

**CHEM202**

**Organic Chemistry**

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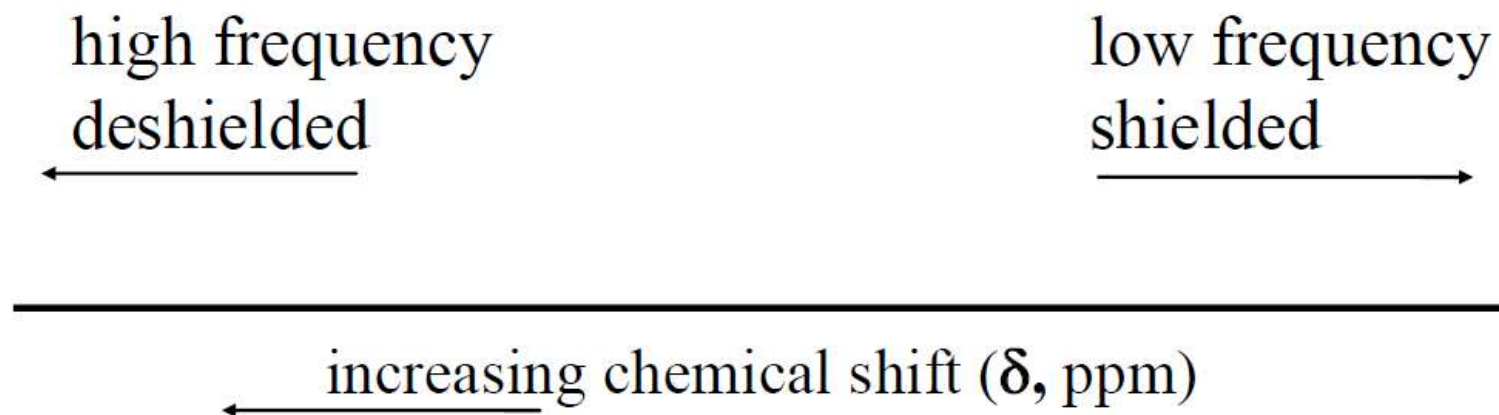
Module 1: Spectroscopy and Characterisation

***Lecture 4:  $^1\text{H}$  NMR Spectroscopy II***

The structure of benzene came to Kekulé in  
a dream, of a snake eating its tail

# Recap: Shielding and deshielding

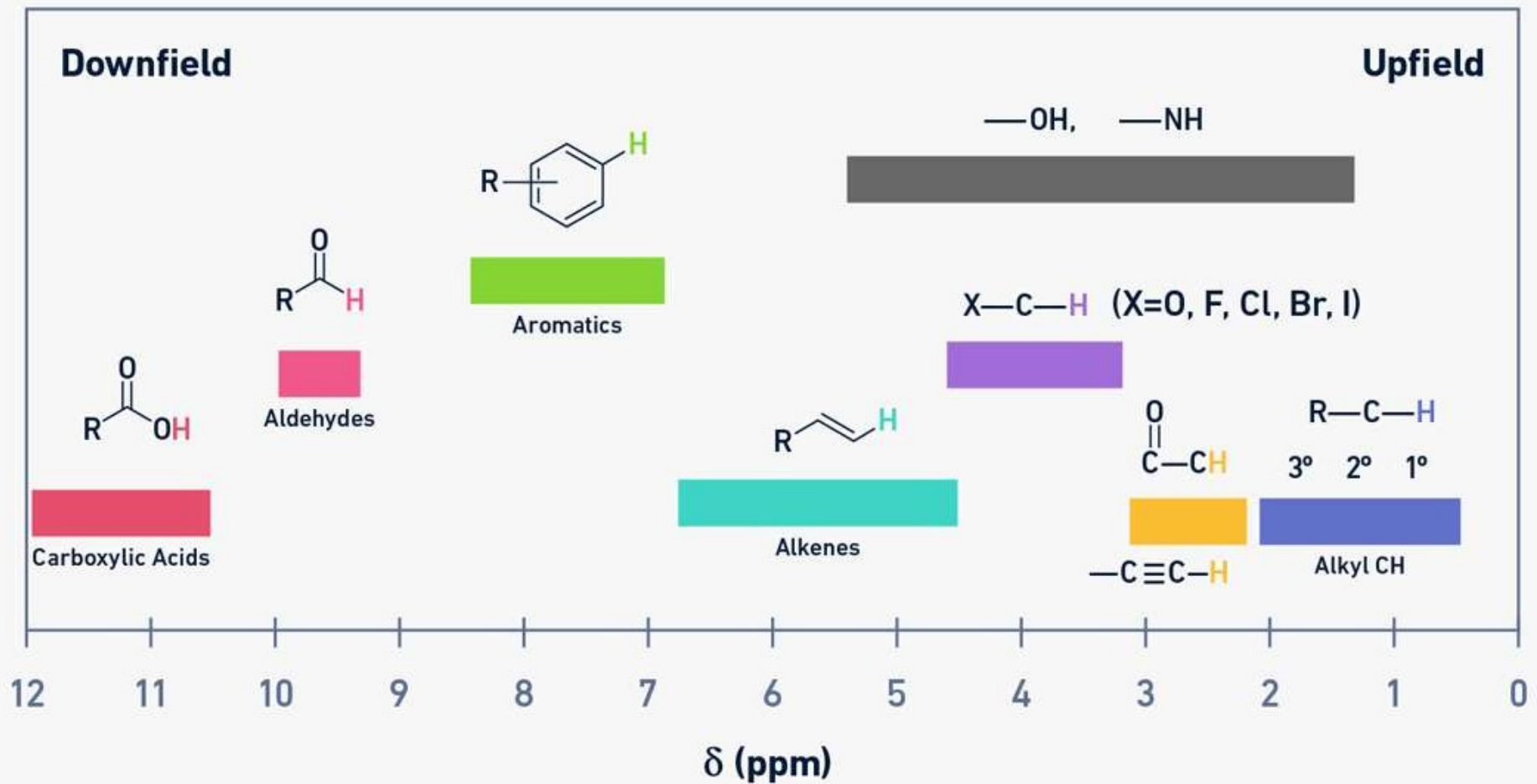
## Nomenclature used when describing chemical shift



### What influences shielding?

- Inductive effects
- Anisotropic effects
- Mesomeric effects
- H-bonding

# Chemical shift is characteristic of structure



## **Anisotropic effects**

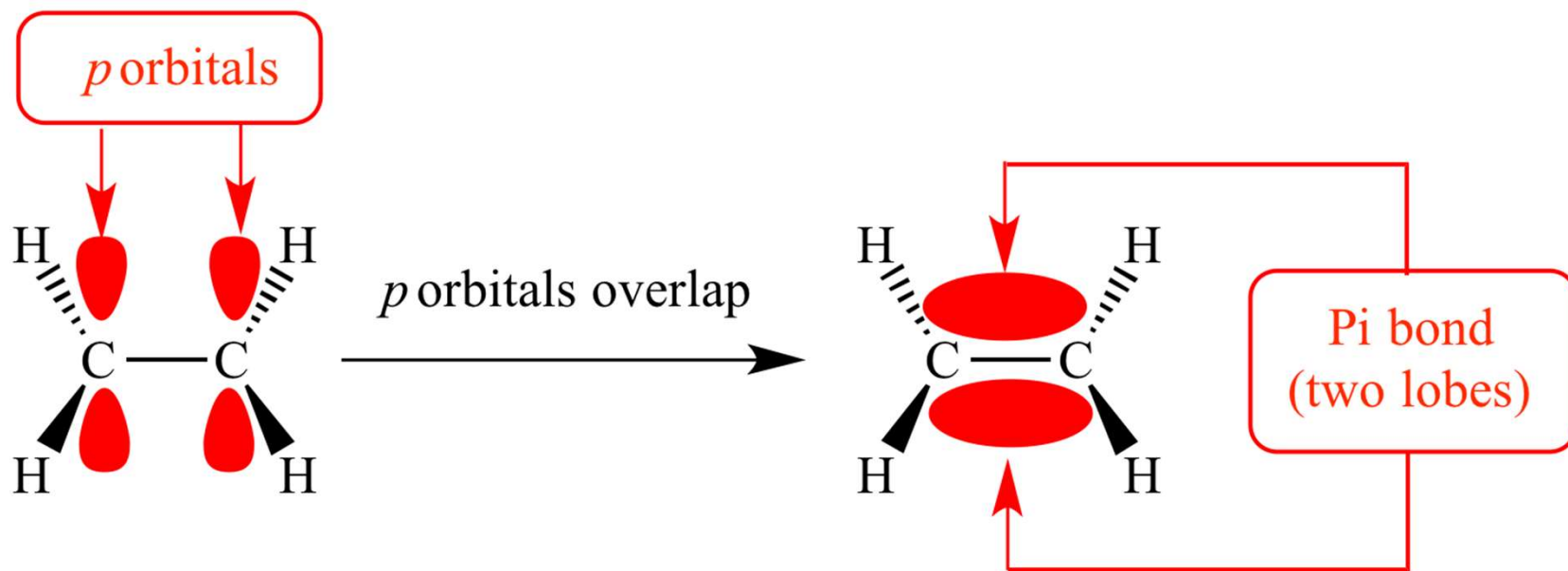
- shielding effects that are highly spatially dependent arising from the circulation of electrons
- in aliphatic systems it accounts for;
  - a) the general observation that an increase in branching leads to an increase in chemical shift ie  $\delta\text{CH} > \delta\text{CH}_2 > \delta\text{CH}_3$
  - b) in ring systems eg cyclohexane  $\delta\text{H}_{\text{equatorial}} > \delta\text{H}_{\text{axial}}$

**Anisotropy means that the electron distribution (and effect on the magnetic field) is not the same in each direction about, for example, a carbon atom.**

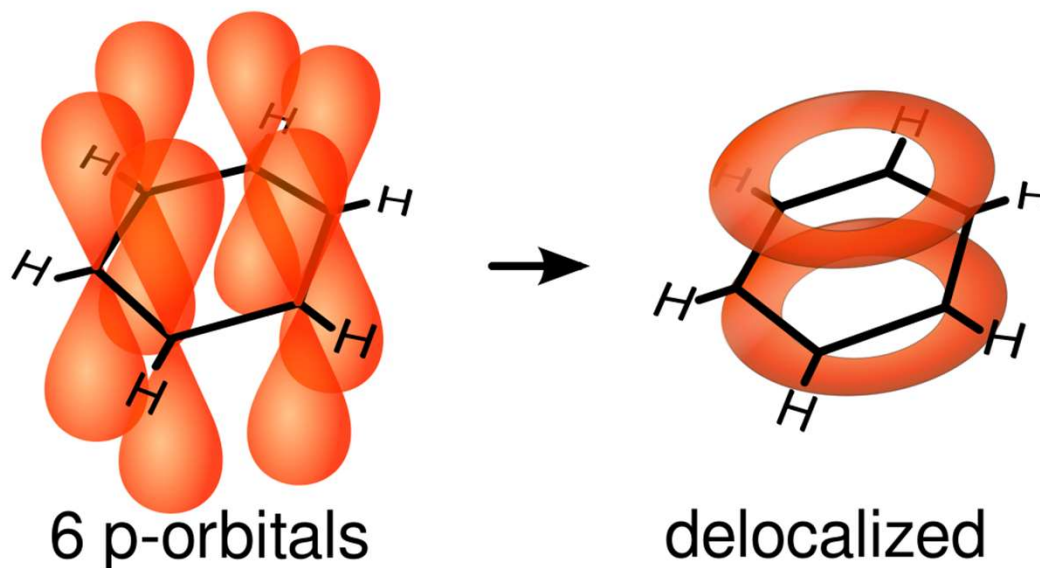
**Hence, protons in different directions relative to that carbon atom experience different shielding effects.**

# Pi bond anisotropy (electronic)

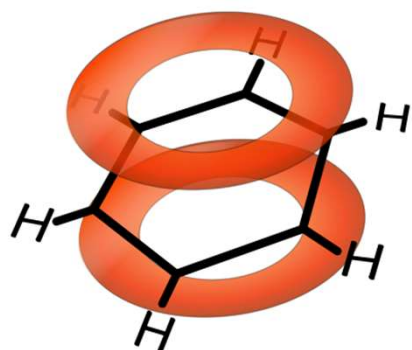
**Alkene**



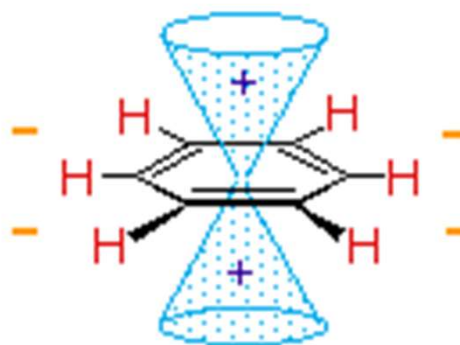
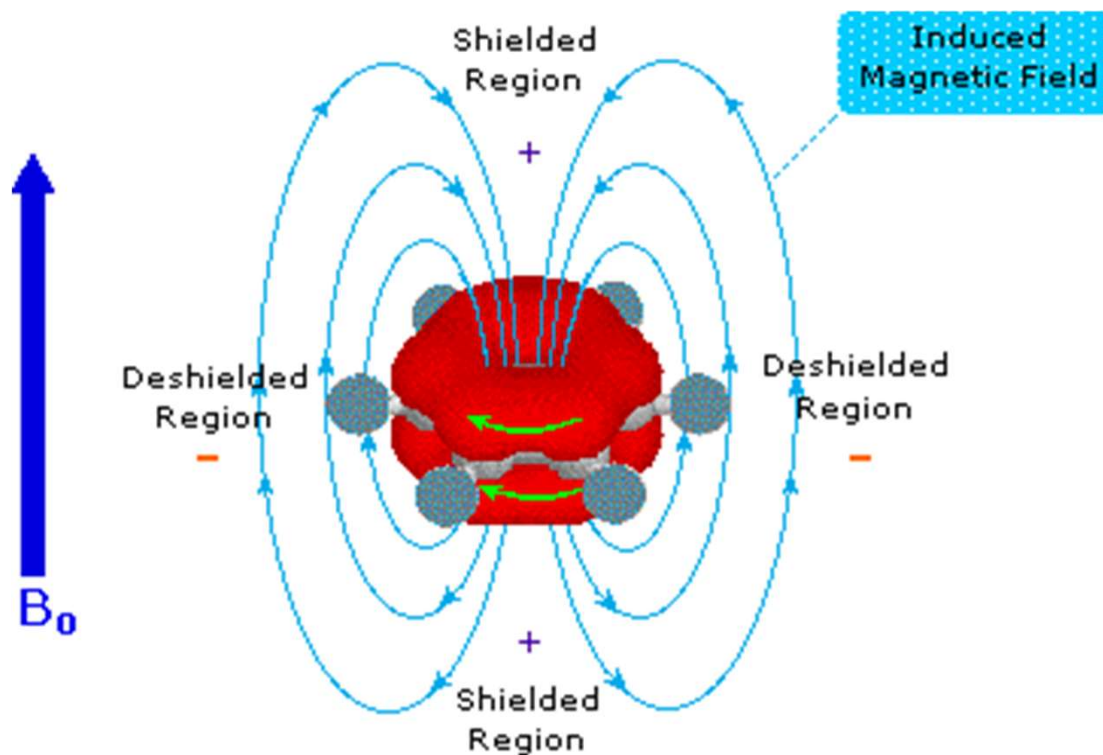
**Aromatic**



# Pi bond anisotropy (magnetic)



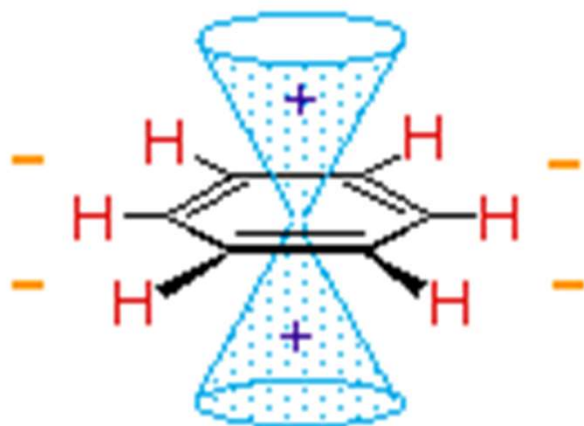
delocalized



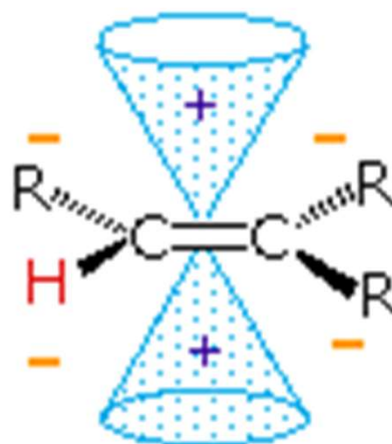
$\delta = 7-8$  ppm

Anisotropic effects are most prominent in unsaturated systems, which possess pi electrons.

Pi electrons are more readily polarisable than sigma electrons in saturated systems.



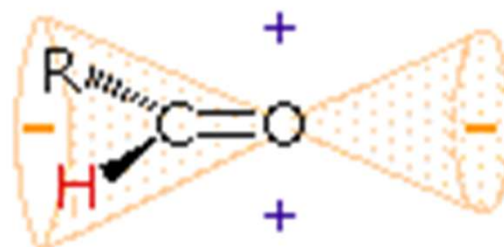
$\delta = 7-8$  ppm



$\delta = 5-7$  ppm



$\delta = 2-3$  ppm

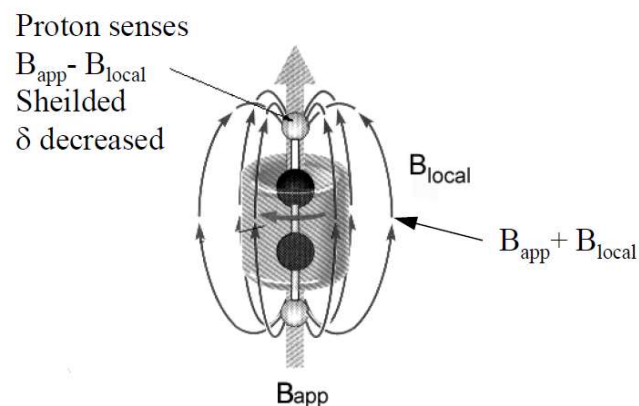


$\delta = 9-10$  ppm



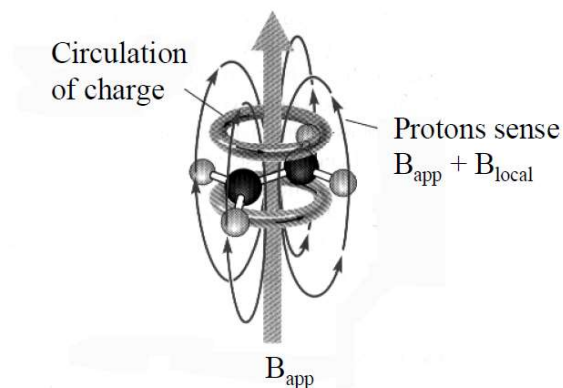
## Magnetic induction in $\pi$ -electron systems

- In alkyne bonds the electrons circulate about the  $\text{C}\equiv\text{C}$ .



Note that outside the charge circulation the local field helps the applied field.

- In alkene bonds electrons circulate perpendicular to the  $\text{C}=\text{C}$ .



The greater the charge circulation the stronger  $B_{\text{local}}$ .

$\delta$  for benzene 7.3 ppm

$\delta$  for  $\text{C}=\text{CH}_2$  5 ppm

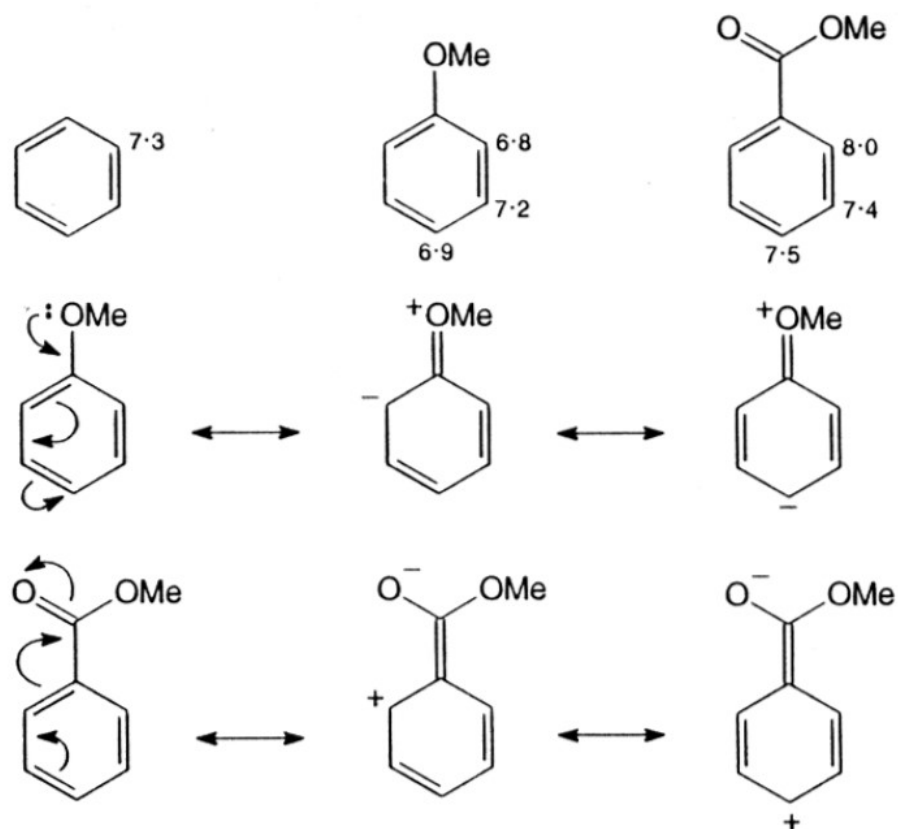


## Mesomeric Effects (Resonance)

In unsaturated systems the electron density may be influenced by the presence of groups which induce mesomeric effects

Examples	methoxybenzene (anisole)	+ <b>M</b> effect
	methylenbenzoate	- <b>M</b> effect

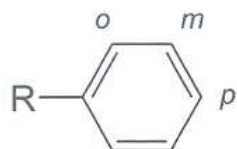
*Note ortho and para: 1,3-relationships between donor and acceptor*



Mesomeric effects influence electron distribution and hence chemical shifts.

– indicates an increase in electron density, and hence increased shielding whereas + indicates a decrease in density and hence deshielding of the protons.



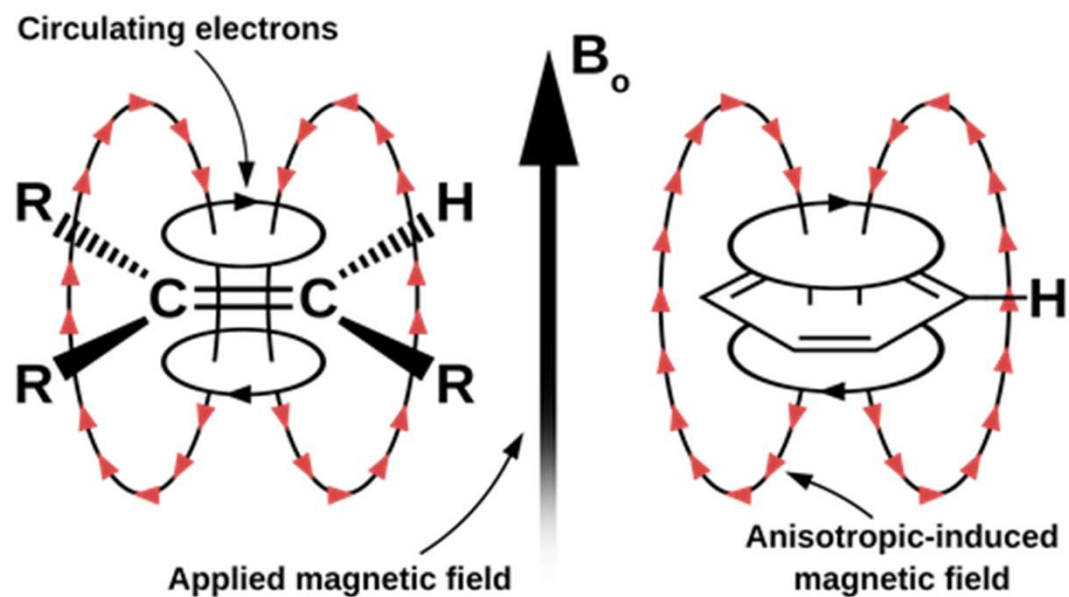
Estimation of  $^1\text{H}$  NMR chemical shifts in substituted benzenes

$$\delta_{\text{H}} = 7.27 + \sum z_i \quad (\text{Equation 3})$$

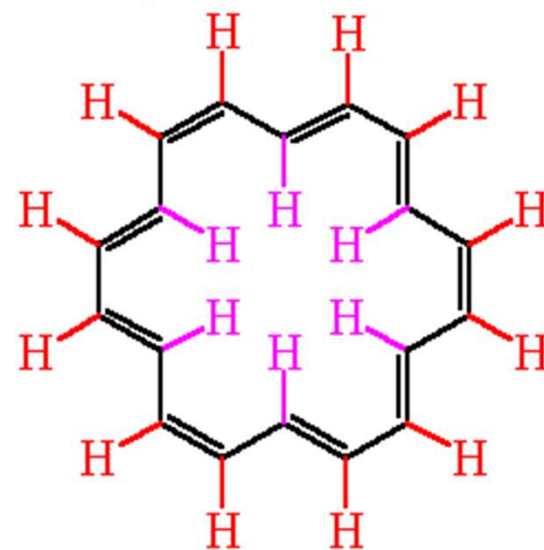
Substituent constants  $z$  for **Equation 3**:

	$\text{R}^i$	$z_{\text{ortho}}$	$z_{\text{meta}}$	$z_{\text{para}}$
C	—H	0.00	0.00	0.00
	—Me	-0.20	-0.12	-0.22
	—Et	-0.14	-0.06	-0.17
	—Pr <sup>i</sup>	-0.13	-0.08	-0.18
	—Bu <sup>t</sup>	0.02	-0.08	-0.21
	—CH <sub>2</sub> NH <sub>2</sub> or —CH <sub>2</sub> OH	-0.07	-0.07	-0.07
	—CH <sub>2</sub> Cl	0.00	0.00	0.00
	—CF <sub>3</sub>	0.32	0.14	0.20
	—CCl <sub>3</sub>	0.64	0.13	0.10
	—CH=CH <sub>2</sub>	0.06	-0.03	-0.10
	—Ph	0.37	0.20	0.10
	—CHO	0.56	0.22	0.29
	—COMe	0.62	0.14	0.21
	—CONH <sub>2</sub>	0.61	0.10	0.17
	—CO <sub>2</sub> H	0.85	0.18	0.27
	—CO <sub>2</sub> Me	0.71	0.10	0.21
	—COCl	0.84	0.22	0.36
	—CC	0.15	-0.02	-0.01
	—CN	0.36	0.18	0.28
N	—NH <sub>2</sub>	-0.75	-0.25	-0.65
	—NMe <sub>2</sub>	-0.66	-0.18	-0.67
	—NHAc	0.12	-0.07	-0.28
	—NO <sub>2</sub>	0.95	0.26	0.38

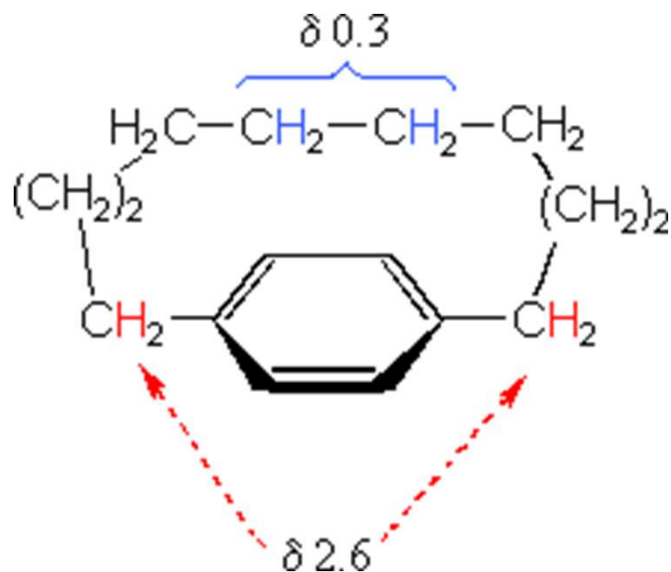
## Compelling evidence of ring currents



### [18]Annulene



6H -1.9  $\delta$  Highly Shielded  
 12H 8.2  $\delta$  Highly Deshielded

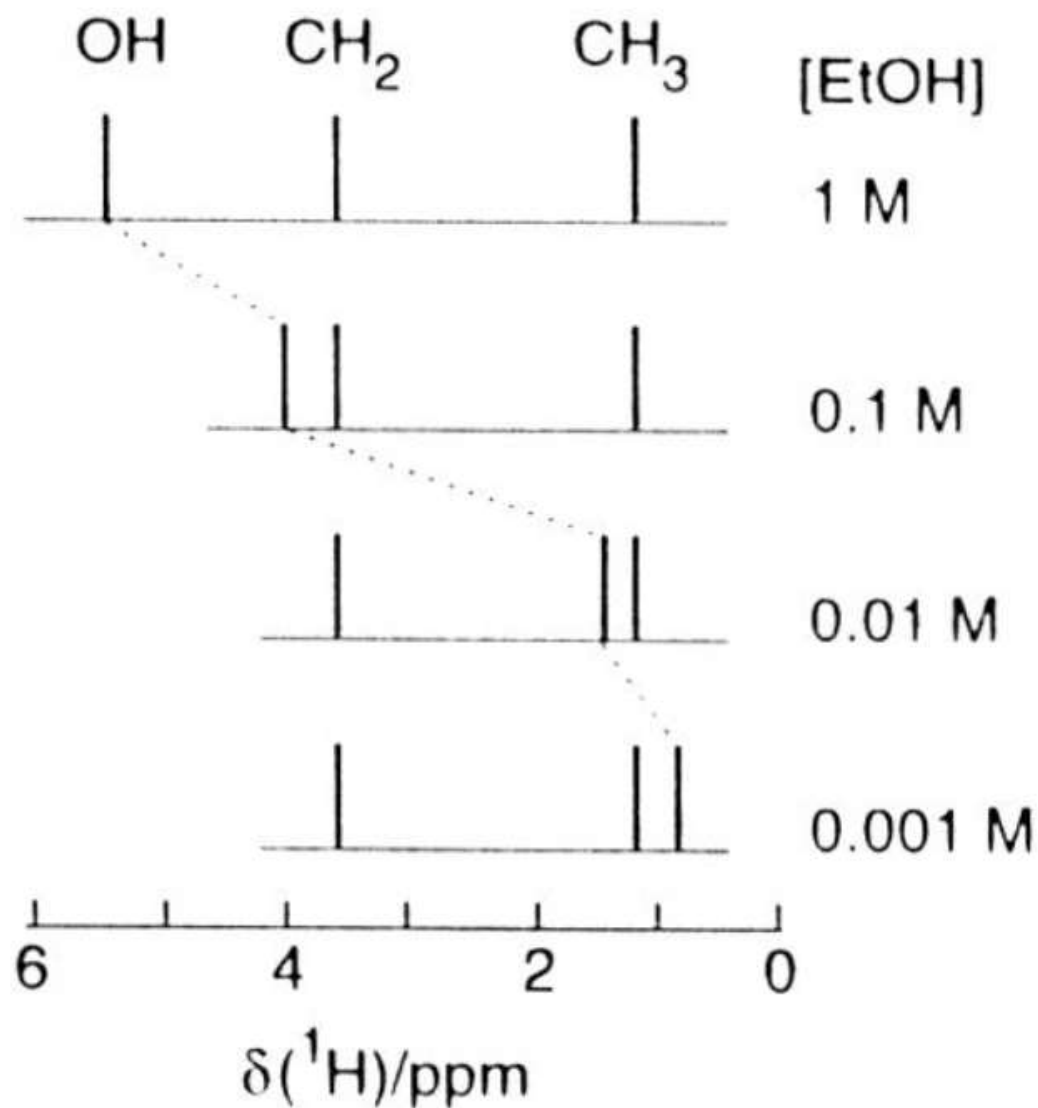


## H-bonding (D-H---A)

- H-bonds, usually involve OH, NH or SH groups have an electron withdrawing effect on the proton involved and may move such protons to higher frequencies (ie deshielding influence)
- H-bonding may be inter- or intra-molecular
- intermolecular H-bonding which is generally weaker than intra-molecular
- intermolecular H-bonding is concentration dependent. Hence, chemical shift can be, and vary between samples
- the origin of the deshielding is unclear. Probably the acceptor (A) draws the hydrogen away from the electron density of the D-H bond, so reducing the immediate electron density around it.

# Concentration effects

H-bonding shifts in ethanol



# Hydrogen bond donors needs acceptors

<sup>1</sup>H Chemical Shifts of Methanol in Selected Solvents

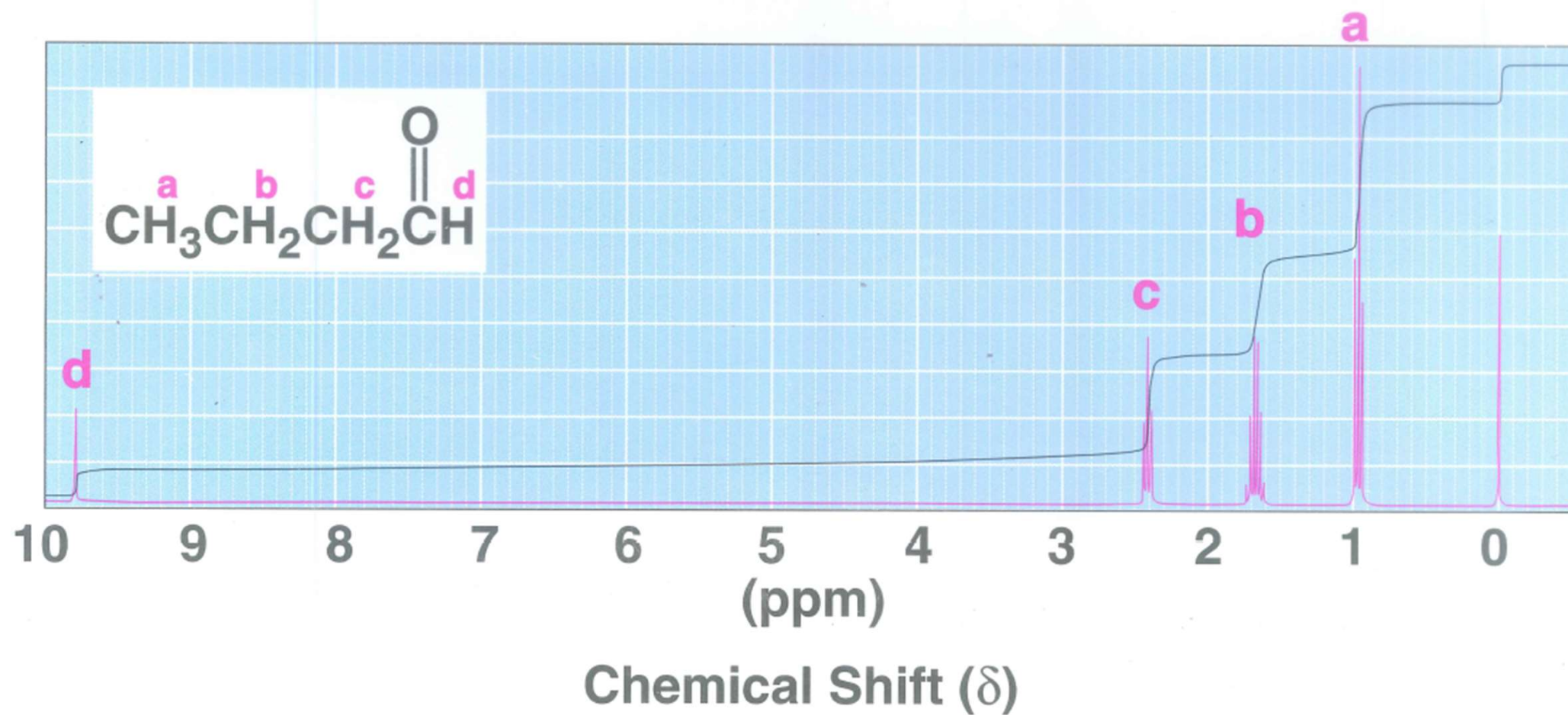
Solvent	CDCl <sub>3</sub>	CD <sub>3</sub> CO CD <sub>3</sub>	CD <sub>3</sub> SO CD <sub>3</sub>	CD <sub>3</sub> C≡ N
CH <sub>3</sub> -O-H CH <sub>3</sub> O-H	3.40 1.10	3.31 3.12	3.16 4.01	3.28 2.16

What can you say about the relative hydrogen bond acceptor ability of chloroform, acetone, and acetonitrile?

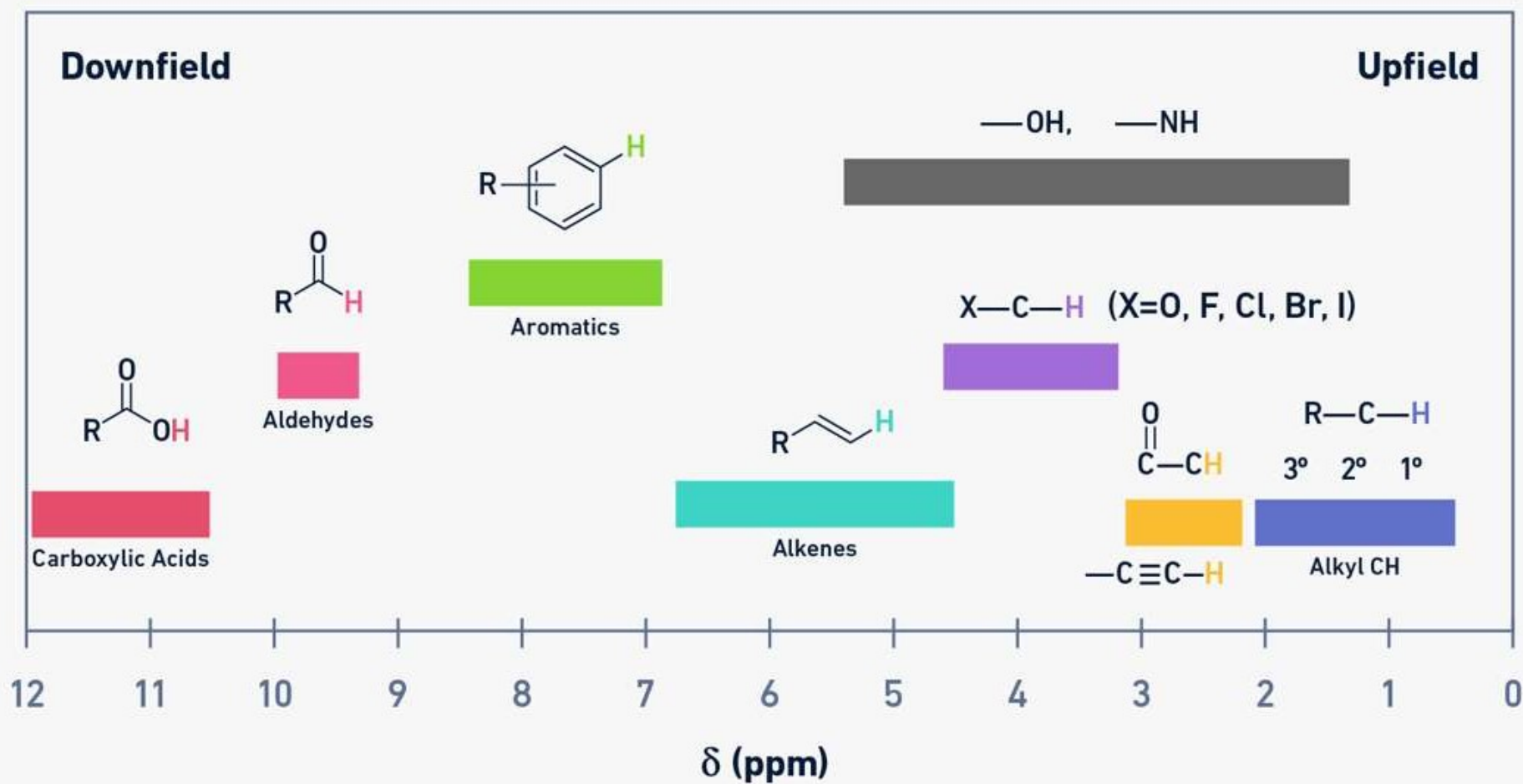
Bottom line: hydrogen bonded protons are fickle and variable to analyse by NMR, this variation can be useful and diagnostic, or confusing.



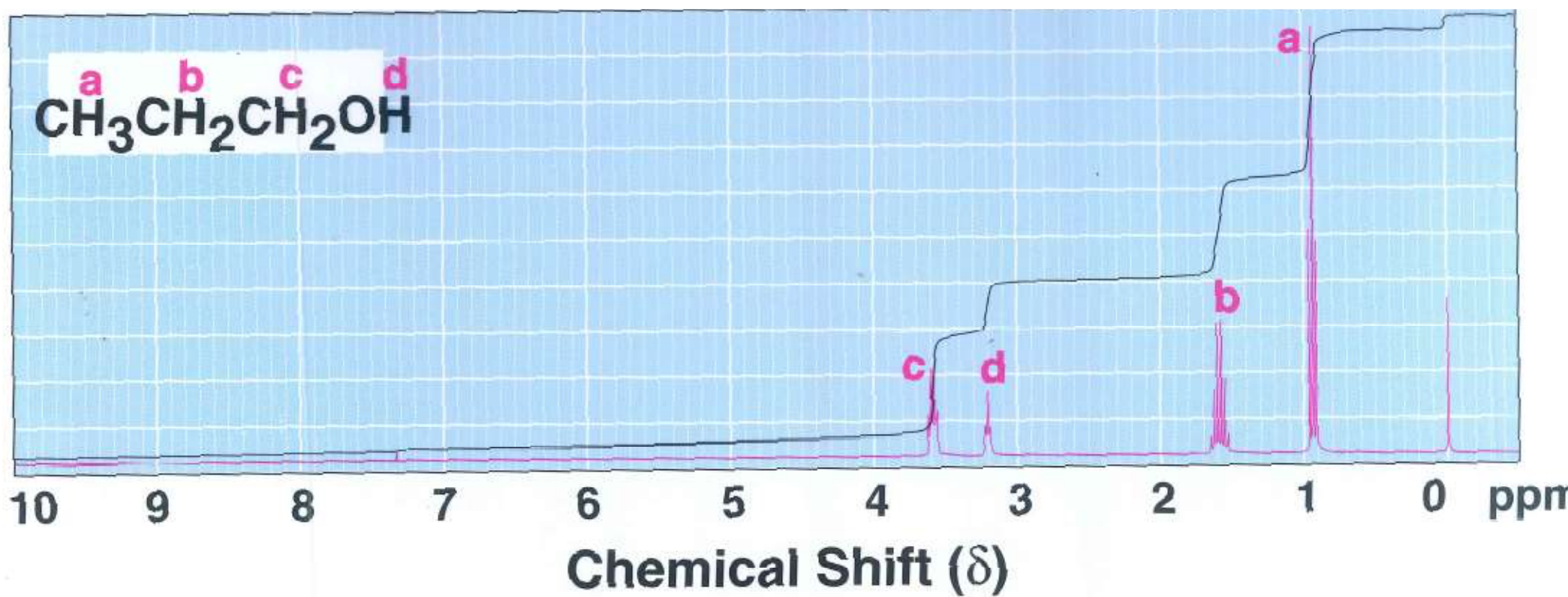
# $^1\text{H}$ NMR of butanal

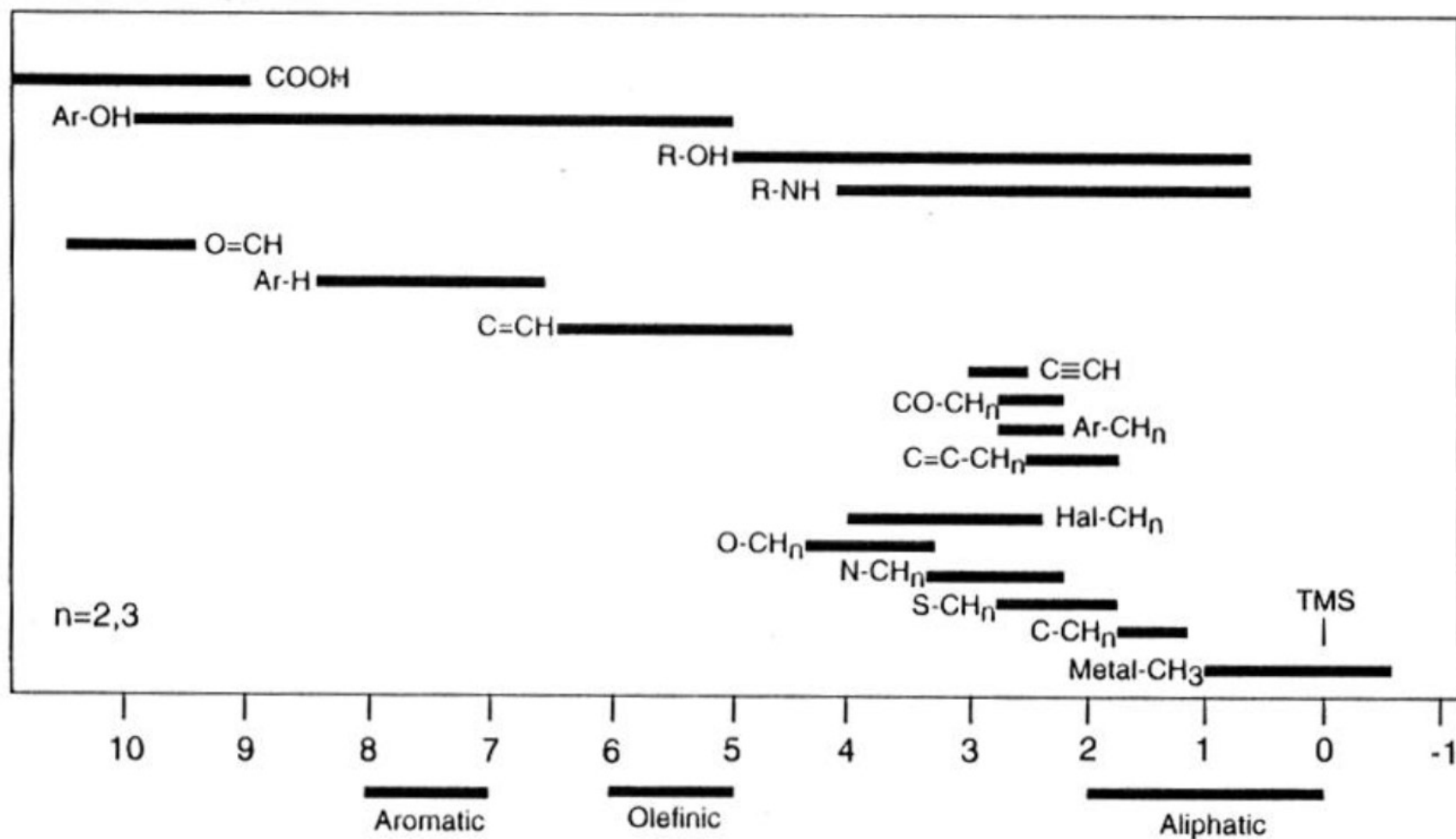


# Chemical shift is characteristic of structure



# $^1\text{H}$ NMR of propanol





Typical proton chemical shift ranges for various chemical environments.

Refer to Lab Manual, Appendix 12 (p82) for detailed chemical shift data

