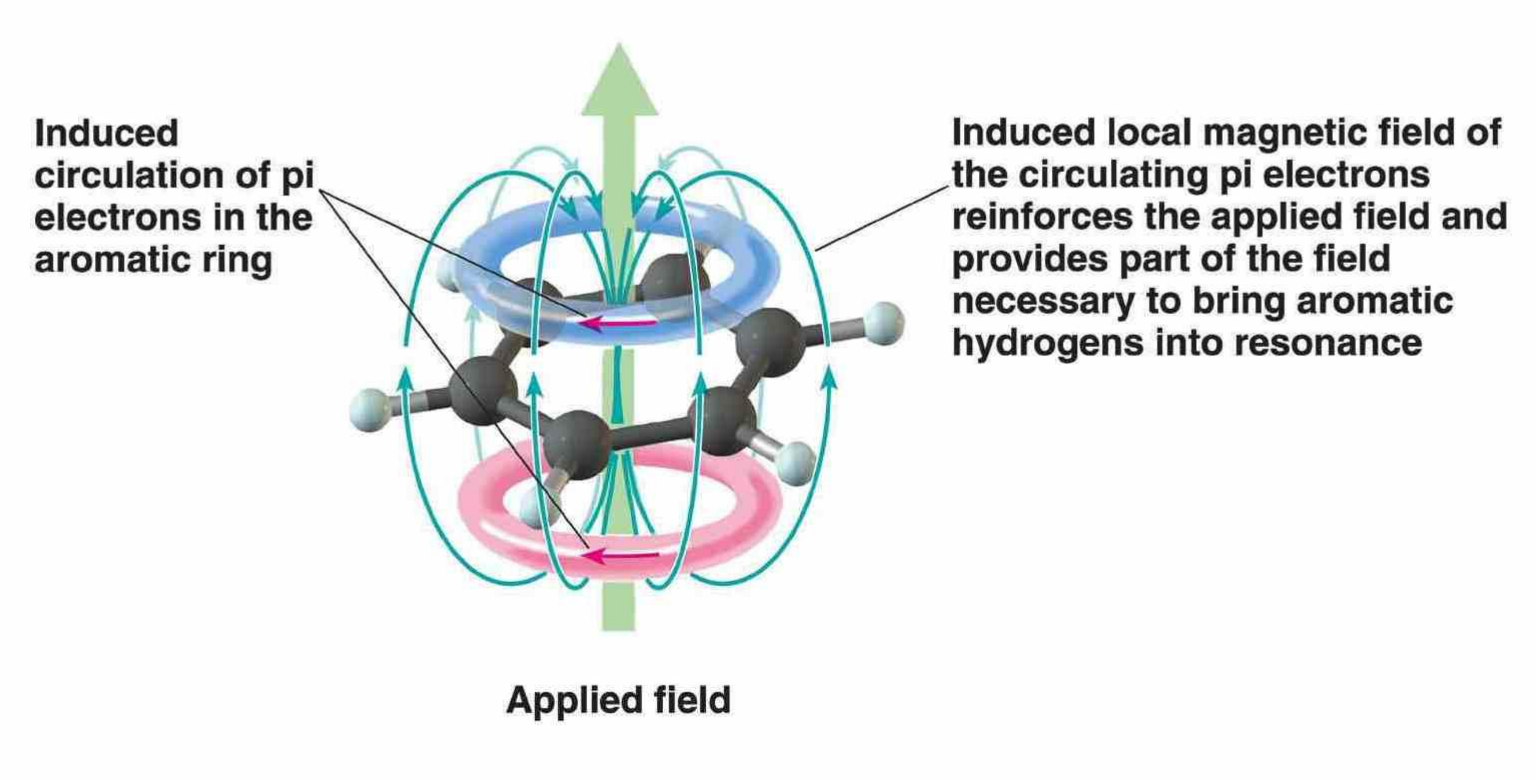
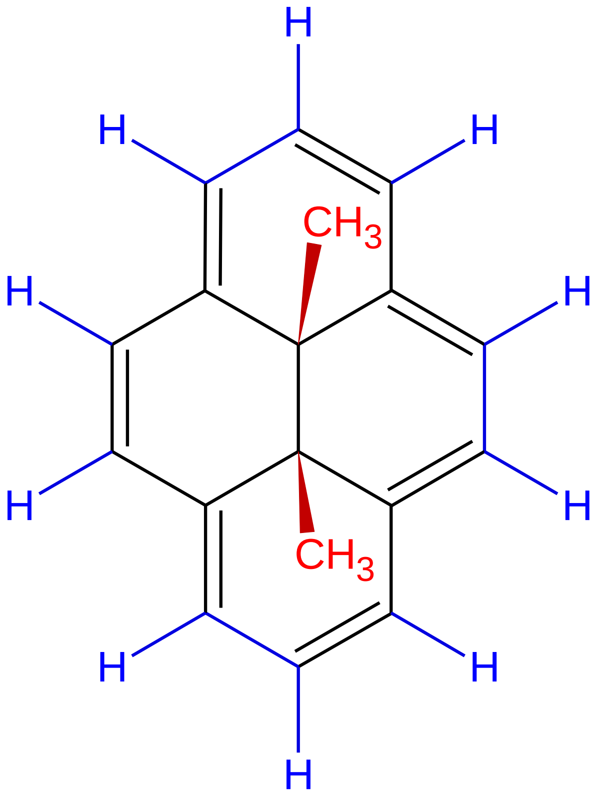
Chemical Shift

– magnetic induction of the pi electrons in an aromatic ring (Fig. 13.11)

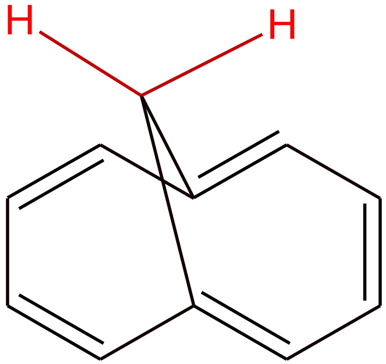


Anisotropy of Aromatic compounds: in plane and above



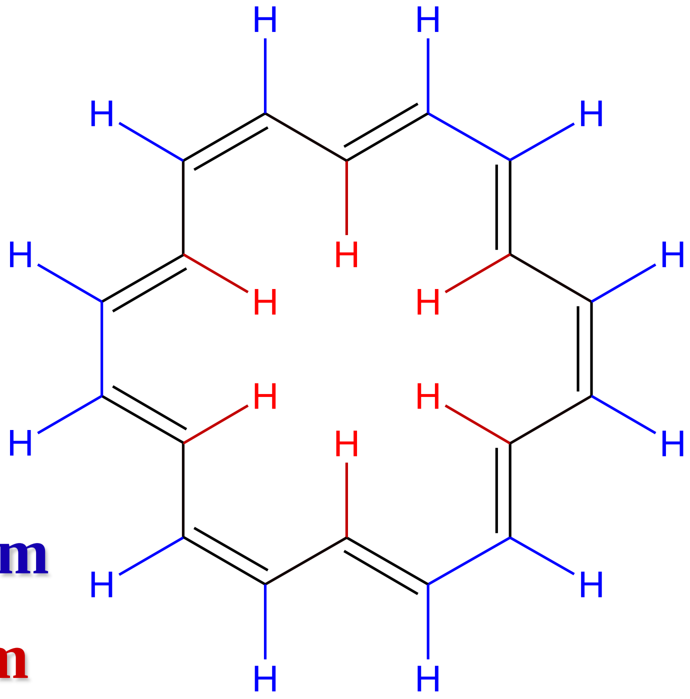
δ_{ring} → 8.14-8.64 ppm

δ_{Me} → -4.25 ppm



δ_{ring} → 7.27-6.95 ppm

δ_{CH_2} → -0.51 ppm



$\delta_{OUTSIDE}$ → 9.28 ppm

δ_{INSIDE} → -2.99 ppm

Anisotropy: Aromatic

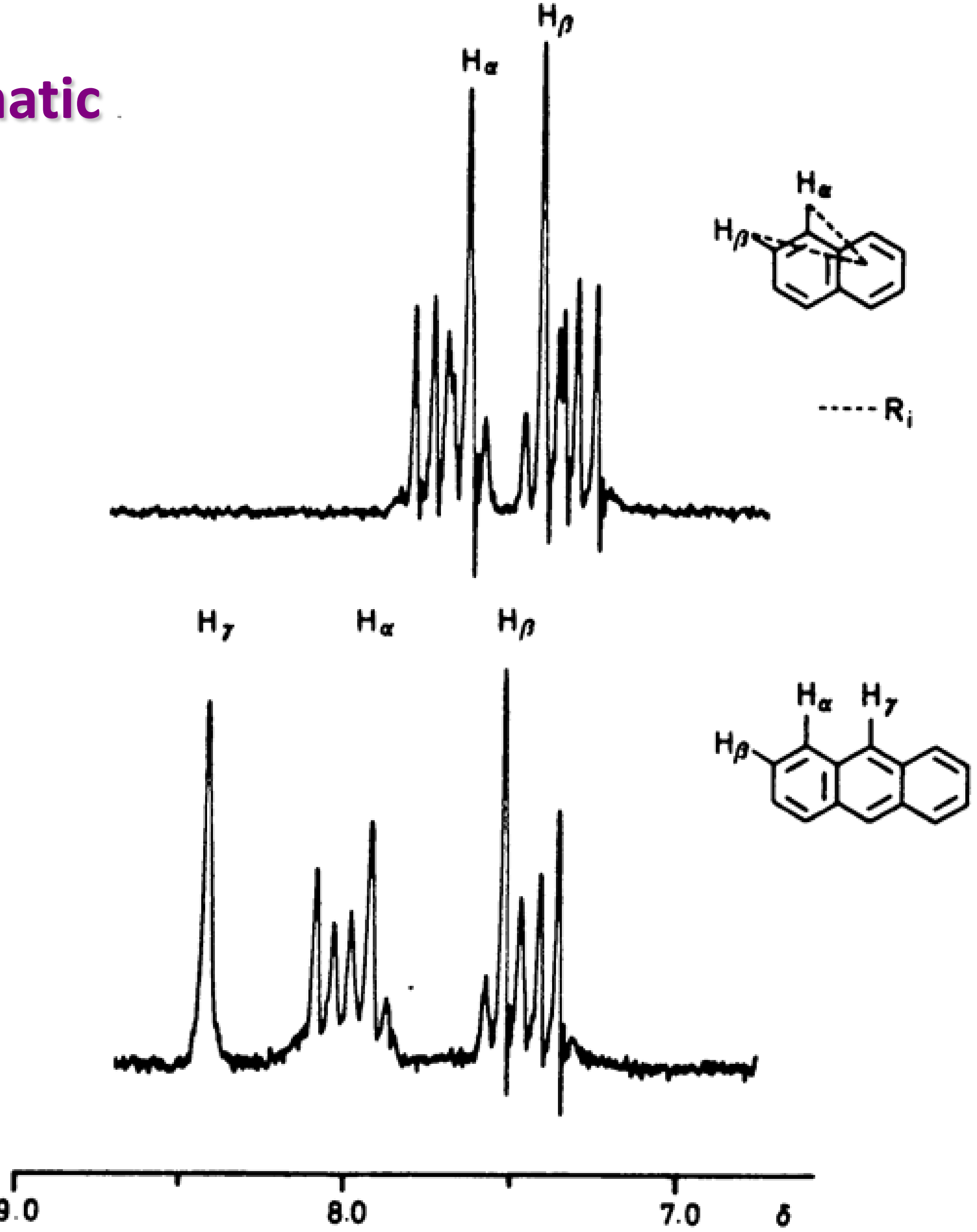
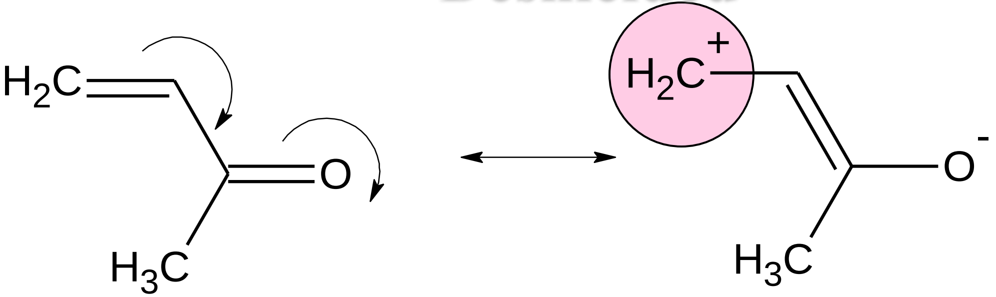


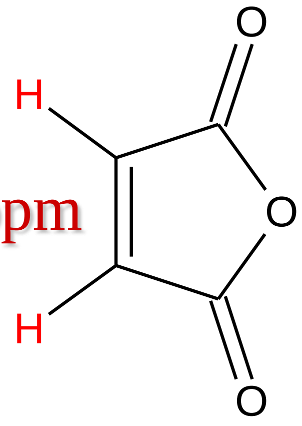
Figure 4.11 Correlation between the relative chemical shifts of the proton resonances in naphthalene and anthracene and the distance R_i of the proton from the centre of a specific benzene ring

Electronic effects

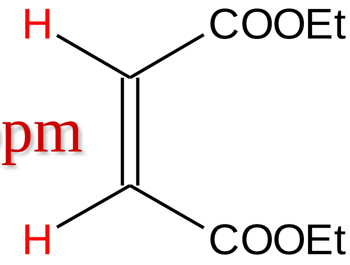
Deshielded

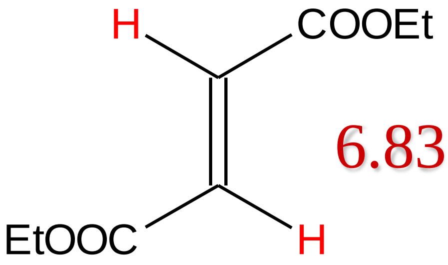


7.10 ppm



6.28 ppm

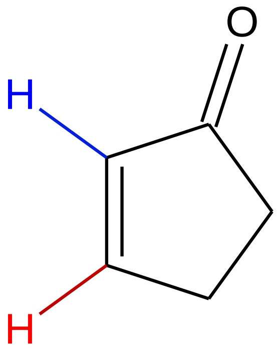




6.83 ppm

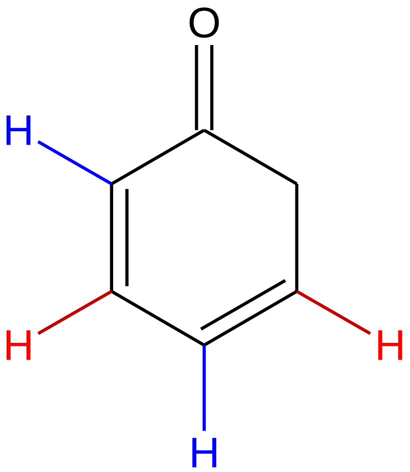
6.10 ppm

7.71 ppm



5.93 ppm

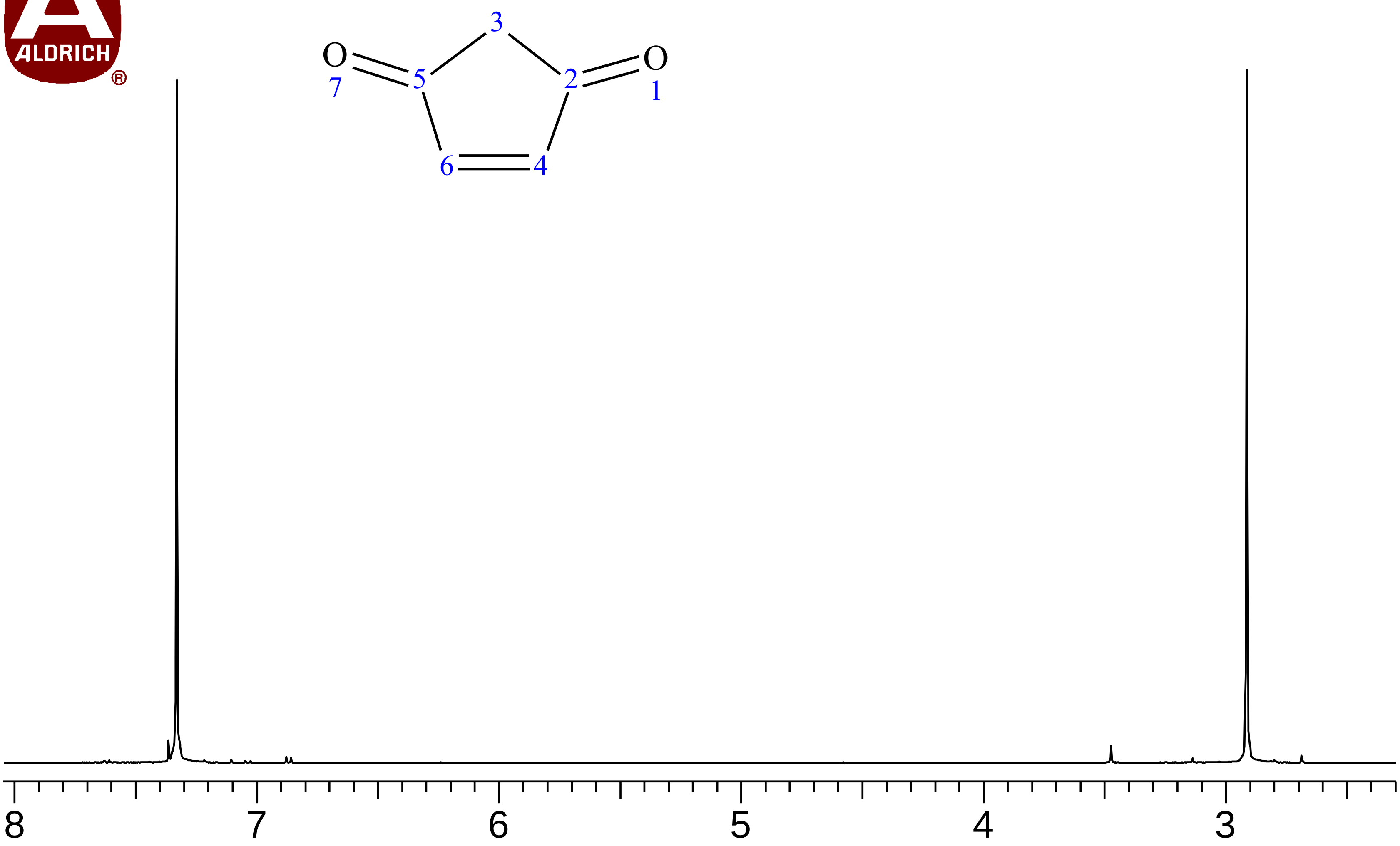
7.07 ppm



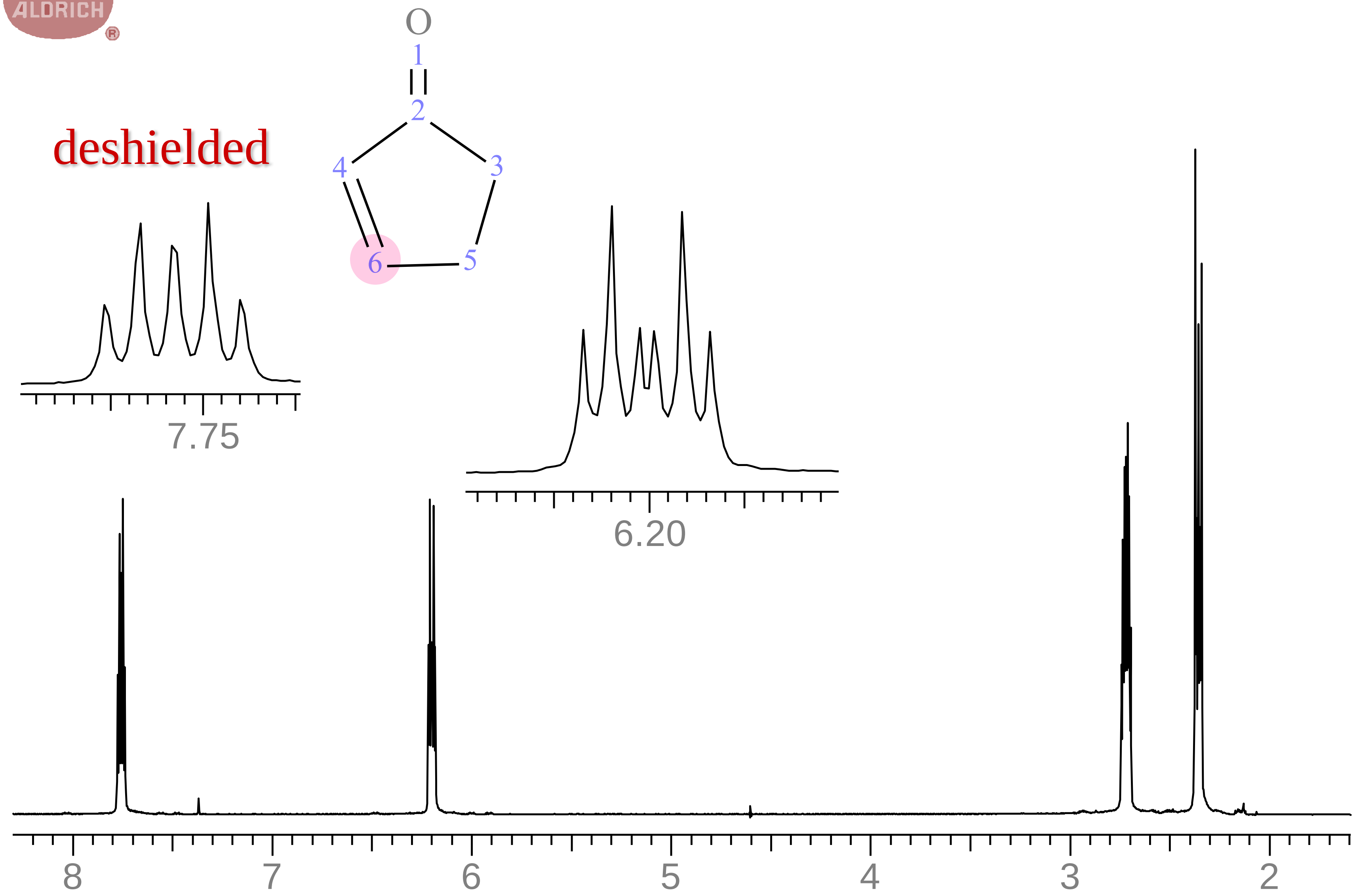
6.38 ppm

6.28 ppm

Electronic effects: conjugation with carbonyl

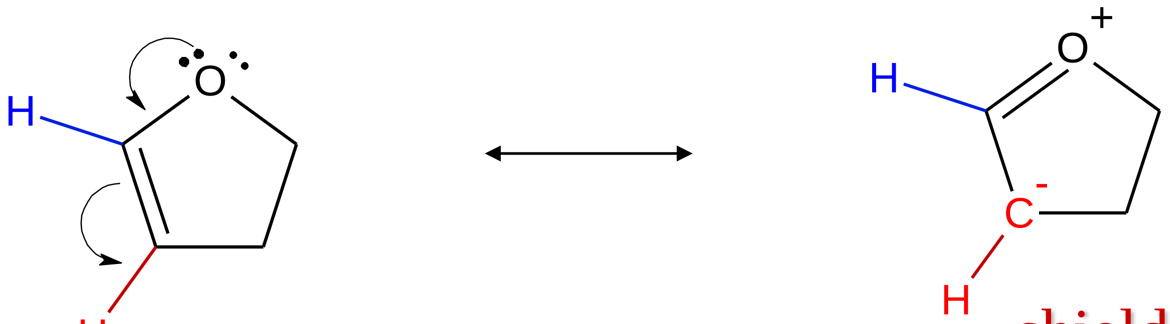


Electronic effects: conjugation with carbonyl

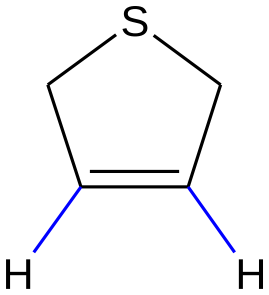


deshielded

Electronic effects: conjugation with heteroatom

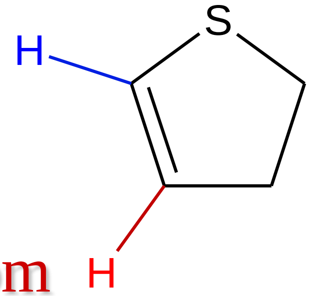


shielded

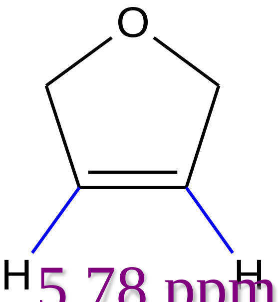


5.81 ppm

6.06 ppm

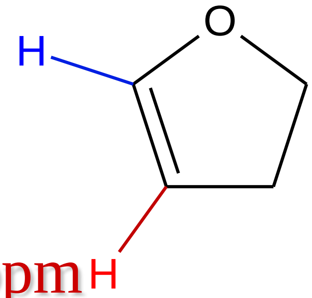


5.48 ppm



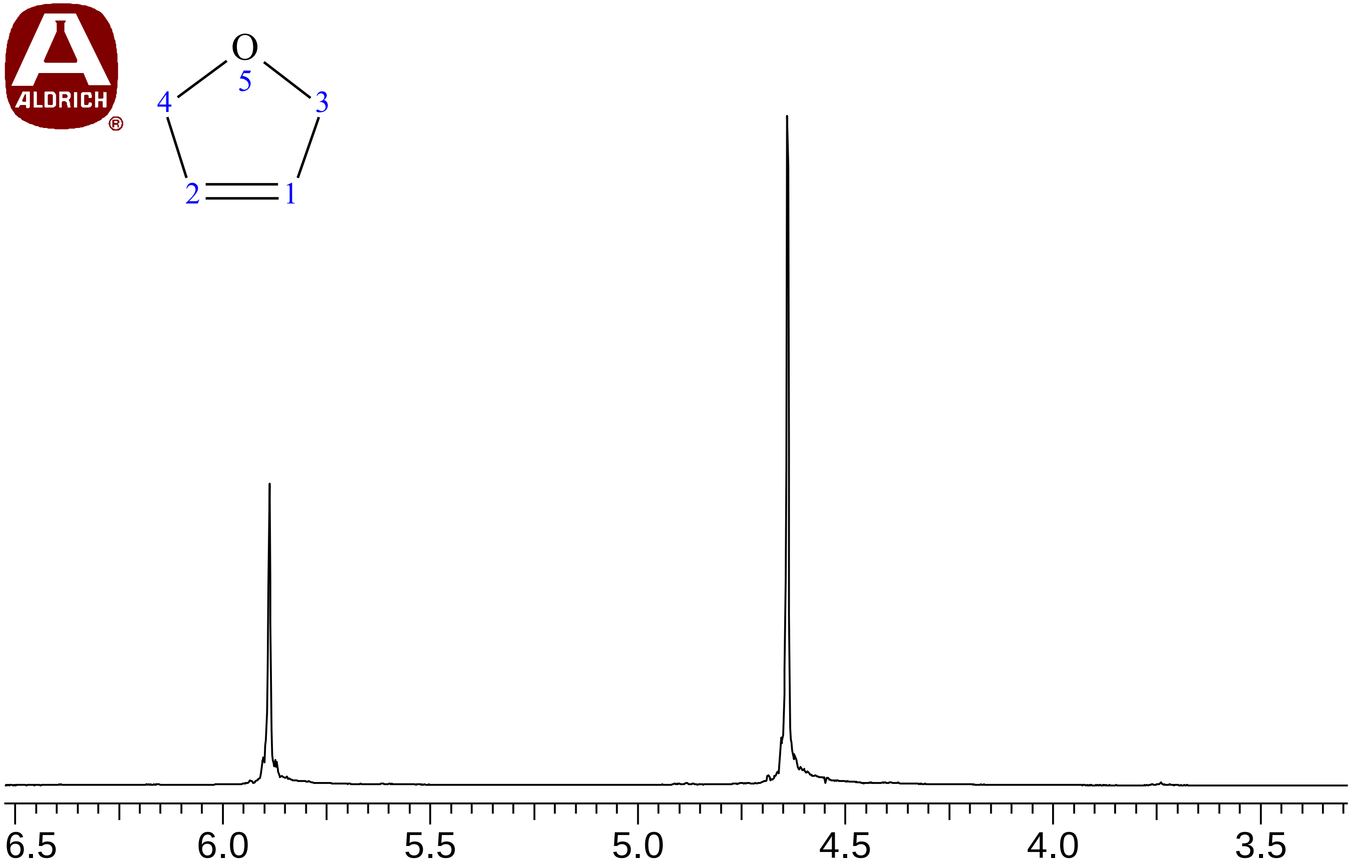
5.78 ppm

6.22 ppm

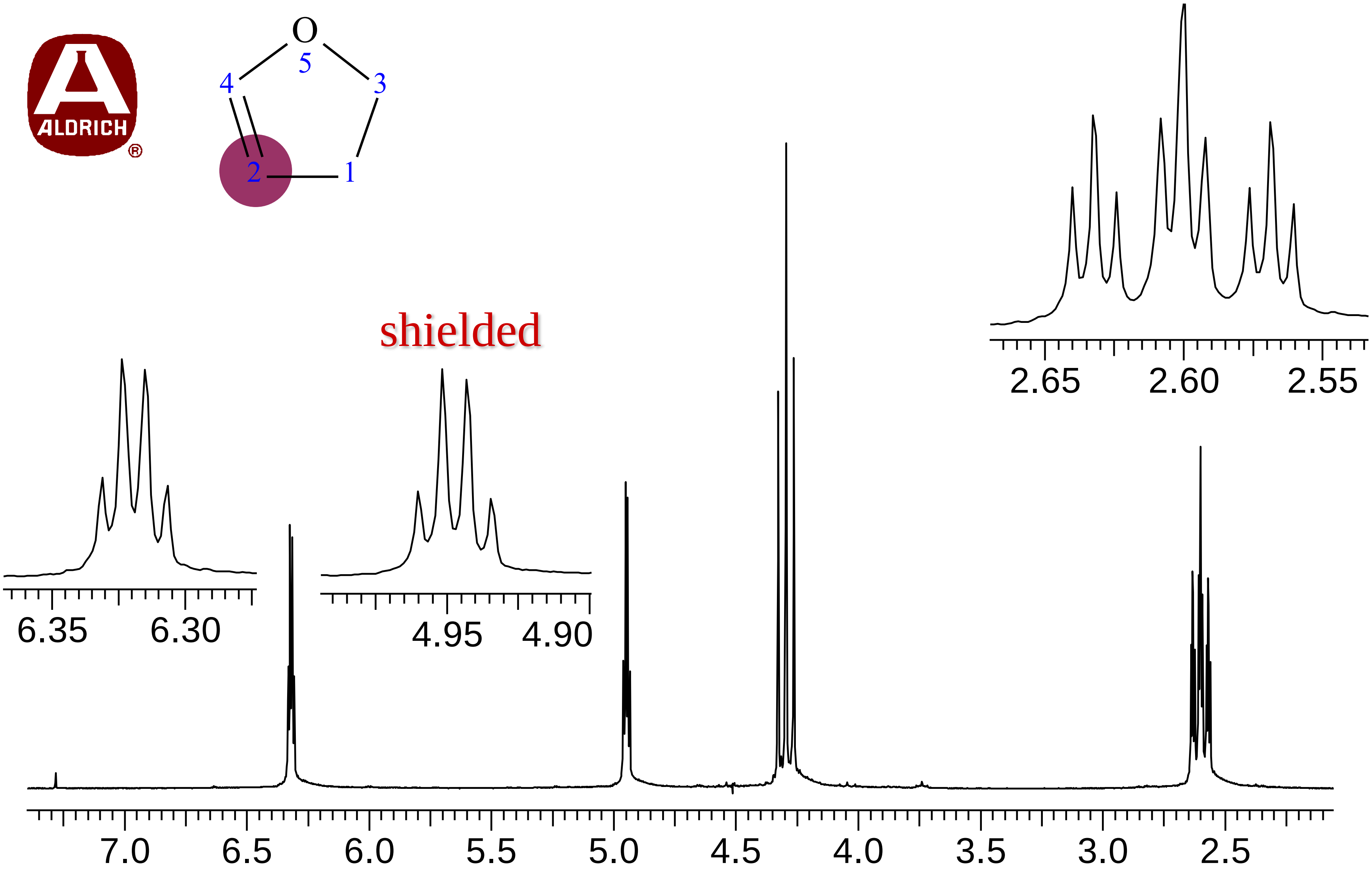


4.82 ppm

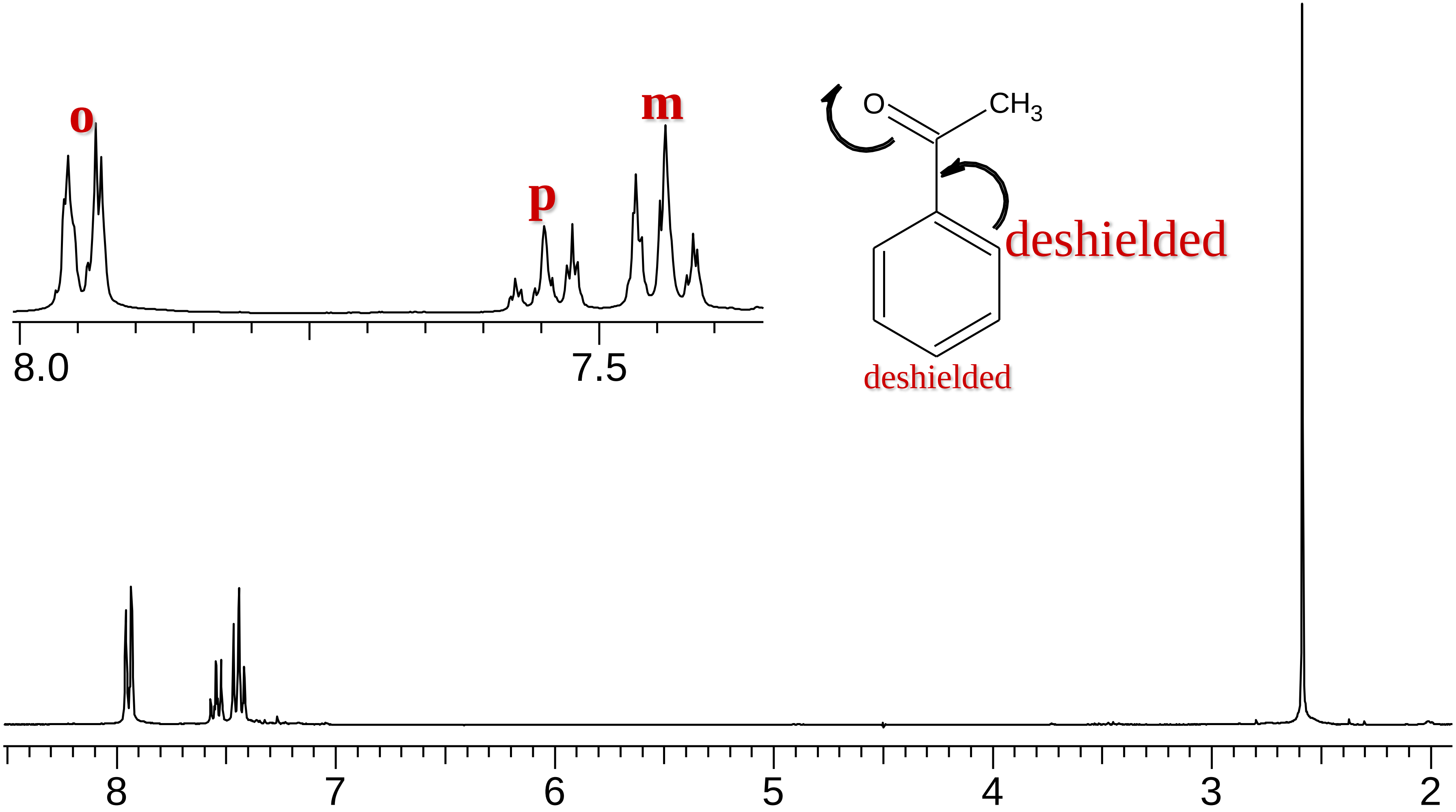
Electronic effects: no conjugation with heteroatom



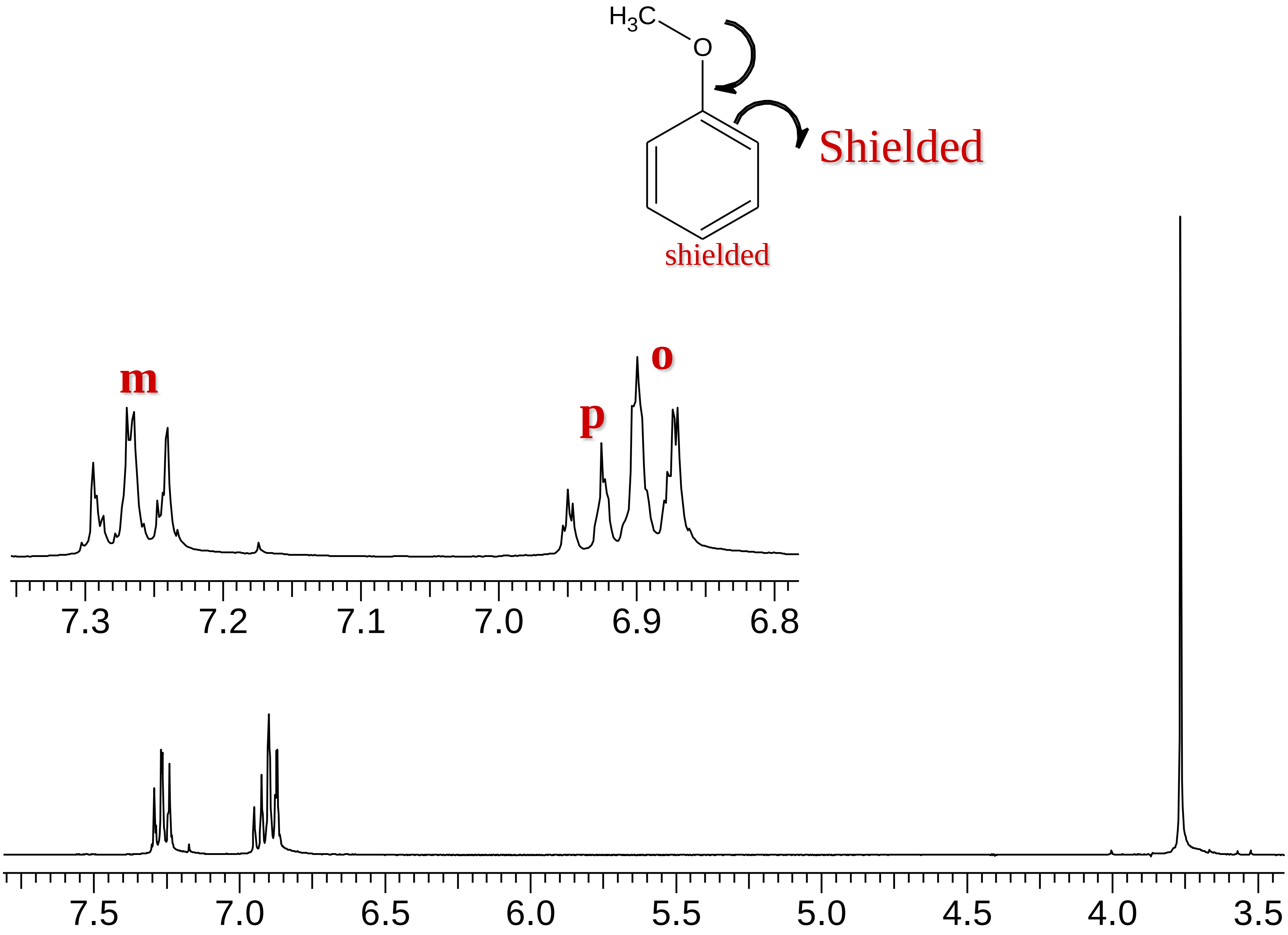
Electronic effects: conjugation with heteroatom



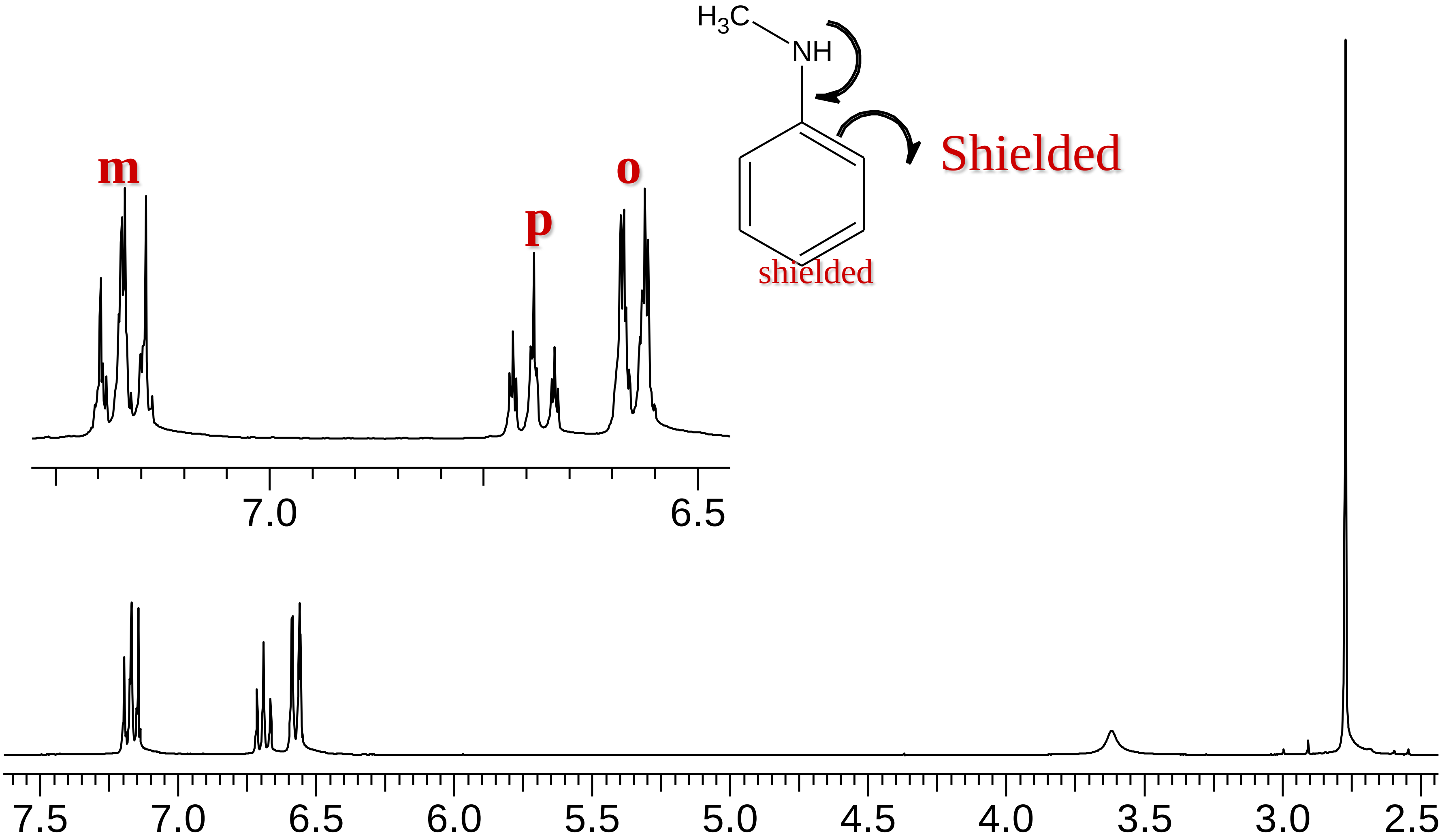
Electronic effects: conjugation with carbonyl



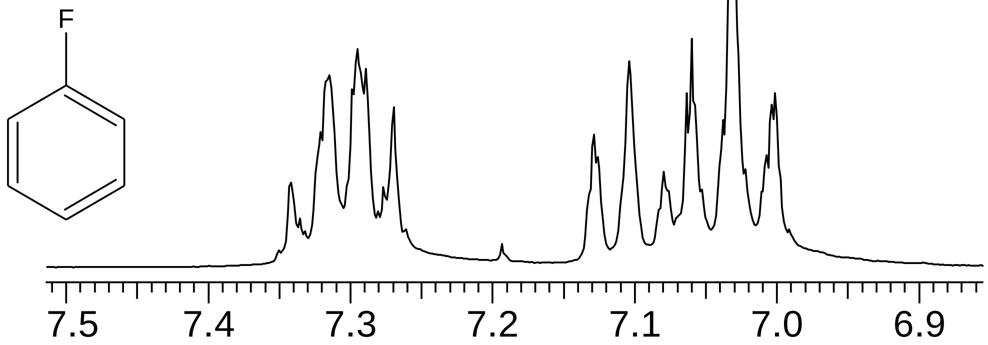
Electronic effects: conjugation with heteroatom

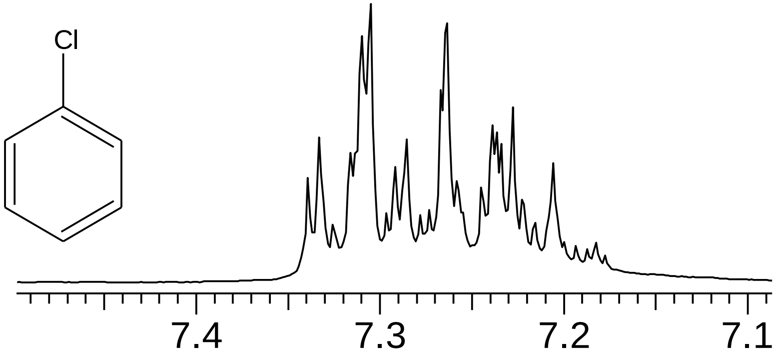


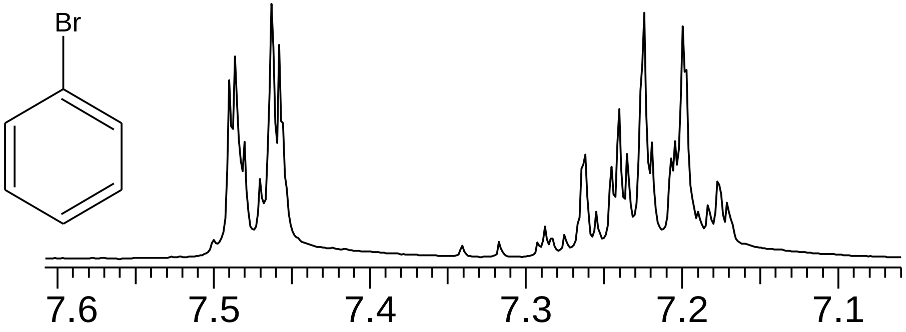
Electronic effects: conjugation with heteroatom



Aromatic: inductive effect and resonance effect







Calculating Shifts for aromatic compounds

Chemical Shift Calculation for Aromatic compounds

$$\delta = 7.27 + \sum S(\delta)$$

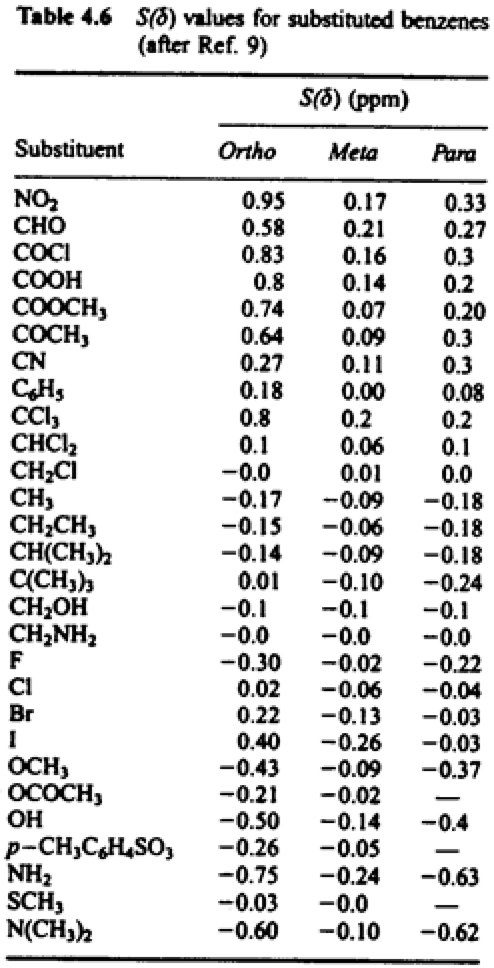
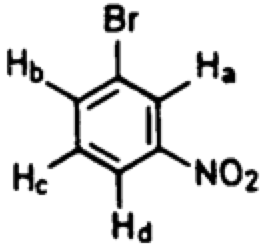


Table 4.6 *S(δ)* values for substituted benzenes (after Ref. 9)

Substituent	*S(δ)* (ppm) *Ortho*	*Meta*	*Para*
NO_2	0.95	0.17	0.33
CHO	0.58	0.21	0.27
COCl	0.83	0.16	0.3
COOH	0.8	0.14	0.2
$COOCH_3$	0.74	0.07	0.20
$COCH_3$	0.64	0.09	0.3
CN	0.27	0.11	0.3
C_6H_5	0.18	0.00	0.08
CCl_3	0.8	0.2	0.2
$CHCl_2$	0.1	0.06	0.1
CH_2Cl	−0.0	0.01	0.0
CH_3	−0.17	−0.09	−0.18
CH_2CH_3	−0.15	−0.06	−0.18
$CH(CH_3)_2$	−0.14	−0.09	−0.18
$C(CH_3)_3$	0.01	−0.10	−0.24
CH_2OH	−0.1	−0.1	−0.1
CH_2NH_2	−0.0	−0.0	−0.0
F	−0.30	−0.02	−0.22
Cl	0.02	−0.06	−0.04
Br	0.22	−0.13	−0.03
I	0.40	−0.26	−0.03
OCH_3	−0.43	−0.09	−0.37
$OCOCH_3$	−0.21	−0.02	—
OH	−0.50	−0.14	−0.4
$p{-}CH_3C_6H_4SO_3$	−0.26	−0.05	—
NH_2	−0.75	−0.24	−0.63
SCH_3	−0.03	−0.0	—
$N(CH_3)_2$	−0.60	−0.10	−0.62



$$\delta(H_a) = 7.27 + 0.22 + 0.95 = 8.44$$

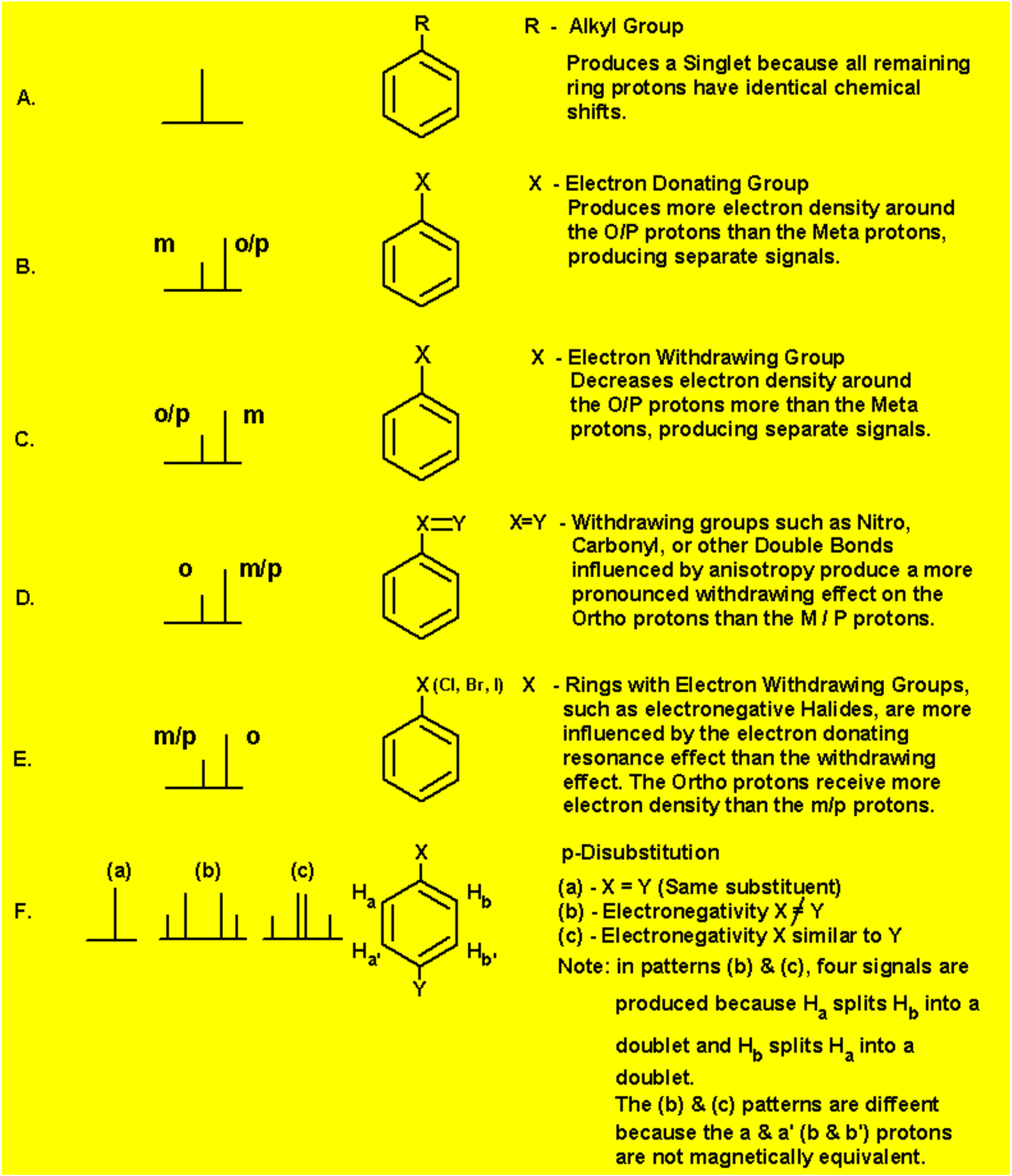
$$\delta(H_b) = 7.27 + 0.22 + 0.33 = 7.82$$

$$\delta(H_c) = 7.27 - 0.13 + 0.17 = 7.31$$

$$\delta(H_d) = 7.27 - 0.03 + 0.95 = 8.19$$

NMR

- Common Aromatic Patterns



A. R - Alkyl Group

Produces a Singlet because all remaining ring protons have identical chemical shifts.

B. X - Electron Donating Group

Produces more electron density around the O/P protons than the Meta protons, producing separate signals.

C. X - Electron Withdrawing Group

Decreases electron density around the O/P protons more than the Meta protons, producing separate signals.

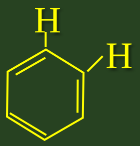
D. X=Y - Withdrawing groups such as Nitro, Carbonyl, or other Double Bonds influenced by anisotropy produce a more pronounced withdrawing effect on the Ortho protons than the M / P protons.

E. X - Rings with Electron Withdrawing Groups, such as electronegative Halides, are more influenced by the electron donating resonance effect than the withdrawing effect. The Ortho protons receive more electron density than the m/p protons.

F. p-Disubstitution

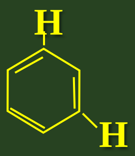
(a) - X = Y (Same substituent)
(b) - Electronegativity $X \neq Y$
(c) - Electronegativity X similar to Y

Note: in patterns (b) & (c), four signals are produced because H$_a$ splits H$_b$ into a doublet and H$_b$ splits H$_a$ into a doublet.
The (b) & (c) patterns are diffeent because the a & a' (b & b') protons are not magnetically equivalent.

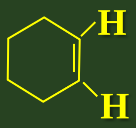


Ortho
6-10 Hz

para
1-4
Hz



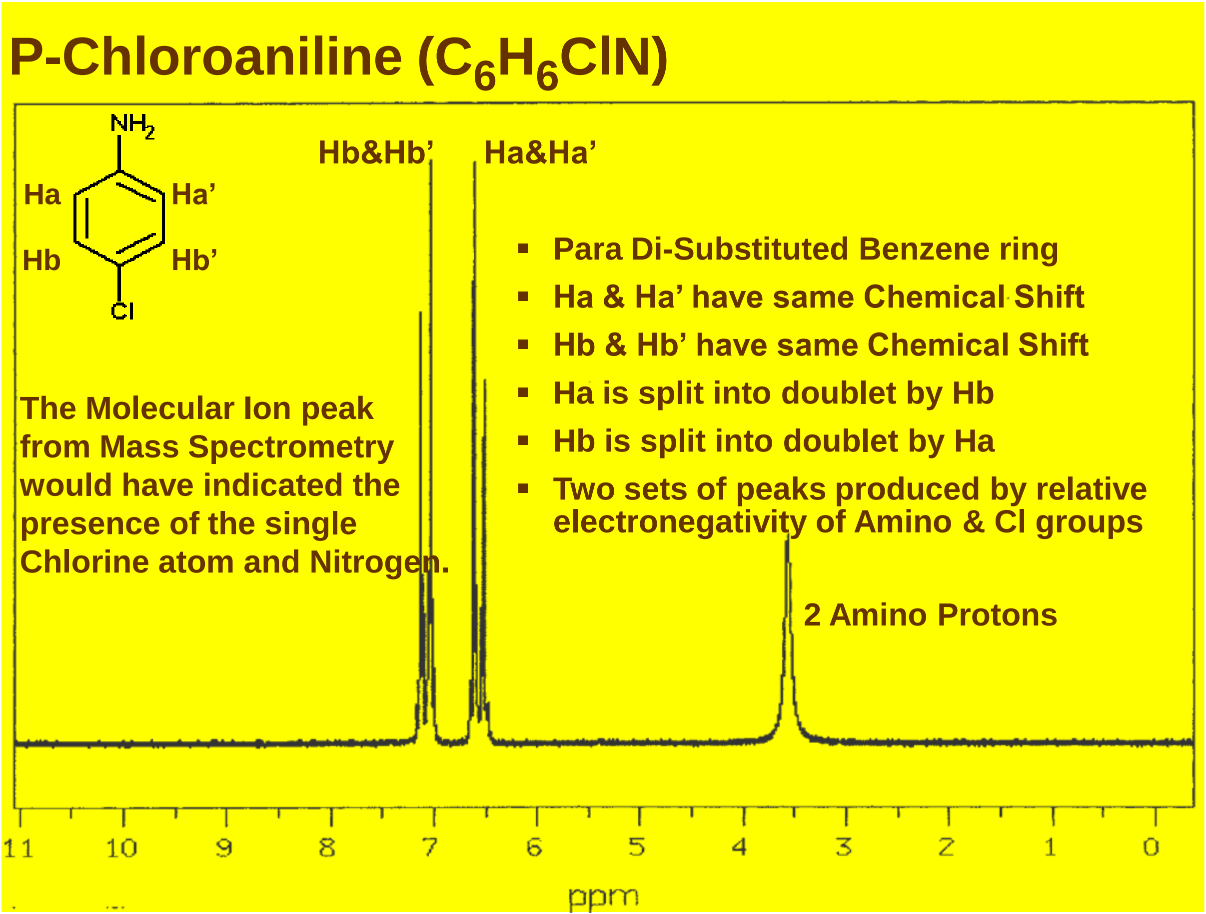
meta
0-2 Hz



8-10 Hz

NMR

- “Activating” and “Deactivating” groups and the impact of the changing electron density in the Benzene ring on Chemical Shift of ortho, meta, para protons



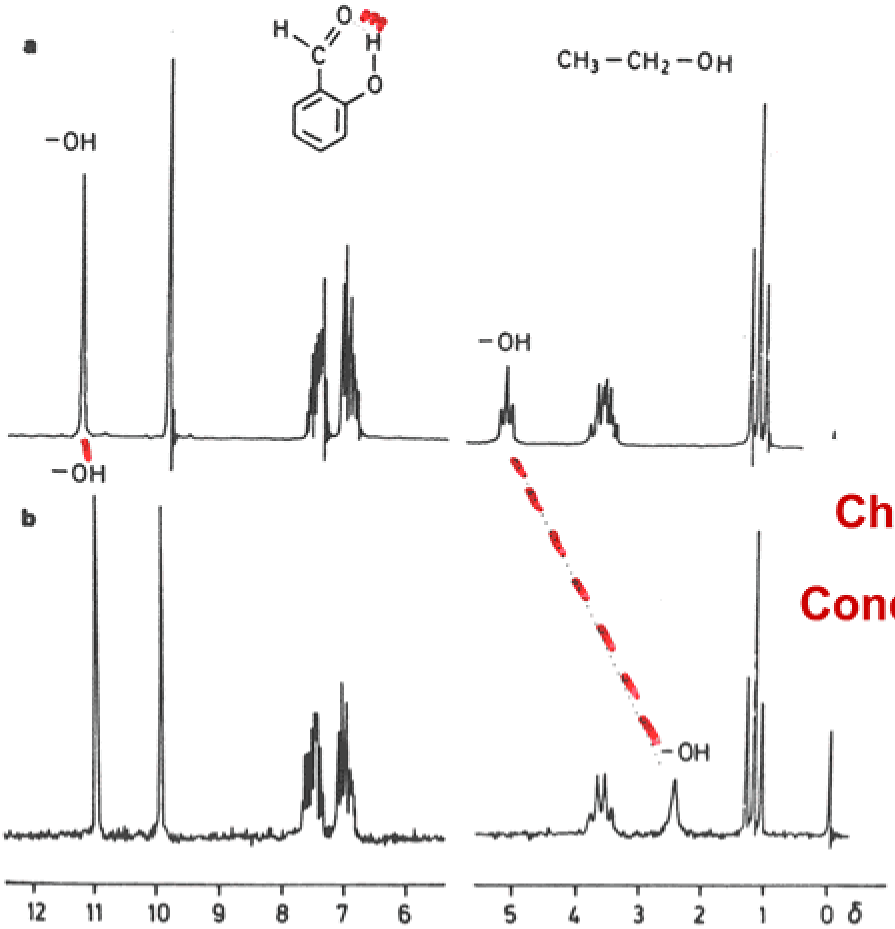
P-Chloroaniline (C_6H_6ClN)

- Para Di-Substituted Benzene ring
- Ha & Ha’ have same Chemical Shift
- Hb & Hb’ have same Chemical Shift
- Ha is split into doublet by Hb
- Hb is split into doublet by Ha
- Two sets of peaks produced by relative electronegativity of Amino & Cl groups

The Molecular Ion peak from Mass Spectrometry would have indicated the presence of the single Chlorine atom and Nitrogen.

Hydrogen bond

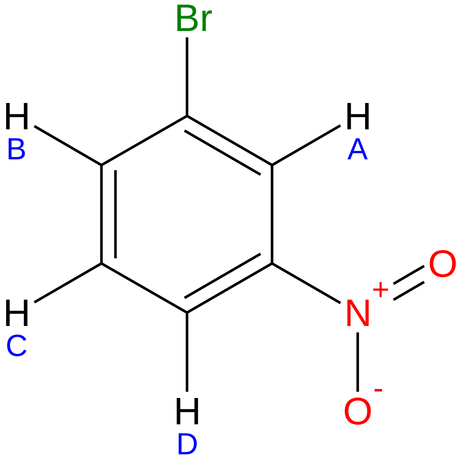
Hydrogen Bond



Chem Shift
vs
Concentration

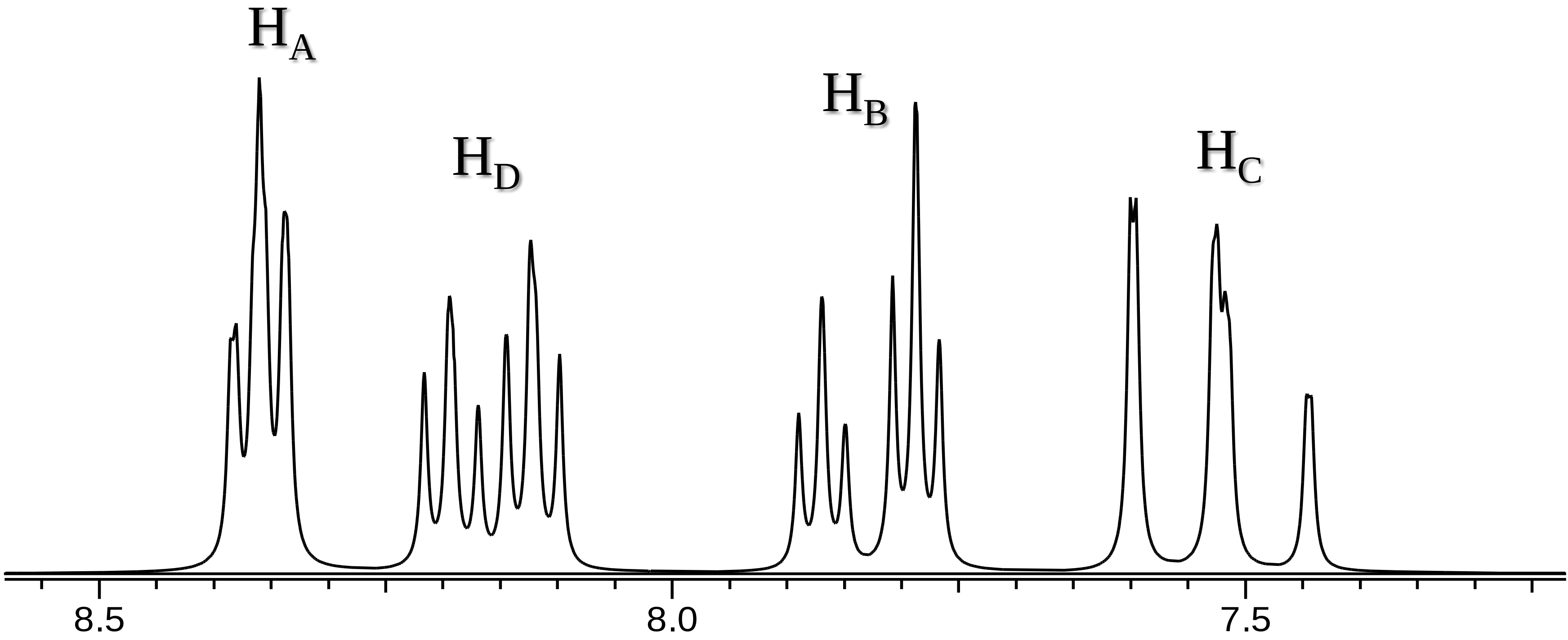
Figure 4.19 Concentration dependence of the proton resonance frequency of the hydroxyl protons of salicylaldehyde and ethanol: (a) neat; (b) 5% by volume in CCl_4

meta bromo nitro benzene



Calculated shifts

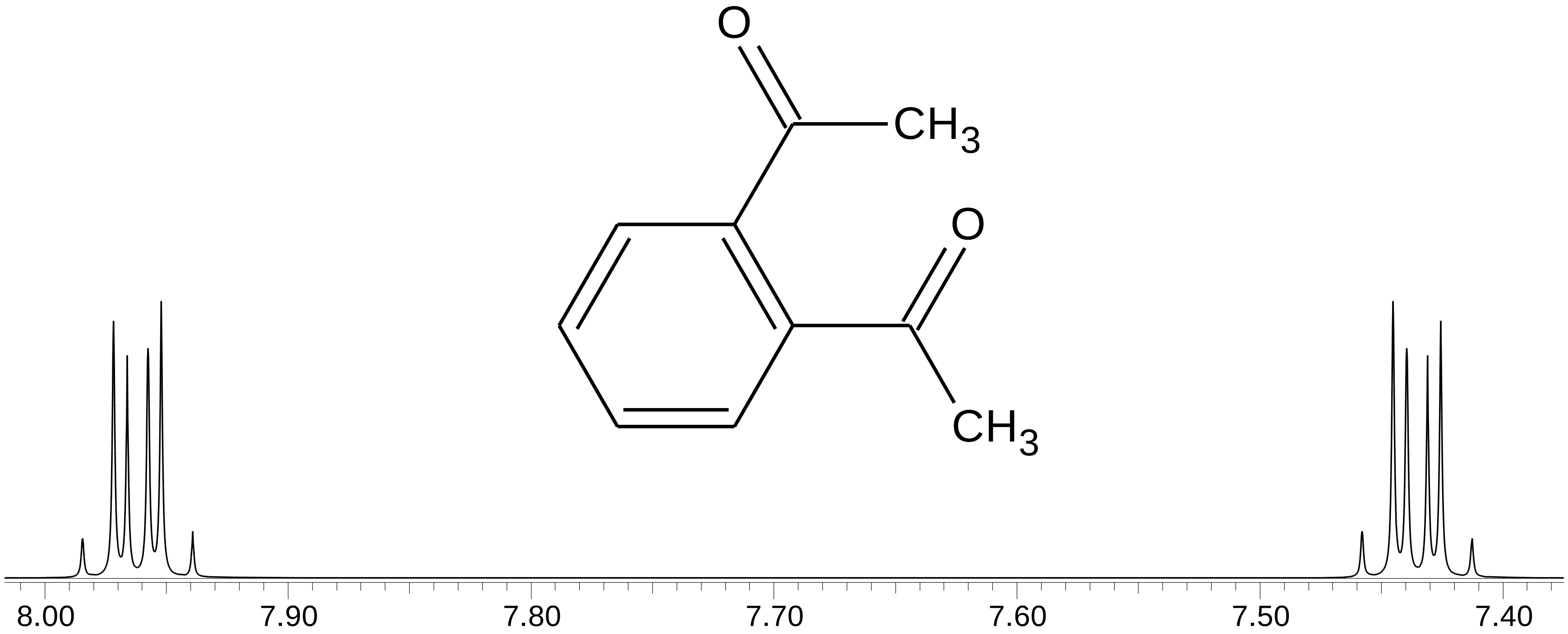
$\delta H_A = 8.44$ $\delta H_B = 7.82$ $\delta H_C = 7.31$ $\delta H_D = 8.19$



Aromatic substitution pattern: ortho

AA’ XX’

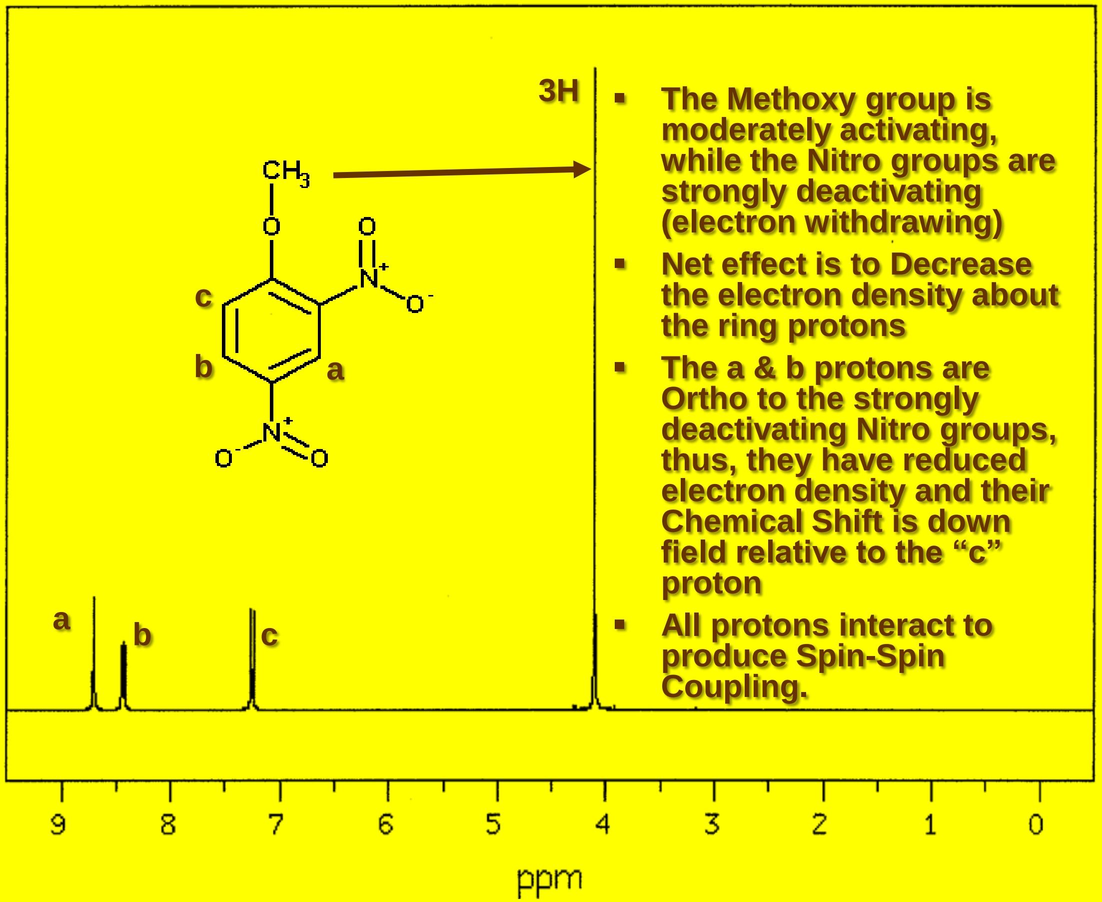
Typical spectra for ortho (symmetrical)



NMR

- “Activating” and “Deactivating” groups and the impact of the changing electron density in the Benzene ring on Chemical Shift of ortho, meta, para protons

2,4-Dinitroanisole ($C_7H_6N_2O_5$)



- The Methoxy group is moderately activating, while the Nitro groups are strongly deactivating (electron withdrawing)
- Net effect is to Decrease the electron density about the ring protons
- The a & b protons are Ortho to the strongly deactivating Nitro groups, thus, they have reduced electron density and their Chemical Shift is down field relative to the “c” proton
- All protons interact to produce Spin-Spin Coupling.

AB-Spectra

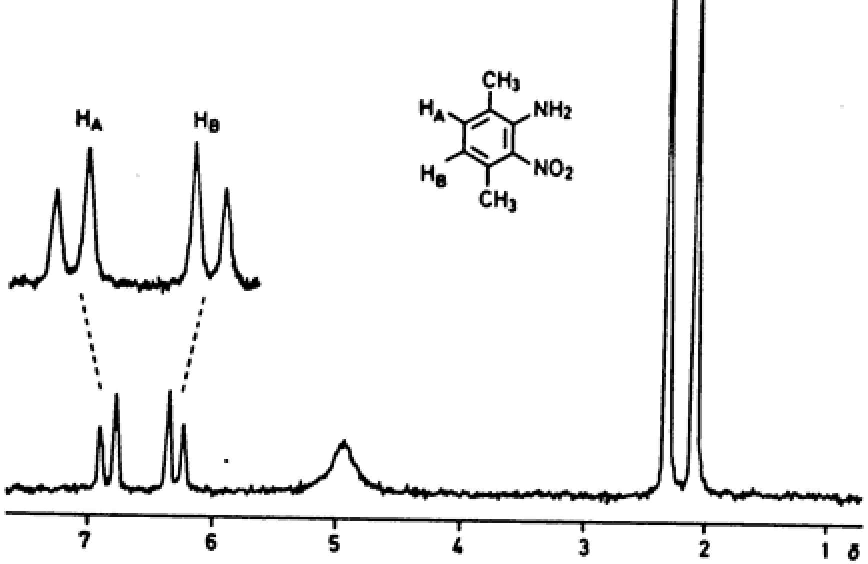


Figure 5.4 ^{1}H n.m.r. spectrum of 1-amino-3,6-dimethyl-2-nitrobenzene at 60 MHz

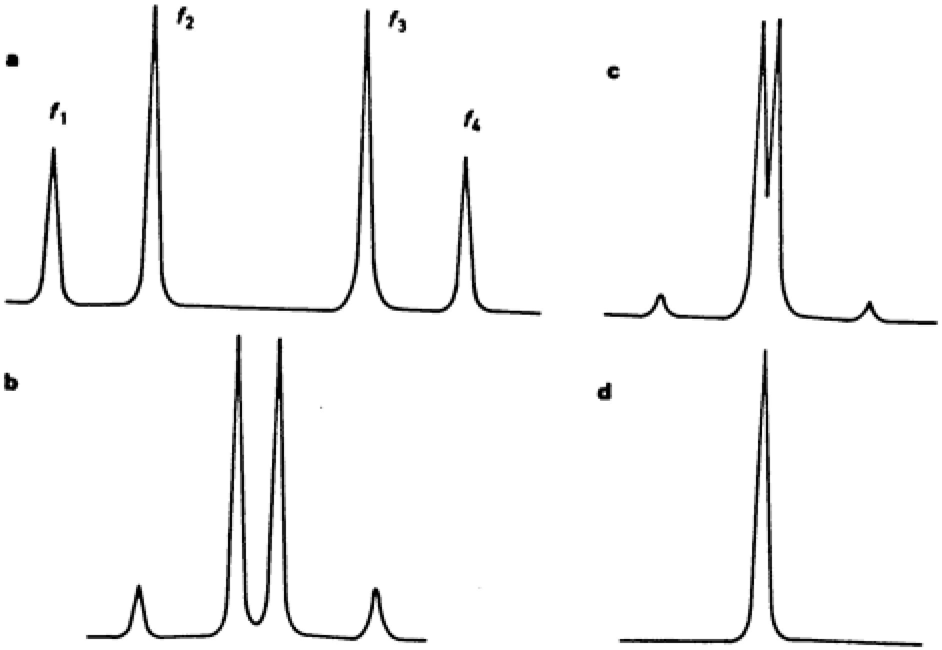


Figure 5.5 Dependence of the AB system on the ratio $J/\nu_0\delta$; spectra illustrated are for values of $J/\nu_0\delta$ of (a) 1:3, (b) 1:1, (c) 5:3, and (d) 5:1.

AMX

$C_6H_4O_5N_2$

I = 6 - 4/2 + 2/2 +1

I = 6

Phenyl = 4 I

NO2 = 1 I

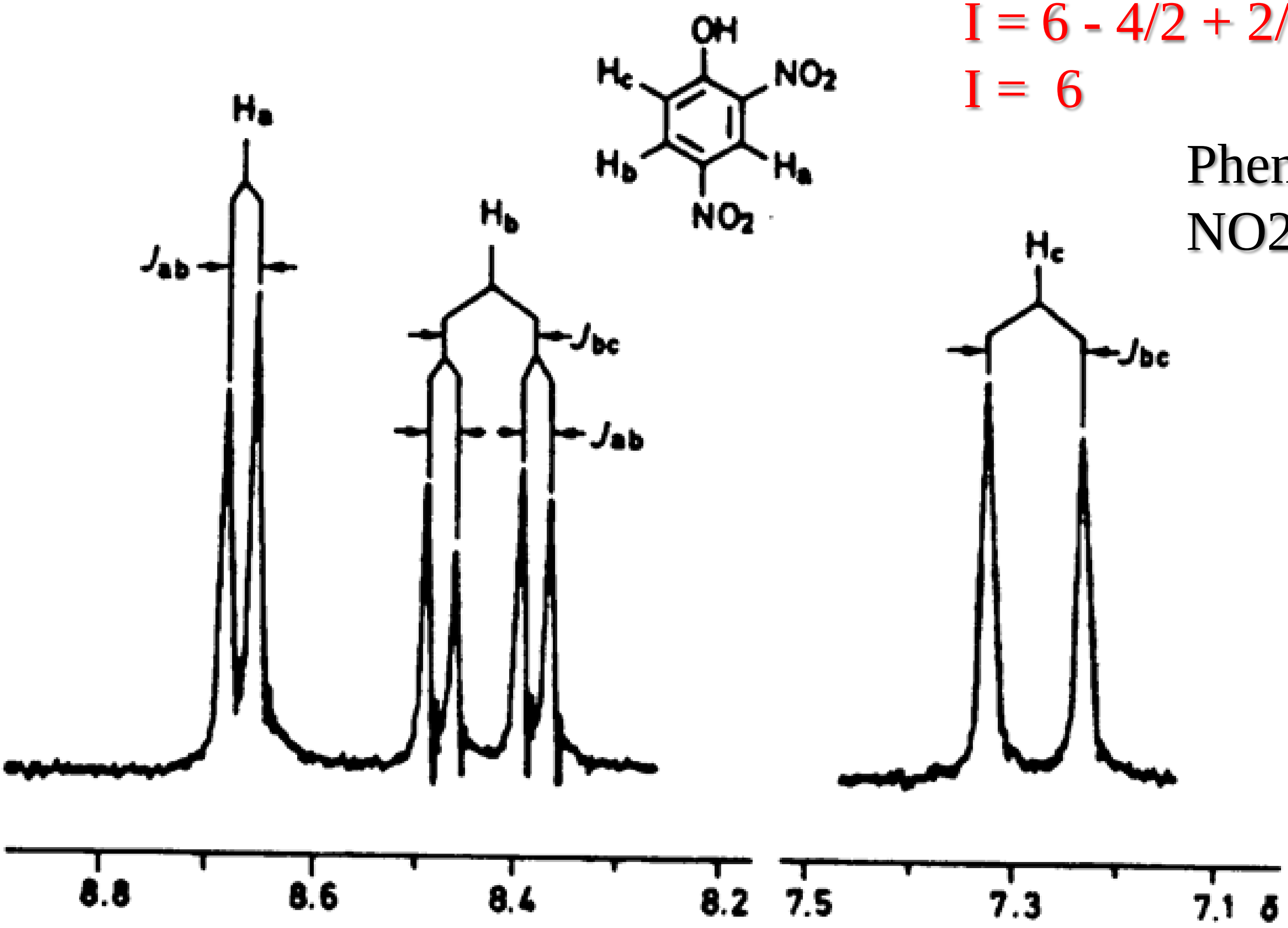
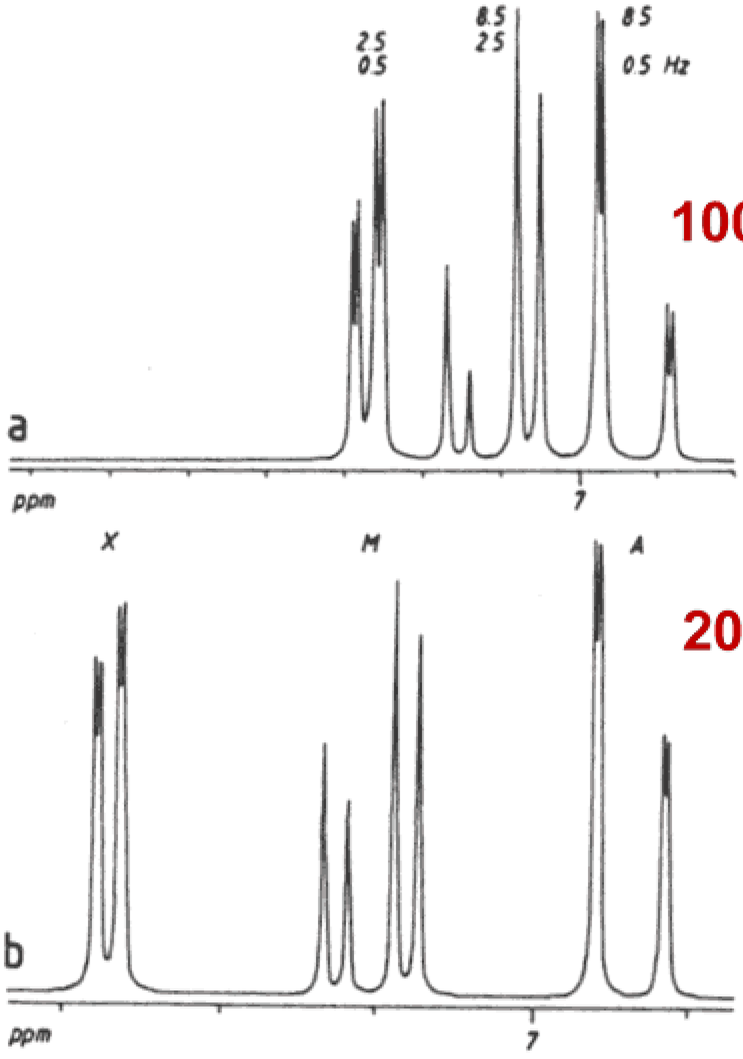


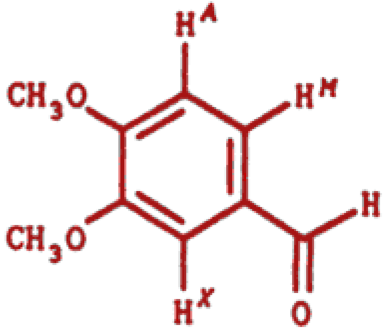
Figure 2.14 Signal splitting due to spin–spin coupling in the 100 MHz proton magnet resonance spectrum of 2,4-dinitrophenol. One finds J_{bc} = 9.1 Hz and J_{ab} = 2.8 Hz. J_{ac} is n observed (rule 4)

AMX



100 MHz

200 MHz



6

$^3J_{AM}$ = 8.5 (ortho)
$^4J_{MX}$ = 2.5 (meta)
$^5J_{AX}$ = 0.8 (para)

Fig. 2.7. ^1H NMR spectrum of 3,4-dimethoxybenzaldehyde (6) [aromatic shift range, $CDCl_3$, 25 °C, (a) 100 MHz (b) 200 MHz]

AFMX

C5 H4 N Br

I = 5 – 4/2 – 1/2 +1/2 +1

I = 4 (aromatic ring)

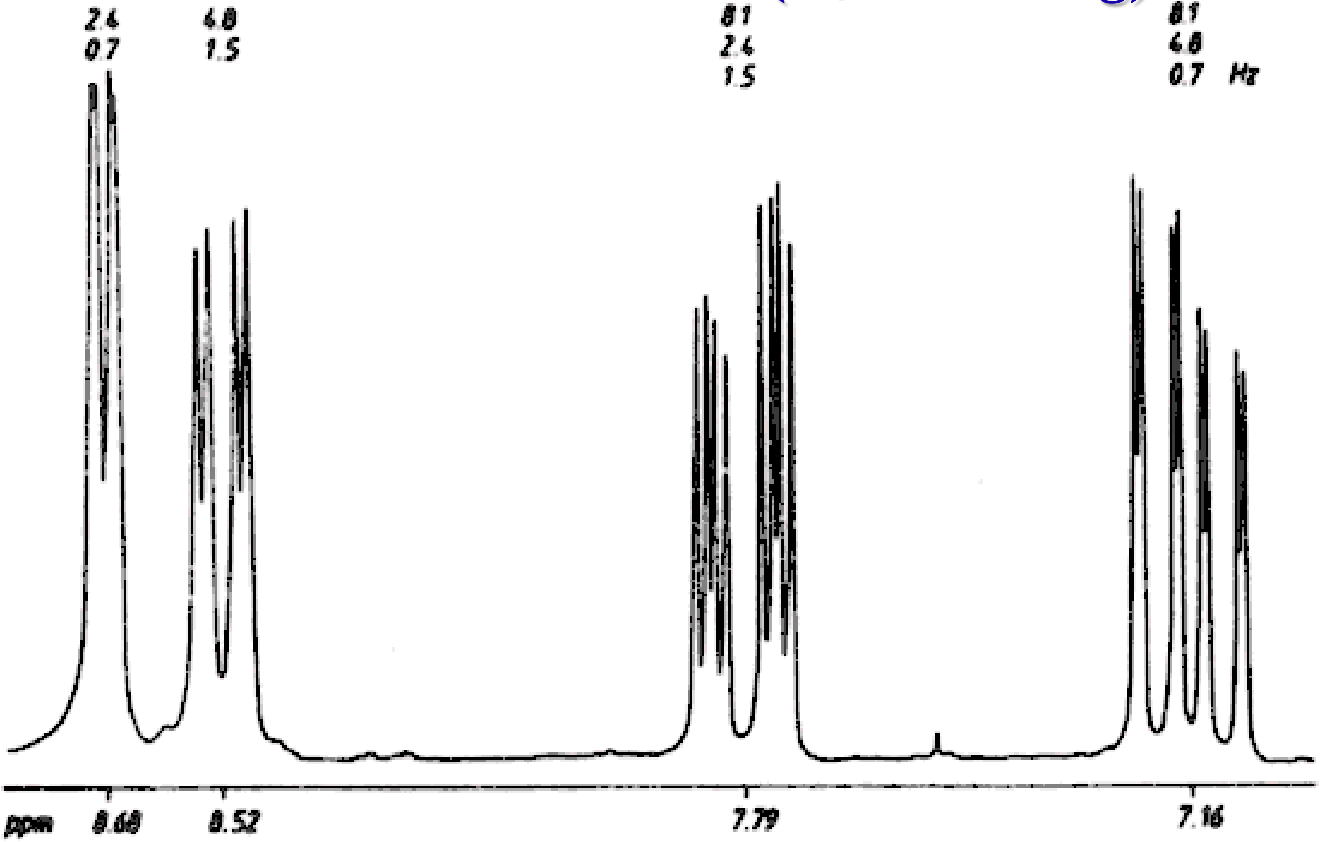
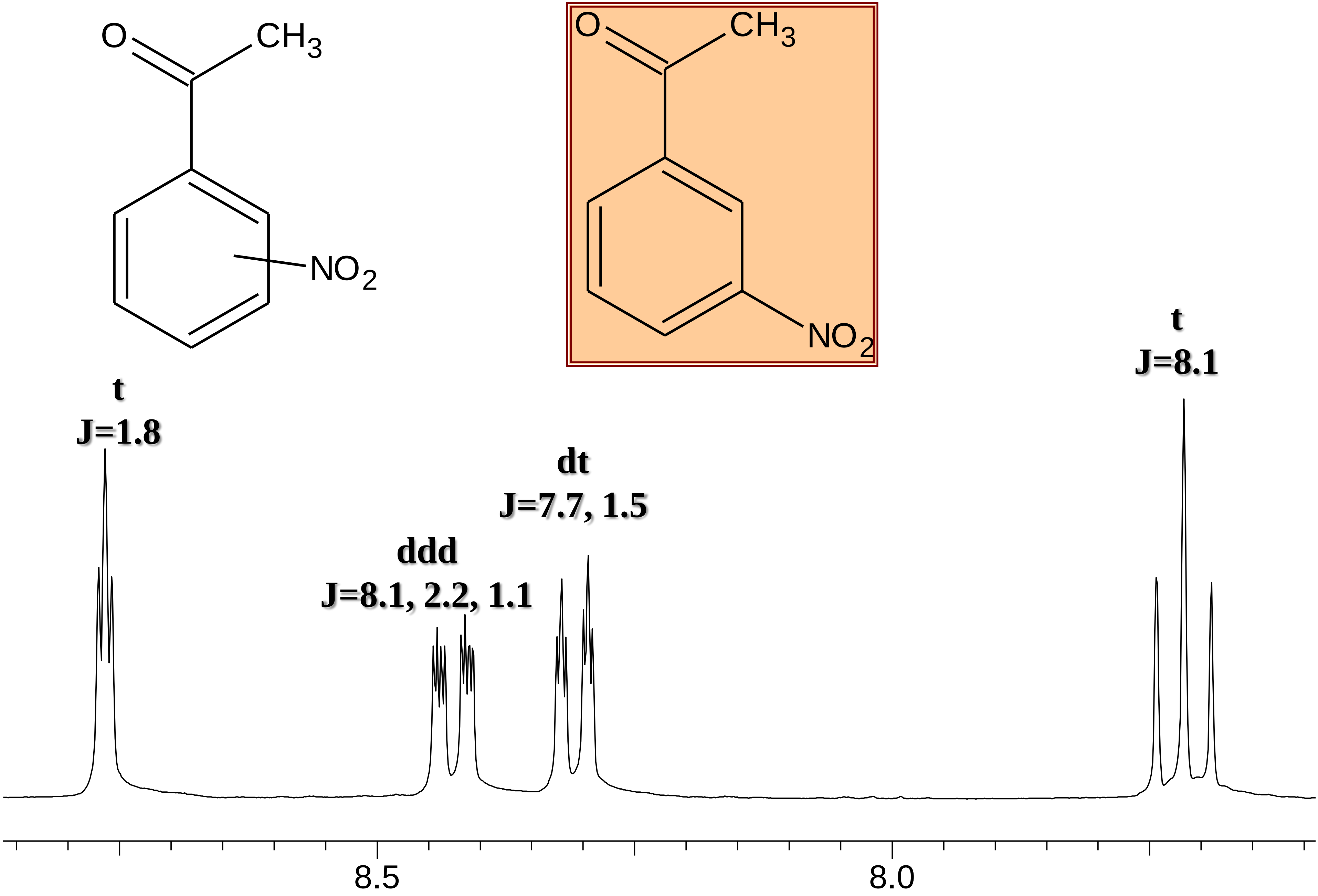


Fig. 2.8. ^{1}H NMR spectrum of 3-bromopyridine (8) ($CDCl_3$, 25 °C, 90 MHz)

δ

J

Aromatic substituent pattern



Aromatic substituent pattern