APPENDIX 2

^{1}H NMR Spectral parameters for substituted benzenes.

Most of the unknown carboxylic acids that you will work with are benzoic acid derivatives. Below is a brief introduction on the pattern of ^{1}H NMR of benzoic acids analogs.

The shielding constant σ from equation (6) is written as a sum of a diamagnetic contribution, σ_{dia}, and a paramagnetic contribution σ_{para}. When the magnetization induced by an external field causes an electronic current in the molecule that opposes the external field, the shielding constant is diamagnetic. Paramagnetic currents generate magnetic field that augment the external magnetic field.

In the vicinity of the benzene ring, the applied magnetic field is non-uniform (anisotropic). The benzene protons experience three magnetic fields: one strong due to the NMR magnetic field, and two weaker fields: 1) produced by the protons andvalence electrons, and 2) the anisotropic magnetic field produced by the π electron ring current.

In benzene, the protons resonate at δ=7.28 ppm. Compared with the resonance of protons attached to a double bond (as ethene: δ=5.28 ppm), the aromatic protons are considerably less shielded (see Fig. 4a). The π electrons of benzene can sustain large electronic currents. The magnetic field produced this way is shown below:

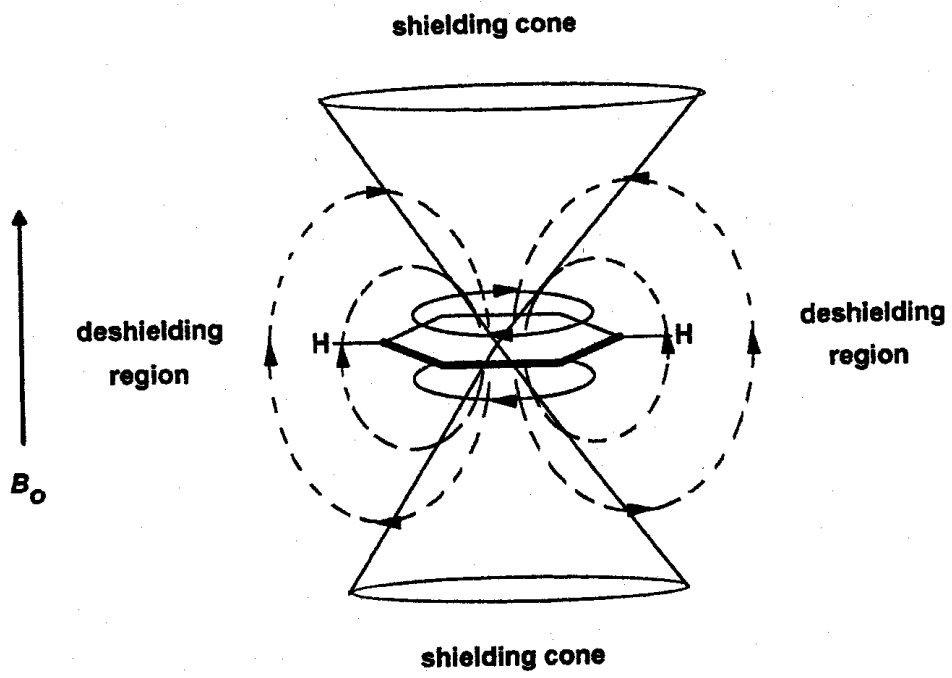
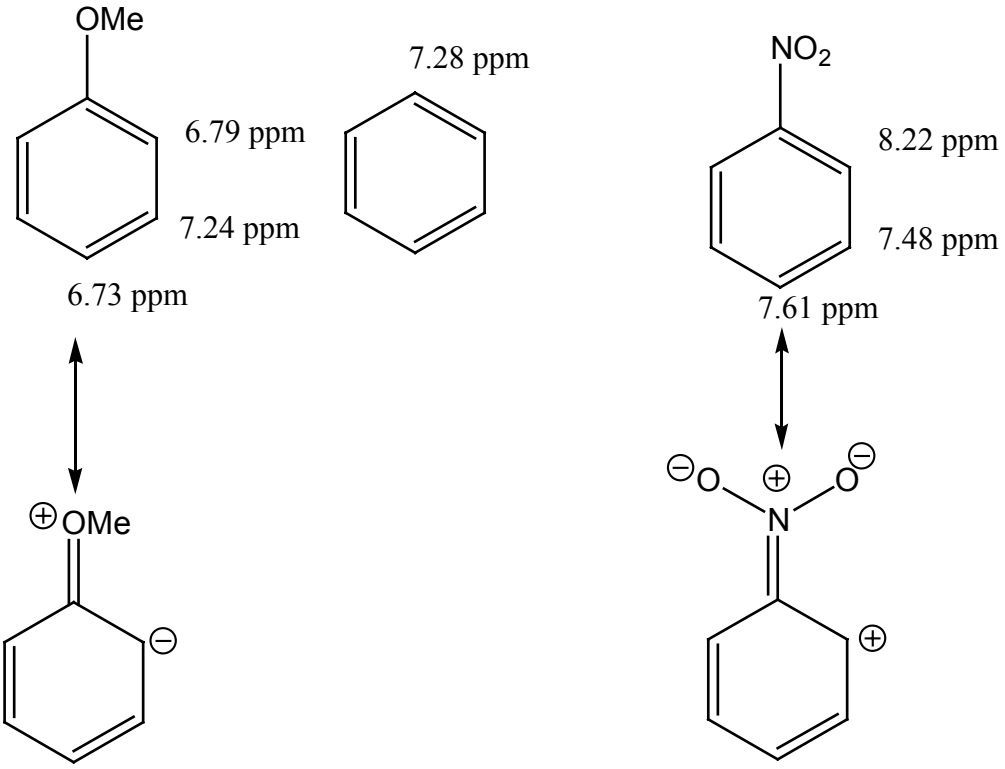


Fig. 1-Appendix. The external magnetic field B_o induces an anisotropic diamagnetic effect. Protons that fall into the deshielding region resonate at a lower field, while protons that experience the shielded cone resonate at higher fields.

Substituted benzenes.

Mesomeric effects dramatically influence the chemical shifts of the aromatic protons. An electron donating group such as MeO- (+M effect), increases the electron density in *o*- and *p*- positions. As result, the chemical shift of the *o*-proton (δ=6.79 ppm) and *p*- proton (δ=6.73 ppm) appear more shielded than the benzene proton (δ=7.28 ppm).



An electron withdrawing group (-M effect) such as NO_2, depletes the *o*- and *p*- positions of electron density. Clearly, the chemical shifts of these protons (*o*- δ=8.22 ppm and *p*- (δ=7.61 ppm) are more deshielded than those of benzene (δ=7.28 ppm).

Aromatic proton chemical shifts can be calculated empirically by adding the substituent parameters to the shift of benzene proton:

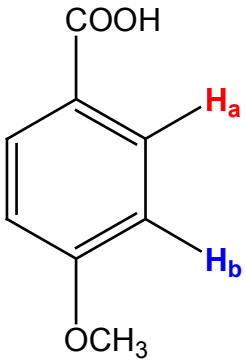
$$\delta = 7.27 + \sum_i \mathbf{S}_i \qquad \text{(1)-Appendix}$$

Equation (1)-Appendix is valid for any aromatic compound not having the substituents *ortho* to each other (steric crowding).

Table 1-Appendix. Substituent Parameters for Aromatic Proton Shifts

Substituent	S_{ortho}	S_{meta}	S_{para}
CH_3	-0.17	-0.09	-0.18
CH_3CH_2	-0.15	-0.06	-0.18
NO_2	0.95	0.17	0.33
Cl	0.02	-0.06	-0.04
Br	0.22	-0.13	-0.03
I	0.40	-0.26	-0.03
CHO	0.58	0.21	0.27
OH	-0.50	-014	-0.40
NH_2	-0.80	-0.25	-0.64
CN			
COOH	0.80	0.14	0.20
$COOCH_3$			
$COCH_3$	0.60	0.11	0.19
OCH_3	-0.43	-0.09	-0.38
$OCOCH_3$	-0.19	-0.03	-0.19
$N(CH_3)_2$	-0.67	-0.18	-0.66

Take as example the spectrum of 4-methoxybenzoic acid:



exp. calculated

8.08 δ_a=7.27+0.80-0.09=7.98 ppm

6.98 δ_b=7.27-0.43+0.14=6.98 ppm

Fig. 1. Experimental and calculated chemical shifts for H_a and H_b of 4-methoxybenzoic acid.

The observed resonance for H_a is at δ=8.08 ppm and that of H_b is at δ=6.98 ppm. The calculated chemical shifts (see Fig. 1) are δ_a=7.98 ppm and δ_b=6.98 ppm.

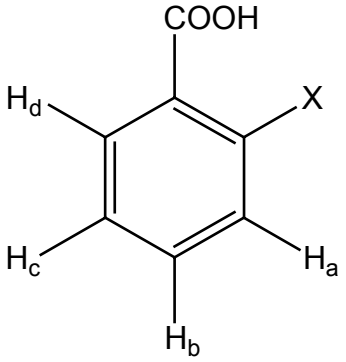
–Carboxylic Acid Proton

In solution most of the carboxylic acids exist as dimers or oligomers that are hydrogen bondedtogether. The acid proton resonates at δ=10-14 ppm. A convenient procedure to identify acidic protons is to add a few drops of D_2O (that is in a large molar excess versus the organic acid) to the $CDCl_3$ solution to replace all the acidic hydrogen atoms with deuterium atoms, which removes the signal. . Shake the NMR tube well and allow the layers to separate. The aqueous layer will separate out on top and is positioned above the receiver coil.

Coupling constants.

Typical magnitudes for coupling constants are: J_{ortho}=6.0-9.0 Hz, J_{meta}=1.0-3.0 Hz, J_{para}=0-1.0 Hz.

Ortho-substituted benzoic acids. If the X substituent is an electron donating group, then the most deshielded proton is H_d. If the X substituent is electron withdrawing, then the chemical shift of proton H_a is deshielded too.



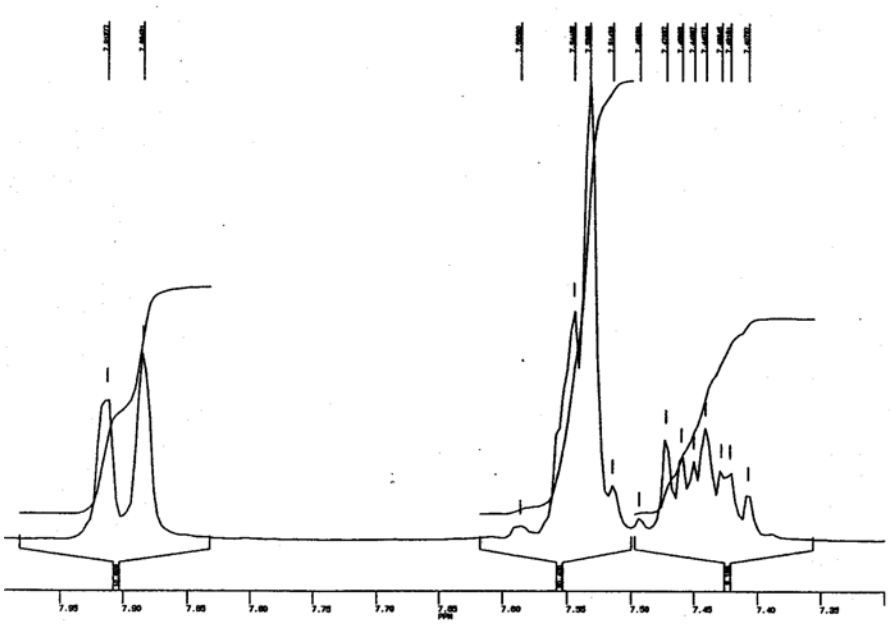
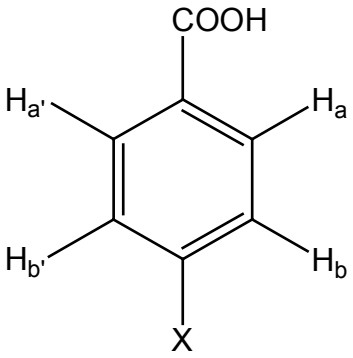


Fig. 1. The ^{1}H NMR for an ortho substituted benzoic acid (in d_6-acetone).

Chemical shift assignments:

δ_{Hd}= 7.898 ppm [calc. 8.01 see Table and eq. (1)-Appendix]
δ_{Hc}= 7.898 ppm [calc. 7.37 see Table and eq. (1)-Appendix]
δ_{Hc}= 7.898 ppm [calc. 7.35 see Table and eq. (1)-Appendix]
δ_{Hc}= 7.898 ppm [calc. 7.43 see Table and eq. (1)-Appendix]

Para-Disubstituted benzoic acids. Chemical shifts of H_a and $H_{a'}$ protons are around δ= 8 ppm. If the second substituent is electron donating, the chemical shifts of H_b and $H_{b'}$ are relatively shielded and deshielded. Note that H_a does not interact equally with H_b and $H_{b'}$. Therefore, H_b and $H_{b'}$ are magnetically nonequivalent. Similarly, H_a and $H_{a'}$ are magnetically nonequivalent because they interact differently with H_b, for example. This kind of spectrum is named AA'BB'.



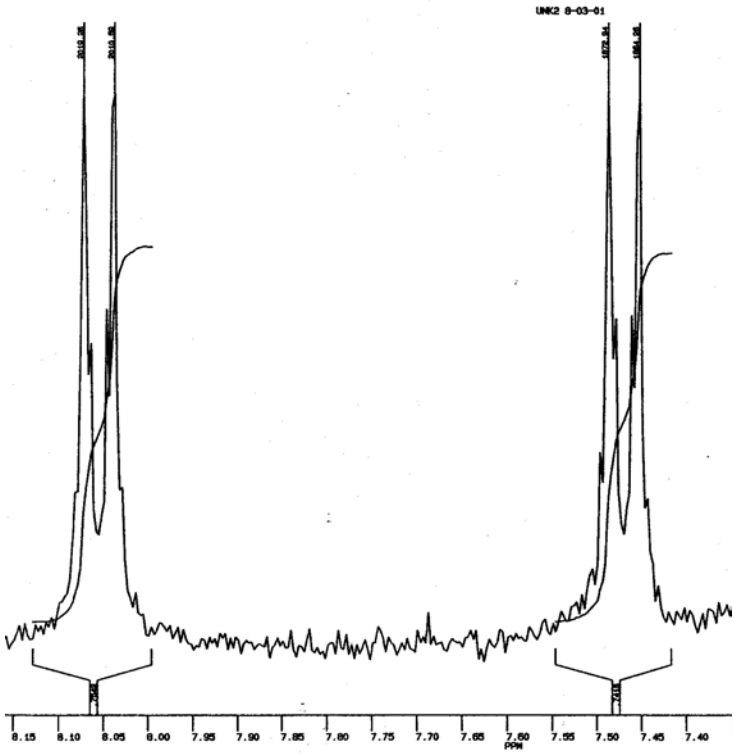
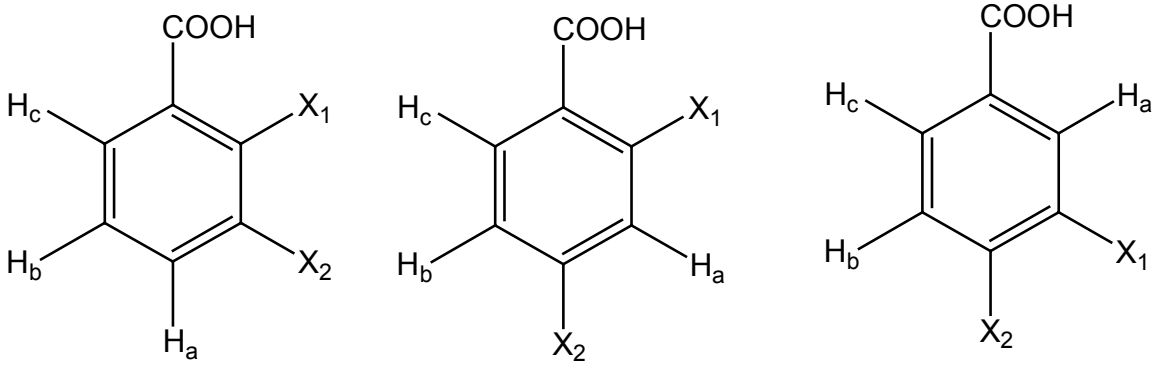


Fig. 2. The ^{1}H NMR for a para substituted benzoic acid (in d_6-acetone)

Disubstituted benzoic acids.

Some constitutional isomers for disubstituted benzoic acids are presented in structures **1**,**2** and **3**, respectively. The pattern of the ^{1}H NMR (chemical shift and coupling constant magnitude) for the three compounds differ and is structure dependent.



1 **2** **3**

For example, the ^{1}H NMR of a compound closely related to structure (X_1=X_2, moderate electron releasing group) is presented in fig. 3.

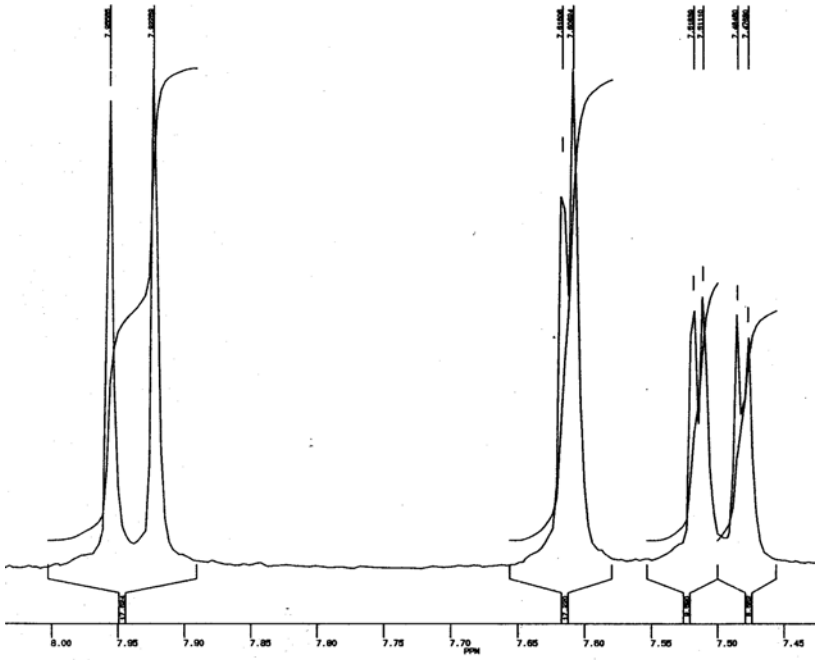


Fig. 3. The ^{1}H NMR for a 2,4-disubstituted benzoic acid (in d_6-acetone).

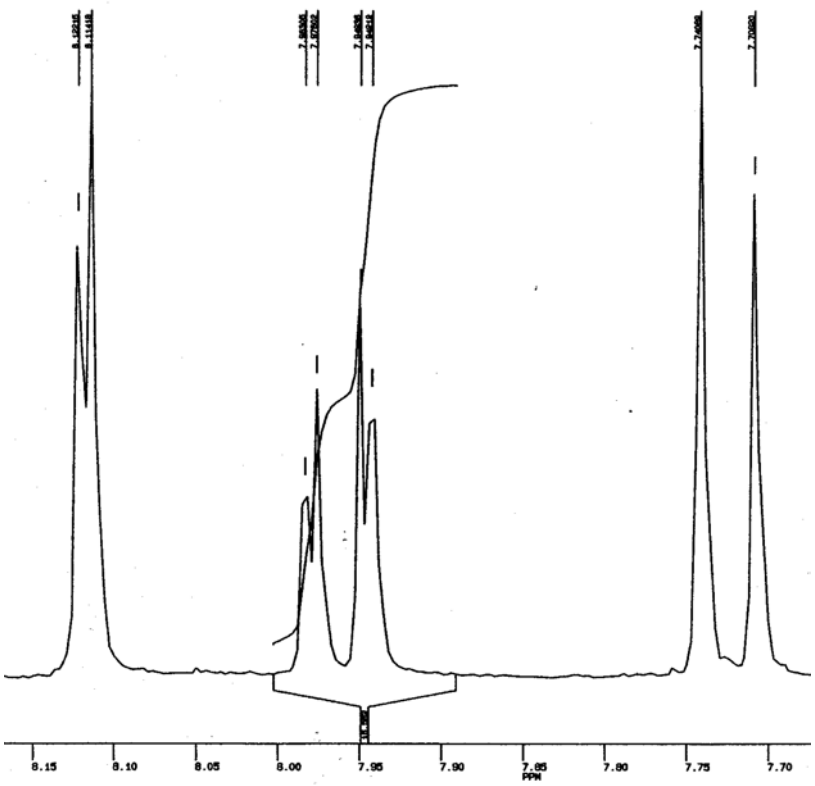


Fig. 4. The ^{1}H NMR for a 3,4-disubstituted benzoic acid (in d_6-acetone)