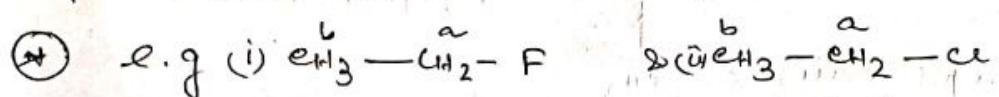


NMR Spectra.Effect of Inductive effect on NMR spectra.

★ A proton is said to be deshielded if it is attached with an electronegative atom or groups. Greater the electronegativity of the atom, greater is the deshielding caused to the proton. If the deshielding is more for a proton, then its δ value will also be more.



Here two signals are expected for each of the two compounds. Deshielding for proton 'a' in compound (i) is more than that for similar protons in compound (ii).

$\text{CH}_3 - \text{F}$	$\frac{\delta}{4.25}$
$\text{CH}_3 - \text{Cl}$	3.10
$\text{CH}_3 - \text{Br}$	2.61

★ As the distance from the electronegative atom increases, the deshielding effect due to it diminishes. Protons 'b' are comparatively less deshielded and hence will resonate at comparatively lower value of δ .

ANSWER

Reasons : Hydrogen nuclei in a molecule are surrounded by electronic charge and shields the nucleus slightly from the influence of applied field. Thus to bring this proton to resonance, the applied field must be increased to overcome the shielding effect. In a magnetic field, the electrons around the proton are induced to circulate, and thus generate induced magnetic field which opposes the magnetic field. Greater the electron density around the proton; greater is the induced magnetic field (opposing the external field) and greater will be the applied field required to overcome the shielding effect. On the other hand electronegative atoms or groups withdraw electron density around the proton and thus, causes deshielding (reverse shielding). Due to deshielding smaller value of applied field will be needed to bring the proton to resonance.

- ④ Greater the electronegativity of the atom or group, greater will be the deshielding effect on a proton.
- ⑤ Greater the distance of the electronegative atoms or group from a particular proton, smaller is the deshielding effect on it.
- ⑥ In TMS, $\text{CH}_3 \rightarrow \begin{matrix} \text{CH}_3 \\ \downarrow \\ \text{Si} \leftarrow \text{CH}_3 \\ \uparrow \end{matrix}$, four electron releasing ($-I_{+3}$) groups causes CH_3 powerful shielding effect and hence TMS proton (low δ value) (all equivalent) resonate at high field (low frequency).
- ⑦ Silicon is also electropositive and pushes electrons into the methyl groups of TMS by $+I$ effect and also causes powerful shielding effect.
- ⑧ Protons adjacent to -N^+ are strongly deshielded (high δ value) while those near $\text{C}=\text{O}$ are powerfully shielded. (low δ value).

Hydrogen Bonding effect on nmr spectra

It has been found that a hydrogen atom exhibiting property of hydrogen bonding in a compound absorbs at a lower field in comparison to the one which does not. The hydrogen bonded proton being attached to a highly electronegative atom will have smaller electron density around it.

Being less shielded, the field felt by such a proton will be more and hence resonance will occur downfield. The downfield shift depends on the strength of hydrogen bonding.

- ⑨ Intermolecular and intramolecular hydrogen bonding can easily be distinguished as the latter does not show any shift in absorption due to change in concentration. At lower concentration intermolecular hydrogen bonding is diminished in simple -OH , NH & SH compd. since hydrogen bonding involves electron cloud transfer from the hydrogen atom to neighbouring electronegative atom, the hydrogen experience a net deshielding effect when H-bonding is strong & is less when deshielded when hydrogen bonding is diminished.

- (*) In case of phenoles absorption occurs between 4 to 8 δ . But if the concentration is decreased, i.e. if the volume of solvent, say CCl_4 is increased, then absorption for -OH protons occur up-field.
- (*) Again if -OH group on Benzene is intramolecularly bonded with some other group in the ortho position, the absorption for OH proton may occur even at greater than 10. e.g. the -OH proton in salicylic acid absorbs at 10.6 δ .
- (*) Enols show strong intramolecular hydrogen bonding which is further stabilised by resonance. Due to this a great shielding effect is caused and absorption for such a proton occur at very high δ value (10.5-128).
- (*) A signal for carboxylic acid also appear high δ value (10.95 δ). This is due to the fact that acids exist as dimer as a result of hydrogen bonding.

A. Vander Waal's deshielding

In overcrowded molecules, it is possible that some protons may be occupying sterically hindered position. Clearly, electron cloud of bulky group (hindering group) will tend to repel the electron cloud surrounding the proton. Thus, such a proton will be deshielded and will resonate at slightly higher value of δ than expected in the absence of this effect.

A general Survey of the chemical shift of the more common type of protons

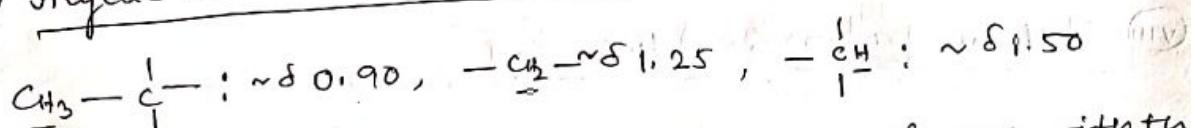
The different types of protons may be divided into two broad types:

Type 1: Proton attached to carbon atoms.

Type 2: Proton attached to atom other than carbon atom.

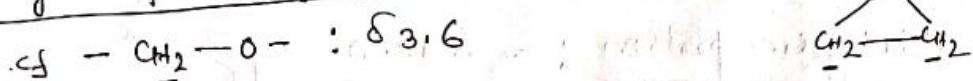
Type 1: (i) Aliphatic protons — In the absence of any other deshielding effect the aliphatic protons usually appear at the highest field. Local diamagnetic circulation of the bonded electron is the main cause of shielding.

(a) Acyclic saturated hydrocarbons

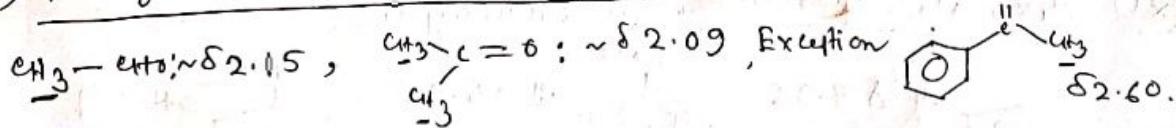


(b) Methylene protons of cycloalkanes: chemical shift vary with the size of the ring. cyclopropane: $\sim \delta 0.2 - 0.5$, cyclohexane: $\sim \delta 1.43$, cycloheptane and higher homologues: $\sim \delta 1.53$.

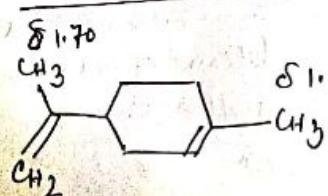
(ii) Methylene proton of an epoxide (oxirane): $\sim \delta 2.30$



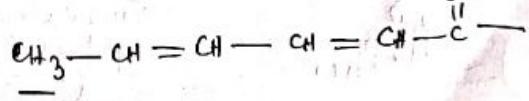
(iii) Methyl protons attached to C=O : $\sim \delta 1.9 - 2.2$

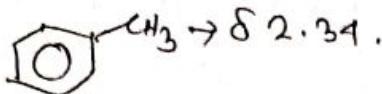


(iv) Methyl attached to C=C : $\delta 1.6 - 1.8$

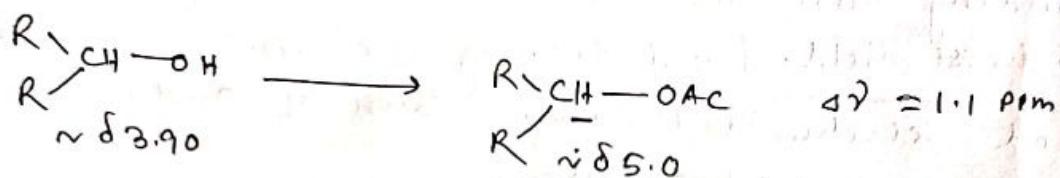
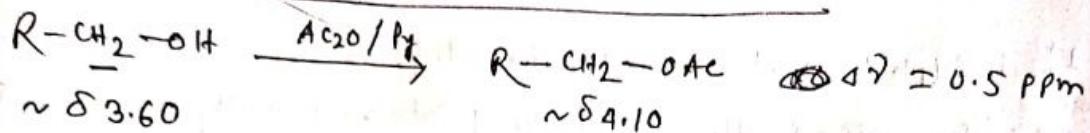
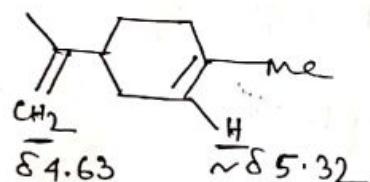


In case of extended conjugation such methyl signals are shifted downfield to $\delta 1.8 - 2.1$

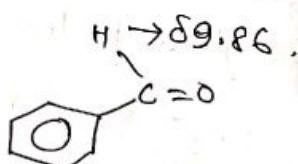
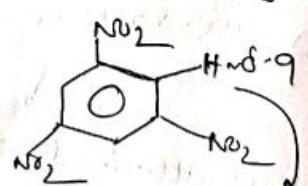
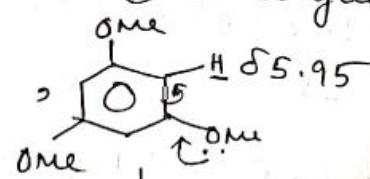
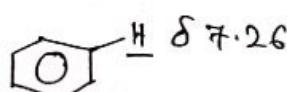


(v) Methyl attached to aromatic rings $\sim \delta 2.34$ (vi) Methyl attached to O & N

- OMe	<u>Aliphatic</u> $\sim \delta 3.50$	<u>aromatic</u> $\sim \delta 3.70-4.0$	<u>Methyl ester</u> $\sim \delta 3.65-3.75 (\text{R}-\overset{\underset{\delta}{\text{C}}}{\text{O}}-\text{R}')$
- NMe	$\sim \delta 2.2$	$\sim \delta 3.0$	

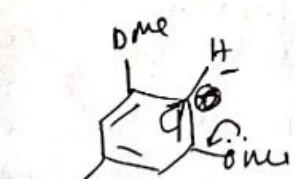
(vii) CH_2 and CH attached to OH and OAc(viii) Olefinic protons : $\sim \delta 4.6-6.4$ 

In case of extended conjugation olefins, the olefinic proton signal merge with those of aromatic proton ($\sim \delta 6.5-8.5$)

(ix) Acetylenic protons : $\sim \delta 2.5-3.0$ (x) Aldehydic protons : $\sim \delta 10.0$ (xi) Aromatic protons : @ Carboyclic : $\sim \delta 6.5-8.5$ 

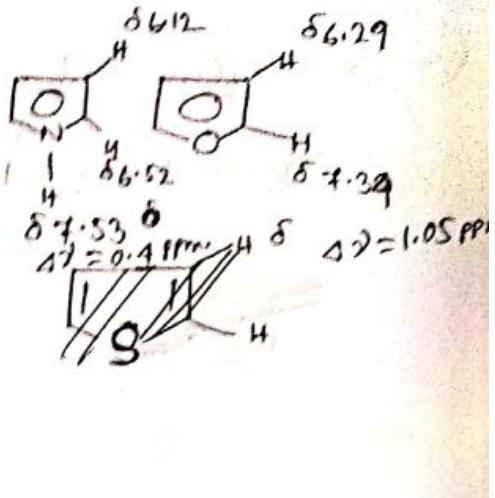
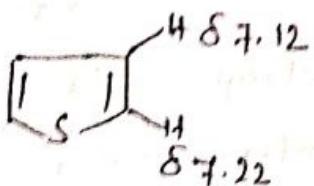
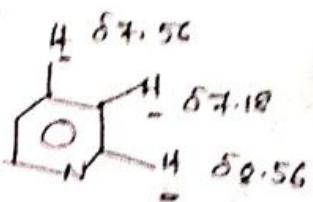
(Due to +R gr.)
the protons
are more shielded
so resonance
upfield

more deshielded
because of electron
withdrawing
 $-\text{NO}_2$ gr.



more shielded
due to increased
charge density.

(b) Heterocyclic

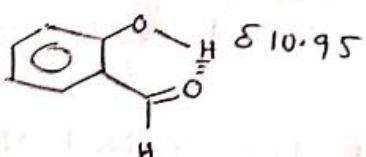
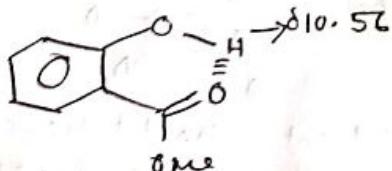
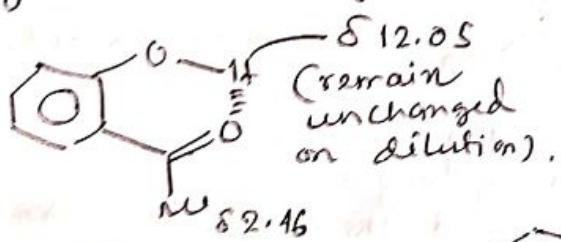


Type 2 : Protons attached to atoms other than carbon
atom

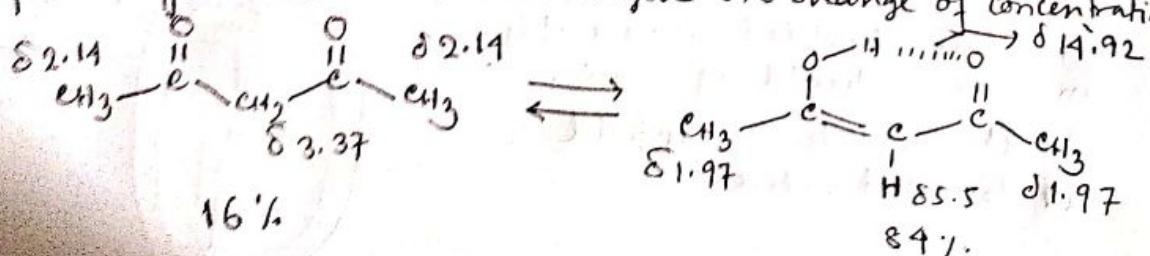
- (i) Aliphatic alcohols $\text{R}-\text{OH} \sim \delta 2-5$ (shifted upfield)
(generally 4-5.5 ppm) (on dilution).
- (ii) Aromatic " $\text{Ph}-\text{OH} \sim \delta 4-10$

(a) Phenols $\sim \delta 6.0-7.7$ (in moderate conc; shifted upfield on dilution; on infinite dilution)

(b) O-substituted phenol | they appear at $\delta 4-5$.
a capable of strong intramolecular hydrogen bond, the phenolic -OH proton shifted to downfield ($\sim \delta 10.5-12.5$) and position of signals are independent on concentration.

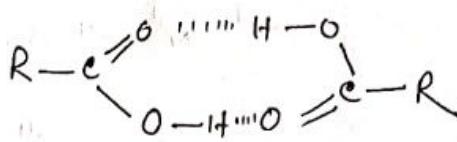
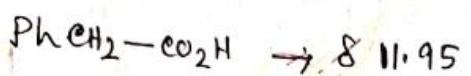


- (iii) Enols in $\delta 15-16$, Enols owe their existence to strong intramolecular hydrogen bonding. The enolic hydrogen appears at a very down-field position and the position of the signal remains unchanged on change of concentration.



(iv)

Carboxylic acid - CO_2H : $\sim \delta 10.5 - 12.0$

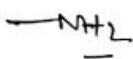


Carboxylic acid [Dimer].

exist as dimer by
intramolecular hydrogen bonding.

(v)

Amines : aliphatic aromatic

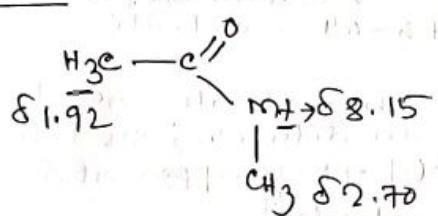


$\sim \delta 0.3 - 2.2$

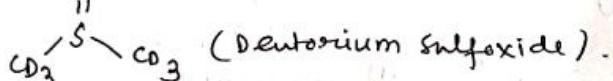
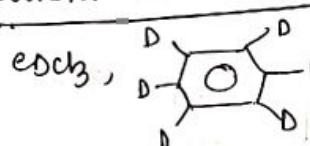
$\delta 2.6 - 4.7$

(vi)

Amides : $\sim \delta 5 - 8.5$



Solvent in NMR Spectra :



- i) solvent should be chemically inert.
- ii) it should be devoided of any H.
- iii) solvent should dissolve the sample to a reasonable extent.

(vii)

Although the $-I$ effect of $\text{-C}\equiv\text{N}$ is greater than -Cl , But CH_3 proton of methyl chloride resonate at higher δ value compare to CH_3 proton of CH_3CN .

Anisic this can be explained on the basis of anisotropic effect.

Due to anisotropic effect, CH_3 on $\text{C}\equiv\text{N}$ is more shielded because it is in the shielding zone.

so it resonate at upfield

i.e. lower δ value

