344 | Organic Chemistry Laboratory

Introduction to ^{1}H-NMR Spectroscopy Part 2

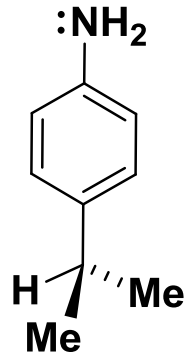
Main topics

- Spin-spin coupling, *J* values

- Spectra of alkenes and aromatic molecules

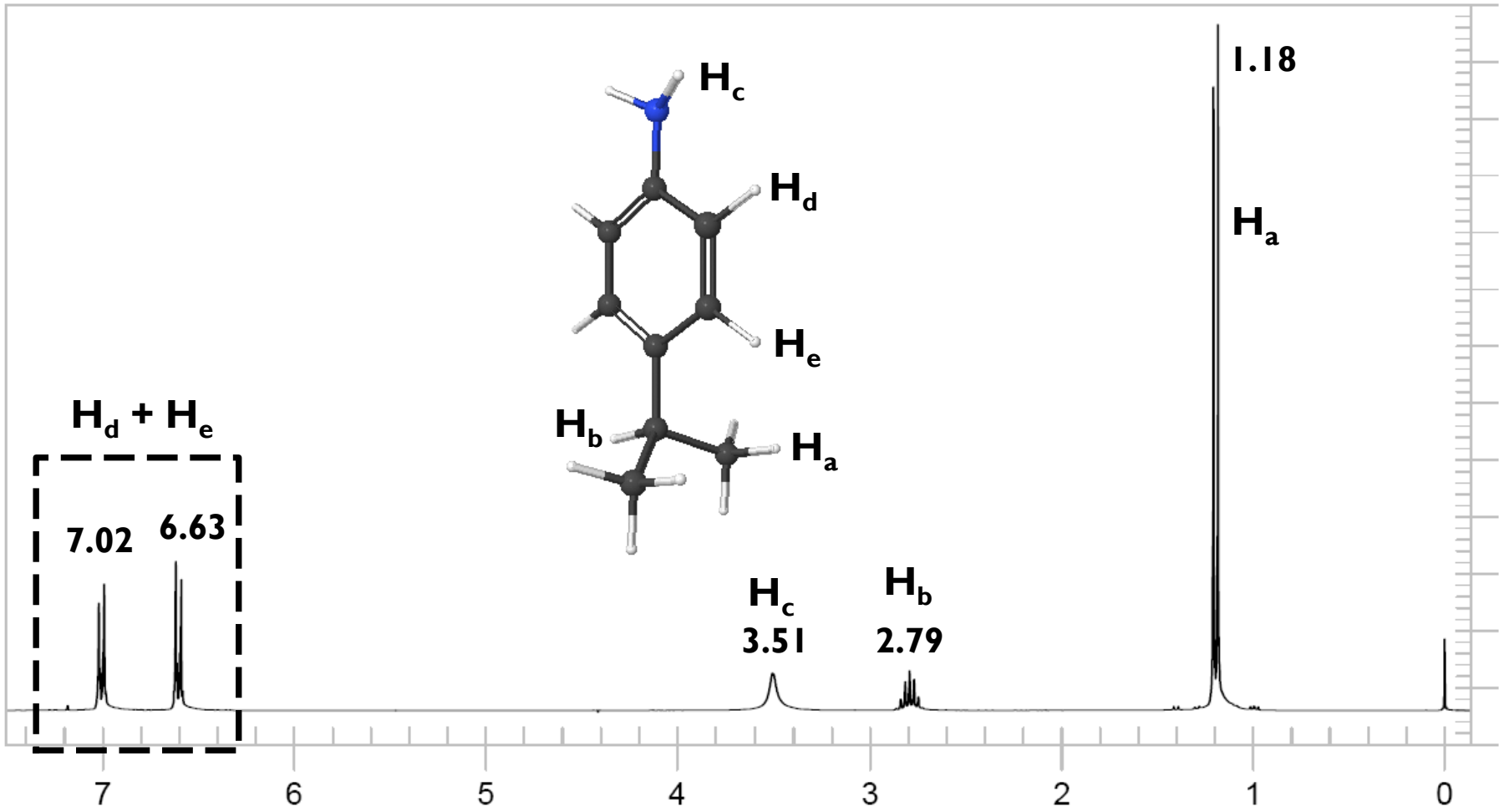
- Putting it all together

From Part I



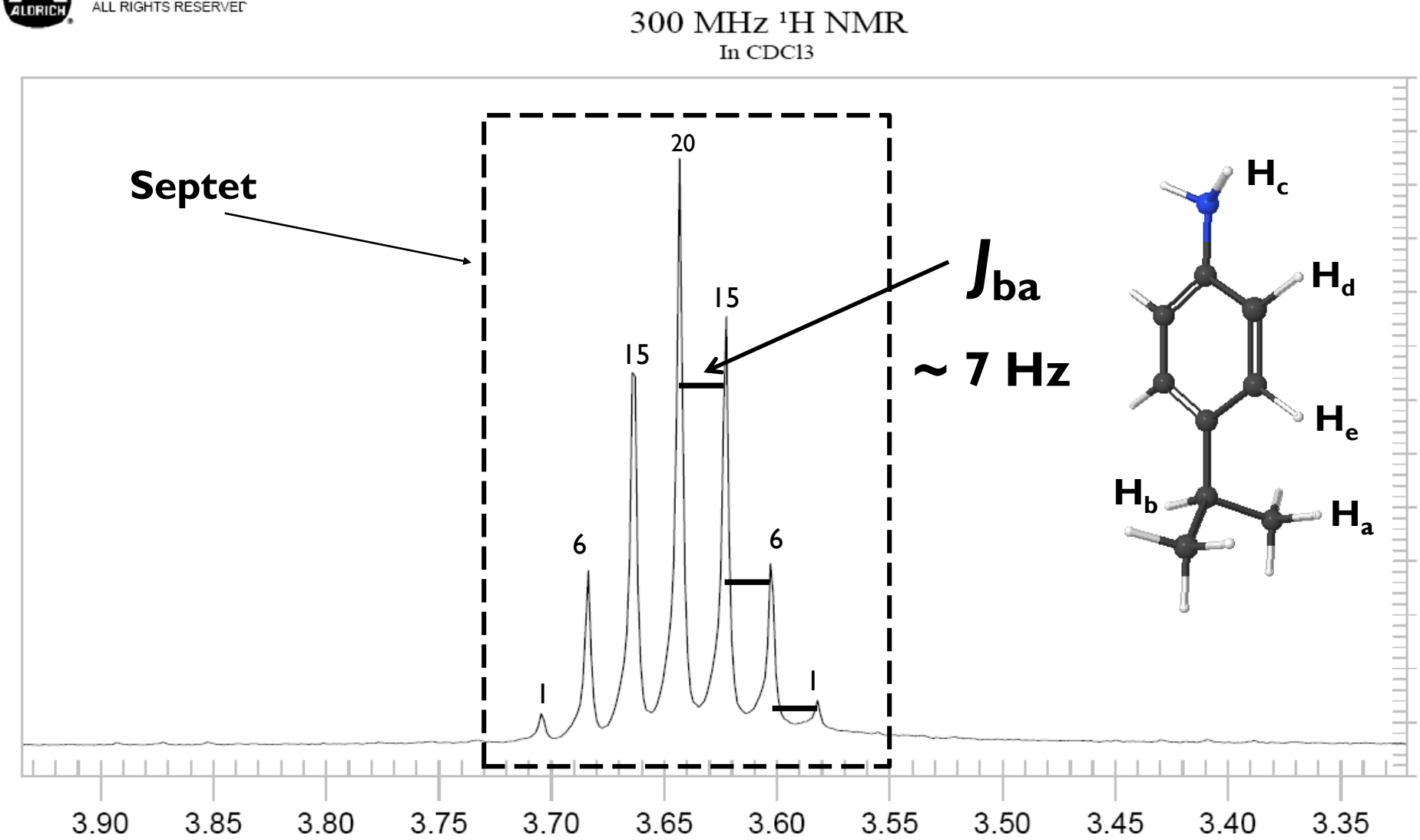
4-*iso*propylaniline

300 MHz ^{1}H NMR
In CDCl3

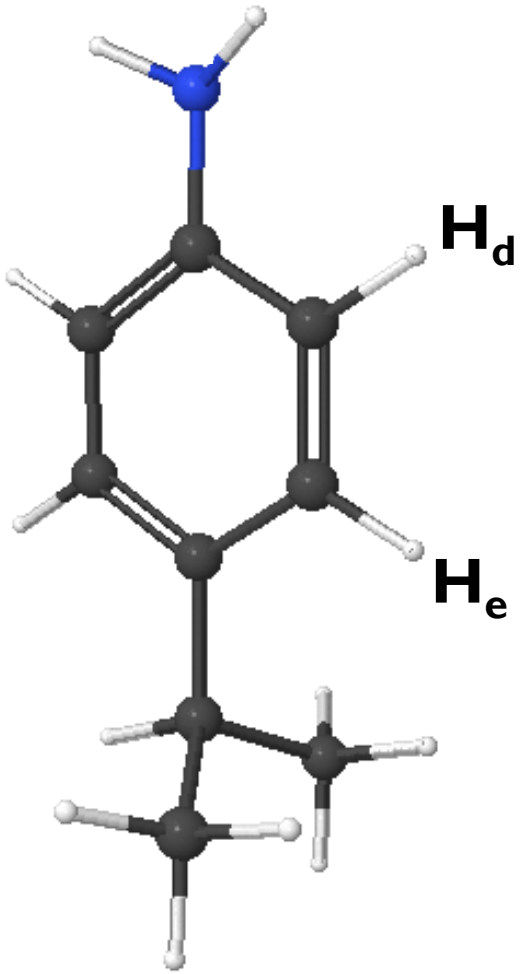


Coupling constant *J* (Hz) – indicates strength of coupling

J ~ 7 Hz for alkyl (sp^3) systems



Coupling constants in aromatic systems



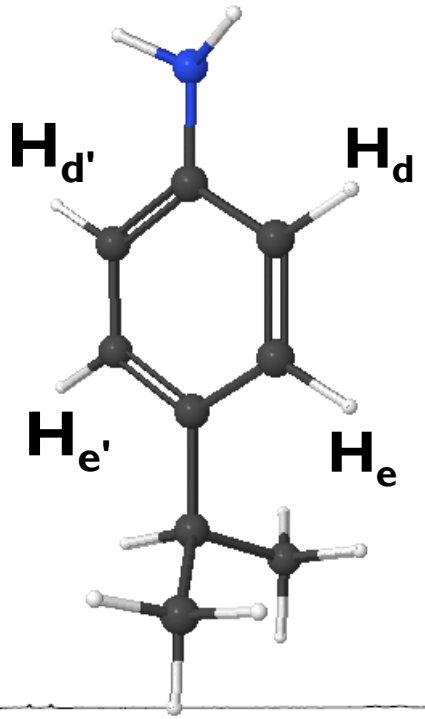
Splitting patterns in aromatic systems

Which signal is shielded more than H_e?

Consider the ring substituents and resonance structures (when applicable)

300 MHz ^{1}H NMR
In CDCl3

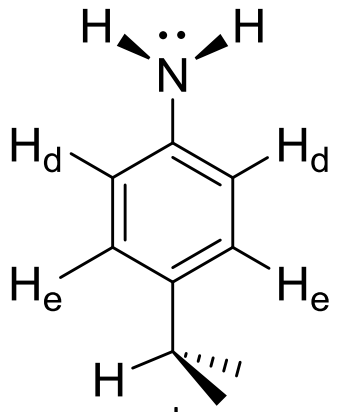
H_d is coupled to H_e, $H_{d'}$, and $H_{e'}$

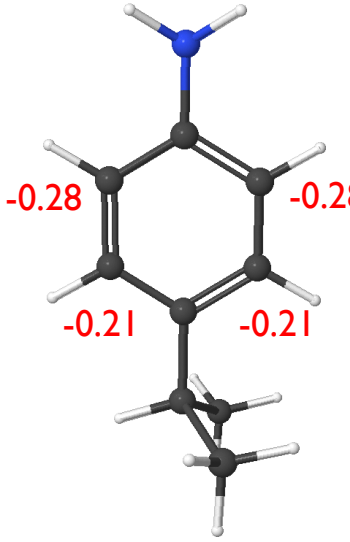


NH_2 is an electron-donating group through the π-system.

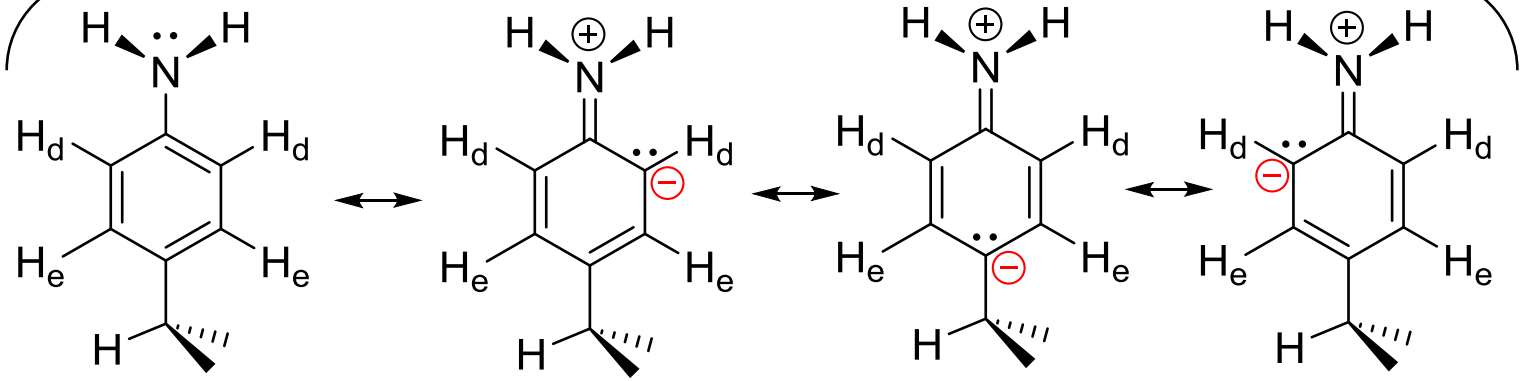
H_d shielded relative to H_e can be rationalized by resonance effects.

Benzene





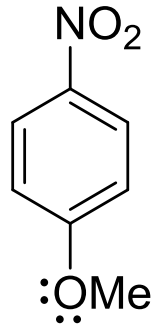
NBO charges
B3LYP/6-31G(d)



-NH_2, -NR_2, -OMe, -OH, etc. are electron-donating groups via the π-system.

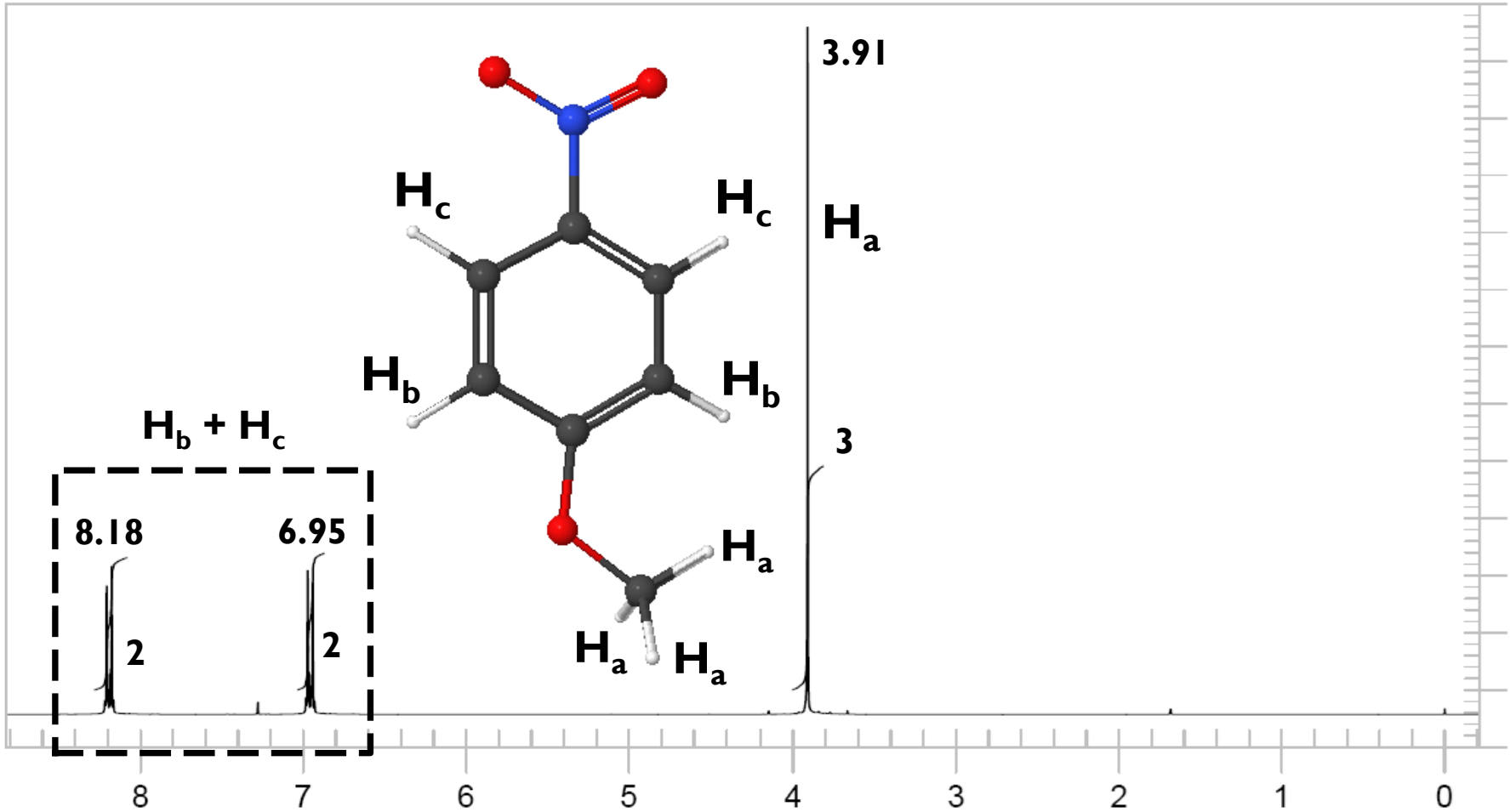
Electron-donating groups increase e^- density at the *ortho* and *para* C-atoms.

H-atoms at *ortho* and *para* positions are shielded relative to benzene H-atoms.



4-Nitroanisole

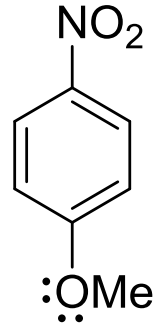
300 MHz ^{1}H NMR
In CDCl3



Why is H_b more shielded than H_c?

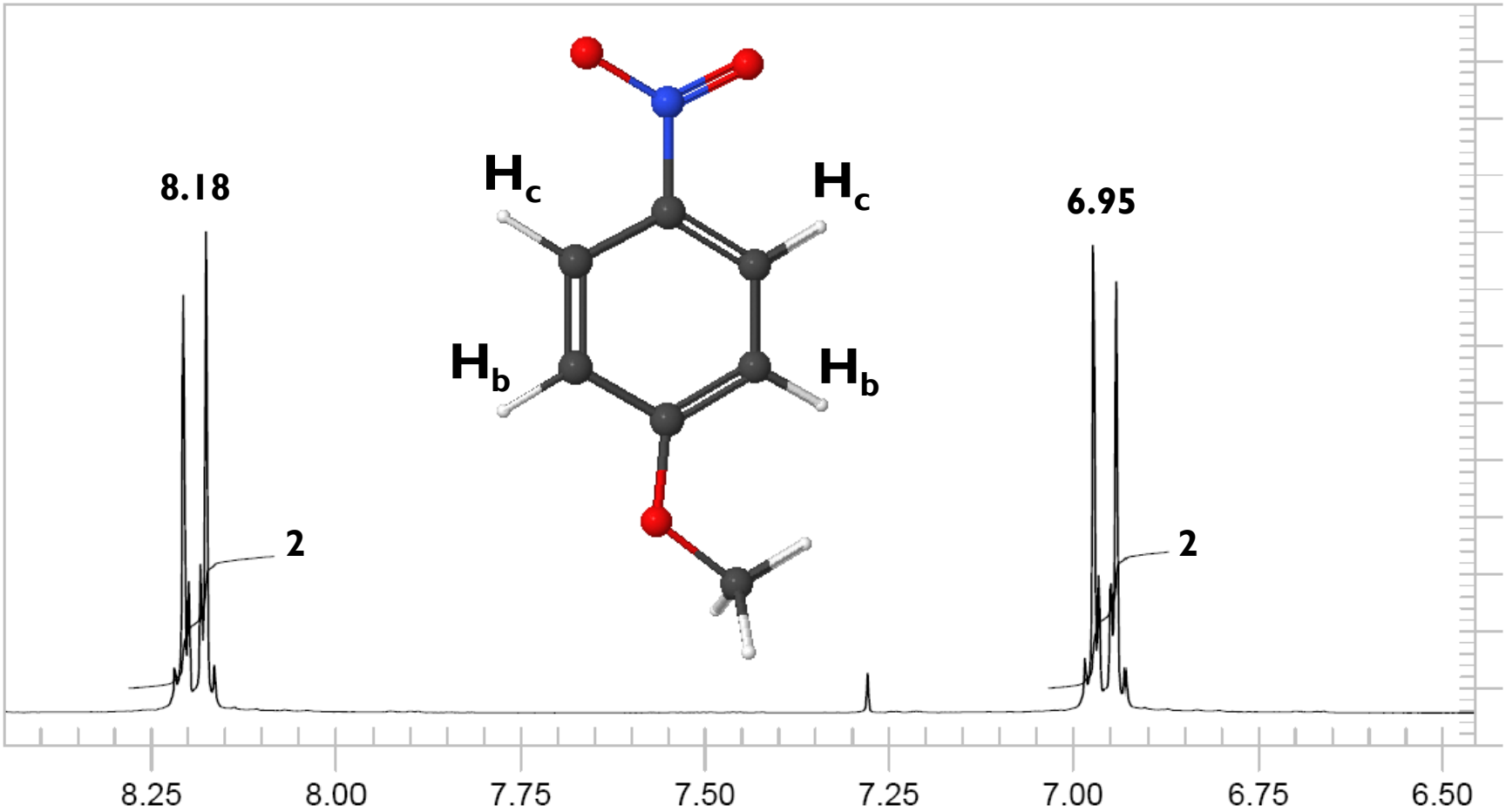
Why is H_c <u>so deshielded</u>?

Consider the ring substituents and resonance structures

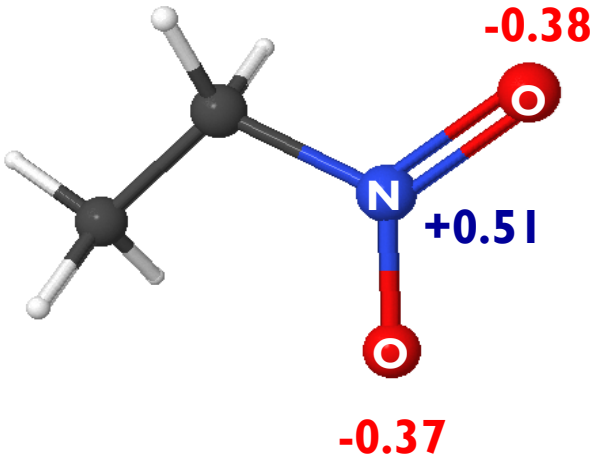


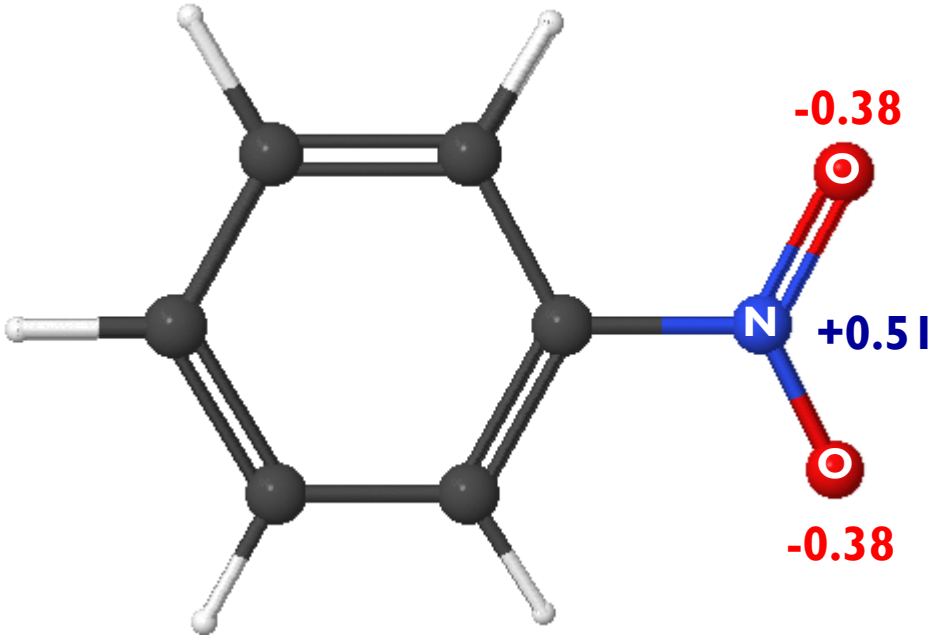
4-Nitroanisole

300 MHz ^{1}H NMR
In CDCl3



Resonance structures of the nitro group



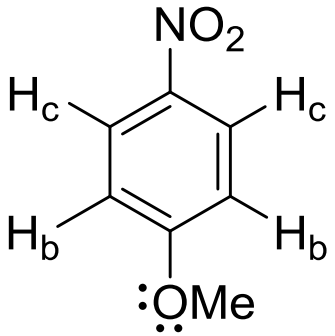


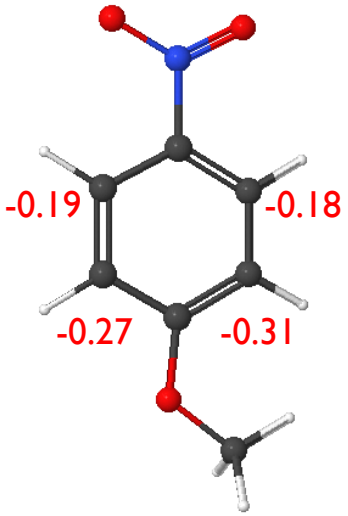
NBO charges
B3LYP/6-31G(d)

NO_2 is an electron-withdrawing group through the π-system.

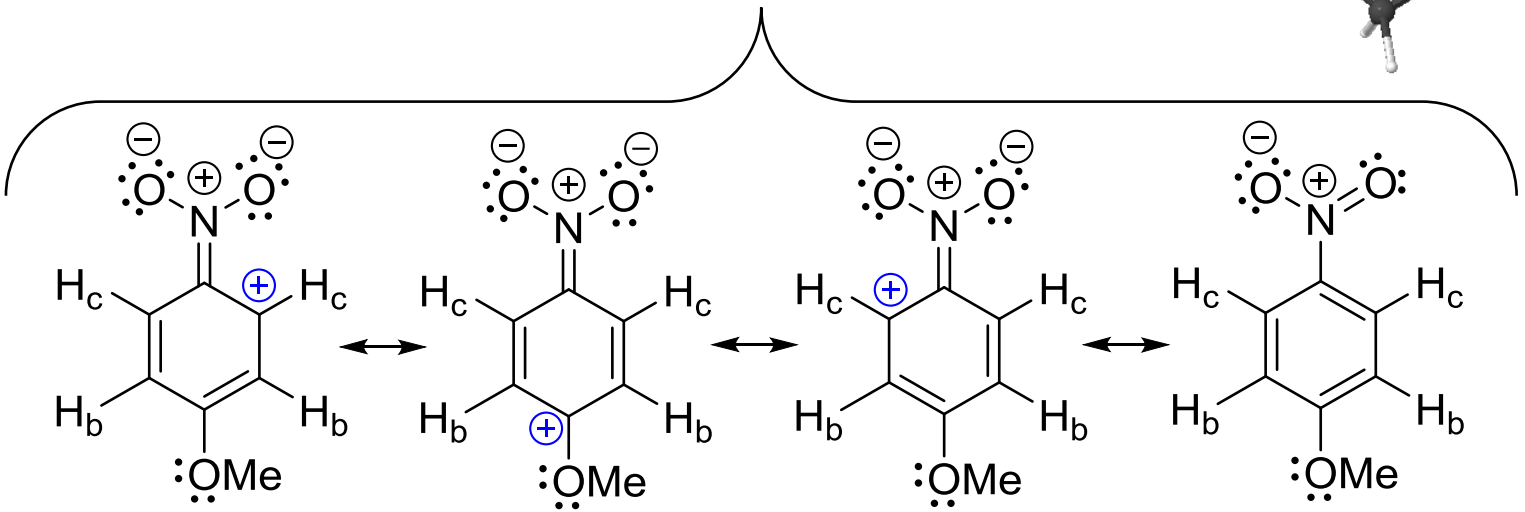
H_c deshielded relative to H_b can be rationalized by resonance effects.

Benzene





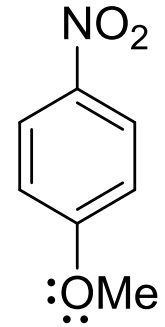
NBO charges
B3LYP/6-31G(d)



-NO_2, -CO_2R groups are electron-withdrawing groups via the π-system.

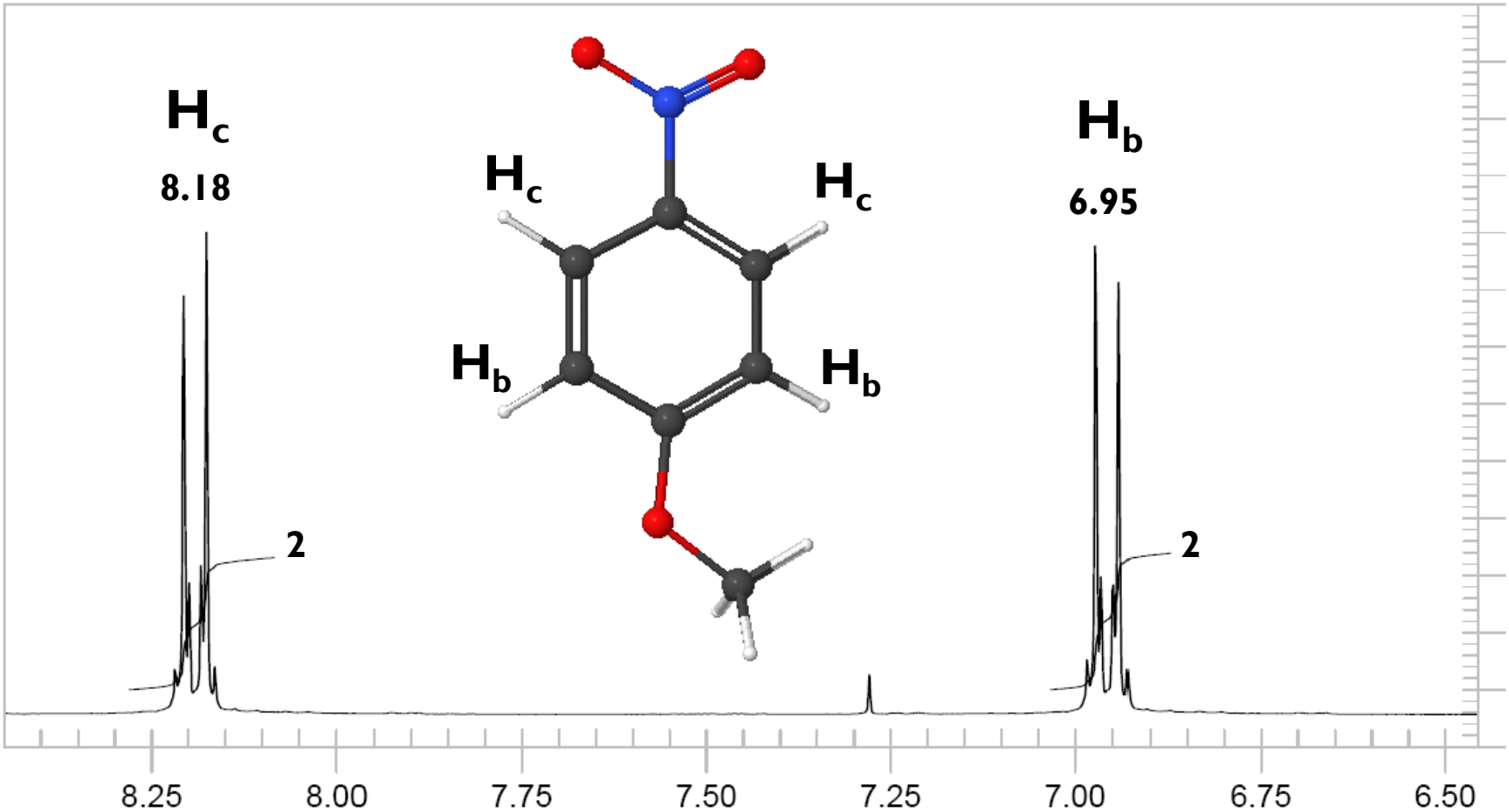
Electron-withdrawing groups reduce e^- density at the *ortho* and *para* C-atoms.

H-atoms at *ortho* and *para* positions are deshielded relative to benzene H-atoms.

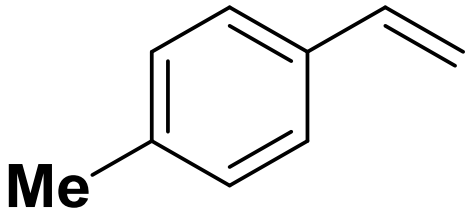


4-Nitroanisole

300 MHz ^{1}H NMR
In CDCl3

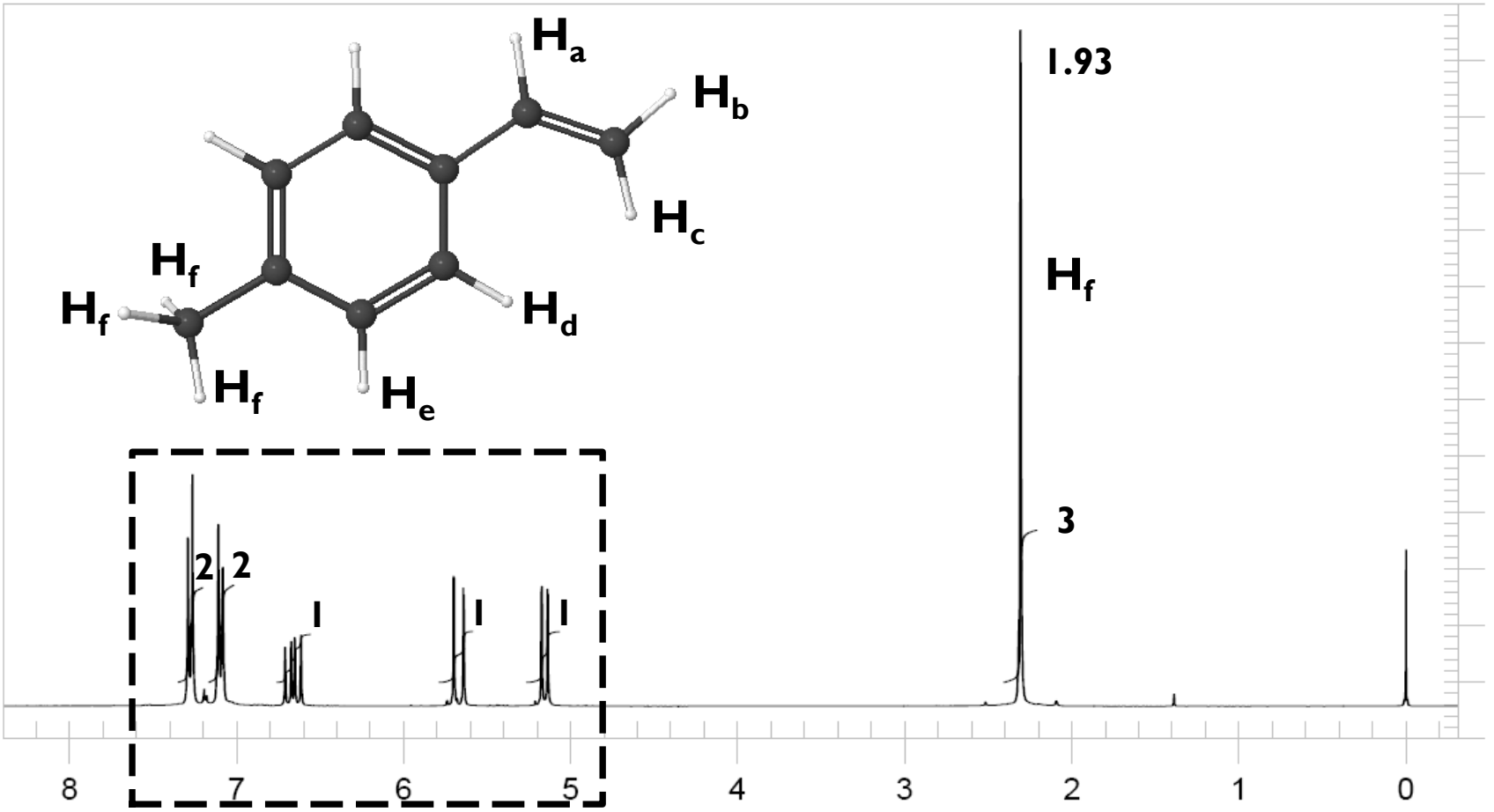


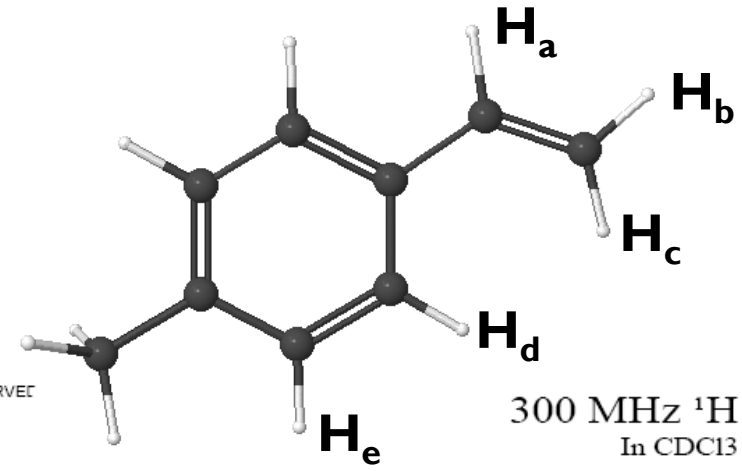
Splitting patterns in alkene systems



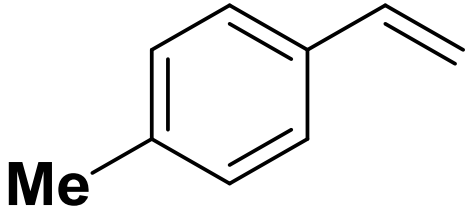
4-Methylstyrene

300 MHz ^{1}H NMR
In CDCl3

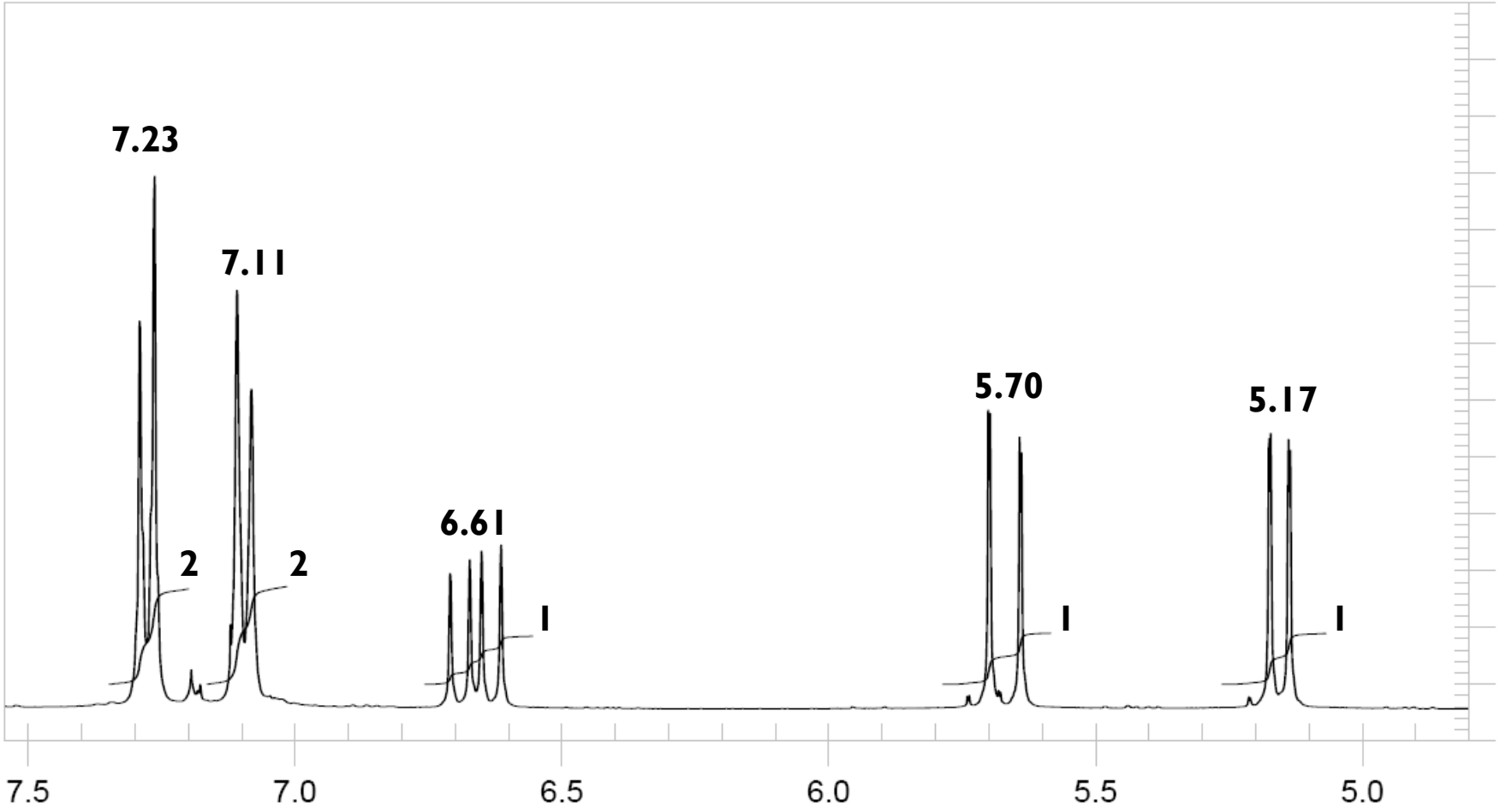




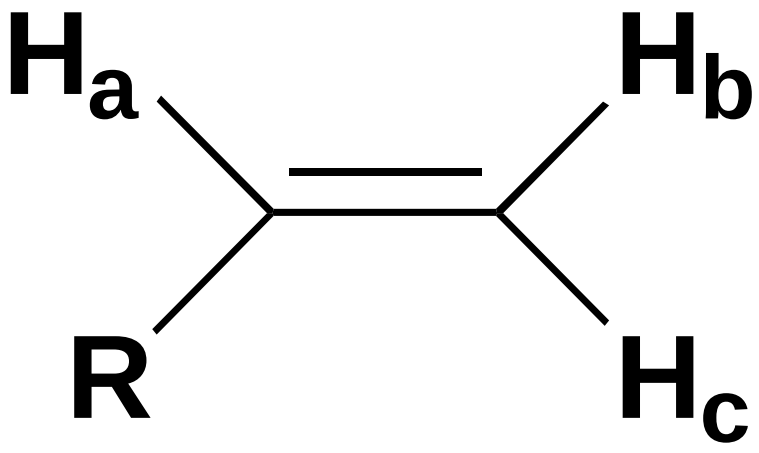
300 MHz ^{1}H NMR
In CDCl3



4-Methylstyrene

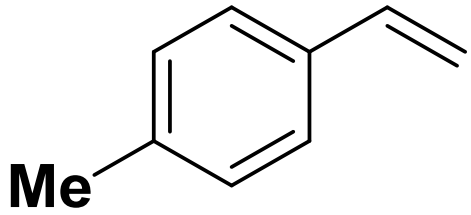


Coupling constants in alkene systems



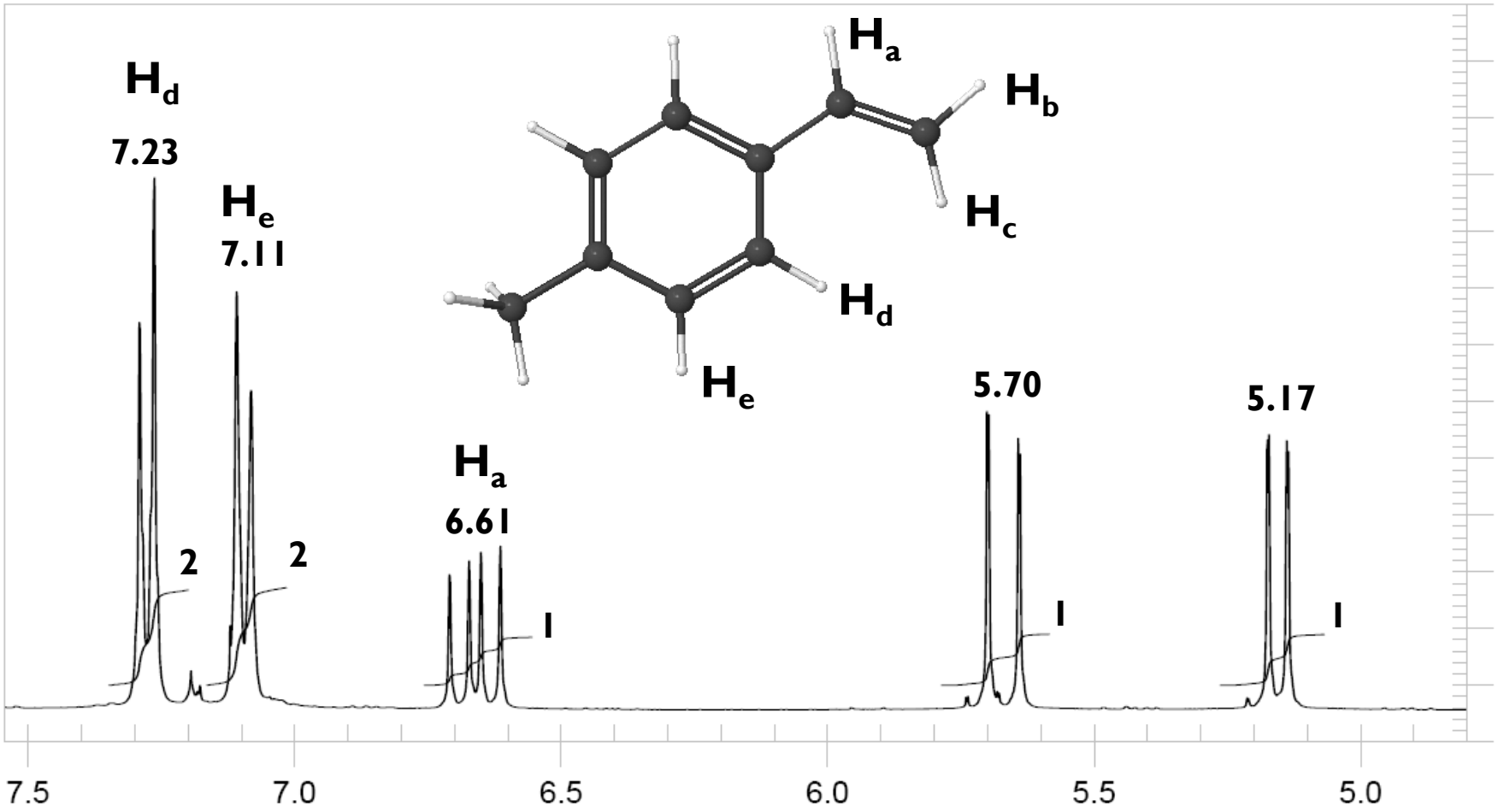
Write down the relationships between the alkene protons

List all couplings, strongest first



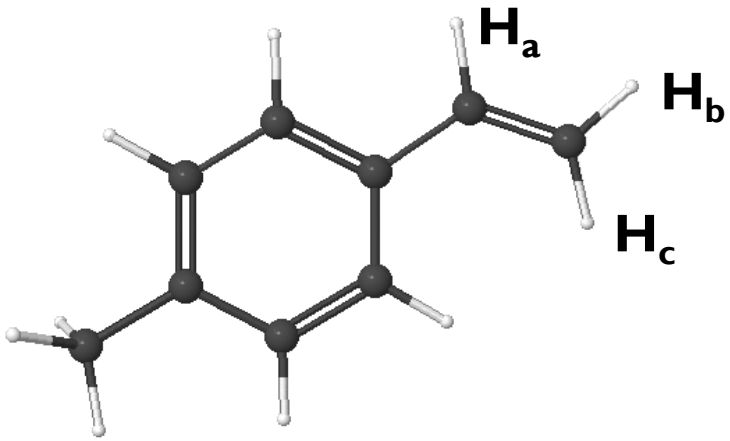
300 MHz ^{1}H NMR
In CDCl3

4-Methylstyrene

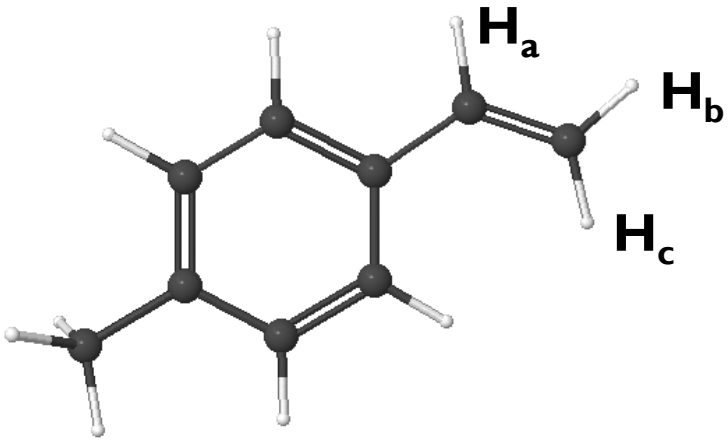


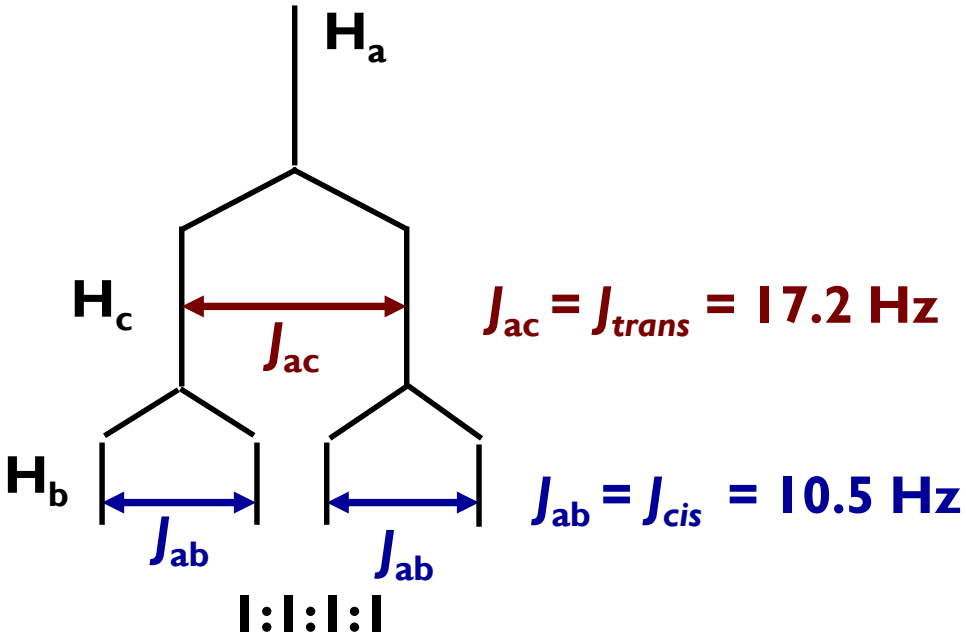
Write down the relationships between the alkene protons

List all couplings, strongest first



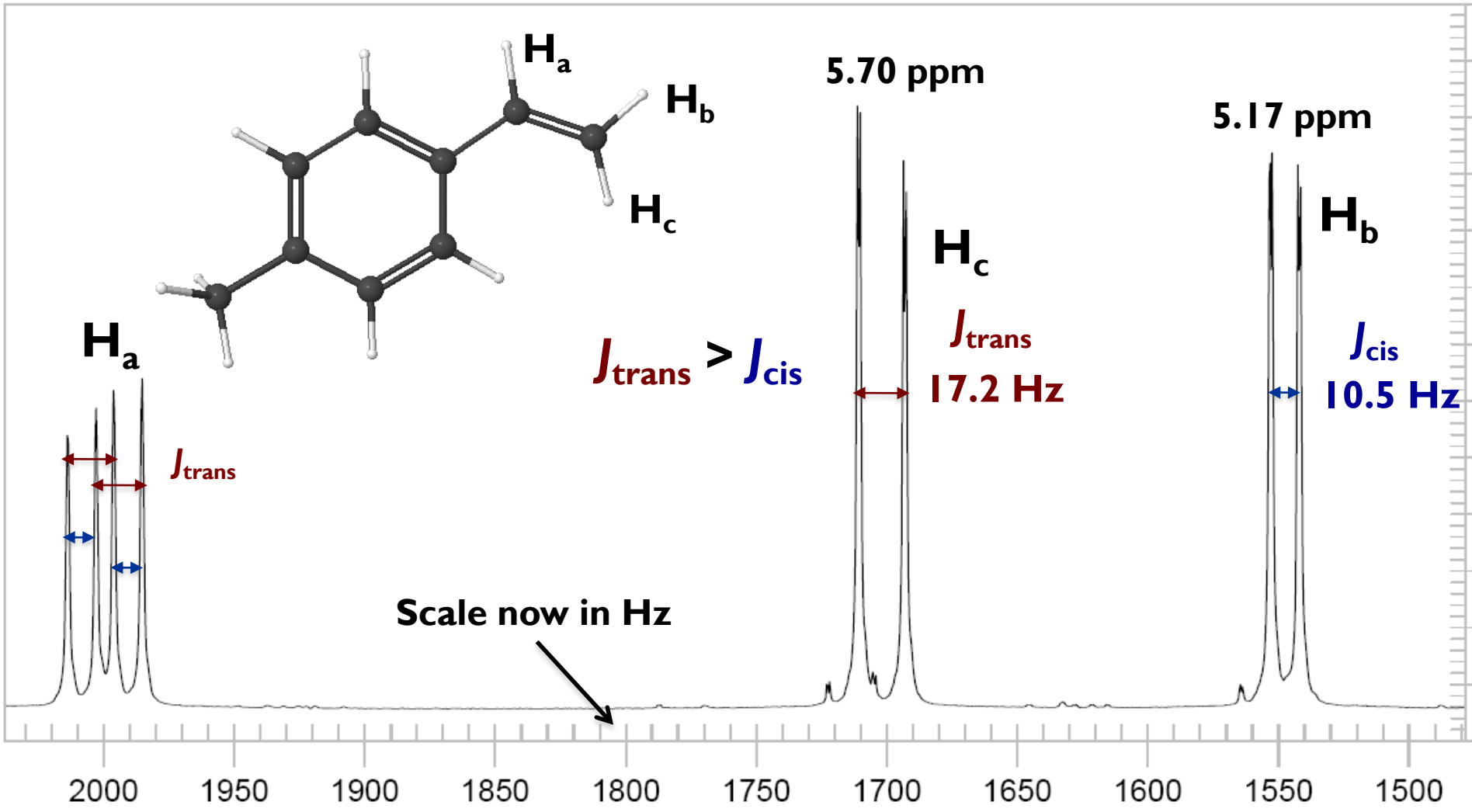
Derivation of splitting diagrams - H_a

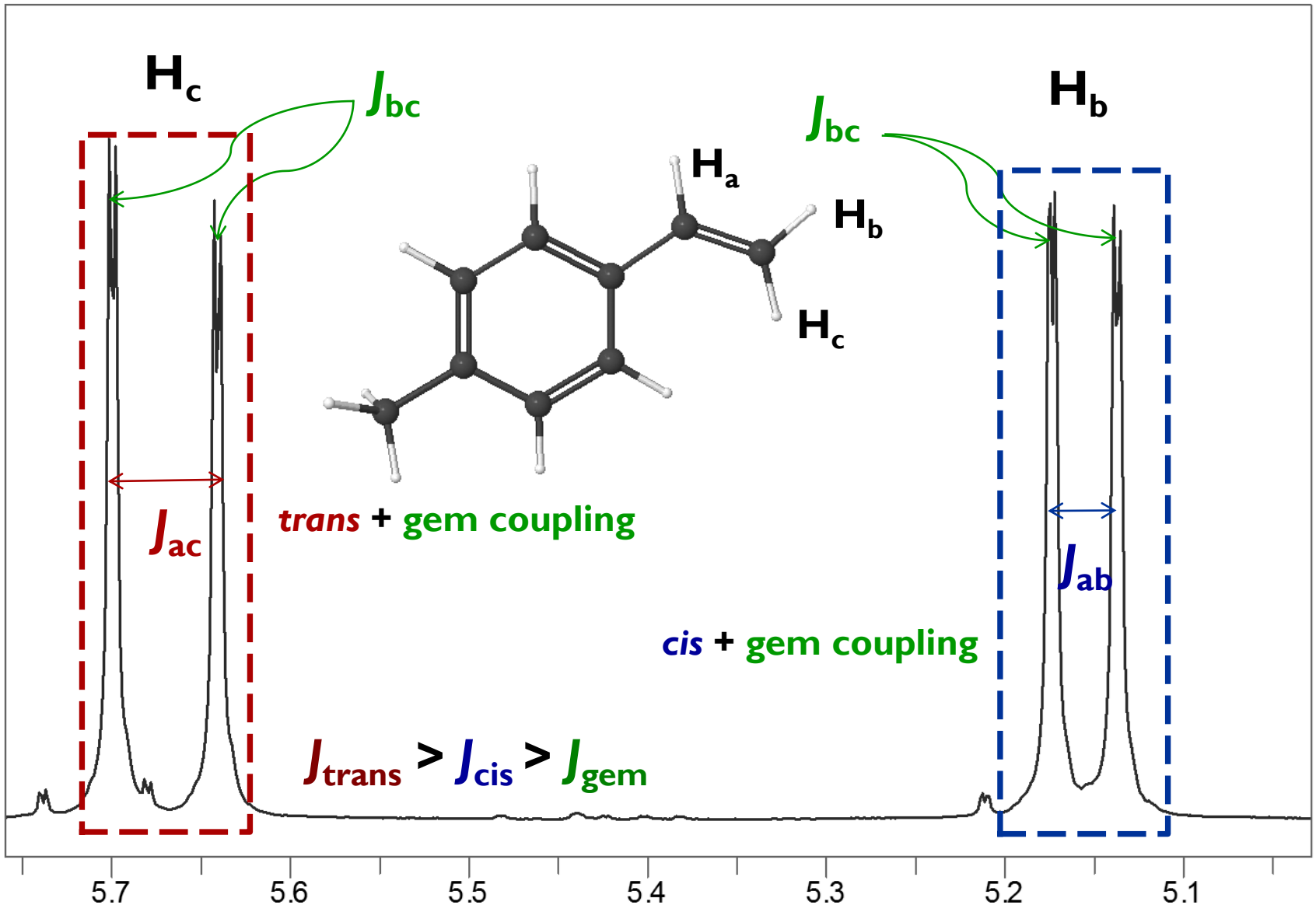




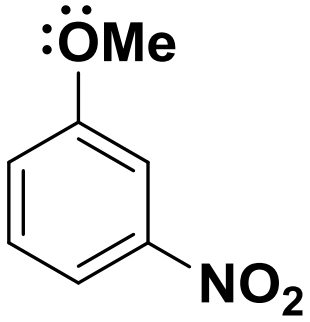
300 MHz ^{1}H NMR

In CDCl3



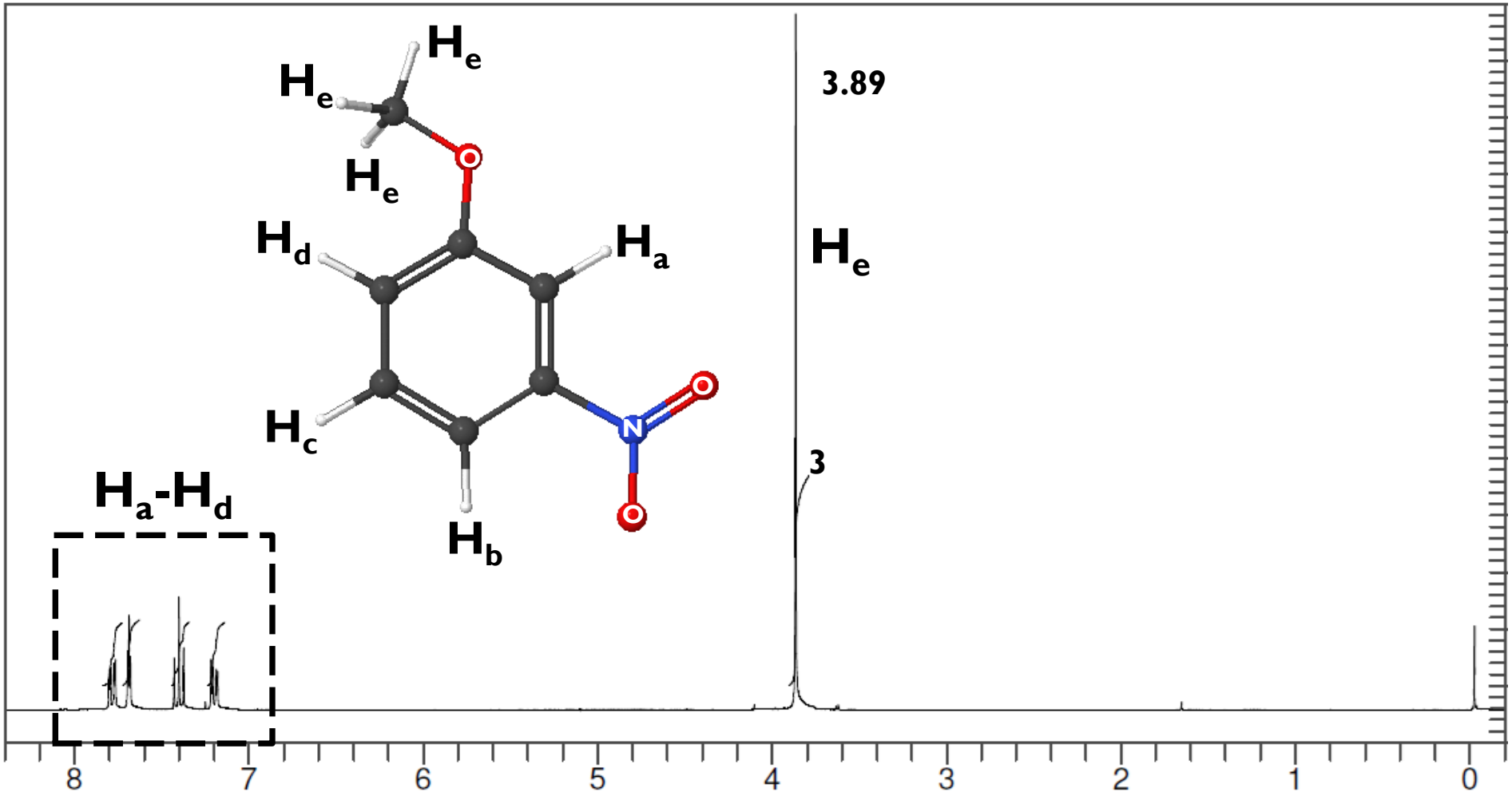


Splitting patterns in aromatic systems

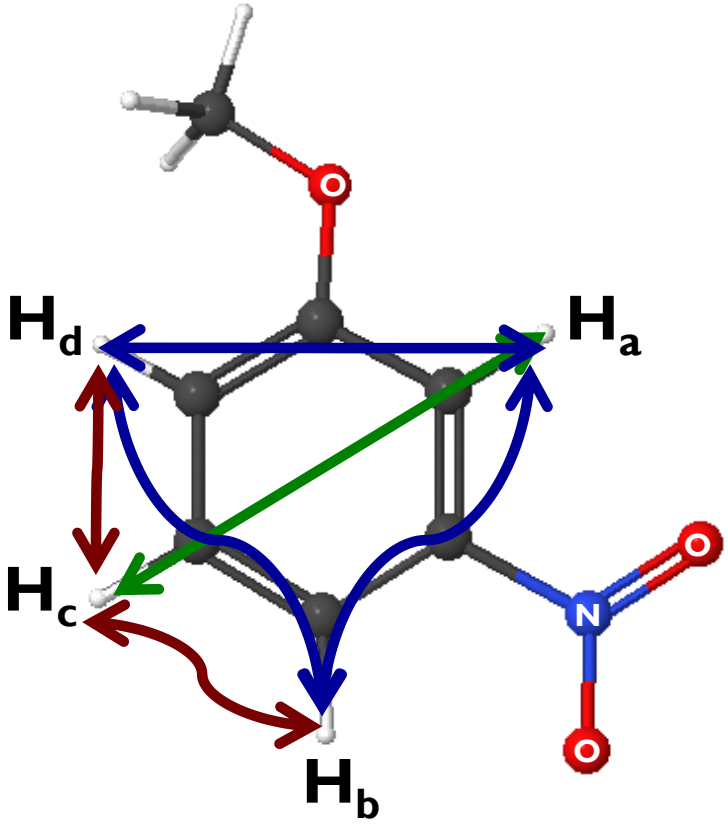


3-Nitroanisole

300 MHz ^{1}H NMR
In CDCl3

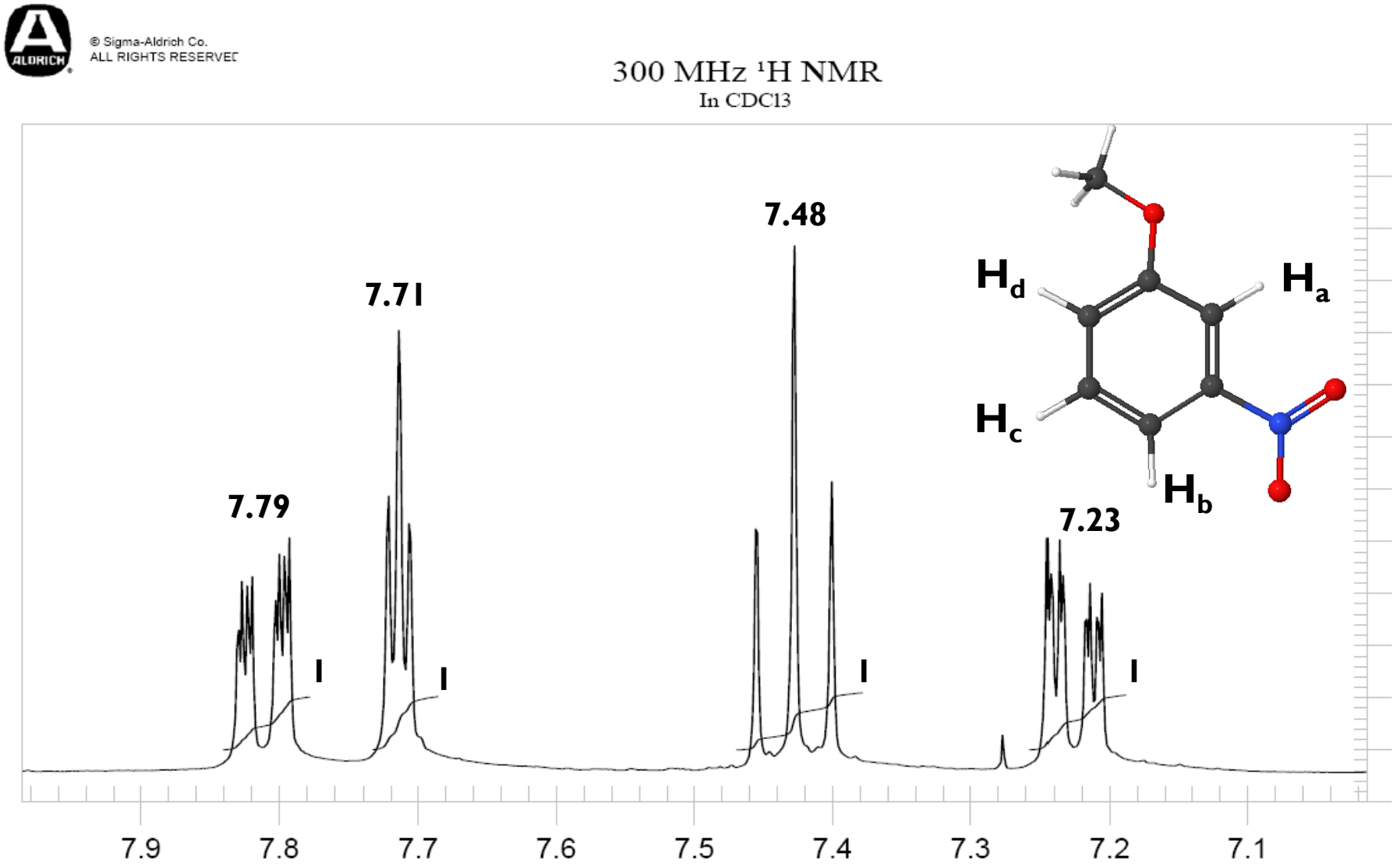


Coupling constants in aromatic systems



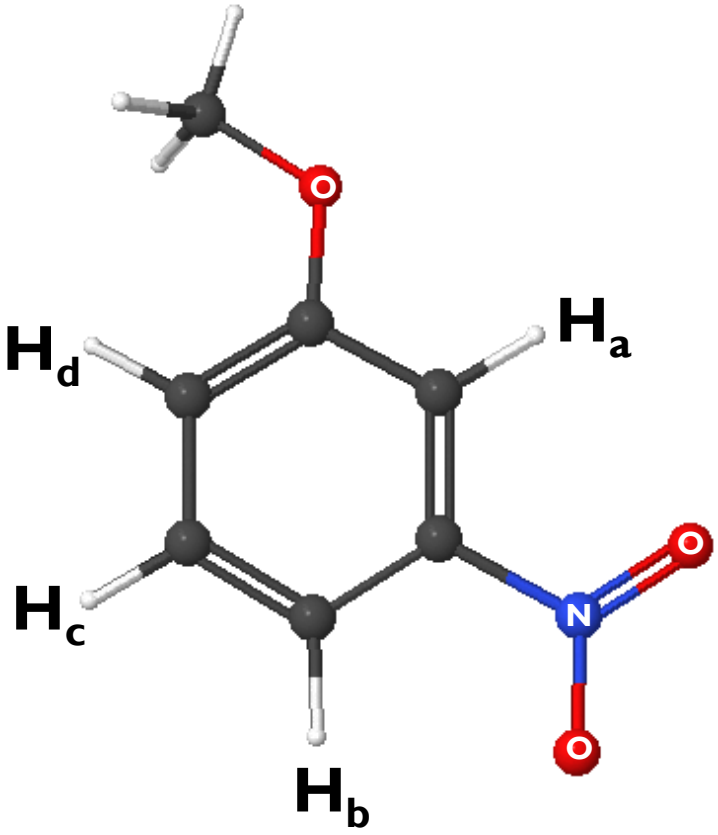
Write down the relationships between the protons!

List all couplings, start with the strongest coupling



Write down the relationships between the alkene protons

List all couplings, strongest first



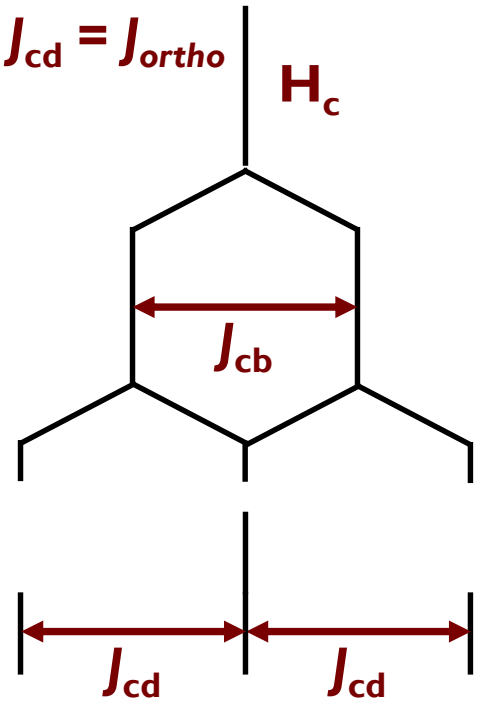
Derivation of splitting diagrams - H_c

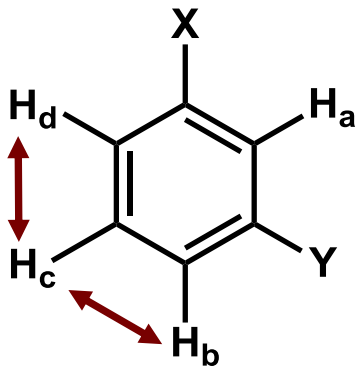
To predict the appearance of H_c:

Apply the n+1 rule to each different coupling

Apply largest coupling first

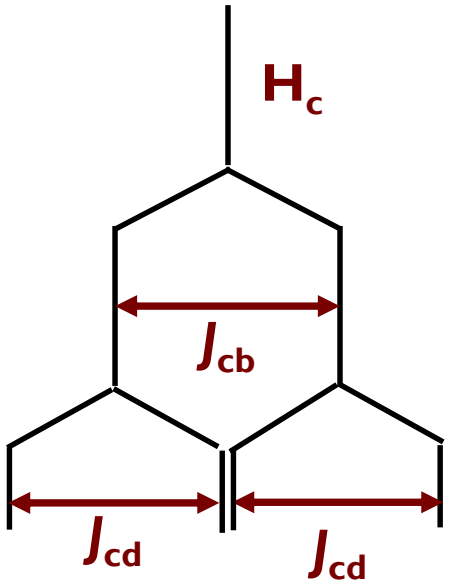
$J_{cb} = J_{cd} = J_{ortho}$





$J_{cb} \approx J_{cd} = J_{ortho}$

$J_{cd} < J_{cb}$



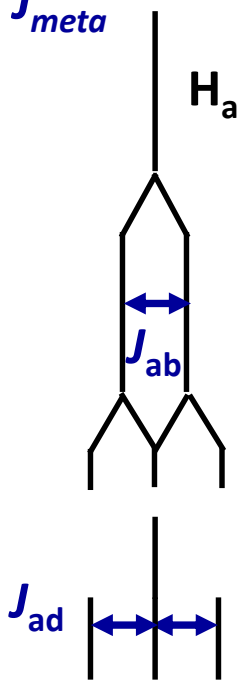
Derivation of splitting diagrams - H_a

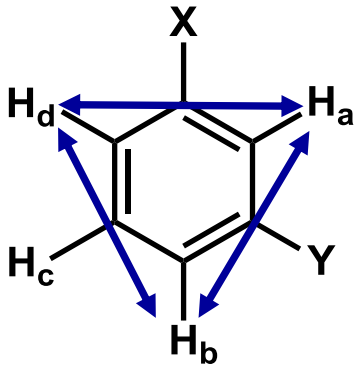
To predict the appearance of H_a:

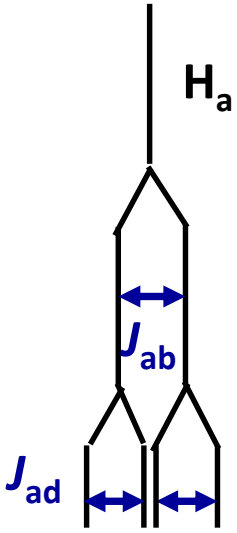
Apply the n+1 rule to each different coupling

Apply largest coupling first

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







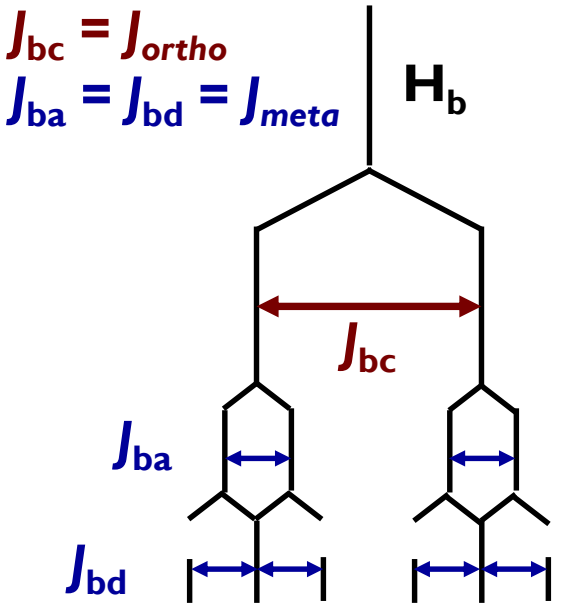
$J_{ab} \approx J_{ad} = J_{meta}$

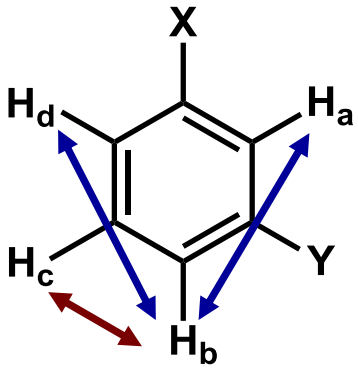
$J_{ad} < J_{ab}$

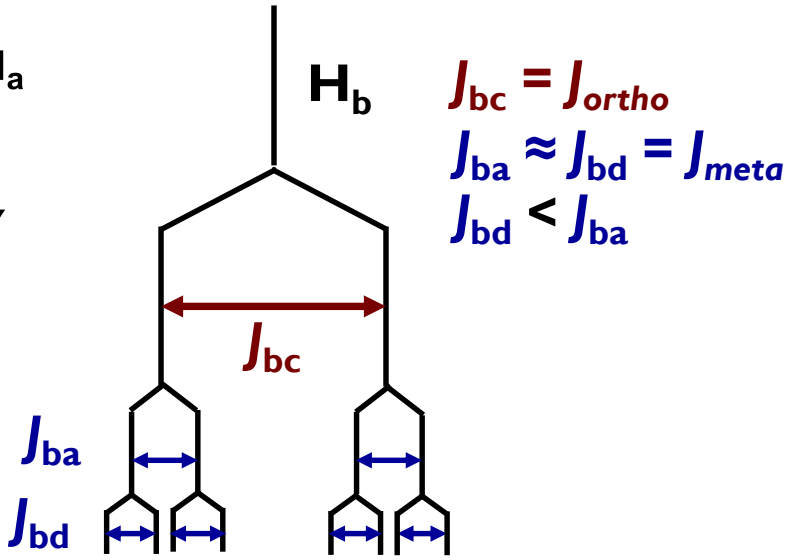
Derivation of splitting diagrams - H_b

To predict the appearance of H_b:

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







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**