CHEMICAL SHIFT OF ^{1}H NMR SPECTROSCOPY
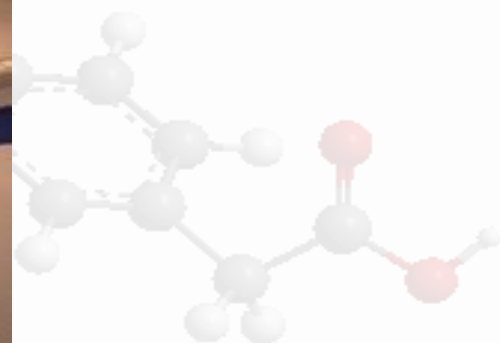
BY

Dr. Sanjay S. Ankushrao

M.Sc., SET, GATE, PhD

Assistant Professor in Chemistry

Vivekanand College, Kolhapur (Autonomous)

Outline

1. **Concept of Chemical shift**
2. **Measurement**
3. **Methods of Measurement**
4. **Characteristic d values of H**
5. **Factors Affecting**

CONCEPT OF CHEMICAL SHIFT

- *The difference in peak position or resonance position of proton w. r. t. an arbitary std. chosen is called as Chemical Shift.*

- *Chemical shift is also called as Position of Signals.*

- *Not measured in Gauss or Tesla.*

- *Even it is not actual frequency required to resonate specific proton*

- *Instead of actual frequencies of resonances, a reference is taken and the frequencies are calibrated with respect to the reference and normalized with respect to the spectrometer frequency.*

- *Equivalent Proton: identical electronic environ. & same chemical shift*

- *Non Equivalent: Diff. electronic environ. & diff chemical shift*

Measurement of Chemical Shift

- **Non equivalent protons absorbs at diff. field strength**

- **But this field diff could be as small as 0.02 gauss.**

- **But an NMR producing 14000 gauss field strength can not accurately measure field strength diff 0.02 gauss.**

- **Even it is not possible to measure actual frequency required to resonate proton.**

- **Therefore, A std proton reference (TMS) is used.**

- **The freq or m. f. of TMS proton- considered as zero**

- **The position of peak of sample proton is measured w. r. t. TMS proton**

Why TMS?

❑ *Tetramethylsilane (TMS) is used as a reference*

❑ *The chemical shift of TMS is lower than most protons in organic molecules, so it is taken as zero*

❑ *The protons in TMS are equivalent and hence only one signal for all the 12 protons-high signal intensity*

❑ *TMS is a liquid and miscible with most solvents*

❑ *It is also volatile and hence easy to remove*

❑ *It is inert and does not react with the samples*

Methods of Chemical Shift

1) Delta Scale (δ):

- Mostly used.

- δ = Freq shift/ operating freq of intrument.

- δ = $(\nu_s - \nu_{TMS})$ in H_z/ operating freq of intrument (ν_{instr} in MHz)* 10^6

- δ value expressed in dimensionless unit (i.e. ppm)

- Independent on field strength

- δ of TMS considered zero arbitarily.

- δ of most sample in the range 0-10

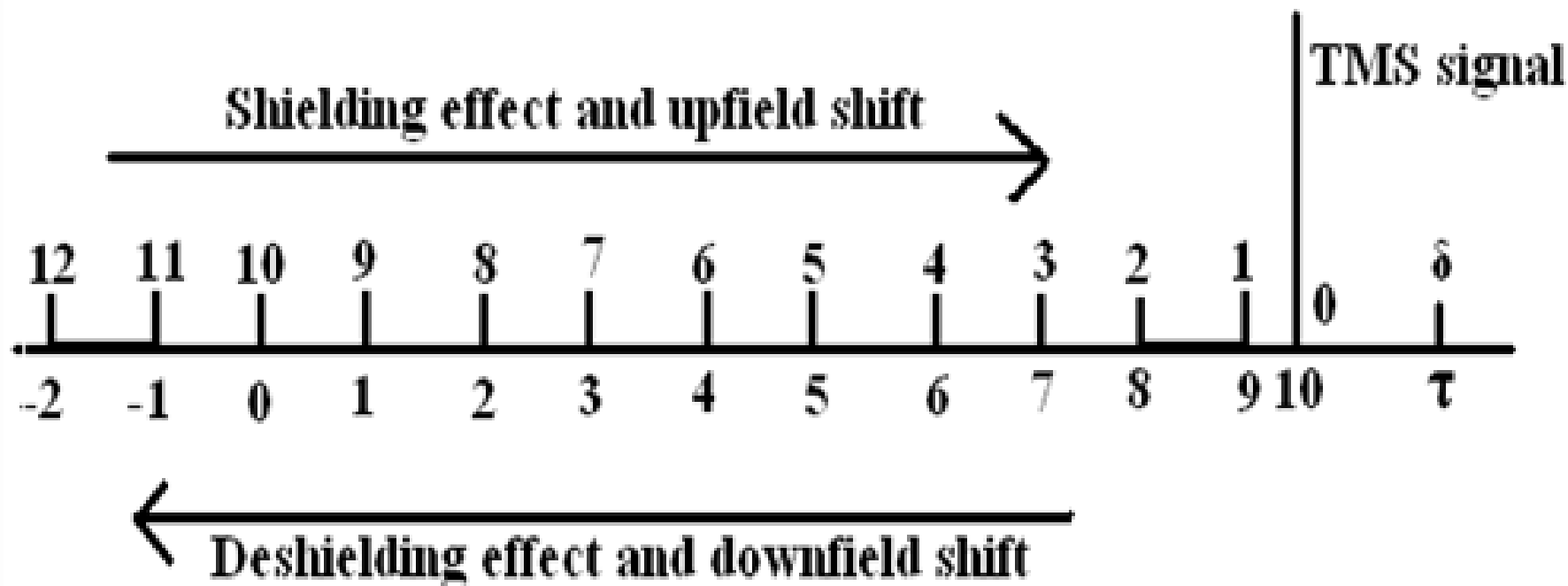- Proton absorbs at downfield than TMS gives +ve δ values

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- ❑ TMS Peak (Shielded)- High Field strength (Upfield)- lower δ values
- ❑ Sample Peak (Deshielded)- Less field strength (Downfield)- higher δ values

2)Tau Scale (τ):

- *To avoid misleading of delta scale.*

- *$\tau = 10-\delta$*

Shielding effect and upfield shift

TMS signal

| 12 | 11 | 10 | 9 | 8 | 7 | 6 | 5 | 4 | 3 | 2 | 1 | 0 | δ |

| -2 | -1 | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 10 | τ |

Deshielding effect and downfield shift

NMR Correlation Chart

DOWNFIELD

DESHIELDED

UPFIELD

SHIELDED

$CHCl_3$, $\overset{|}{H}$

-OH   -NH

TMS

12 11 10 9 8 7 6 5 4 3 2 1 0 δ (ppm)

RCOOH   RCHO

$C=C\overset{H}{\underset{}{}}$

CH_2F
CH_2Cl
CH_2Br
CH_2I
CH_2O
CH_2NO_2

CH_2Ar
CH_2NR_2
CH_2S
$C\equiv C\text{-}H$
$C=C\text{-}CH_2$
$CH_2\text{-}\overset{\|}{\underset{O}{C}}\text{-}$

$C\text{-}\overset{|}{\underset{C}{CH}}\text{-}C$

$C\text{-}CH_2\text{-}C$
$C\text{-}CH_3$

8
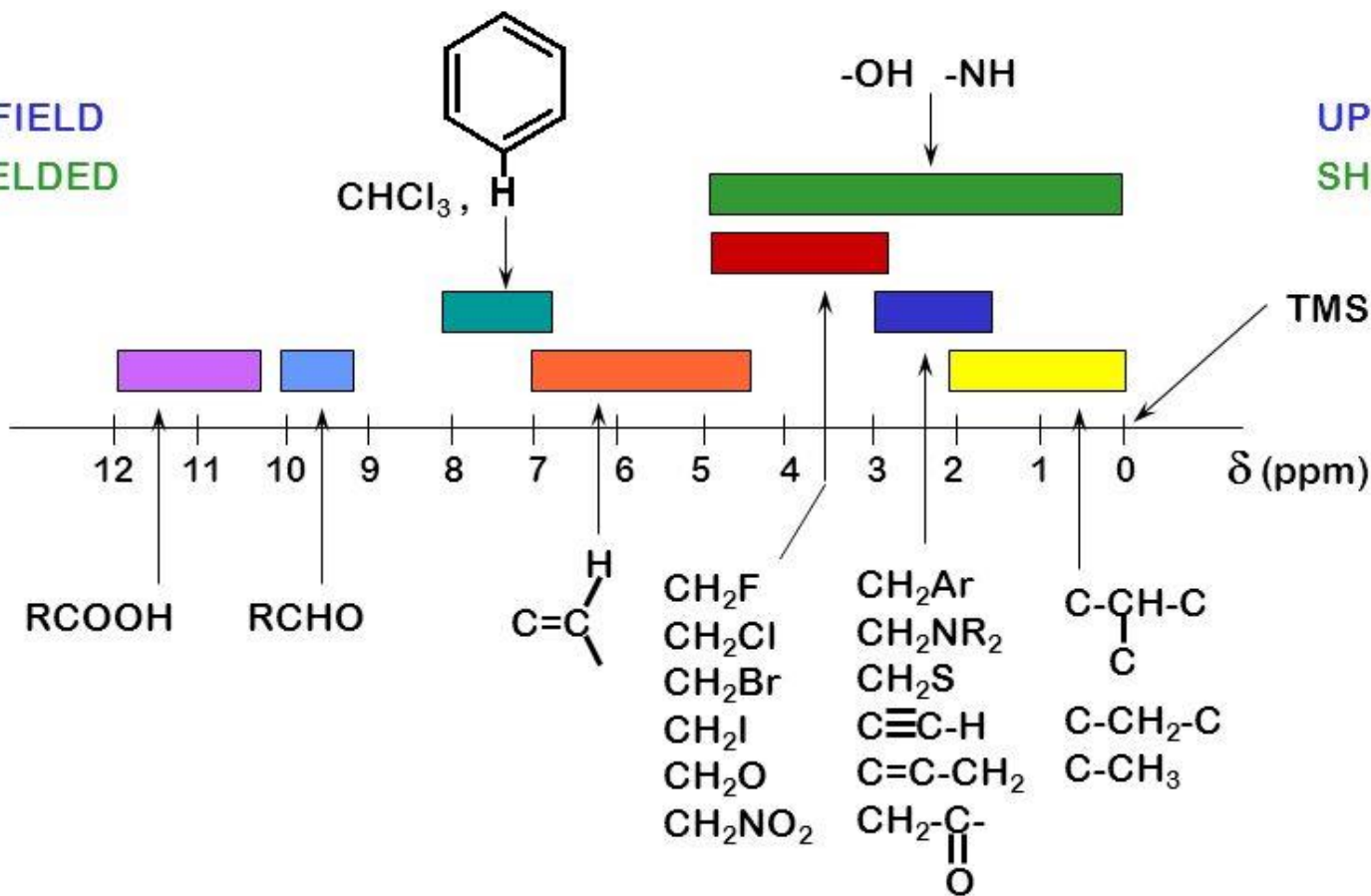
Shielding & Deshielding

Shielding

For example:- _Acetylene molecule_

Shielded Proton of acetylene:-

electron circulation

Proton experiencing diamagnetic shielding

Induced magnetic field
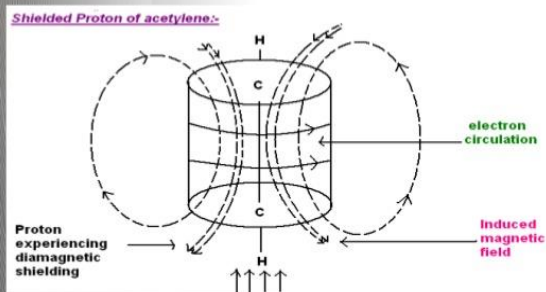
Deshielding

Example:- Benzene molecule

electron circulation

Paramagnetic deshielding of Proton

Induced magnetic field

Deshielded proton of benzene
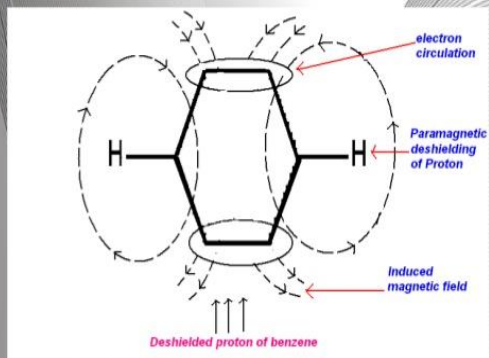
❑ *Diamagnetic Shielding:* **It is due to e_s^- present surrounding to H.**

• **The phenomenon of partially protecting protons from applied field by induced field or sec field generated due to circulation of surrounding e_s^- is called as Diamagnetic shielding.**

• *Degree of shielding depends on strength of induced field*

• *Induced field depends on strength of applied field & e-density around H .*

• *e- density depends on nature of neighbouring atom & its electronegativity.*

• *If induced field align to Applied Field-* Shielding

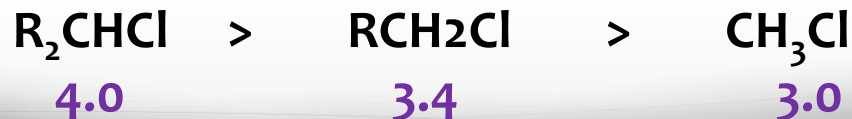• *If induced field align opposite to applied field- deshielding*
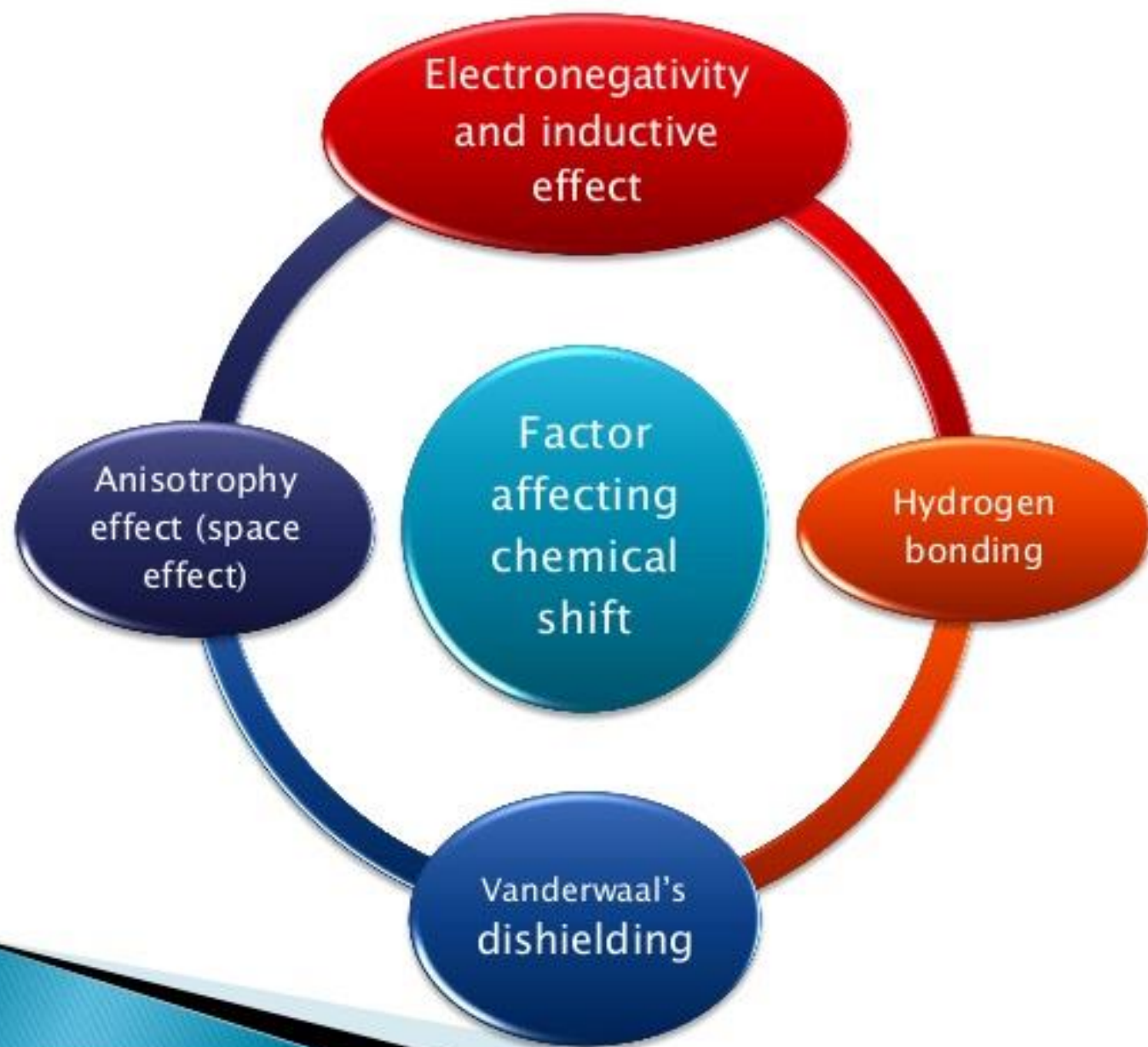
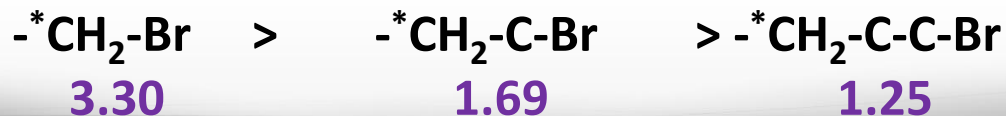# 1) *Electronegativity, inductive and resonance effects*

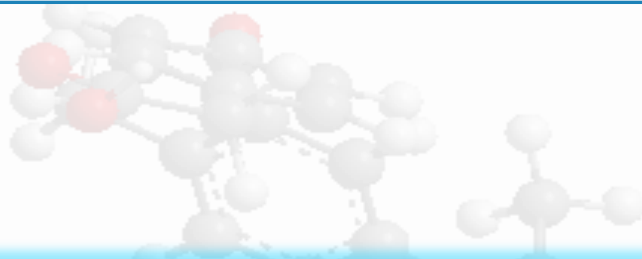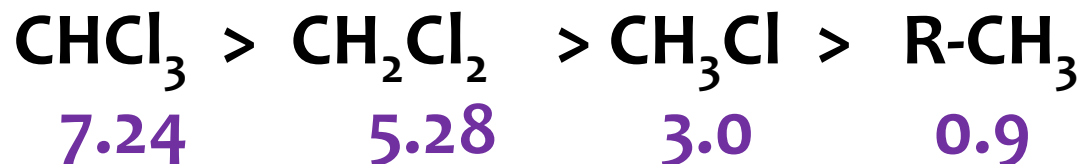- *Electronegative Group- deshields proton- Proton shifts move towords downfield (higher d values)*

CH_3F >	CH_3Cl >	CH_3Br >	CH_3I >	CH_3-CH_3 >	CH_4 >	CH_3SiMe_3 >	CH_3Li
4.26	3.05	2.69	2.19	0.96	0.2	0.0	-0.4
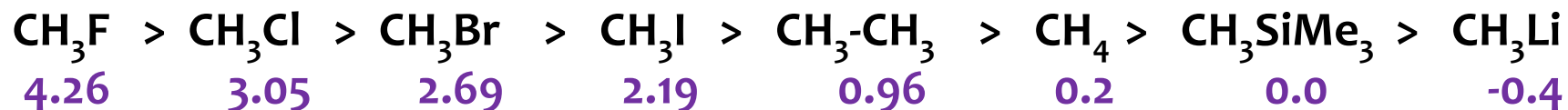
- *More H atoms- more shielding- lower d values*

R_2CHCl >	$RCH2Cl$ >	CH_3Cl
4.0	3.4	3.0

- *As e- withdrawing group goes away shielding increases-* lower *d values*

$-^*CH_2$-Br >	$-^*CH_2$-C-Br	> $-^*CH_2$-C-C-Br
3.30	1.69	1.25

- *Electron withdrawing group increases- increases δ values*

CHCl$_3$ > CH$_2$Cl$_2$ > CH$_3$Cl > R-CH$_3$
7.24   5.28   3.0   0.9

2) *Van der Waal's Deshielding- increases δ values*
- *In overcrowded molecule H occupying hindered position gives higher δ values*
- *It is due to e- cloud of bulky group tend to repel e- cloud of surrounding proton.*
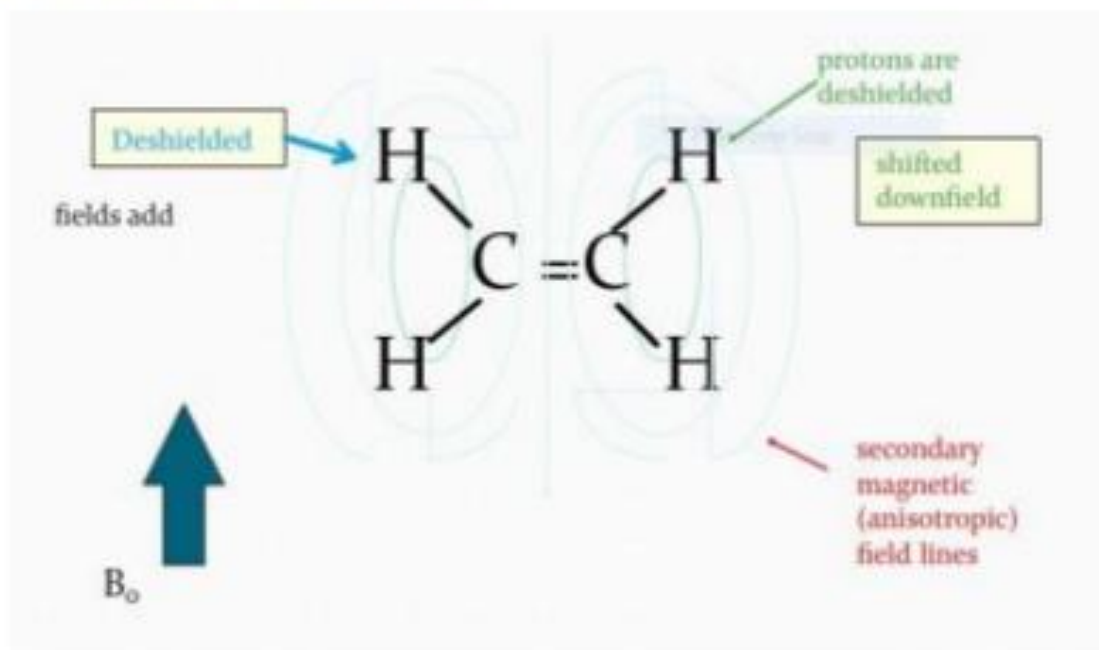
3) ANISOTROPIC EFFECT *OR SPACE EFFECT*

❖ The opposite of isotropy which means uniformity in all directions.
❖ So, anisotropy is non-uniformity.
❖ Now for different compounds this anisotropy is different as different distribution of electrons around nuclei.
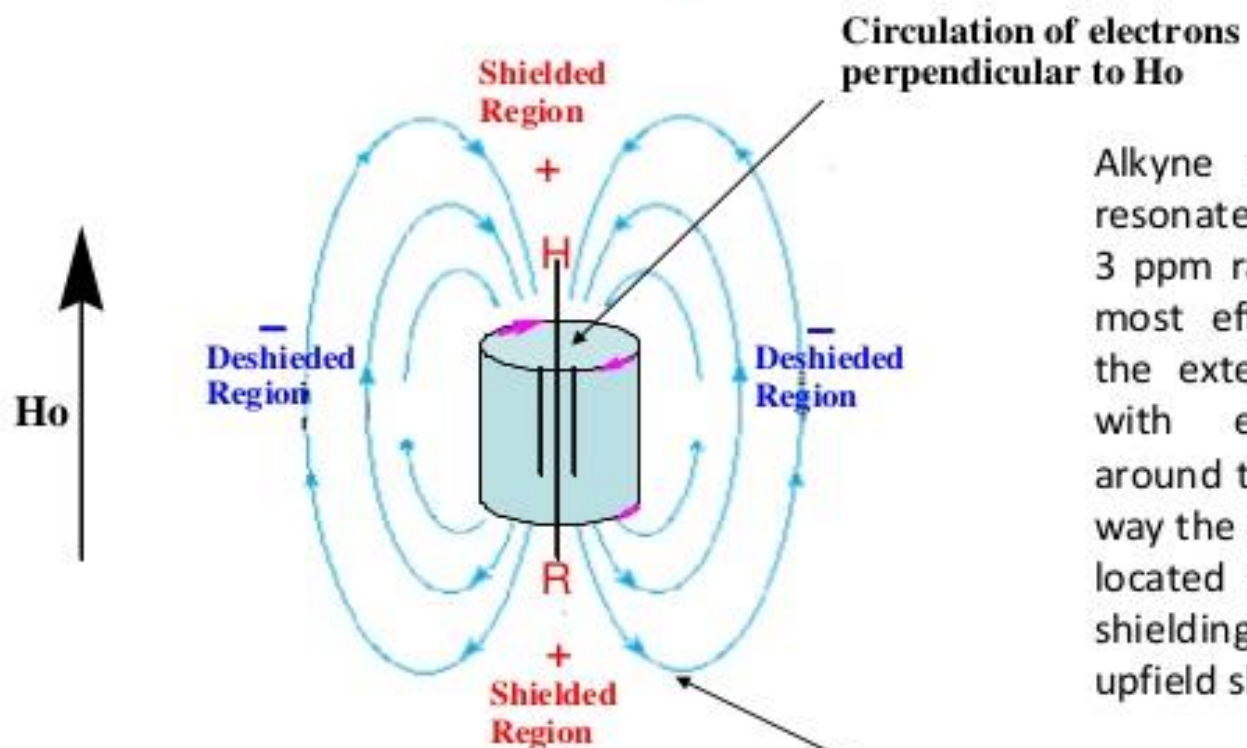
Anisotropy effect of

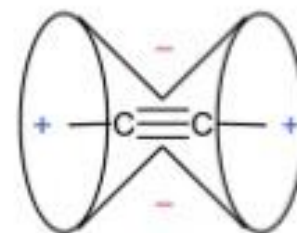- Alkene
- Alkyne
- Benzene
- ketone/Aldehyde

ALKENES:

❖ protons adjacent to alkene ($C=C-H$)are deshielded by anisotropy effect,so, chemical shift will be induced.

Alkyne -C≡C-H

Circulation of electrons perpendicular to Ho

Shielded Region

+

Deshieded Region −

H

Ho

Deshieded Region −

+

Shielded Region

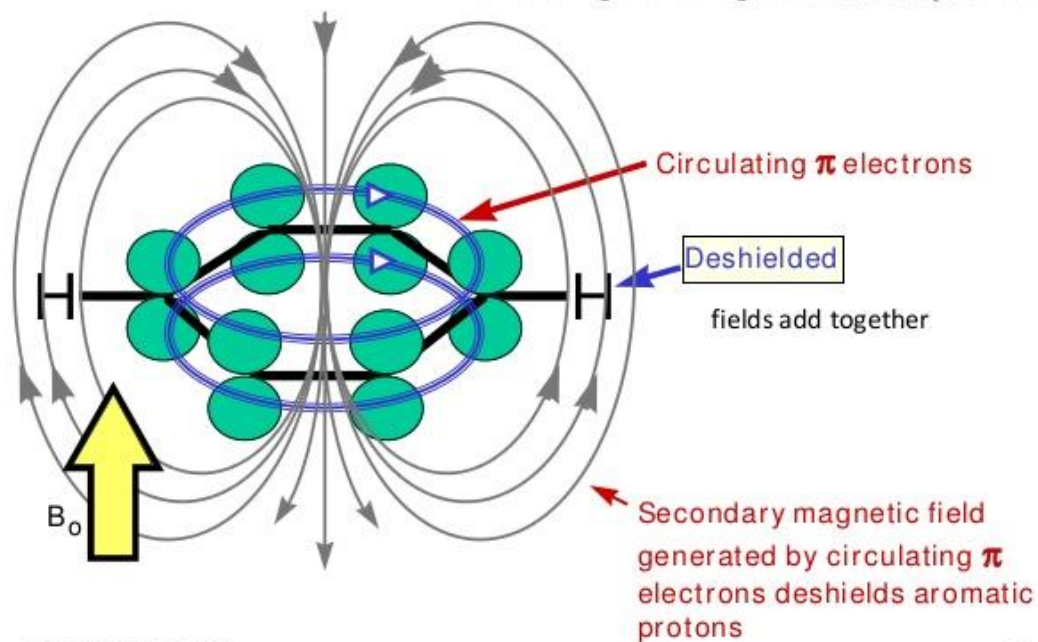Acetylenic Protons at δ 2.5-3.0

Induced Magnetic Field

Alkyne protons by contrast resonate at high field in a 2–3 ppm range. For alkynes the most effective orientation is the external field in parallel with electrons circulation around the triple bond. In this way the acetylenic protons are located in the cone-shaped shielding zone hence the upfield shift
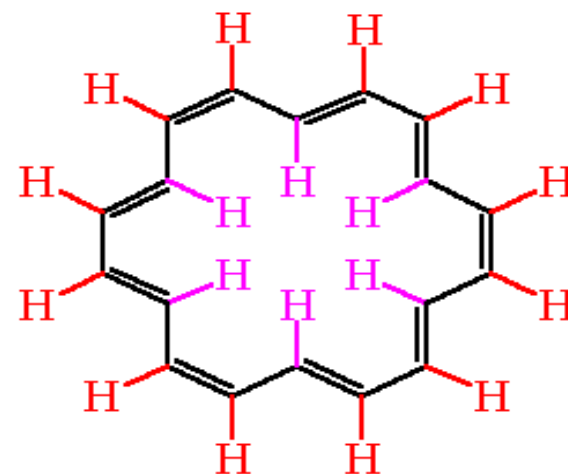
Ring Current in Benzene

Benzene rings have the greatest **anisotropic** effect.

Circulating π electrons

Deshielded

fields add together

Secondary magnetic field generated by circulating π electrons deshields aromatic protons
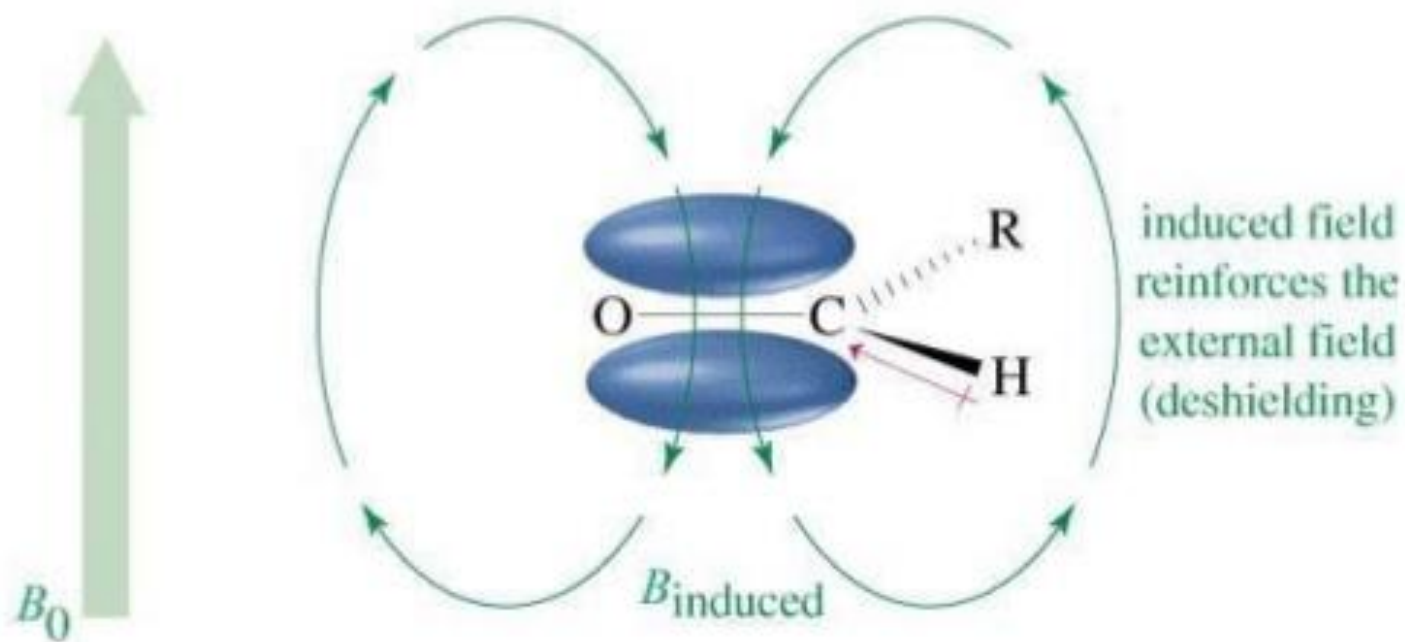
B_o

[18]Annulene
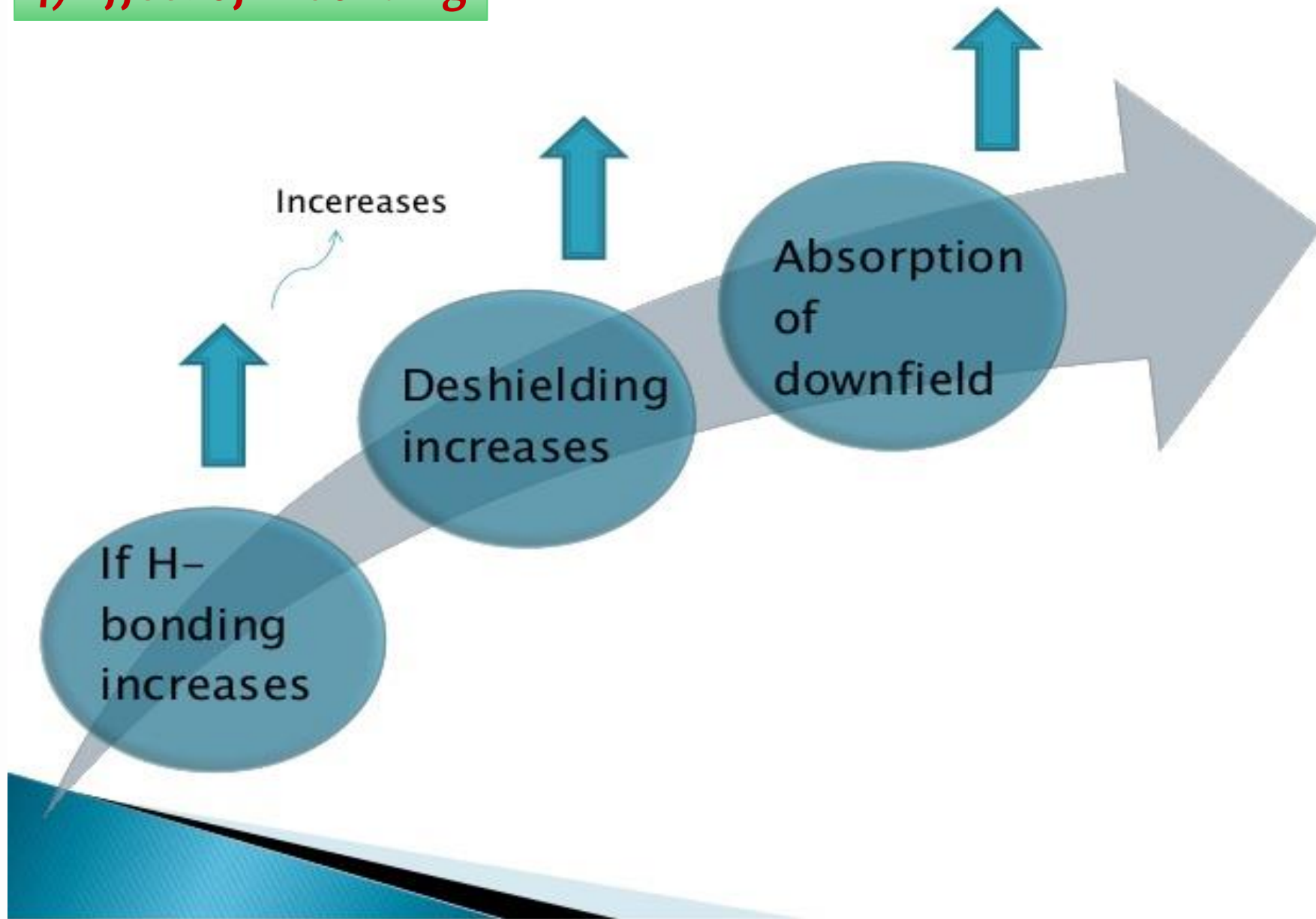

6H   -1.9 δ Highly Shielded
12H   8.2 δ Highly Deshielded

Good evidence of a ring current. Deshielded protons are a property of Aromatic Compounds.
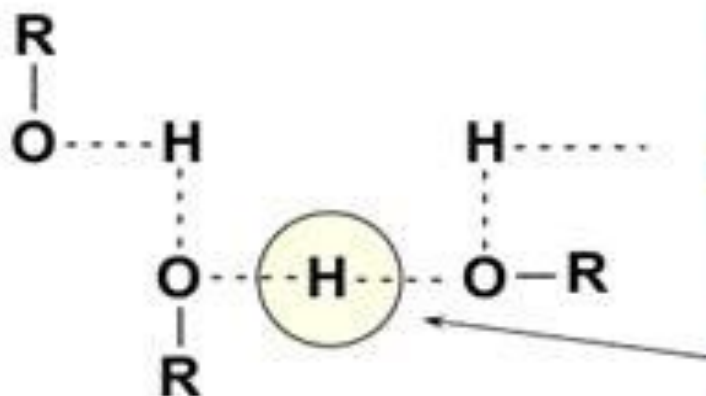
Aldehyde proton

4) *Effect of H-bonding*

If H– bonding increases → Deshielding increases → Absorption of downfield

Increeases

HYDROGEN BONDING
O–H and N–H Signals
HYDROGEN BONDING DESHIELDS PROTONS

R
|
O----H   H------

O----H----O–R
|
R

The chemical shift depends on how much hydrogen bonding is taking place (observed in high concentrated solutions).

Hydrogen bonding lengthens the O–H bond and reduces the valence electron density around the proton

It is deshielded and shifted downfield in the NMR spectrum.

Alcohols vary in chemical shift from 0.5 ppm (free OH) to about 5.0 ppm (lots of H bonding).

D_2O–exchangeable (peak for OH proton in alcohol and NH in amines disappears upon shaking with D_2O)

:::Thank You::: :::Keep Learning:::