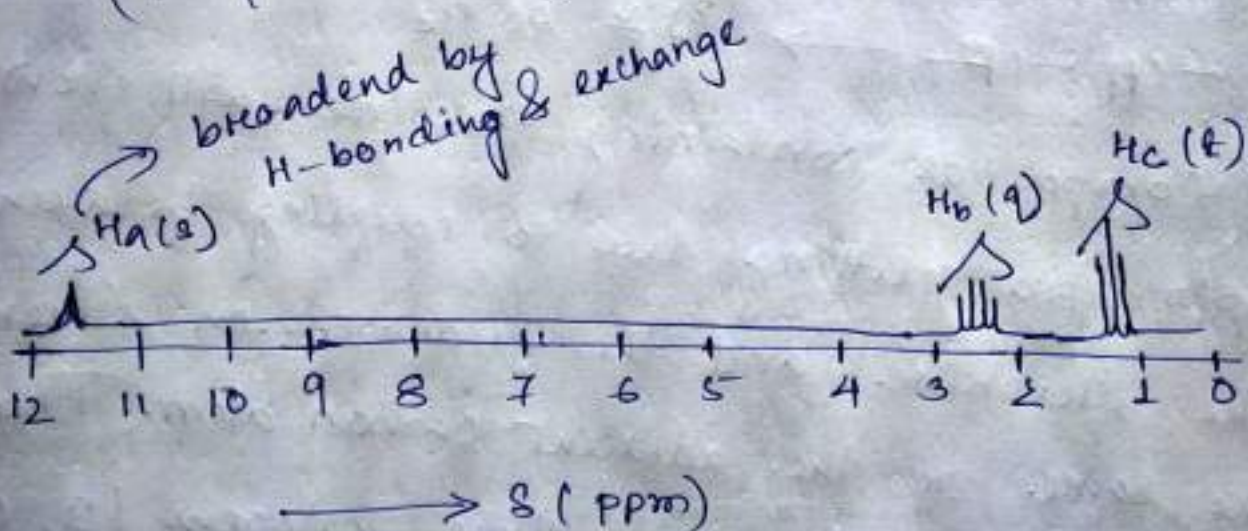
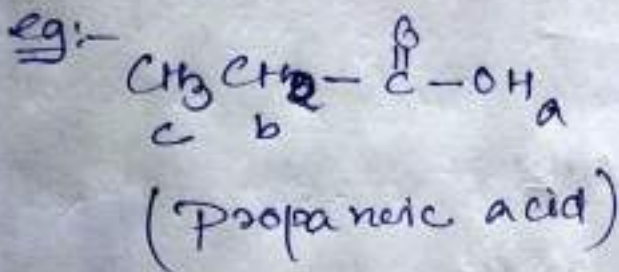
eg:-



3) Carboxylic Acids —

↳ Carboxylic acids have the acid proton (the one attached to the $-\text{COOH}$ group) and the α -hydrogens (those attached to the same carbon as the ~~carb~~ carboxyl group)

↳ Chemical shift



a) Alkyl halides —

↳ In alkyl halides the α -hydrogen (the one attached to the same carbon as the halogen) will be deshielded.

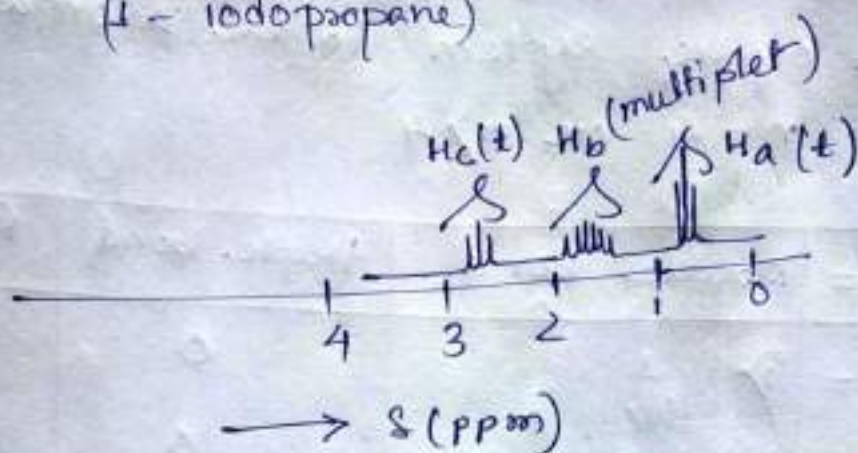
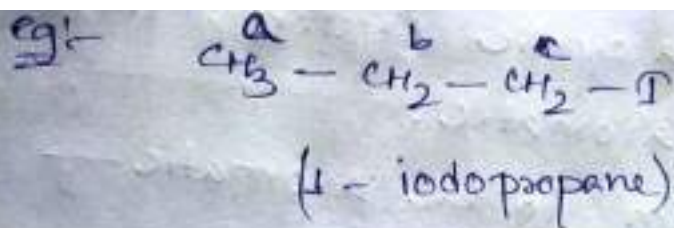
↳ Chemical shifts



↳ Coupling behaviour —



(Compounds containing fluorine will show spin-spin splitting due to coupling between the fluorine and the hydrogens on either the same or the adjacent carbon atom. Fluorine has a spin of $\frac{1}{2}$. The other halogens (I, Cl, Br) do not show any coupling.)



Double Bond Equivalent (DBE) -

$$\text{DBE} = N_{\text{tetra}} - \frac{N_{\text{mono}}}{2} + \frac{N_{\text{tri}}}{2} + 1$$

Where,
 N_{tetra} = Number of tetravalent atoms, eg:- C

N_{mono} = " " monovalent "

eg:- (Cl, Br, I, H) etc.

N_{tri} = Number of trivalent atoms

eg:- N.

eg:-

⇒



C_5NH_5

$$\text{DBE} = 5 - \frac{5}{2} + \frac{1}{2} + 1$$

$$= 5 - 2.5 + 0.5 + 1$$

$$= 4 \text{ (aromatic), i.e., ring}$$

is considered as equivalent of double bond.

→ If $DBE = 4$ for a cyclic system, then the system will be aromatic.

For a cyclic system to be aromatic —
 $n = 4$ or $n > 4$

DBE =	Double bond	Triple bond	Ring
1	i) 1	0	0
	ii) 0	0	1
2	i) 2	0	0
	ii) 0	1	0
	iii) 1	0	1
	iv) 0	0	2 etc.

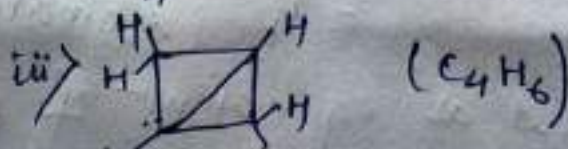
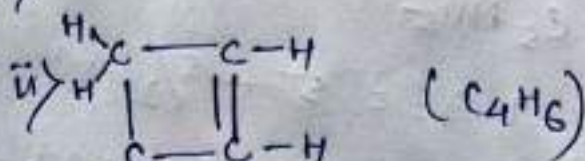
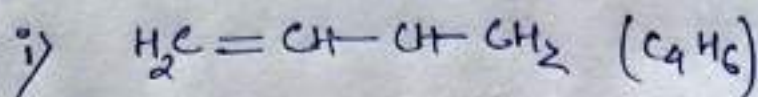
→ Possible structures of C_4H_6 —

$$DBE = 4 - \frac{6}{2} + \frac{0}{2} + 1$$

$$= 4 - 3 + 1$$

$$= 2$$

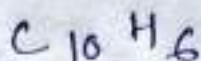
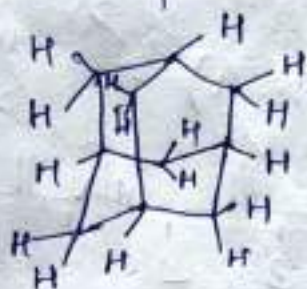
Possible structures —



↳ Find the number of rings in —



⇒ Molecular formula —



$$\therefore \text{DBE} = 10 - \frac{16}{2} + 1$$

$$= 10 - 8 + 1$$

$$= 3$$

Since, no double or triple bond present.

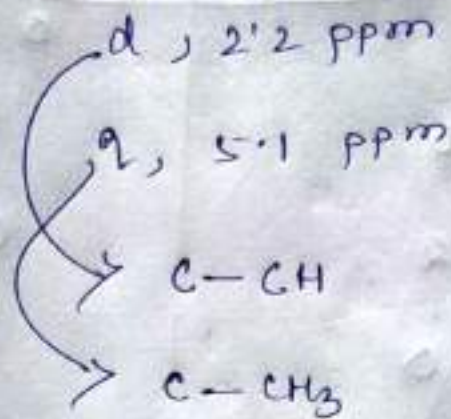
Therefore, ~~no~~ $\text{DBE} \cong \text{No. of rings}$

$$\therefore \text{No. of Ring} = \underline{\underline{3}}$$

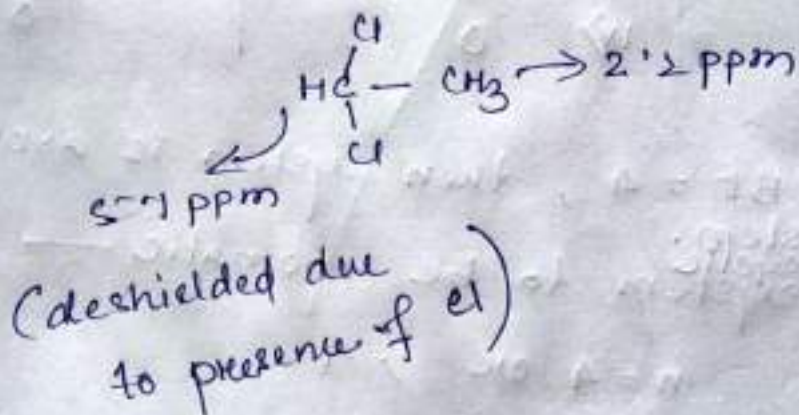
↳ For $C_2H_6Cl_2$, gives two $^1\text{H-NMR}$ signals —
(d, 2.2 ppm) & (q, 5.1 ppm), find the structure —

$$\begin{aligned} \Rightarrow \text{DBE} &= 2 - \frac{6}{2} + 1 \\ &= 2 - 3 + 1 \\ &= \underline{\underline{0}} \end{aligned}$$

Given —



∴ Possible structure —



↳ Given, Mol. wt = 120, ¹H-NMR signals —
(multiplet, 5H at 7.1-7.3 ppm), (d, 6H, at 1.2 ppm) & (septet, 1H at 2.8 ppm)

⇒

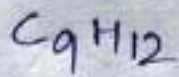
Mol. wt. = 120

divisor ← 13 $\sqrt{\begin{array}{r} 9 \rightarrow \text{quotient} \\ 120 \rightarrow \text{dividend} \\ 170 \\ 3 \rightarrow \text{remainder} \end{array}}$

∴ No. of Carbon = 9 (quotient)

& " " Hydrogen = 9 + 3 = 12 (remainder + quotient)

∴ The molecular formula will be —

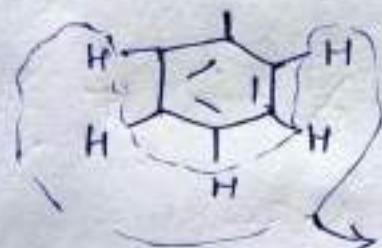


$$\therefore DBE = 9 - \frac{12}{2} + 1$$

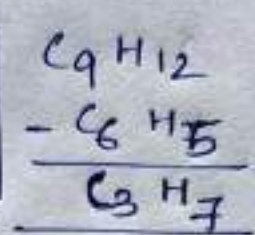
$$= 9 - 6 + 1$$

$$= 4 \text{ (Aromatic)}$$

Therefore, possible structure —

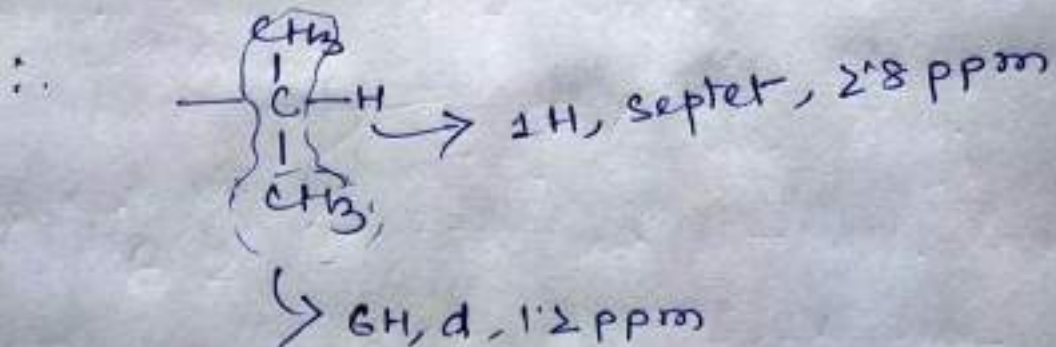


7.1 — 7.3 ppm, 5H
(multiplet)



Given, 6H, d, 1.2 ppm &

1H, septet, 2.8 ppm



Therefore, the structure will be

