FACTORS AFFECTING TO CHEMICAL SHIFT IN ^{1}H NMR SPECTROSCOPY

BY

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Chemical Shifts ^{1}H-NMR

Type of Hydrogen	Chemical Shift (δ)	Type of Hydrogen	Chemical Shift (δ)
$(CH_3)_4Si$	0 (by definition)	$RCOCH_3$	3.7-3.9
RCH_3	0.8-1.0	$RCOCH_2R$	4.1-4.7
RCH_2R	1.2-1.4	RCH_2I	3.1-3.3
R_3CH	1.4-1.7	RCH_2Br	3.4-3.6
$R_2C{=}CRCHR_2$	1.6-2.6	RCH_2Cl	3.6-3.8
$RC{\equiv}CH$	2.0-3.0	RCH_2F	4.4-4.5
$ArCH_3$	2.2-2.5	$ArOH$	4.5-4.7
$ArCH_2R$	2.3-2.8	$R_2C{=}CH_2$	4.6-5.0
ROH	0.5-6.0	$R_2C{=}CHR$	5.0-5.7
RCH_2OH	3.4-4.0	ArH	6.5-8.5
RCH_2OR	3.3-4.0	$RCHO$	9.5-10.1
R_2NH	0.5-5.0	$RCOH$	10-13
$RCOCH_3$	2.1-2.3		
$RCOCH_2R$	2.2-2.6		

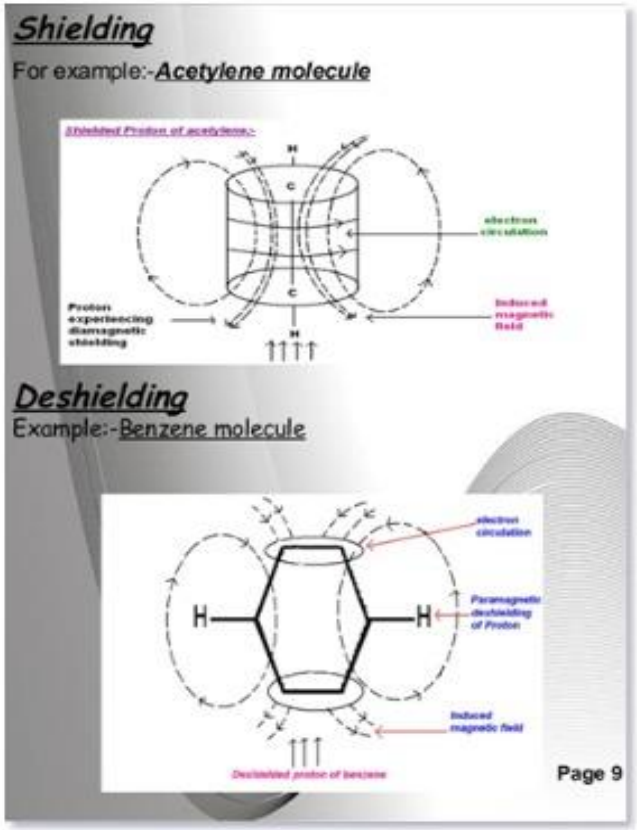
Shielding & Deshielding

Diamagnetic Shielding

The phenomenon of partially protecting protons from applied field by induced field or sec field

Paramagnetic Deshielding

It is phenomenon of partially **deprotecting** proton from applied field by induced or sec. field.

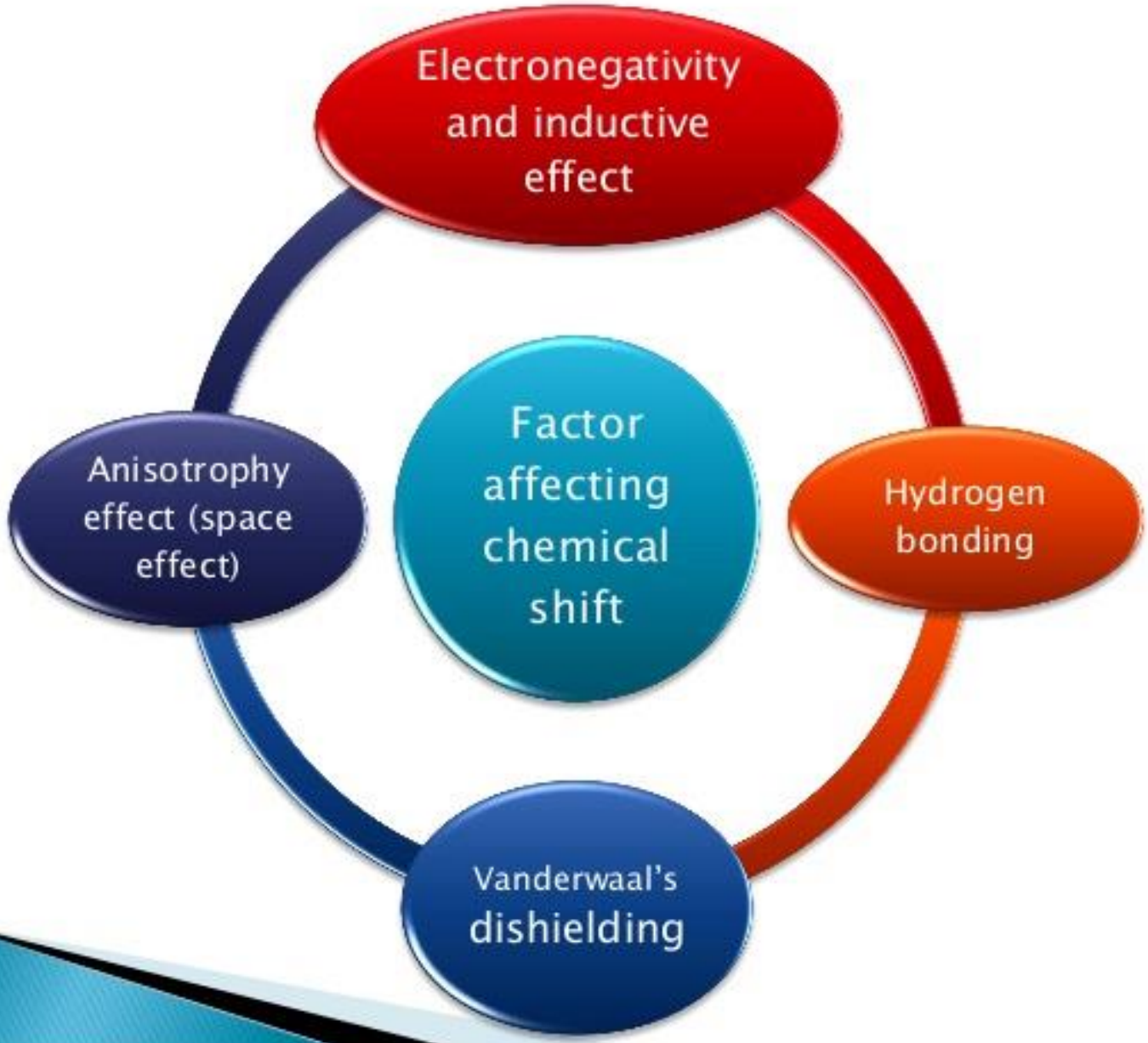


Degree of shielding depends on strength of induced field

Strength of Induced field depends on strength of applied field and electron density around H

Electron density depends on nature of neighbouring atom and its electronegativity

- Deshielding- If induced field align to Applied Field-
- Shielding- If induced field align opposite to applied field-


Electronegativity and inductive effect
Hydrogen bonding
Vanderwaal's dishielding
Anisotrophy effect (space effect)
Factor affecting chemical shift

1) Electronegativity, inductive and resonance effects

- *Electronegative Group- deshields proton- Proton shift moves towards downfield (higher δ 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 δ values*

R_2CHCl	>	RCH2Cl	>	CH_3Cl
4.0		3.4		3.0

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

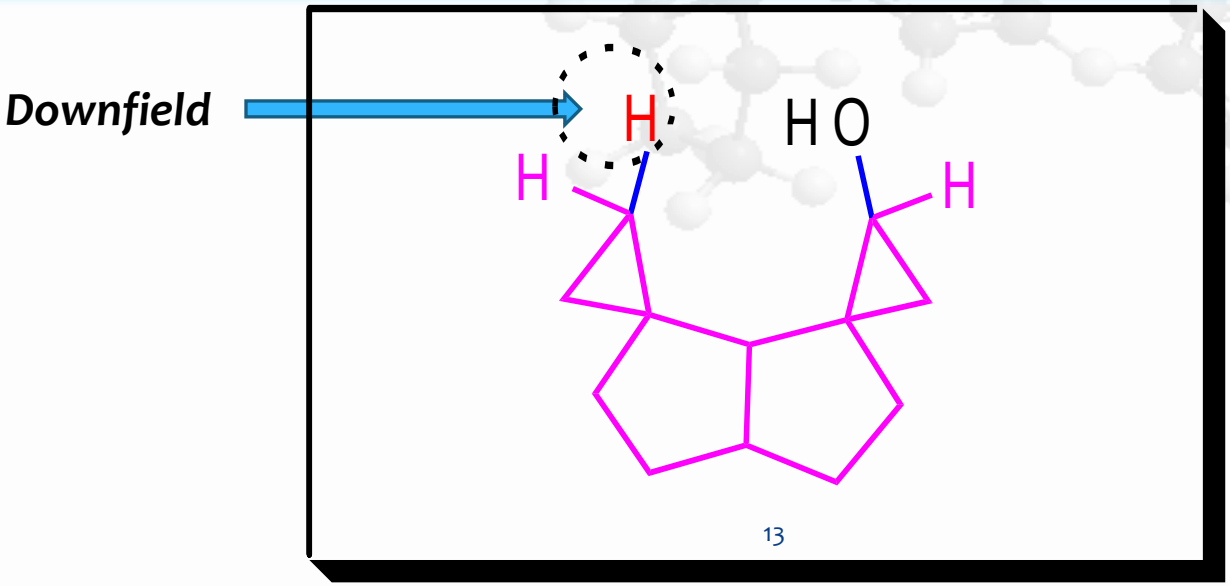
-*CH_2-Br	>	-*CH_2-C-Br	> -*CH_2-C-C-Br
3.30		1.69	1.25

- *Electron withdrawing group increases- increases δ values*

$CHCl_3$	>	CH_2Cl_2	>	CH_3Cl	>	$R\text{-}CH_3$
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

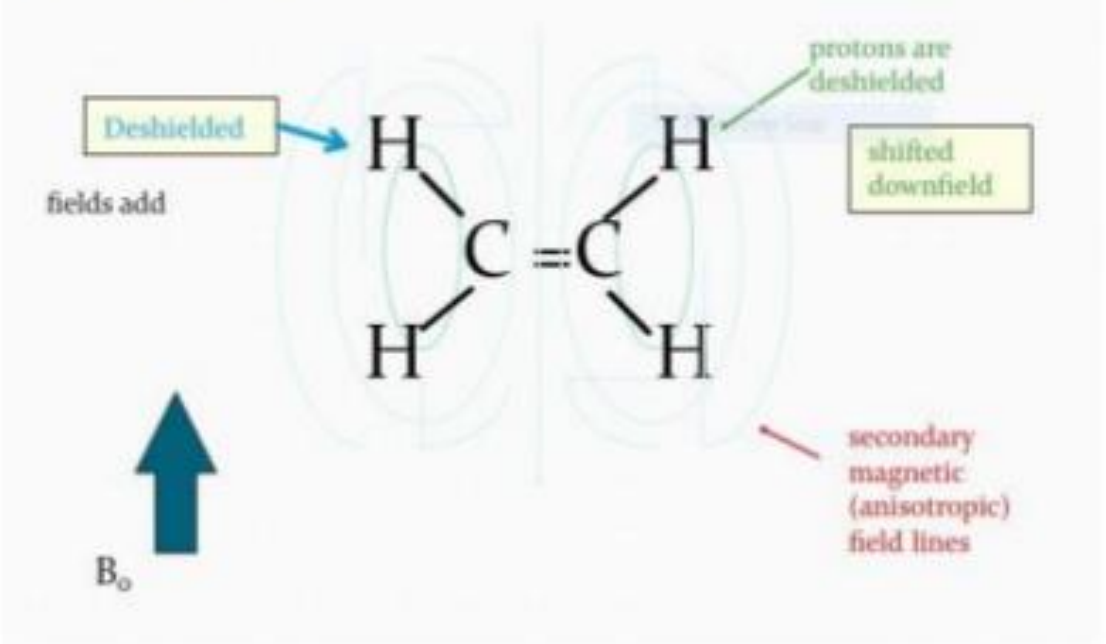
- The opposite of isotropy which means uniformity in all directions.
- So, anisotropy is non-uniformity.
- Now for different compounds this anisotropy is different as different distribution of electrons around nuclei.

Anisotropy effect of

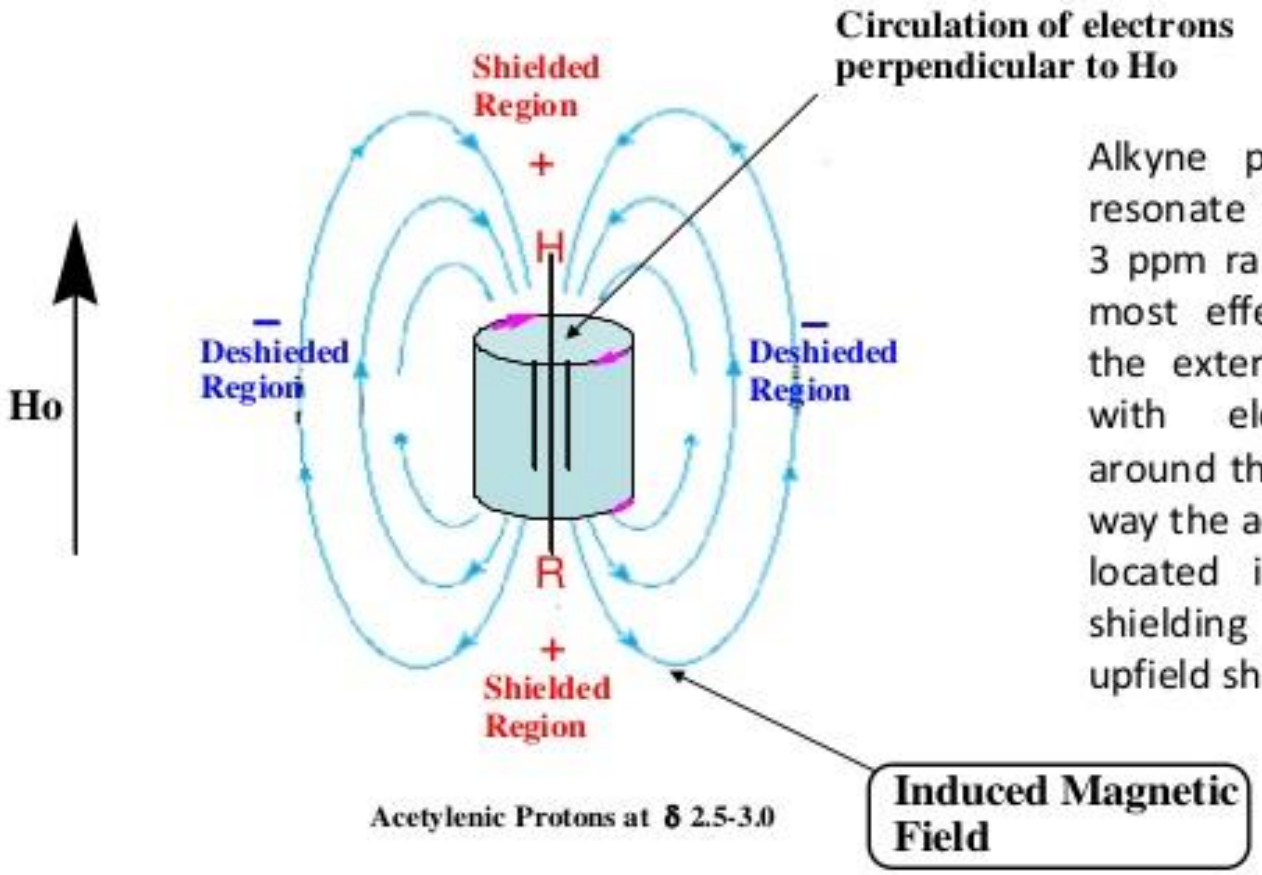
- Alkene
- Alkyne
- Benzene
- ketone/Aldehyde

ALKENES:

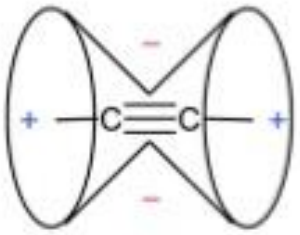
- protons adjacent to alkene (C=C-H)are deshielded by anisotropy effect,so, chemical shift will be induced.



Alkyne -C≡C-H

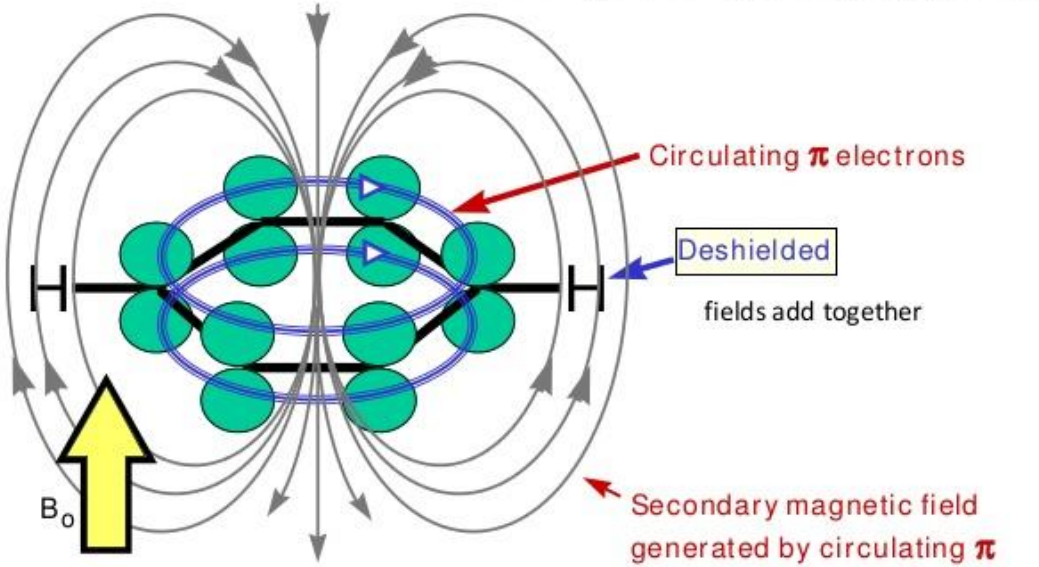


Alkyne protons by contrast resonate at high field in a 2–3 ppm range. For alkynes the most effective orientation is the external field in parallel with electrons circulation around the triple bond. In this way the acetylenic protons are located in the cone-shaped shielding zone hence the upfield shift



Ring Current in Benzene

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



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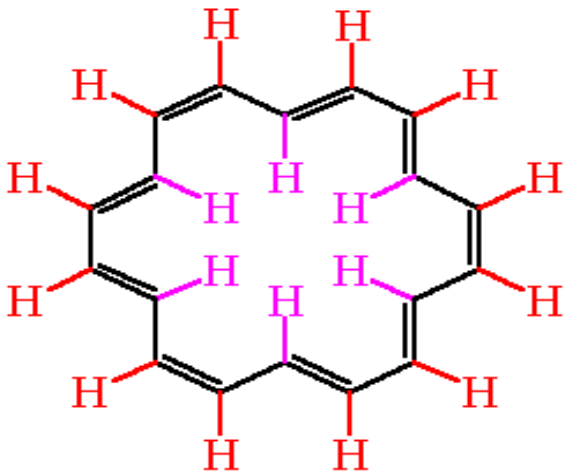
[18]Annulene

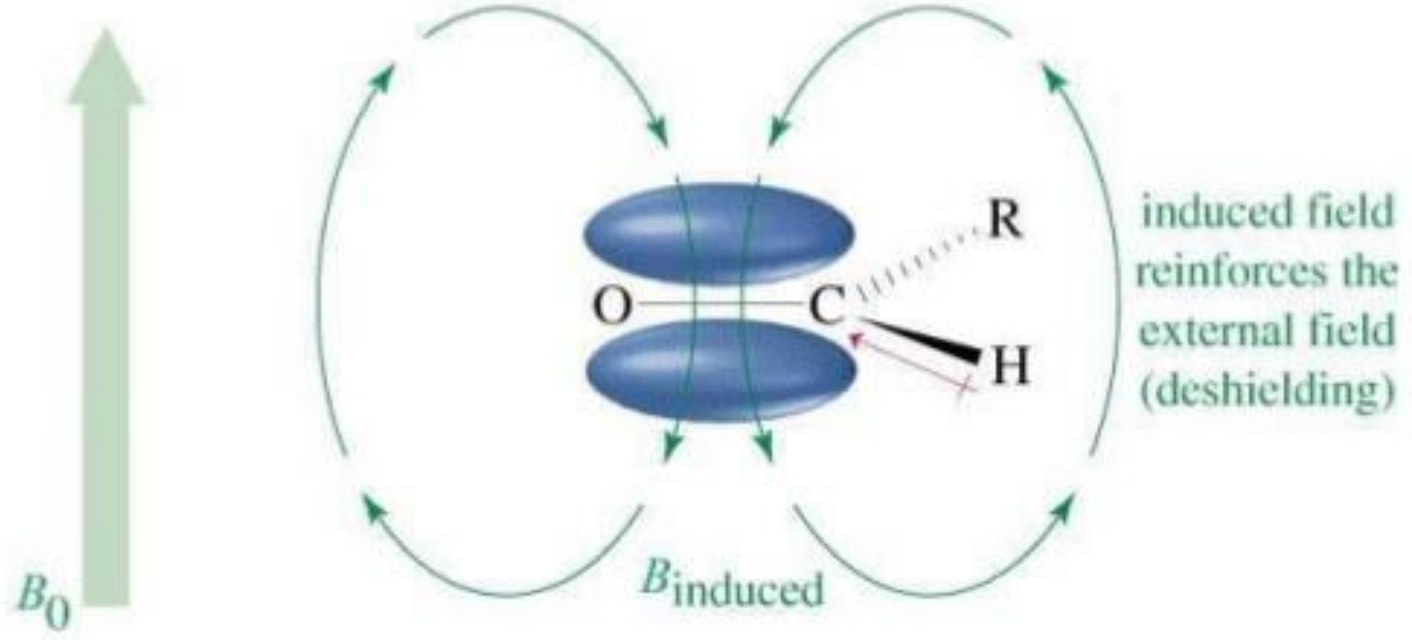


6H -1.9 δ Highly Shielded

12H 8.2 δ Highly Deshielded

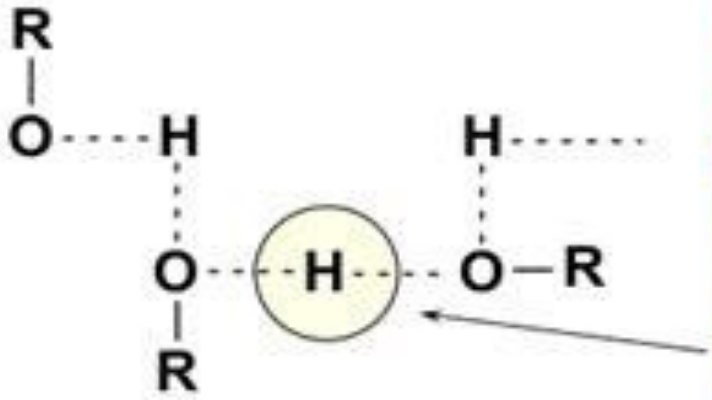
Good evidence of a ring current. Deshielded protons are a property of Aromatic Compounds.

Aldehyde proton



4) Effect of H-bonding

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



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:::::