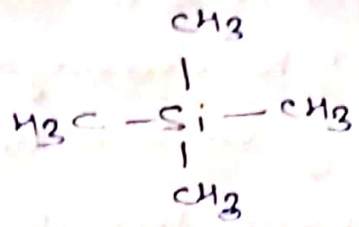
* Tetramethyl Silane (TMS)



Generally, TMS is taken as a reference. It is due to following facts:

1) It is chemically inert and miscible with a large range of solvents.
2) Its twelve (H-atom) protons are all magnetically equivalent.
3) It is highly volatile and can be easily removed to get back the sample.
4) It doesnot take part in intermolecular association with the sample.
5) Its resonanance position is far away from absorption due to protons in most organic molecules. Thus, assigning TMS = 0 (chemical shift value).

* factors which affect chemical shift value.:-

following are the factors which influences the chemical shift.

(1) Inductive effect
(2) Vander Waal's deshielding

(3). Anisotropic effect

(4). Hydrogen bonding.

(1). Inductive effect :-

A proton is said to be deshielded if it is attached to an electronegative atom/group. Greater is the electronegativity of the atom, greater is the deshielding caused to the proton. If the deshielding is more for proton, then its chemical shift value (δ-value) also be more.

For example-

(a) $CH_3^{b}-CH_2^{a}-F$ & (b) $CH_3^{b}-CH_2^{a}-Cl$.

Deshielding for proton 'a' in CH_3-CH_2-F is more than proton 'a' in CH_3-CH_2-Cl.

Reason- F is more electronegative than Cl.

(2). Vander Waal's deshielding :-

In overcrowded molecule, it is possible that some proton may be occupy sterically hindered position, Electron cloud of bulky group will tend to repel the electron cloud surrounding the proton. Thus, such a proton will be deshielded and will resonate higher chemical shift (δ-value) value.

(3). Anisotropic effect :-

The deshielding effect on proton attached to $>C=C<$ double bond is higher than that can be accounted for by Inductive effect alone.

Aldehydic and aromatic protons are much more deshielded. Alkyne proton appears at low δ-value.

The π-electrons circulate under the influence of the applied magnetic field.

for example-

In case of alkene, $>C=C<$, the plane of the double bond is at right angle to the applied field. Induced circulation of π-electrons generates induced magnetic field which is diamagnetic around C-atom and paramagnetic in the region of the proton (H-atom). Thus the proton will feel greater field strength (deshielded) and resonance occurs at higher δ-value.

(4). Hydrogen Bonding

A Hydrogen atom exhibiting property of hydrogen bonding in a compound absorbs at a low field in comparision 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 and resonate at downfield.

Intramolecular hydrogen bonding doesnot show any shift in absorption due to change in concentration.

* Solvent Effect

A substance which is free of proton (H-atom) is used as a solvent i.e. which does not give absorption of its own in NMR spectrum.

following solvents are commonly used in NMR-spectroscopy:

1. Carbon tetra chloride — CCl_4
2. Carbon disulphide — CS_2
3. Deuterochloroform — $DCCl_3$
4. Hexachloroacetone — $Cl_3C-\overset{O}{\overset{\|}{C}}-CCl_3$

NMR-spectrum of a compound measured in one solvent may be slightly different from that measured in another solvent of different polarity.

Hydrogen bonding also affects the value of chemical shift (δ-value) in this technique.

At higher concentrations of -OH, -NH compounds, deshielding of proton is greater and signals appear at high (δ-value).

With increase in temperature, the extent of H-bonding falls. and hence signals in nmr. spectra appears at smaller δ-value.

DMSO (dimethyl sulphoxide) can also be used in nmr-spectroscopy. This is due to —

1. It should be chemically inert and magnetically isotropic.
2. It should be devoid of H-atom
3. It should dissolve the sample to a reasonable extent.

—x—

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