B.Sc. Semester-VI
Paper CC-XIV
Organic Chemistry-V

III. Nuclear Magnetic Resonance Spectroscopy

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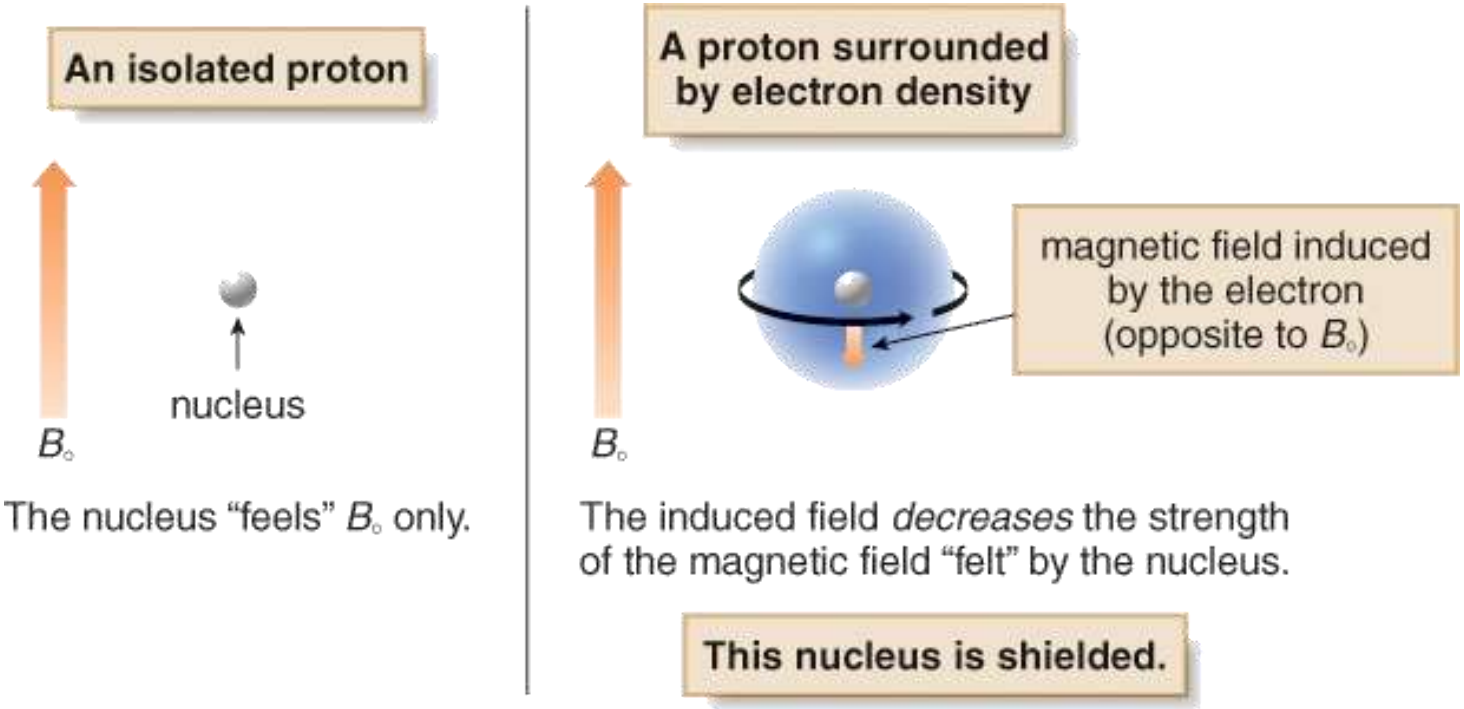
Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Position of Signals

- In the vicinity of the nucleus, the magnetic field generated by the circulating electron decreases the external magnetic field that the proton "feels".
- Since the electron experiences a lower magnetic field strength, it needs a lower frequency to achieve resonance. Lower frequency is to the right in an NMR spectrum, toward a lower chemical shift, so shielding shifts the absorption upfield.



Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Position of Signals

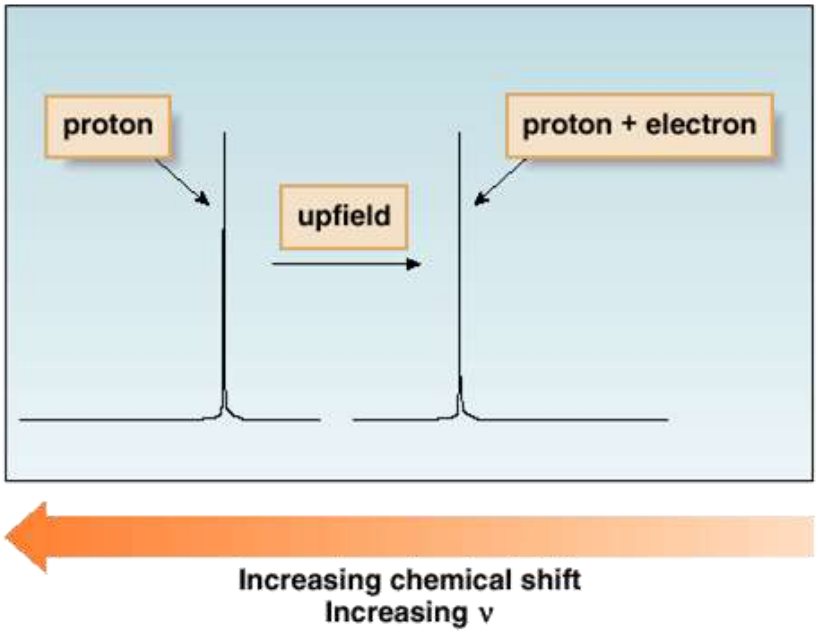
- The less shielded the nucleus becomes, the more of the applied magnetic field (B_0) it feels.
- This deshielded nucleus experiences a higher magnetic field strength, to it needs a higher frequency to achieve resonance.
- Higher frequency is to the left in an NMR spectrum, toward higher chemical shift—so deshielding shifts an absorption downfield.
- Protons near electronegative atoms are deshielded, so they absorb downfield.

Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Position of Signals

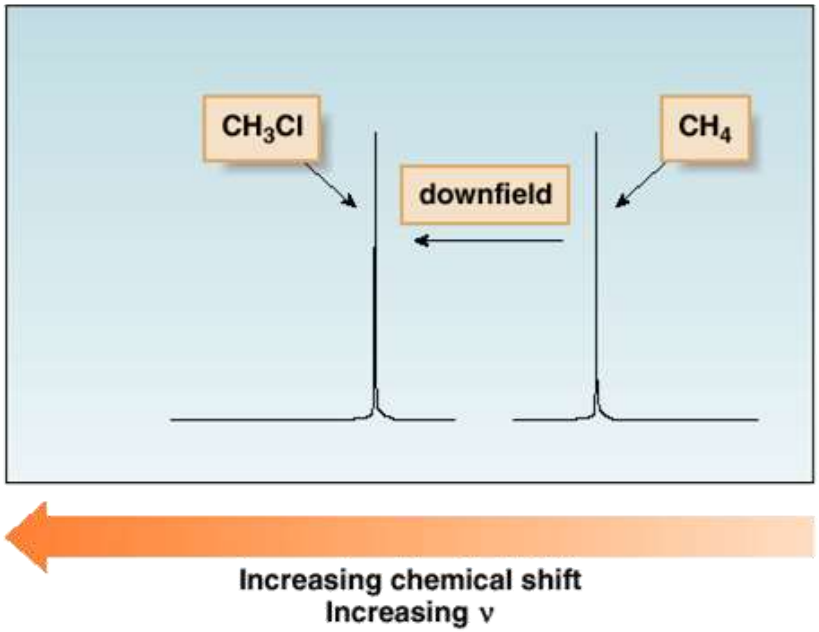
a. Shielding effects

- An electron shields the nucleus.
- The absorption shifts *upfield*.



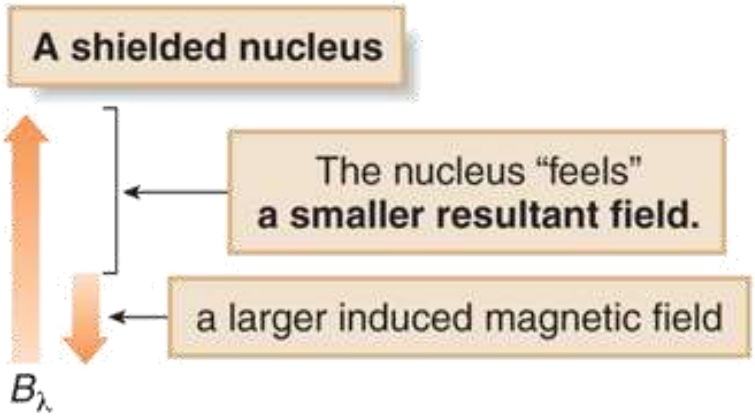
b. Deshielding effects

- Decreased electron density deshields a nucleus.
- The absorption shifts *downfield*.

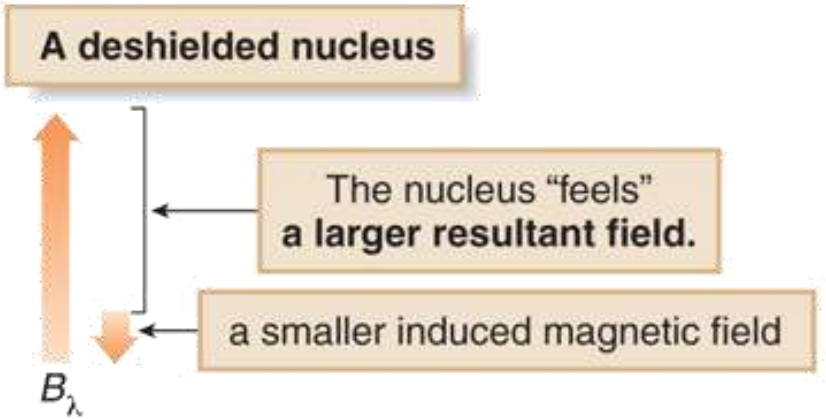


Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR–Position of Signals

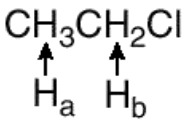


- As the electron density around the nucleus increases, the nucleus feels a smaller resultant magnetic field, so a lower frequency is needed to achieve resonance.
- **The absorption shifts upfield.**

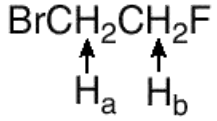


- As the electron density around the nucleus decreases, the nucleus feels a larger resultant magnetic field, so a higher frequency is needed to achieve resonance.
- **The absorption shifts downfield.**

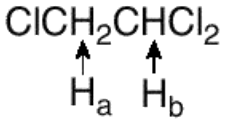
^{1}H NMR—Position of Signals



- The H_b protons are **deshielded** because they are closer to the electronegative Cl atom, so they absorb **downfield** from H_a.



- Because F is more electronegative than Br, the H_b protons are more **deshielded** than the H_a protons and absorb farther **downfield.**

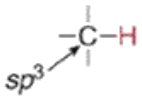
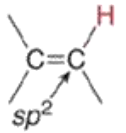
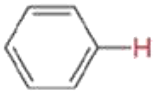
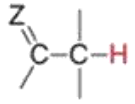
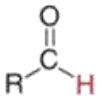
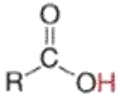
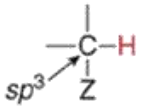
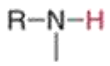


- The larger number of electronegative Cl atoms (two versus one) **deshields** H_b more than H_a, so it absorbs **downfield** from H_a.

Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Chemical Shift Values

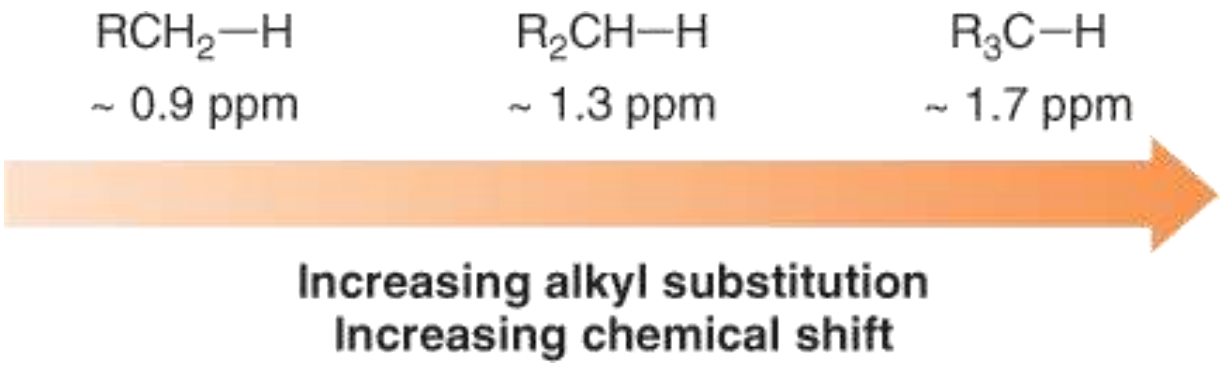
- Protons in a given environment absorb in a predictable region in an NMR spectrum.

Type of proton	Chemical shift (ppm)	Type of proton	Chemical shift (ppm)
	0.9–2		4.5–6
• RCH_3 • R_2CH_2 • R_3CH	~0.9 ~1.3 ~1.7		6.5–8
 Z = C, O, N	1.5–2.5		9–10
—C≡C–H	~2.5		10–12
 Z = N, O, X	2.5–4	RO–H or 	1–5

Nuclear Magnetic Resonance Spectroscopy

^{1}H NMR—Chemical Shift Values

- The chemical shift of a C—H bond increases with increasing alkyl substitution.



Calculating ^{1}H NMR–Chemical Shift Values

- Tchemical shift of a C–H can be calculated with a high degreeprecision he if a chemical shift additivity table is used.
- The additivity tables starts with a base chemical shift value depending on the structural type of hydrogen under consideration:

		Methylene	Methine
	CH_3-	$-C(H_2)-$	$-C(H)-$
Base Chemical Shift	0.87 ppm	1.20 ppm	1.20 ppm

Nuclear Magnetic Resonance Spectroscopy

Calculating ^{1}H NMR—Chemical Shift Values

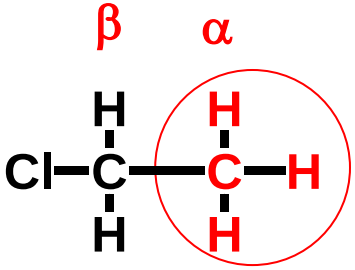
- The presence of nearby atoms or groups will effect the base chemical shift by a specific amount:
  - The carbon atom bonded to the hydrogen(s) under consideration are described as alpha (α) carbons.
  - Atoms or groups bonded to the same carbon as the hydrogen(s) under consideration are described as alpha (α) substituents.
  - Atoms or groups on carbons one bond removed from the a carbon are called beta (β) carbons.
  - Atoms or groups bonded to the β carbon are described as alpha (α) substituents.

Nuclear Magnetic Resonance Spectroscopy

Calculating ^{1}H NMR–Chemical Shift Values

Additional Chemical Shifts

Substituent	Type of Hydrogen	α-Shift	β-Shift
C=C–	CH_3	0.78	—
	CH_2	0.75	-0.10
	CH	—	—
Y RC–C=C– [Y = C or O]	CH_3	1.08	—
Aryl-	CH_3	1.40	0.95
	CH_2	1.45	0.59
	CH	1.98	—
Cl-	CH_3	2.49	0.69
	CH_2	2.90	0.59
	CH	2.55	0.09
Br-	CH_3	1.80	0.89
	CH_2	2.18	0.60
	CH	2.68	0.25
I-	CH_3	1.28	1.29
	CH_2	1.95	0.58
	CH	2.75	0.00
OH-	CH_3	2.50	0.99
	CH_2	2.90	0.19
	CH	2.20	—
RO- (R is saturated)	CH_3	2.49	0.99
	CH_2	2.95	0.15
	CH	2.00	—
O R-CO– or ArO–	CH_3	2.88	0.98
	CH_2	2.98	0.49
	CH	9.49 (ester only)	—
O R-C–	CH_3	1.28	0.18
where R is alkyl, aryl, OH, OR', H, CO, or N	CH_2	1.05	0.91
	CH	1.05	—



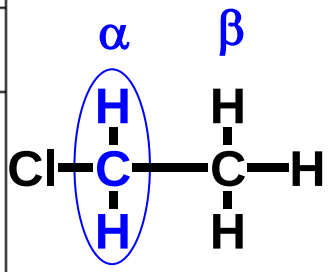
(Hydrogen under consideration)

Base Chemical Shift = 0.87 ppm

no α substituents = 0.00

one β -Cl (CH_3) = 0.63

TOTAL = 1.50 ppm



(Hydrogen under consideration)

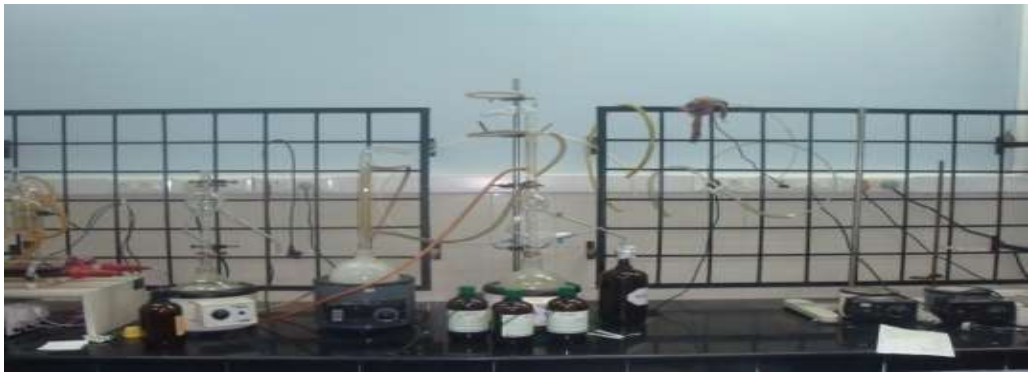
Base Chemical Shift = 1.20 ppm

one α -Cl (CH_2) = 2.30

no β substituents = 0.00

TOTAL = 3.50 ppm

Thank You



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