Relaxation Process :

It involves some non radioactive transitions by which a nucleus in an ~~uper~~ upper transition state returns to the lower spin state. Two kinds of relaxation processes are —

I Spin - spin Relaxation :-

In this case excited nucleus get relaxed by imparting its energy to the nucleus of the lower state and thus there is always a bit greater number of nuclei in ground state to continue the n.m.r. spectra. (It is due to the mutual exchange of spins by two precessing nuclei which are in close proximity to each other).

II Spin- lattice Relaxation (Longitudinal Relaxation) :-

In this case an excited nucleus (proton) imparts its energy to the lattice and returns to the ground state. Here lattice stands for solvents, other electrons or atoms present in the sample. This energy is eventually converted into translational energy, rotational energy, vibrational energy etc.. ~~In this In this~~

In this way, the two mechanisms assume the excess number of nuclei in the ground state for the absorption of energy from radiofrequency and causing the fliping of protons.

$$h\nu = \gamma H_0 = ar$$

$$\nu = \frac{\gamma H_0}{h}$$

and $\gamma = g_n \beta_n$ $\therefore$ $\boxed{\nu = \frac{g_n \beta_n H_0}{h}}$ — I (When H_0 fixed)

$$\boxed{\therefore H_0 = \frac{h\nu}{g_n \beta_n}}$$ — II (When ν is fixed)

g_n = nuclear splitting factor or nuclear g-value, which is a constant for a particular nucleus.

e.g. $^1H \rightarrow g_n = 5.5856$; $^{13}C \rightarrow g_n = 1.4048$

$^{19}F \rightarrow g_n = 5.257$

$\beta_n = \frac{qh}{4\pi m_p c}$, q = charge of nucleus = charge of protons.

$= 5.05 \times 10^{-24}$ erg gauss^{-1}

$= 5.05 \times 10^{-27}$ JT^{-1} (T = Tessela)

$\because$ 1 erg gauss^{-1} = 10^{-3} JT^{-1}

(erg gauss^{-1} → c.g.s. unit; JT^{-1} → SI unit)

Unit of mag. moment = Am^2

$1T = 1NA^{-1}m^{-1} = 1NC^{-1}s\,m^{-1}$

$= 1Kg\,s^{-1}C^{-1}$

; A = Ampere

coulomb = A × sec

$A = C\,s^{-1}$

* In c.g.s. unit, mag. moment has unit erg gauss^{-1} while in S.I. unit it is J. Tessela^{-1}.

It is also expressed in Wb/m^2

$1T = 10^{+4}$ Gauss (Wb = Weber)

- If mag. field of 15,000 gauss is applied, calculate the radio frequency to resonate a proton (^1_1H).

we know that, $\nu = \frac{g_n \beta_n H_0}{h} = \frac{5.5856 \times 5.05 \times 10^{-24} \text{ erg gauss}^{-1} \times H_0 \text{ gauss}}{6.6 \times 10^{-27} \text{ erg. sec}}$

$= 4.26 \times 10^3 \times H_0 \; sec^{-1}$

$= 4.26 \times 10^3 \times 15000 \; sec^{-1}$

$= 63.9 \times 10^6$ c.p.s. or Hz

$=$ 64 MHz.

Q calculate mag. field strength required to precessional frequency for a proton of 220 M.c.p.s or MHz.

We know that, $\nu = \frac{g_n \beta_n H_0}{h}$

$\therefore H_0 = \frac{h\nu}{g_n \beta_n} = \frac{6.6 \times 10^{-27} \times 220 \text{ erg.sec} \times \text{MHz}}{5.5856 \times 5.05 \times 10^{-24} \text{ erg/gauss}}$

$= \frac{14.52 \times 10^{4}}{5.5856 \times 5.05}$ gauss

$= 5.1476 \times 10^{4}$ gauss

$= 5.15$ T $\quad (\because 1T = 10^4 \text{ gauss})$

Number of Signals:

The number of signals in the nmr spectrum tell the number of different set of equivalent protons in a molecule. Each signal corresponds to a set of equivalent protons. It may be noted that magnetically equivalent protons are chemically equivalent.

Find the various set of equivalent protons (signals) in the following compounds.

(i) $\overset{a}{CH_3}$, $\overset{a}{CH_3}$ > C=O ($(CH_3)_2C=O$)
No. of signal / nmr signal = 1
Acetone

(ii) $\overset{a}{CH_2}$—$\overset{a}{CH_2}$ | $\overset{a}{CH_2}$—$\overset{a}{CH_2}$
(1)
Cyclobutane

(iii) $\overset{a}{CH_2}$—$\overset{a}{CH_2}$ (each with Br: $BrCH_2-CH_2Br$)
(1)

(iv) $\overset{a}{CH_3}-\overset{b}{OH}$
(2)

(v) $\overset{c}{CH_3}-\overset{b}{CH_2}-\overset{a}{NH_2}$
(3)

(vi) $\overset{c}{CH_3}\overset{b}{CH_2}\overset{a}{CH_2}Cl$
(3)

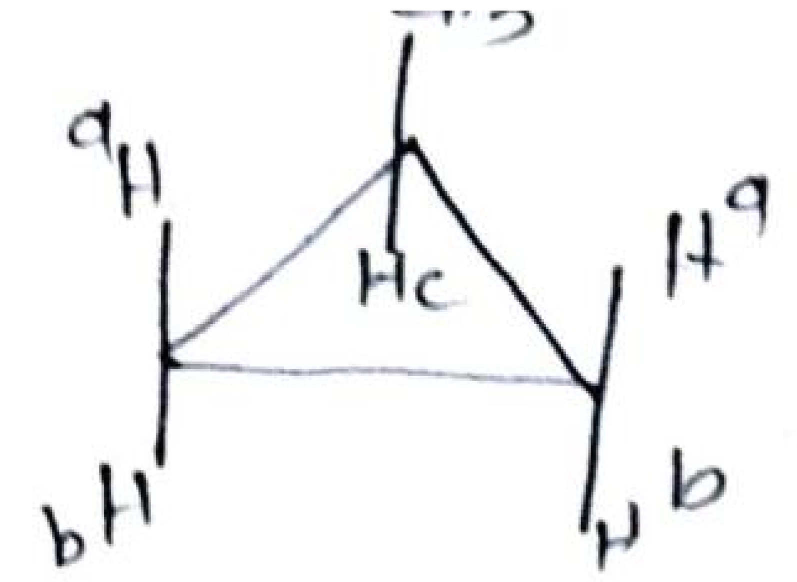
(vii) $\overset{b}{CH_3}-\overset{c}{CH}(\overset{a}{OH})-\overset{b}{CH_3}$
(3)

(viii) $\overset{a}{CH_3}$, Cl > C = C < $\overset{b}{H}$, $\overset{c}{H}$
(3)

(ix) $\overset{a}{CH_3}-C(\overset{a}{CH_3})(\overset{a}{CH_3})-\overset{b}{NH_2}$
(2)

(x) $\overset{b}{CH_3}\overset{a}{CH}Br$
(2)

(XI)

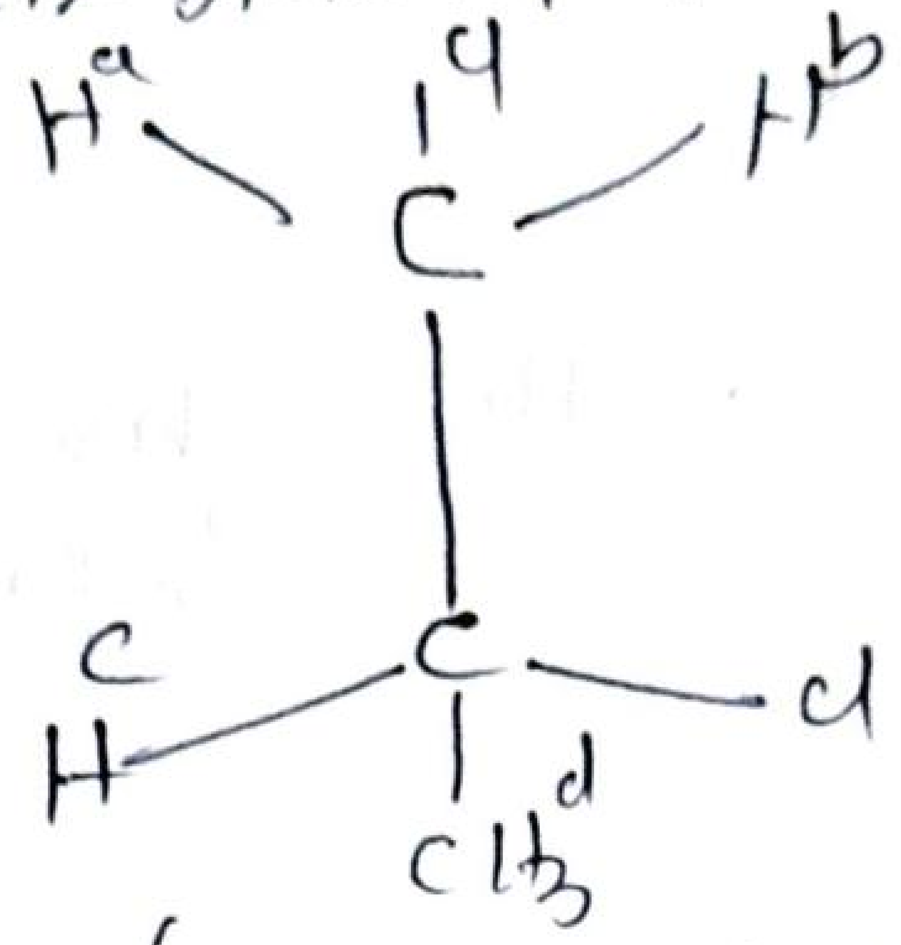


methyl cyclopropane

(4)

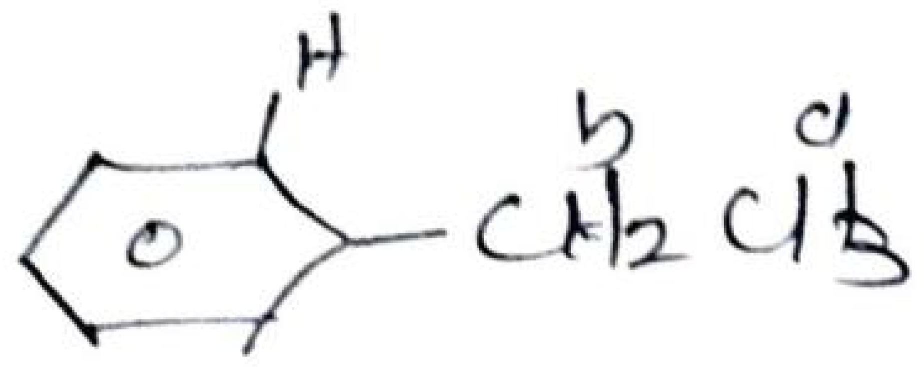
(XII) $CH_3CHCl-CH_2Cl$

1,2-Dichloropropane



(4 - signals)

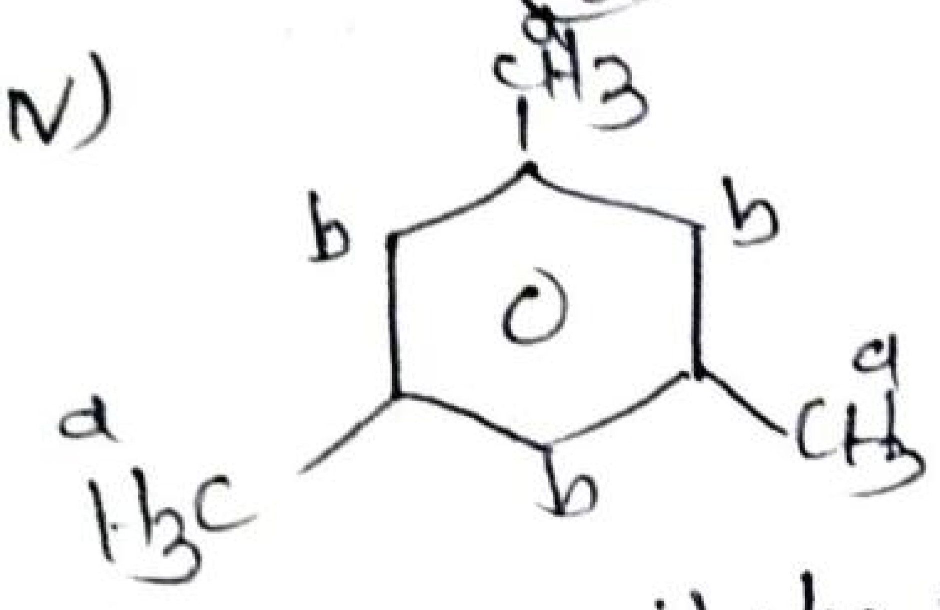
(XIII)



ethyl benzene

(3)

(XIV)



mesitylene

(2)

(XV) $\overset{a}{CH_3}\overset{b}{CH_2}-O-\overset{b}{CH_2}\overset{a}{CH_3}$

(2)

(XVI) $\overset{c}{CH_3}\overset{b}{CH_2}\overset{a}{CHO}$

(3)

(XVII) $\overset{d}{CH_3}\overset{c}{CH_2}-O-\overset{b}{CH_2}-\overset{O}{\overset{\|}{C}}-O\overset{a}{H}$

ethoxyacetic acid

(4)

(XVIII) $\overset{a}{H}-\overset{O}{\overset{\|}{C}}-O-\overset{b}{CH_2}\overset{c}{CH_2}\overset{d}{CH_3}$

propyl formate

(4)

(XIX)

$$\begin{array}{l}\overset{a}{CH_2}-\overset{O}{\overset{\|}{C}}-O-\overset{b}{CH_2}\overset{c}{CH_3}\\ |\\ \overset{a}{CH_2}-\underset{O}{\underset{\|}{C}}-O-\overset{b}{CH_2}\overset{c}{CH_3}\end{array}$$

(3).