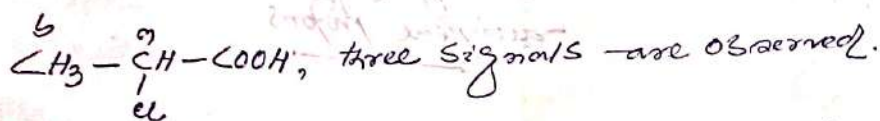


\* What do you mean by Chemical Shift?

Shifts in the positions of NMR absorption which are due to the shielding or deshielding of protons by the electrons are called chemical shifts. For measuring chemical shifts of various protons in a molecule, the signal for tetramethylsilane (TMS) is taken as reference. Due to the low electronegativity of Silicon, the shielding of equivalent protons in TMS is greater than most of the organic compounds. Therefore, NMR signal for TMS is taken as reference and chemical shift for different kinds of protons are measured relative to it. Clearly, the NMR signal for a particular proton in a molecule will appear at different field strengths compared to a signal from TMS. This difference in the absorption position of the proton with respect to TMS signal is called chemical shifts. It is not measured in gauss but is measured in equivalent frequency units which is then divided by the frequency of spectrometer used. This gives the value of  $\delta$ .

\* How many signals are appeared in  $^1\text{H}$ -NMR spectrum for 2-chloropropanoic acid? Give splitting pattern.



The carboxylic proton will appear as a singlet at a  $\delta$  value between 10.5 to 12. The multiplicity of other signals for protons 'a' and 'b' are:

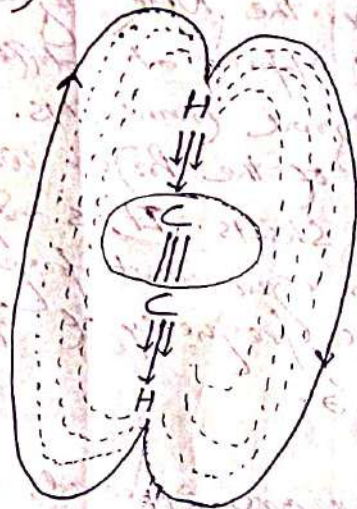
i. A one proton quartet  
Downfield  
Area = 1

ii. Three proton doublet  
upfield  
Area = 3

From the above example, it is clear that the chemical shifts for various protons are exactly in accordance with the factors on which the values of chemical shifts depend. The presence of electronegative atoms or groups near the protons, bring the absorption downfield and the effect diminishes with the increasing distance of the said atom or group from the concerned protons.

\* The chemical shift value of protons in acetylene appears at 1.5-3.5 ppm though it contains  $\sigma$ -bonds. Explain the fact.

In alkynes, electronic circulation around triple bond takes place in such a way that the protons experience diamagnetic shielding effect. When the axis of the alkyne group lies parallel to the direction of the applied field, the  $\pi$  electrons are induced to circulate around the axis in such a way that the induced field opposes the applied field. Thus, protons feel smaller field strength (shielding) and hence resonance occurs at higher applied field (low  $\delta$  value).



$\uparrow \uparrow \uparrow H_0$

Shielding of  
acetylene protons

\* A compound of molecular formula  $C_4H_7BrO_2$  gives different peaks in  $^1H$ -NMR spectra:

$\delta = 1.2$  (t, 3H), 2.5 (m, 2H), 4.3 (t, 1H), 12.0 (s)

Suggest the structure with explanation.

\* From the data, it is clear that there are four set of equivalent protons in the compound. A one proton singlet at  $\delta = 12.0$  ppm indicate the presence of acidic proton. A one proton triplet at  $\delta = 4.3$  indicate that this proton attached to carbon, which also has a bromine atom attach to it ~~directly~~ and contain

or  $\text{CH}_2$  groups in its neighborhood. From all this  
 clear that the structure of the compound is



$$d = 12.0 (3, 1\text{H})$$

$$a = 4.3 (2, 1\text{H})$$

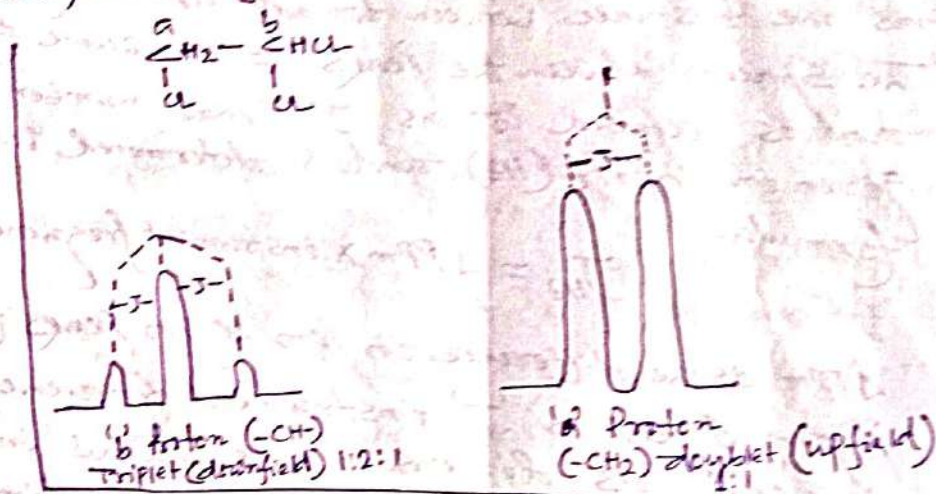
$$b = 2.3 (m, 2\text{H})$$

$$c = 1.2 (t, 3\text{H})$$

\* Define coupling constant ( $J$ ) and explain with example.

The distance between the centres of the two adjacent peaks in a multiplet is usually constant and is called coupling constant. The value of coupling constant is independent of the external field. It is measured in Hertz (Hz) or cps (cycle per second).

In the NMR spectrum of 1,1,2-trichloroethane two multiplets are observed. The value  $J$  in each of its multiplets is found to be constant.



→ Upfield ( $\delta$  value decreases)

NMR spectrum of 1,1,2-trichloroethane

\* Explain why unit of chemical shift is dimensionless but that of coupling constant has dimension. - Explain.

Ans:

Chemical shift may be defined as the difference in the absorption position of the proton with respect to TMS signal. It is expressed in dimensionless ppm unit.

The value of  $\delta$  for a substance with respect to TMS can be obtained by measuring  $\nu_s - \nu_{TMS}$ , where,

$\nu_s$  = Resonance frequency of the sample

$\nu_{TMS}$  = Resonance frequency of TMS

Keeping the radio-frequency constant, an NMR signal for a particular set of protons in the sample will appear at different field strength than the signal obtained from TMS. Thus the value of  $\nu_s - \nu_{TMS}$  can be expressed in the corresponding field strength in gauss. Since the operating frequency of the instrument is directly proportional to the strength of magnetic field

$$\delta = \frac{\nu_{\text{sample}} - \nu_{\text{ref}}}{\text{operating frequency in megacycles/sec}}$$

Since dimension in above ~~is~~ and below are cancelled out,  $\delta$  is expressed in dimensionless unit. So chemical shift are dimensionless.

On the other hand coupling constant is defined as the distance between two adjacent peaks in a multiplet. The spacing between the peaks is the same for both protons and is referred to as  $J$ . This number is always given in hertz (Hz), and is determined by the following formula.

$$J_{\text{Hz}} = \Delta \text{ppm} \times \text{instrument frequency}$$

$\Delta \text{ppm}$  is the difference in ppm of two peaks for a given proton. Since in ' $J$ ' instrument frequency parameter is used, its dimension is always included in coupling constant value. So it has a dimension.

\* How will you distinguish between intermolecular and intramolecular hydrogen bonding using  $^1\text{H-NMR}$  spectroscopy?

Intermolecular and intramolecular hydrogen bonding can be easily distinguished as the latter does not show any absorption shift in absorption due to the change in concentration. In case of phenols, absorption occurs between 2 to 6 $\tau$ . But if the concentration is decreased, i.e. if the volume of solvent, say  $\text{CCl}_4$  is increased, then the absorption for  $-\text{OH}$  proton occurs upfield. In case the  $-\text{OH}$  group of benzene is intramolecularly bonded with some other group in the ortho position, the absorption for  $-\text{OH}$  proton may occur even at the negative tau value. But the value remains unchanged on dilution.

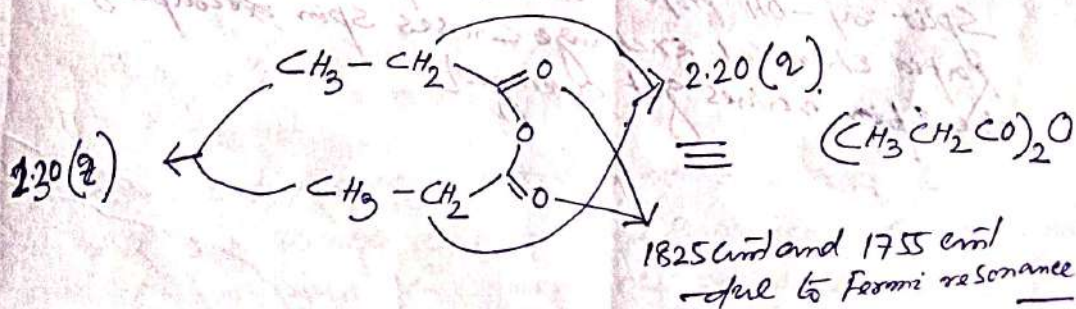
\* An organic compound ( $\text{C}_6\text{H}_{10}\text{O}_3$ ) shows the following spectral data:

IR: 3082-2860, 1825, 1755, 1455  $\text{cm}^{-1}$

$^1\text{H NMR}$ :  $\delta$  1.30 (t, 3H), 2.20 (quartet, 2H)

Establish the structure of the compound.

The above organic compound <sup>exists</sup> ~~give~~ two frequency peaks in the region 1825-1750  $\text{cm}^{-1}$  (in IR spectra), which clearly indicates that the compound is an acid anhydride. This is further supported by the  $^1\text{H NMR}$  data of the compound which shows two sets of equivalent proton for 10H. The peaks at  $\delta$  2.20 (q, 2H) indicate the presence of 'methylene' proton ~~which is~~ and  $\delta$  1.30 (t, 3H), indicate the presence of 'methyl' proton. From the above data we can conclude that the structure of the given compound is:



IR peaks at 3082-2860  $\text{cm}^{-1}$  is due to C-H stretching frequency and at 1455  $\text{cm}^{-1}$  is due to C-O str. vibration.

\* The proton NMR spectrum of ethyl alcohol in the presence of traces of acid shows different splitting patterns compared to the spectrum of ethyl alcohol in its pure form.

In case of pure anhydrous ethanol  $\text{CH}_3\text{CH}_2\text{OH}$ , three signals are observed

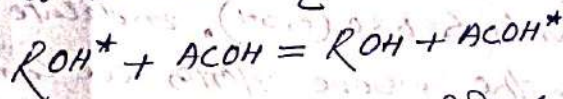
(i) a triplet for  $-\text{CH}_3$  proton at  $8.82 \tau$  due to coupling with  $-\text{CH}_2-$  protons.

(ii) A multiplet consisting of eight lines for  $-\text{CH}_2-$  protons at  $6.38 \tau$ . The  $-\text{CH}_2-$  protons are under the influence of two kinds of proton in different chemical environments. Thus, the multiplet consists of  $(n+1)(m+1) = (3+1)(1+1) = 8$  lines.

(iii) a triplet for  $-\text{OH}$  proton at  $4.72 \tau$ . The OH proton appears as a triplet because of coupling to  $-\text{CH}_2-$  protons.

Now if we scan the spectrum of ethyl alcohol in the presence of traces of acid, the  $-\text{OH}$  signal appears as a singlet and its coupling with adjacent  $-\text{CH}_2-$  does not take place.

The exchange of  $-\text{OH}$  protons among ethanol and acid is normally so rapid that a particular proton does not reside on a particular oxygen atom long enough for the nuclear coupling to be observed.



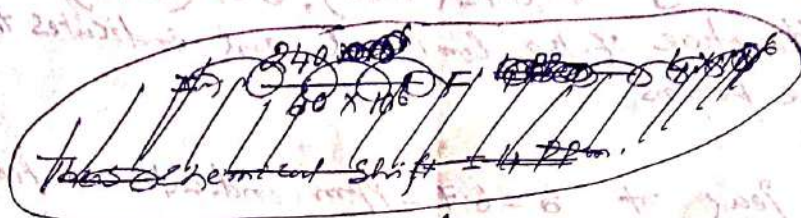
Similarly, absorption due to  $-\text{CH}_2-$  protons will not be split by  $-\text{OH}$  proton due to rapid chemical exchange. Rapid chemical exchange causes spin decoupling, because the spin values get averaged.



\* The chemical shift of a proton is 240 Hz from TMS in an NMR spectrometer operating at 60 MHz. Calculate its chemical shift in terms of  $\delta$  (in ppm). What would be its chemical shift value in an NMR spectrometer operating at 300 MHz?

The chemical shift ( $\delta$ ) can be calculated by applying the relation:

$$\delta = \frac{\Delta\nu \text{ (in cps)} \times 10^6}{\text{Frequency of spectrophotometer in cps (or Hz)}}$$

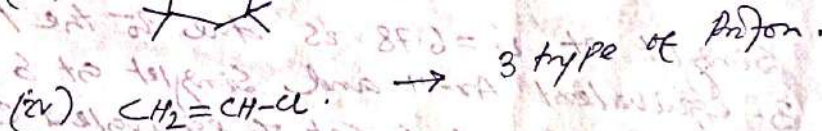
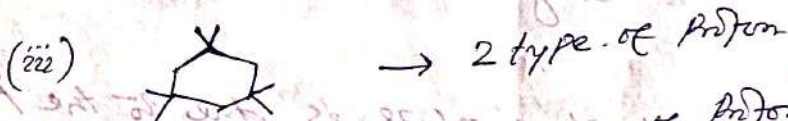
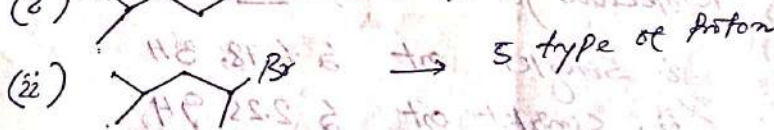


$$= \frac{240 \times 10^6}{60 \times 10^6} = 4 \text{ ppm}$$

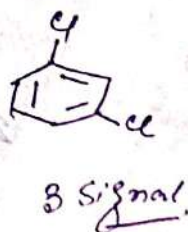
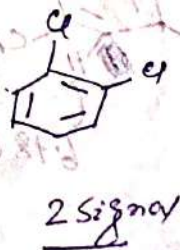
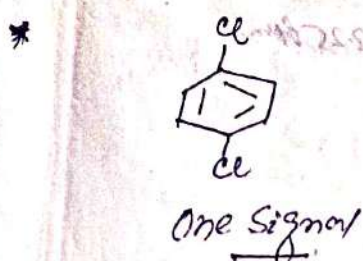
Thus chemical shift = 4 ppm.

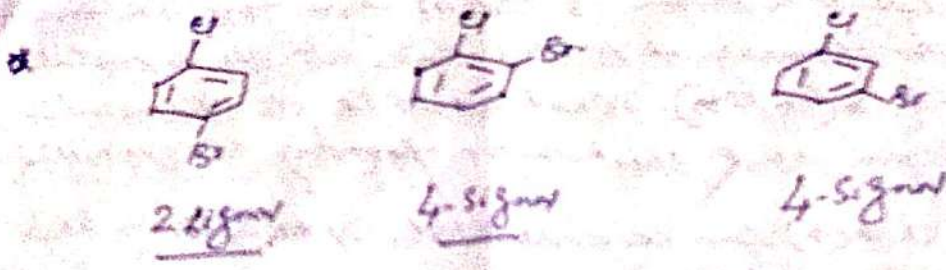
Since chemical shift is independent of the operating frequency of the instrument, so the above chemical shift value will remain unchanged in an NMR spectrometer operating at 300 MHz.

\* Predict the types of protons to be observed in  $^1\text{H-NMR}$  spectra of the following compounds:



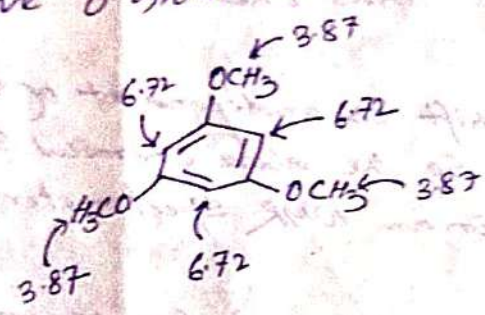
\* Mention the types of protons that you would observe in NMR spectra of o-, m- and p-isomers of dichlorobenzenes and o-, m- and p-isomers of bromochlorobenzenes.





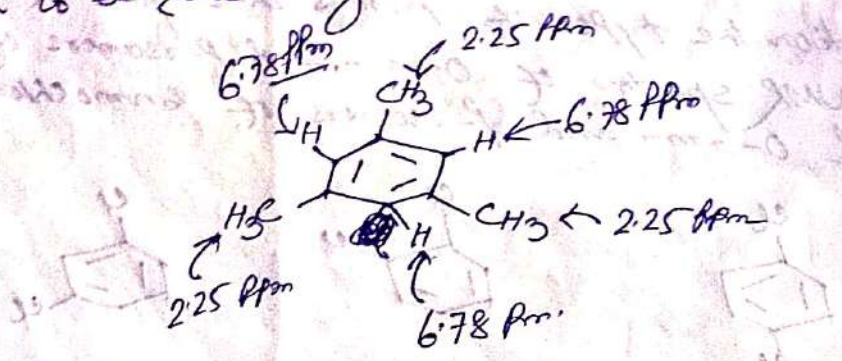
\* A compound of m.f.  $C_9H_{12}O_3$  display  $^1H-NMR$  sp. in  $CDCl_3$ :  $\delta$  6.72 (s, 3H), 3.87 (s, 9H). Identify the structure of the compound and indicates the  $\delta$  values the protons.

The peak at  $\delta = 6.72$  ppm indicates the presence of the Aromatic proton (Ar-H), on the other hand peak at  $\delta$  3.87 ppm due to the presence of (methyl) group attached to electronegative 'O' atom. So the structure of compound is:



\* Give a structure consistent with the following data and explain:  
 Molecular formula  $C_9H_{12}$   
 i. Singlet at  $\delta$  6.78, 3H  
 ii. Singlet at  $\delta$  2.25, 9H

Ans  
 Singlet at  $\delta = 6.78$  is due to the presence of 3-equivalent Ar-H and singlet at  $\delta$  2.25 due to the presence of 3 set of equivalent  $CH_3$  group attached to benzene ring. So the structure of the compound is:





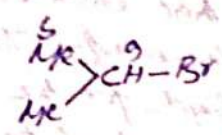
\* Suggest structure on the basis of given NMR data:

(i)  $C_9H_{17}Br$   
 $\delta$  1.7 (d, 6H),  $\delta$  4.3 (septet, 1H)

(ii)  $C_9H_{10}O$   
 $\delta$  1.28 (s, 9H),  $\delta$  1.95 (s, 1H)

(iii)  $C_5H_9Cl_3$   
 $\delta$  0 (1.0) (d, 6H)  
 $\delta$  1.5 (m, 1H)  
 $\delta$  8.3 (s, 2H)

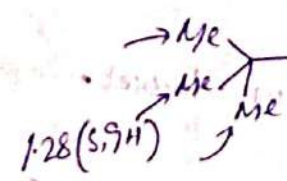
Ans (i) Structure of  $C_9H_{17}Br$  on the basis of given data



Proton 'a' appears as one peak as septet due to the presence of two -CH<sub>3</sub> groups in its neighbours and it is slightly deshielded due to presence of R electron withdrawing system.

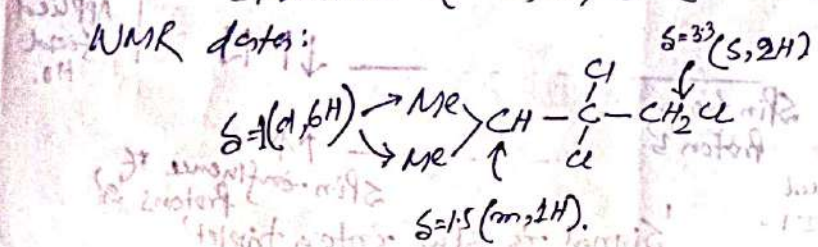
Proton 'b' appears as 6 proton doublet due to the presence of one -CH- proton in its neighbour.

(ii) Structure of  $C_9H_{10}O$  on the basis of given data



This would be  $\delta$  11 (data given) since no intermolecular H-bonding possible due to its bulk.

(iii) Structure of  $C_5H_9Cl_3$  on the basis of given

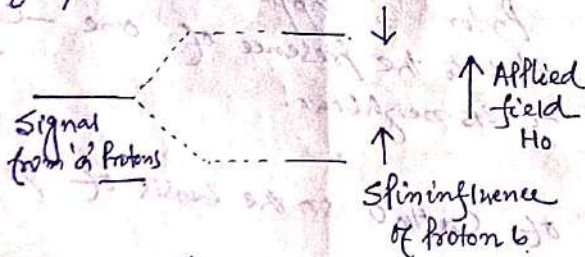


# What are 'spin-spin' coupling' and Coupling constants?

1,1,2-trichloroethane ( $\text{C}^{\text{a}}\text{HCl}_2\text{C}^{\text{b}}\text{HCl}_2$ ) has two types of protons

The mutual magnetic influence between the protons 'a' and 'b' is not transmitted through space but through the electrons in the intervening bonds. The nuclear spin of protons 'a' first couples with the electron spin of C-H<sub>a</sub> bonding electrons and these in turn couple with C-C bonding electrons and then with C-H<sub>b</sub> bonding electrons. Thus, the coupling is eventually transmitted to the spin of H<sub>b</sub> nucleus. The magnetic field that the proton 'a' feels at a particular instant is slightly increased or decreased by the spin of the neighbouring proton 'b'. The field felt by proton 'a' is increased if the proton 'b' happens to be aligned at that instant with the applied field. If the proton 'b' is aligned against the applied field, then at that instant, the field felt by the proton 'a' will be slightly decreased. Thus, absorption by proton 'a' is shifted slightly downfield for the half the molecules and slightly upfield for other half of the molecules. Thus, the signal for 'a' kind of protons is split into two peaks i.e., into doublet with equal peak intensity.

Splitting by protons 'b'



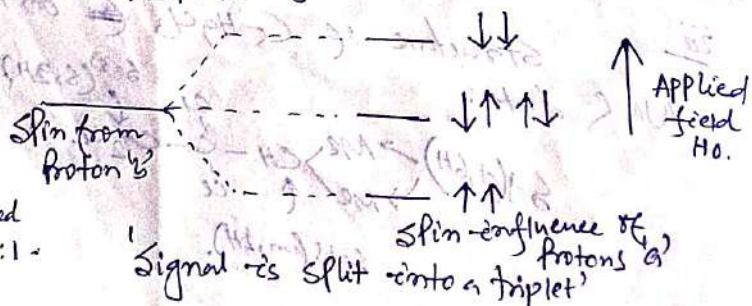
Signal is split into a doublet.

Thus coupling with proton 'b' gives 1:1 doublet.

Splitting by proton 'a':

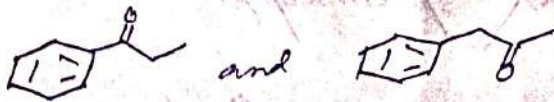
Now let us see, how the signal from 'b' protons is effected by 'a' kind of proton (two protons). These two protons can be aligned with applied field in three different ways and will consequently influence the proton 'b'.

Thus, a signal for 'b' proton will be split into three peaks (triplet) which are equally spaced with peak intensities 1:2:1.

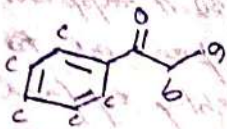


Signal is split into a triplet

\* Consider the following two isomers:



How many type of protons along with spin-multiplicity are expected (consider aromatic protons in one type)



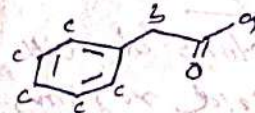
3 types of proton

c → Ar-H proton

b → 2 protons ~~doublet~~ quartet

a → 3 protons triplet

'b' proton will appear slightly downfield region compared to 'a'



3 types of proton

c → Ar-H proton

b → 2 proton singlet

a → 3 proton singlet

'b' protons will appear a downfield region compared to 'a' due to the adjacent phenyl ring and carbonyl group.

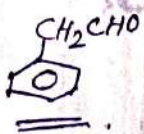
\* A compound with molecular formula  $C_8H_8O$  gives the following PMR data:

i. Multiplet at  $\delta$  7.28 (5H)

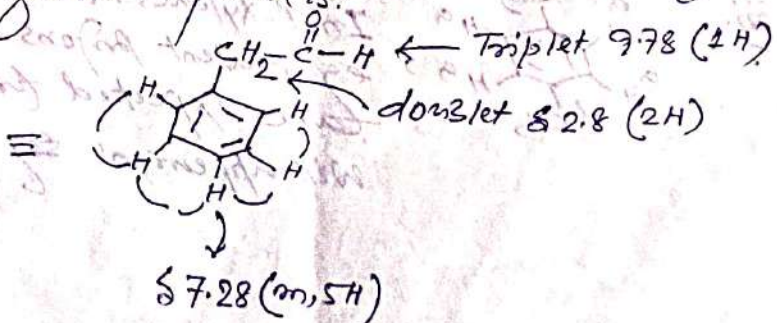
ii. Doublet at  $\delta$  2.8 (2H)

iii. Triplet at  $\delta$  9.78 (1H)

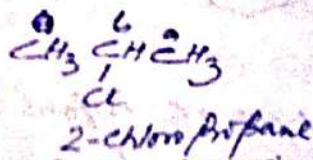
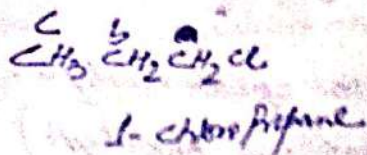
From the given NMR data it is clear that compound has three set of equivalent proton. A peak at  $\delta$  9.78 (1H) is due to aldehydic hydrogen. The peak at  $\delta$  7.28 (m, 5H) are due to Ar-H. The peak at doublet at  $\delta$  2.8 (2H), are attached to aromatic ring and carbonyl group. From the given data it is clear that given compound is:



$\equiv PhCH_2CHO$



\* How will you differentiate 1-chloropropane and 2-chloropropane by NMR Spectroscopy.



1-chloropropane:

The protons 'a' will appear as triplet and will appear in downfield region, the protons 'b' will appear as doublet of triplet (dt) and it will appear ~~to~~ slightly upfield compared to 'a' set of protons. ~~to~~ The protons 'c' will appear as triplet and it will appear most shielding region compared to other region.

2-chloropropane:

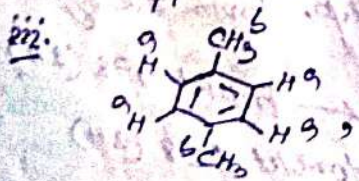
2-chloropropane will show two set of protons - a six proton doublet and a one proton septet due to proton directly attached with ~~carbon~~ carbon attached with chlorine.

\* How many NMR signals do you expect in each of the following compounds

i. n-butane    ii. 1,1-dichloroethane    iii. p-xylene

i. In  $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$ , there are two kinds of equivalent protons and thus two signals are expected for it. The two signals are, a 6H triplet and a 4H quartet.

ii. In  $\text{CH}_2\text{Cl} - \text{CH}_2\text{Cl}$ , there are only one kind of equivalent protons and only one signal are expected for it and it will appear as singlet.



In p-xylene, there are two kinds of equivalent protons and thus two signals are expected for it. Both the peaks will appear as singlet.

\* Give a structure consistent with the following NMR data in each case.

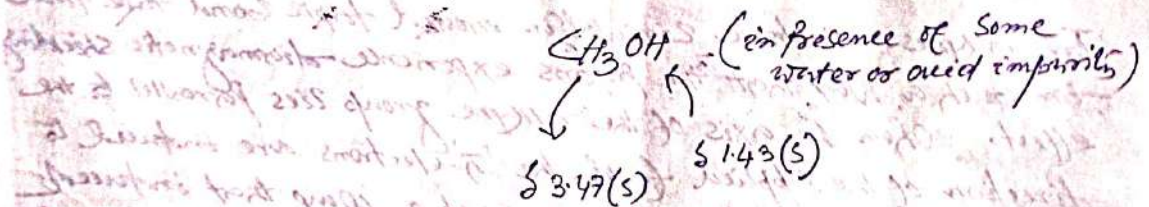
- i. Molecular formula  $\text{CH}_4\text{O}$ :  
 a. Singlet  $\delta$  1.43 1H  
 b. Singlet  $\delta$  3.47 3H

- ii. Molecular formula  $\text{C}_2\text{H}_5\text{Br}$ :  
 a. doublet  $\delta$  1.71 6H  
 b. septet  $\delta$  4.32 2H

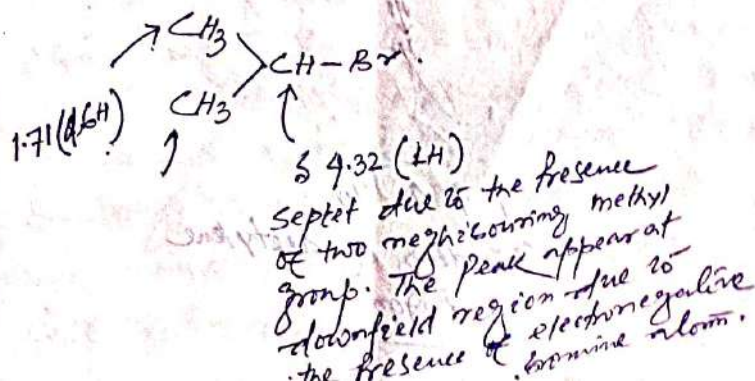
Ans

i. Molecular formula  $\text{CH}_4\text{O}$

a. A one proton singlet at  $\delta$  1.43 possibly due to the presence of -OH proton in presence of water or acid impurity, due to impurity no coupling with neighbouring  $\text{CH}_3$ - group take place. As a result  $\text{CH}_3$ - also appear as a singlet at 3.47 ppm. The higher  $\delta$ -value of  $\text{CH}_3$ -proton due to directly attachment of it with electronegative oxygen atom. From the above data the structure of compound predicted as

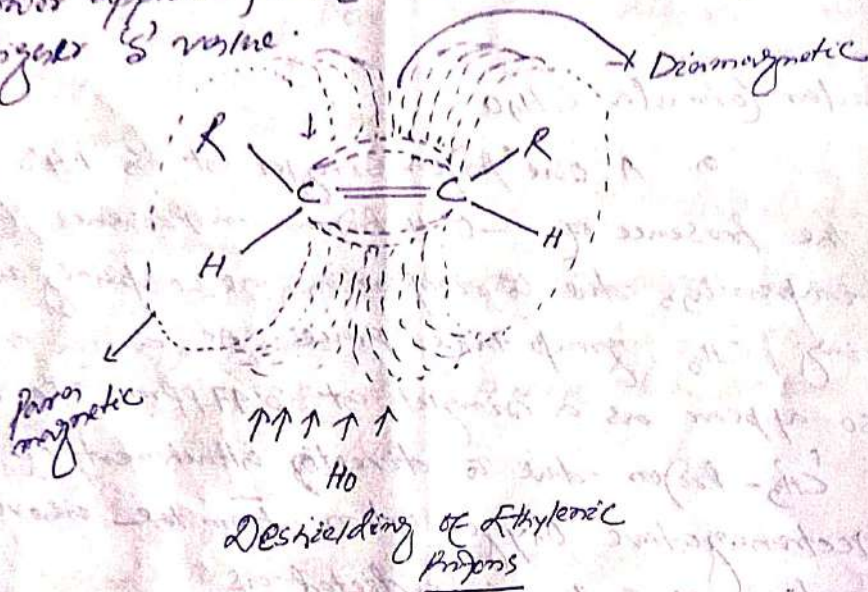


ii. From the given data it is clear that compound has two sets of proton. ~~a one proton~~ A <sup>6H</sup> one proton doublet and a ~~2H~~ <sup>one</sup> proton septet indicated the presence of  $\text{Me}_2\text{CH}$ -group in the compound. From the above data the structure of compound predicted as

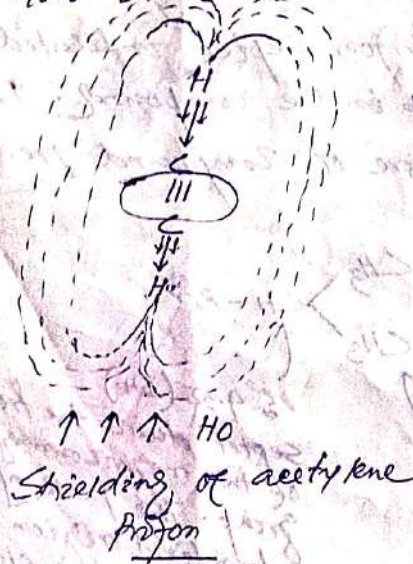


\* In spite of highest electronegativity of sp-carbon atom, the acetylene protons appear at lower value than ethylene protons. Justify the statement.

In alkene the  $\pi$  electron is so oriented that the plane of the double bond is at right angles to the applied field. Induced circulation of  $\pi$  e's generates induced magnetic field which is diamagnetic around carbon atom and paramagnetic in the region of the alkene protons. Thus the proton will feel greater field strength and hence resonance occurs at lower applied field. As a result alkene protons appear at higher  $\delta$  value.



In alkynes, electronic circulation around triple bond takes place in such a way that the protons experience diamagnetic shielding effect. When the axis of the alkyne group lies parallel to the direction of the applied field, the  $\pi$ -electrons are induced to circulate around the axis in such a way that induced field oppose the applied field. Thus, protons feel smaller field strength (shielding) and hence resonance occurs at higher applied field i.e. low  $\delta$  value.



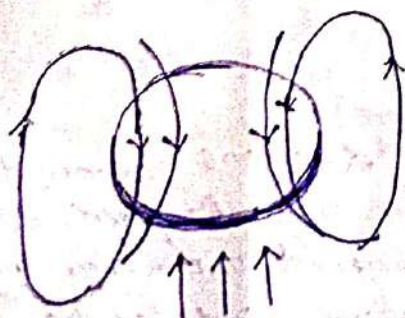
\* Protons in a compound nuclei experience different chemical environments. The different signals in NMR spectrum though they have same nuclear charge. Example:

Ans:

The cause of secondary shielding surrounding an nucleus under the influence of a magnetic field will be orbital and conduction as they generate their own magnetic field. This is opposed to the applied field at the nucleus and known for a proton of a C-13 bond. Because the induced field oppose the applied field, electrons are said to be diamagnetic and the effect on the nucleus is called diamagnetic shielding.

Because the nucleus experiences or weaker magnetic field than that applied by externally, it is said to be shielded. This type of shielding is termed diamagnetic shielding. The externally applied field  $H_0$  is uniform over the entire molecule and therefore, it would create different protons nonequivalent. However, the magnetic field that is induced by the movement of electrons over the molecule is not uniform and this situation makes the protons to be nonequivalent. Thus each nucleus experiences in a different environment experiences a slightly different local magnetic field due to the circulation of electrons in neighbouring bonds and so through space effects. The hydrogen nuclei, near these magnetic field, induced by the molecule may be more highly shielded or deshielded and they experience an effective magnetic field that is either less or greater than that applied externally i.e.  $H_0$  due to the induced field, either opposite or reinforcing  $H_0$ . The ~~shielding~~ shielded nuclei will exceed the application of external magnetic field. Before the spin of these hydrogen nuclei flip and appear as peaks on the spectrum as they absorb energy. Since the effective magnetic field of the shielded proton is always weaker than the external field, therefore, the applied field  $H_0$  must be made stronger before resonance is observed. The reverse effect is deshielding. Thus in short, each nucleus in a different environment requires a slightly different applied magnetic field  $H_0$  for resonance and peaks occur in

different region of the spectrum.



At the proton, the induced magnetic field oppose the external magnetic field

\* An organic compound in the molecular mass 120 absorbs in ultraviolet spectrum at 268 nm (Energy 480). In IR spectrum, medium absorption bands (i) are formed at 3067-3907 cm<sup>-1</sup> (ii) 1608 cm<sup>-1</sup> and 1473 cm<sup>-1</sup>. The NMR spectrum shows absorption as below:

i. at 8.68 ppm singlet

ii. at 8.23 ppm singlet

Two singlets in the are formed in the NMR spectrum are formed in the proton ratio 1:3. Give ~~prob~~ probable structure of the compound.

Ans

From the UV and IR data it is clear the above compound must be an aromatic compound.

Ar-C-H → 3067-3907 cm<sup>-1</sup>

Ar-C=C → 1608 cm<sup>-1</sup>

bending Ar-C=C → 1473 cm<sup>-1</sup>

NMR spectra indicates two sets of  
- one proton singlet at  $\delta = 8.68$  ppm and  
- three proton singlet at  $\delta = 8.23$  ppm.

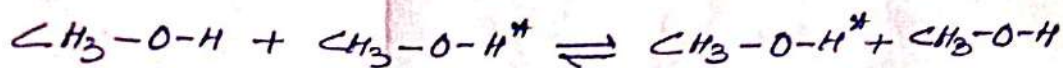


From the above NMR data structure of compound is:

\* Methanol shows two ~~sig~~ singlets in  $\text{CCl}_4$  in the  $^1\text{H}$  NMR spectrum, but methanol gives a doublet and quartet in DMSO. Explain.

Ans:

Exchange of the OH protons among methanol molecules is normally so rapid that one particular proton does not reside for a sufficiently long time on a particular oxygen atom for the nuclear coupling to be observed.



We know that  $\Delta t \cdot \Delta\nu \approx \frac{1}{2} \pi$ . Here  $\Delta t$  is the time needed to resolve accurately the multiplicities in the  $\text{CH}_3$  and OH groups brought about by their coupling and  $\Delta\nu$  is the coupling constant. Provided that the residence time of a particular proton on oxygen is sufficiently long, we can record the coupling. If there is rapid proton exchange, the residence time will be shorter than  $\Delta t$  and the coupling will not be resolved. This <sup>will be</sup> the case if we take  $^1\text{H}$ -NMR of  $\text{CH}_3\text{OH}$  in  $\text{CCl}_4$ . As the coupling not take place two peak appear as a singlet.

In the case of alcohols it is relatively easy to see the OH coupling if the sample is pure, or if the spectrum is recorded with a low-temperature sample, or if the sample is dissolved in a highly polar solvent such as DMSO, when strong solvation presumably stabilizes individual and reduce the exchange.