Quadrant II – Transcript and related material

Programme: Bachelor of Science (Third Year)

Subject: Chemistry

Paper Code: CHC 107

Paper Title: Organic Chemistry

Unit: Spectroscopic methods in Organic Chemistry

Module Name: Position of Signals, Chemical shift (Reference standard, Solvent effect, Shielding + Desheiding effect)

Module No: 22

Name of the Presenter: Mrs. Pranaya Naik

Notes:

Position of Signals- Chemical shift

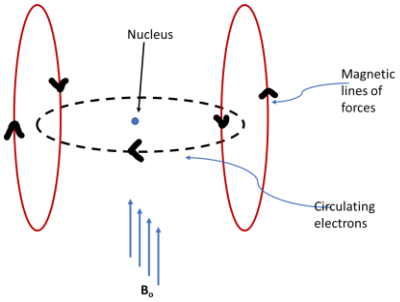
As the number of signal tell about number of different kind of protons present in a molecule, the position of the signal will tell about the nature of protons.

They may be present as follows

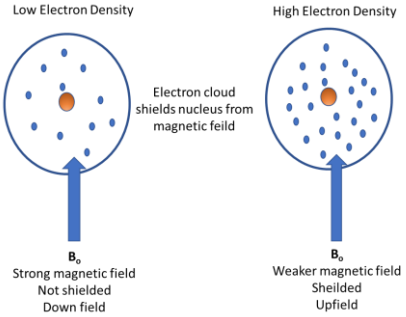
- Aliphatic primary, secondary, tertiary
- Aromatic
- Benzylic, vinylic, acetylenic
- Adjacent to halogen or to other atoms or group

Type of Proton	General structure	Approx. Chemical shifts δ (ppm)
Aliphatic Primary	$R\text{-}CH_3$	0.9
Aliphatic Secondary	R_2CH_2	1.3
Aliphatic Tertiary	R_3CH	1.5
Vinylic	C=C-H	4.5-6
Acetylenic	C=C-H	2-3
Aromatic	Ar-H	6-8.5
Benzylic	Ar-C-H	2.2-3
Allylic	$C{=}C\text{-}CH_3$	1.7

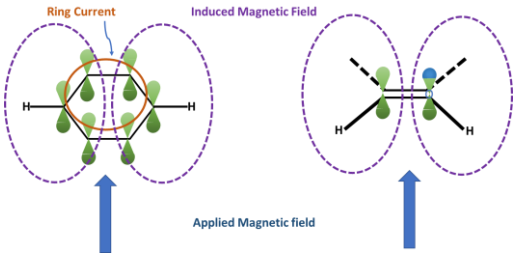
- What makes these protons distinguishable is the chemical environment present around the particular type of proton.
- When a molecule placed in the external magnetic field, the electrons present in it circulate to generate its own magnetic field called induced magnetic field which opposes the magnetic field. As a result “Shielding effect” is observed.



- In organic molecules the degree of shielding for a proton depends on the inductive effect of the groups attached to the carbon containing the particular proton.
- More electron density around the proton nucleus will shield it more from applied field whereas less electron density will shield it less from the applied field.



- If the induced field opposes the applied field, the proton in this region will be “shielded” over the applied field.
- If the induced field is in alignment with the applied field, the proton present in the region will be “deshielded” over the applied field.

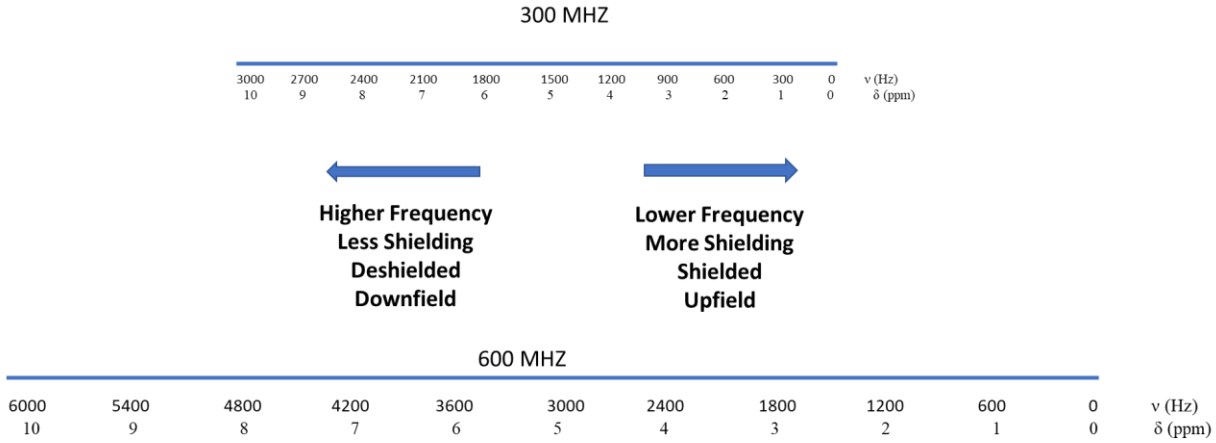


Chemical shift

- In NMR spectrum rather then calculating precessing frequency, difference in Nmr absorbtion is considered.
- In comparison to the naked compound, shielded proton will require higher applied field strength and deshielded will require lower applied field strength.
- This results in difference in absorption position for a particular proton in comparison

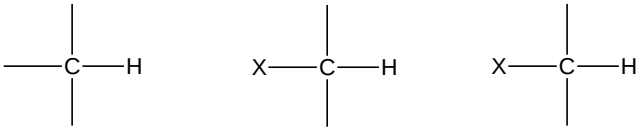
to the reference (naked) proton and is called as chemical shift for particular proton.

- Shielded protons appear in upfield region and deshielded protons appear in downfield region

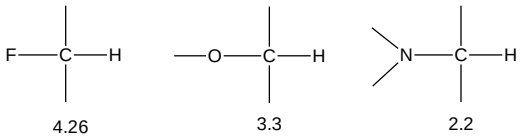


Factor affecting Chemical shift

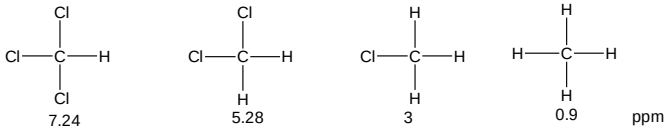
- Electronegativity of the neighboring groups or atom play an important role in chemical shifts.
- Substituents present at sp3 carbon atom influences the degree of shielding of the proton present on the carbon



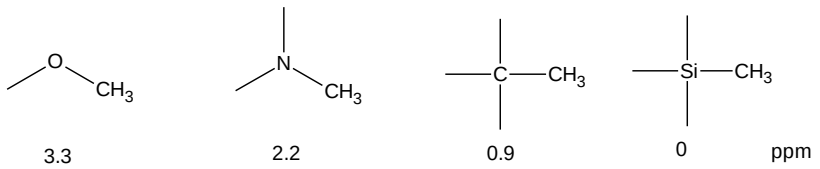
- Proton will be desheilded if X is more electron withdrawing relative to hydrogen
- Consider X being electronegative atoms F, O, N



- Fluorine being most electronegative pulls the electron density towards itself leaving the proton deshielded to applied field, and hence chemical shift is observed in higher field region.
- Increasing number of electronegative substituents also shifts the frequency in downfield region

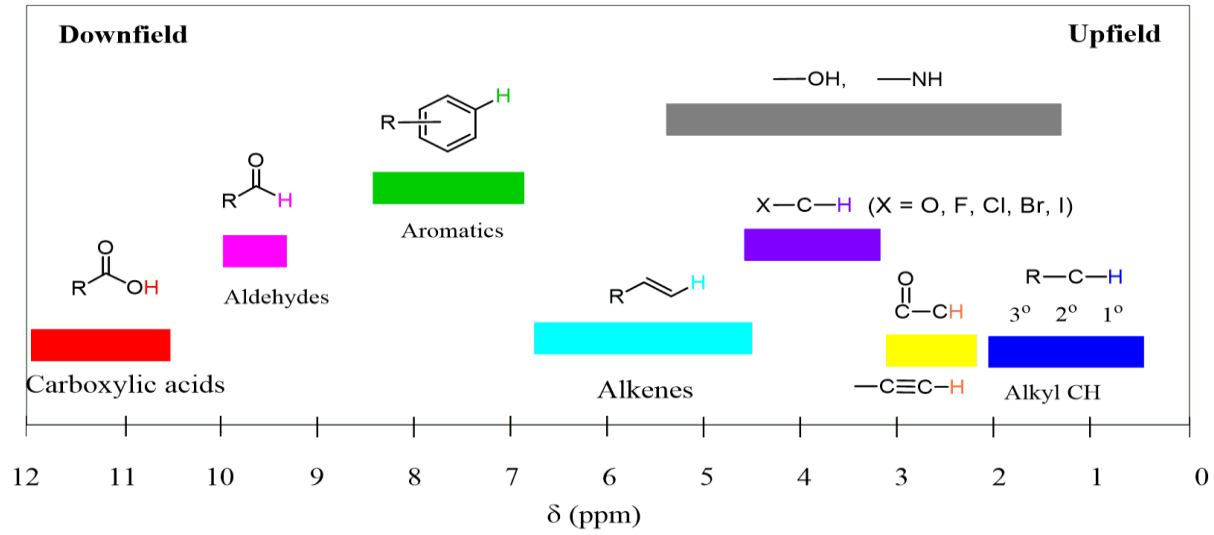


- Increasing electronegativity of the groups attached to methyl group deshields methyl protons showing downfield shift.



- The Unit for chemical shift is given as δ (delta) units, in parts per million.
- δ unit is a proportionality constant and is dimensionless.
- It is independent of the field strength.
- The relation between δ value (ppm) and frequency (Hz) is Given by
- $$\delta_x=(\nu_x-\nu_{TMS})/\nu_0$$
- δ_x is Chemical shift
- ν_x , ν_{TMS} are frequencies (Hz) for X and TMS respectively
- ν_0 is operation Frequency of instrument (MHz)

Chemical shift for Different protons



R-CH_3	0.7 - 1.3
R-CH_2-R	1.2 - 1.4
R_3CH	1.4 - 1.7
R—C=C—CH_3	1.6 - 2.6
R—C(=O)—CH_3	2.1 - 2.5
RO—C(=O)—CH_3	2.1 - 2.6
N≡C—CH_3	2.1 - 3.0
Ar—C—H	2.3 - 2.7
R—C≡C—H	1.7 - 2.7
R—N—C—H	2.2 - 2.9
R—S—C—H	2.0 - 3.0

R= H or alkyl

I—C—H	2.0 - 4.0
Br—C—H	2.7 - 4.1
Cl—C—H	3.1 - 4.1
RO—C—H	3.2 - 3.8

R= H or alkyl

R—C(=O)—O—C—H	3.5 - 4.8
O_2N—C—H	4.1 - 4.3
F—C—H	4.2 - 4.8
R—C=C—H	4.5 - 6.5
Ar—H	6.5 - 8.0
R—C(=O)—H	9.0 - 10

NH and OH peaks are most often broad or may as well be missing completely unless the sample is very dry.

This is also true for any proton capable of making hydrogen bonding:

R—SH (R = alkyl or aryl)	1.0 - 5.0
R—NH_2 1°, 2°	1.0 - 5.0
R—OH 1°, 2°, 3°	1.0 - 5.0
Ar—OH	4.0 - 7.0
R—C(=O)—N(H)—R 1°, 2°	5.0 - 9.0
R—C(=O)—OH	11 - 12

Downfield shifts more common

Solvent Effect

Criteria for solvent selection

- No protons, deuterated solvents used
- Inert solvent
- Low boiling
- Inexpensive

Solvent used in Sample Preparation

Solvents	δ
Acetone-d_6	**2.04(5)**
$CDCl_3$	**7.26(1)**
DMSO-D_6	**2.49(5)**
CH_3CN-d_3	**1.93(5)**
D_2O	**4.82(s)**
CH_3OH-d_4	**4.84(1)** **3.30(5)**
CH_2Cl_2-d_2	**5.32(3)**

Internal Reference Standard

TMS (tetramethylsilane)

- Protons of methyl group more shielded, silicon less electronegative than carbon
- Gives sharp and intense absorption peak at lower concentrations
- Chemically inert solvent
- Symmetrical and only one signal
- Highly volatile (B.P. 27°C), hence can be removed easily from recovery sample
- Soluble in most organic solvents