NMR II

Chemical Shift

Ref 9 : 5, 6; 8th ed.
9 : 6, 7; 9th ed.

Prob HMWK #2

Adv Rdg 9: 7 (8th) / 9: 8 (9th)

Local Magnetic Field, B_{local}

External Field B_0

- interacts with e^-'s of molecule, incl. valence e^- s
- induces **opposing** small local magnetic field, B_{local} (making B_{eff} smaller)

$$B_{local} = \sigma \ B_0$$

where σ is "shielding const."

high e^- density causes:

- large σ
- shielded nucleus
- lge B_{local}
- B_{eff} "greatly" reduced

∴ "high e^- density" = "reduced mag. field"

Shielding Constant, σ

- depends principally on local e^- density (+ other factors)
- if neighboring atoms are e/n
  then, e^- density at H is low,
  = "deshielded"
  = σ, small
- and v.v
  if neighboring atoms are **not** e/n
  then, e^- density at H is high,
  = "shielded"
  = σ, large

Effective Mag. Field Strength, B_{eff}

B_{eff} = "B, actually felt by nucleus"

$$= B_0 - B_{local}$$

$$= B_0 - \sigma \ B_0$$

$$= B_0 \ (\ 1 - \sigma \ )$$

Effect on Resonance Frequency, ν_{res}

must use B_{eff} (*not B_0*)

$$\nu_{res} = \gamma \frac{1}{2\pi} B_{eff}$$

$$= \gamma \frac{1}{2\pi} B_0 (1 - \sigma)$$

$\therefore$ σ, large ⟶ ν_{res}, low

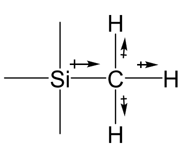
shielding
high e^- density } ⟶ low ν_{res}

Practice

neighbor atoms	are e/n (e.g., Cl)	are less e/n (e.g., Si)
e^- density at H atom	low	high
shielding, σ	low, "deshielded"	high, "shielded"
B_{local}	low ↓	high ↑
B_{eff}	high ↑	low ↓
ν_{res}	high ↑	low ↓

Example

1.) TMS, tetramethylsilane, $Si(CH_3)_4$

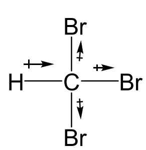


• Si is "electropositive",

• increases e^- density at H,

• H becomes "e^- rich" = "shielded"

2.) bromoform, $CHBr_3$



• Br is "electronegative",

• decreases e^- density at H,

• H becomes "e^- poor" = "deshielded"

shielding effects ...

variable	TMS	$CHBr_3$
e^- density	high	small
nucleus	shielded	deshielded
σ (shielding const)	lge	small
B_{local}	lge	small
B_{eff}	small (reduced)	large (increased)
ΔE	small	lge
ν_{res}	small	lge
resonance occurs	"downfrequency"	"upfrequency"
traditional term	"upfield"	"downfield"
peak occurs on	right side	left side

Quantitative Example

B_0	2.35 T		7.05 T		11.75 T	
ν	100 MHz		300 MHz		500 MHz	
cmpd	TMS	$CHBr_3$	TMS	$CHBr_3$	TMS	$CHBr_3$
B_{eff} (T)	2.350 000 00	2.350 015 84	7.050 0000 00	7.050 047 52	11.750 000 00	11.750 079 20
ν_{res} (Hz)	100 000 000	100 000 674	300 000 000	300 002 022	500 000 000	500 003 370
Δν (Hz)		674		2 022		3 370
δ (ppm)		6.74		6.74		6.74

Δν, absolute shift; δ, relative ("chemical") shift

Explanatory Notes

A.) at 100 MHz

1.) "ν", nominal operating frequency,

as required for PMR

2.) B_0, associated mag. field strength, from

$$\nu = \gamma \frac{B_0}{2\pi} \text{ (use } \gamma \text{ for } {}^1\text{H)}$$

3.) TMS used for calibration,

ν_{res} set at 100 000 000 Hz (= ν_{ref})

($\therefore$ B_{eff} = 2.350 000 00 T)

4.) ν_{res} for $CHBr_3$, (X), experimentally observed

5.) $\Delta\nu = \nu_X - \nu_{ref} = 674$ Hz

6.) $\delta = \frac{\Delta\nu}{\nu_{ref}} \times 10^6 = 6.74$ ppm

Explanatory Notes ...

B.) at 300 MHz

1.) $B_o \propto \nu$

2.) $B_{eff} = B_o(1 - \sigma)$

$\propto B_o$

$\therefore B_o$ triples $\rightarrow B_{eff}$ triples

3.) similarly, $\nu_{res} \propto B_o$, $\Delta\nu_o \propto B_o$ } also triple; convince yourself

4.) at 100 MHz: $\delta = \frac{\Delta\nu}{\nu_{ref}} \times 10^6$

at 300 MHz: $\delta = \frac{3\,\Delta\nu}{3\,\nu_{ref}} \times 10^6$

$\therefore$ δ value does **not** change w/ instrument

C.) at 500 MHz ? Do as HMWK!