Introduction to $^1$H-NMR Spectroscopy Part 2

Main topics

- Spin-spin coupling, $J$ values
- Spectra of alkenes and aromatic molecules
- Putting it all together
From Part I

300 MHz $^1$H NMR
In CDCl$_3$

4-isopropylaniline

$H_d + H_e$
7.02 6.63

$H_c$
3.51

$H_b$
2.79

$H_a$
1.18
Coupling constant $J$ (Hz) – indicates strength of coupling

$J \sim 7$ Hz for alkyl (sp$^3$) systems
Coupling constants in aromatic systems
Why is H_d more shielded than H_e?

Consider the ring substituents and resonance structures (when applicable)

H_d is coupled to H_e, H_d', and H_e'.

300 MHz 'H NMR
In CDC13
NH$_2$ is an electron-donating group through the $\pi$-system.

H$_d$ shielded relative to H$_e$ can be rationalized by resonance effects.

-NH$_2$, -NR$_2$, -OMe, -OH, etc. are electron-donating groups via the $\pi$-system.

Electron-donating groups increase e$^-$ density at the ortho and para C-atoms.

H-atoms at ortho and para positions are shielded relative to benzene H-atoms.
300 MHz $^1$H NMR
In CDCl$_3$

4-Nitroanisole

$\text{H}_b + \text{H}_c$

8.18  6.95

2     2

8  7  6  5  4  3  2  1  0
Why is $H_b$ more shielded than $H_c$?

Why is $H_c$ so deshielded?

Consider the ring substituents and resonance structures.
Resonance structures of the nitro group

NBO charges
B3LYP/6-31G(d)
NO₂ is an electron-withdrawing group through the π-system. H_c deshielded relative to H_b can be rationalized by resonance effects.

-NO₂, -CO₂R groups are electron-withdrawing groups via the π-system.

Electron-withdrawing groups reduce e⁻ density at the ortho and para C-atoms. H-atoms at ortho and para positions are deshielded relative to benzene H-atoms.
300 MHz $^1$H NMR
In CDCl$_3$

4-Nitroanisole

$H_c$ 8.18

$H_c$ 6.95

$H_b$ 2
Splitting patterns in alkene systems

300 MHz $^1$H NMR
In CDCl₃

4-Methylstyrene
300 MHz $^1$H NMR
In CDC$_3$
Coupling constants in alkene systems
Write down the relationships between the alkene protons

List all couplings, strongest first
Write down the relationships between the alkene protons

List all couplings, strongest first
Derivation of splitting diagrams - $H_a$

$J_{ac} = J_{trans} = 17.2$ Hz

$J_{ab} = J_{cis} = 10.5$ Hz

doublet of doublets
300 MHz $^1$H NMR
In CDC13

$H_a$, $H_b$, $H_c$

$J_{trans} > J_{cis}$

$J_{trans}$: 17.2 Hz
$J_{cis}$: 10.5 Hz

Scale now in Hz

5.70 ppm
5.17 ppm
Splitting patterns in aromatic systems

300 MHz $^1$H NMR
In CDCl$_3$

3-Nitroanisole

$H_a - H_d$

$H_b$

$H_c$

$H_d$

$H_e$

$H_e$

$H_e$

$H_e$

$OMe$

Nitroanisole
Coupling constants in aromatic systems
Write down the relationships between the protons!
List all couplings, start with the strongest coupling.
Write down the relationships between the alkene protons

List all couplings, strongest first
Derivation of splitting diagrams - $H_c$

To predict the appearance of $H_c$:
- Apply the n+1 rule to each different coupling
- Apply largest coupling first

\[ J_{cb} \approx J_{cd} = J_{ortho} \]
\[ J_{cd} < J_{cb} \]
Derivation of splitting diagrams - $H_a$

To predict the appearance of $H_a$:
- Apply the n+1 rule to each different coupling
- Apply largest coupling first

$J_{ab} = J_{ad} = J_{meta}$

$J_{ab} \approx J_{ad} = J_{meta}$
$J_{ad} < J_{ab}$
Derivation of splitting diagrams - $H_b$

To predict the appearance of $H_b$:

- Apply the $n+1$ rule to each different coupling
- Apply largest coupling first

\[ \begin{align*}
J_{bc} &= J_{\text{ortho}} \\
J_{ba} &= J_{bd} = J_{\text{meta}}
\end{align*} \]
Derivation of splitting diagrams - $H_d$

To predict the appearance of $H_d$:

- Apply the n+1 rule to each different coupling
- Apply largest coupling first

\[
J_{dc} = J_{ortho}
\]

\[
J_{da} = J_{db} = J_{meta}
\]