MAGNETIC RESONANCE IN CHEMISTRY, VOL. 27, 585–591 (1989)

Correlation of Carbon-13 Substituent-Induced Chemical Shifts: *meta*- and *para*-Substituted Methyl Benzoates

Miloš Buděšínský* and Otto Exner
Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Sciences, 166 10 Prague 6, Czechoslovakia

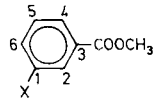
Carbon-13 NMR spectra are reported for 69 substituted methyl benzoates in deuteriochloroform or in its mixture with dimethyl sulphoxide-d_6. The substituent-induced chemical shifts (SCS) of the CO carbon correlate poorly with dual substituent parameters (DSP) in all possible modifications, and for *meta* derivatives in particular this correlation is both overparameterized and imprecise. A much better correlation was obtained with parameters (designated B^m, B^p and C^p) derived previously by principal component analysis (PCA) from a larger set. The SCS of the CH_3 carbon correlate very well with the original simple Hammett equation, and no DSP treatment is needed. The clustering of substituents is not consequential in such a large set.

KEY WORDS Methyl benzoates ^{13}C NMR Substituent effects

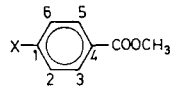
INTRODUCTION

Benzene derivatives represent an important model for studying ^{13}C substituent-induced chemical shifts (SCS), mainly because of their relationship to the Hammett equation and other linear free energy relationships (LFER) (see Refs 1–14 and references listed in a previous paper[3]). The dependence of SCS on structure has been mainly expressed by correlation with dual substituent parameters[15] (DSP), and more recently also by principal component analysis[3,13,14,16–18] (PCA) or by other types of correlations.[10,11,19–25] The use of the DSP treatment has been advocated[26–29] many times and only rarely has its failure[30] or a more profound criticism[17,31] been reported. We have studied a particularly large series of *meta*- and *para*-substituted benzonitriles and showed[3] that DSP analysis is not the best procedure, at least for an extra-annular carbon atom on a multiple bond. For *meta* derivatives the DSP treatment is both overparameterized and imprecise; even for *para* derivatives the fit is significantly worse than with PCA. The components determined by PCA bear some relationship to certain σ constants but also reveal specific deviations, ascribed to 'magnetic' effects.

In this work we have extended the investigation to *meta*- and *para*-substituted methyl benzoates, **1** and **2**, respectively, with 34 substituents. In addition to the experimental data we report here the SCS correlations of the CO and CH_3 carbons. The correlations of the intra-annular carbons will require yet another series to extend the current investigation.[14]



1



2

* Author to whom correspondence should be addressed.

EXPERIMENTAL AND RESULTS

The substituted methyl benzoates **1** and **2** were generally prepared from analytically pure benzoic acids with diazomethane in diethyl ether solution, and after evaporation of the solvent they were not purified further. The following compounds have not been previously characterized (or were now prepared in a different manner): methyl 3-phenoxymethylbenzoate, b.p. 130–133 °C/50 Pa, for $C_{15}H_{14}O_3$ calc. C 74.36, H 5.82, found C 74.32, H 5.85%; methyl 4-phenoxymethylbenzoate, m.p. 85 °C, found C 74.57, H 5.88%; methyl 3-phenylsulphonylmethylbenzoate, m.p. 107 °C, for $C_{15}H_{14}O_4S$ calc. C 62.06, H 4.86, S 11.04, found C 62.17, H 4.78, S 11.04%; methyl 4-phenylsulphonylmethylbenzoate, m.p. 174 °C (lit.[32] m.p. 177 °C), found C 61.88, H 5.00, S 10.89%; 3-methoxycarbonylbenzenesulphonyl fluoride, m.p. 65 °C, for $C_8H_7FO_4S$ calc. F 8.72, S 14.69, found F 8.99, S 14.45%; 4-methoxycarbonylbenzenesulphonyl fluoride, m.p. 84 °C, found F 8.88, S 14.87%; 3-methoxycarbonylbenzenesulphonyl chloride,[33] m.p. 68 °C; 4-methoxycarbonylbenzenesulphonyl chloride, m.p. 69 °C, for $C_8H_7ClO_4S$ calc. C 40.95, H 3.01, S 13.66, found C 41.34, H 3.02, S 13.52%. Most of the parent benzoic acids had been previously characterized,[34,35] and 4-carboxybenzenesulphonyl chloride was prepared according to the literature.[36] 3-methoxycarbonylbenzoyl chloride, (oil, not distilled) was prepared from 1,3-benzenedicarboxylic acid monomethyl ester and thionyl chloride (refluxed only to dissolution), and 4-methoxycarbonylbenzoyl chloride, m.p. 55 °C, was prepared in the same way.

0749-1581/89/060585–07 $05.00

Received 23 November 1988
Accepted 18 January 1989

Table 1. ^{13}C NMR chemical shifts of *meta*-substituted methyl benzoates in deuteriochloroform

Substituent	C-1	C-2	C-3	C-4	C-5	C-6	C=O	OCH_3	Other carbons
H	128.35	129.58	130.24	129.58	128.35	132.88	167.07	52.04	—
H[a]	128.32	129.39	130.06	129.39	128.32	132.88	166.76	51.94	—
CH_3	138.12	130.13	130.13	126.73	128.25	133.64	167.25	51.98	CH_3 21.23
$CH_2C_6H_5$	140.46	130.02	130.39	127.42	128.51	133.48	167.07	51.98	CH_2 41.71; C_6H_5 141.47 (1'), 128.85 (2', 6'), 128.56 (3', 5'), 126.28 (4')
$CH_2SO_2C_6H_5$	128.67	131.91	130.64	129.93	128.72	135.13	162.26	52.20	CH_2 62.47; C_6H_5 137.78 (1'), 128.58 (2', 6'), 129.04 (3', 5'), 133.88 (4')
CF_3 [b]	131.18 (33.1)	126.60 (4.0)	131.14	132.85	129.11	129.47 (3.7)	165.80	52.51	CF_3 123.77 (272.1)
CH_2Cl	137.90	129.65	130.74	129.53	128.88	132.96	166.53	52.21	CH_2Cl 45.50
CH_2Br	138.21	130.06	130.80	129.51	128.94	133.41	166.44	52.21	CH_2Br 32.43
$CH_2OC_6H_5$	137.61	128.49	130.52	129.10	128.67	131.82	166.83	52.12	CH_2O 69.36; C_6H_5 158.57 (1'), 114.88 (2', 6'), 129.52 (3', 5'), 121.16 (4')
C_6H_5	141.47	127.72	130.73	128.24[c]	128.82	131.47	166.99	52.12	C_6H_5 140.10 (1'), 127.13 (2', 6'), 128.87 (3', 5'), 128.33 (4')[c]
$COCH_3$	137.37	129.53	130.75	133.86	128.84	132.28	166.24	52.37	CO 197.12; CH_3 26.67
COC_6H_5	137.98	130.93	130.44	132.77	128.59	134.02	166.21	52.34	CO 195.62; C_6H_5 137.07 (1'), 130.01 (2', 6'), 128.47 (3', 5'), 133.15 (4')
COOH[a]	131.44	130.91	130.46	133.48	128.50	134.00	166.29[c]	52.23	COOH 167.68[c]
$COOCH_3$	130.73	130.66	130.73	133.78	128.61	133.78	166.22	52.34	—
COCl	133.73	132.35	131.38	135.04	129.31	135.98	165.40	52.65	COCl 167.67
CN	113.03	133.27	131.48	133.64	129.45	135.96	165.08	52.69	CN 117.85
F[b]	162.60 (247.3)	116.52 (23.0)	132.40 (7.5)	125.33 (3.2)	130.01 (7.7)	119.98 (21.3)	165.95	52.35	—
Cl	134.55	129.68	131.94	127.70	129.68	132.92	165.83	52.35	—
Br	122.45	132.61	132.11	128.14	129.92	135.84	165.70	52.37	—
I	93.75	138.43	132.01	128.68	129.99	141.67	165.43	52.33	—
OH	156.13	116.47	131.20	121.81	129.75	120.54	[d]	52.44	—
OCH_3	159.64	114.11	131.53	121.99	129.39	119.43	166.92	52.09	OCH_3 55.37
OCH_2CH_3	158.97	114.72	131.47	121.86	129.35	119.97	167.00	52.10	OCH_2 63.70; CH_3 14.75
$OCOCH_3$	150.69	122.86	131.71	126.97	129.43	126.27	166.13	52.25	CO 169.14; CH_3 20.98
NH_2	146.71	115.73	131.11	119.53	129.24	119.40	167.35	51.99	—
$N(CH_3)_2$	150.47	113.19	130.81	117.53	128.97	116.73	167.72	51.92	$N(CH_3)_2$ 40.45
$NHCOCH_3$	139.29	120.58	130.47	124.37	128.78	124.19	166.76	52.00	CO 169.17; CH_3 24.20
NO_2	148.34	124.54	131.94	135.27	129.73	127.39	164.93	52.80	—
NCS	131.97	126.79	131.88	128.17	129.69	129.69	165.61	52.46	NCS[e]
$N{=}NC_6H_5$	152.48[c]	124.04	129.12	131.63	129.12	126.88	166.49	52.28	C_6H_5 152.61[c] (1'), 123.02 (2', 6'), 129.12 (3', 5'), 131.39 (4')
SCH_3	139.37	127.58	130.78	126.06	128.69	130.78	166.61	52.15	SCH_3 15.63
SO_2CH_3	141.31	128.51	131.66	134.51	129.73	131.36	165.20	52.65	SO_2CH_3 44.36
SO_2NH_2 [a]	144.28	127.25	130.82	132.59	129.07	130.27	165.59	52.42	—
SO_2F	134.13	130.05	133.61	136.29	129.59	132.15	164.60	52.90	—
SO_2Cl	144.82	128.10	132.14	135.94	130.10	130.72	164.59	52.90	—
Aza	—	150.94	126.07	137.00	123.27	153.44	165.72	52.38	—

[a] A mixture of $CDCl_3$ with DMSO-d_6 (10%) was used as solvent.
[b] J(CF) values are given in parentheses.
[c] The signal assignments can be interchanged.
[d] Values shift with increasing concentration from 167.51 to 167.97 ppm.
[e] The signal was not observed (probably owing to a long relaxation time).

The ^{13}C NMR spectra were recorded on a Varian XL-200 FT-NMR spectrometer (at 50.3 MHz) in deuteriochloroform or in its mixture with 10% dimethyl sulphoxide-d_6, as previously described.[3] The results are given in Tables 1 and 2. Linear regressions were carried out with a free fitted intercept but its values are not given in Tables 3 and 4.

DISCUSSION

The CO carbon

All the compounds were included in the correlations with two exceptions: OH and Aza substituents. The

Table 2. ^{13}C NMR chemical shifts of *para*-substituted methyl benzoates in deuteriochloroform

Substituent	C-1	C-2 C-6	C-3 C-5	C-4	C=O	OCH_3	Other carbons
H	132.88	128.35	129.58	130.24	167.07	52.04	—
H[a]	132.88	128.32	129.39	130.06	166.76	51.94	—
CH_3	143.51	129.06	129.61	127.51	167.14	51.88	CH_3 21.61
$CH_2C_6H_5$	146.49	128.91	129.80	128.13	166.94	51.89	CH_2 41.89; C_6H_5 140.09 (1'), 128.91 (2', 6'), 128.57 (3', 5'), 126.34 (4')
$CH_2SO_2C_6H_5$	133.93	130.83	129.75	130.56	166.49	52.24	CH_2 62.71; C_6H_5 137.75 (1'), 128.61 (2', 6'), 129.03 (3', 5'), 133.93 (4')
CF_3 [b]	134.52 (32.8)	125.45 (3.8)	130.04	133.47 (1.2)	165.90	52.53	CF_3 123.71 (272.6)
CH_2Cl	142.25	128.45	130.00	130.15	166.53	52.17	CH_2Cl 45.35
CH_2Br	142.61	128.99	130.05	130.09	166.46	52.17	CH_2Br 32.55
$CH_2OC_6H_5$	142.36	126.95	129.88	129.71	166.83	52.10	CH_2O 69.32; C_6H_5 158.50 (1'), 114.90 (2', 6'), 129.55 (3', 5'), 121.24 (4')
C_6H_5	145.65	127.03	130.10	128.91	166.96	52.07	C_6H_5 140.03 (1'), 127.27 (2', 6'), 128.91 (3', 5'), 128.12 (4')
$COCH_3$	140.30	128.20	129.83	133.95	166.20	52.44	CO 197.44; CH_3 26.84
$CO-C_6H_5$	141.35	129.49	129.74	133.25	166.26	52.41	CO 195.91; C_6H_5 137.00 (1'), 130.07 (2', 6'), 128.45 (3', 5'), 132.90 (4')
COOH[a]	134.93	129.67	129.37	133.58	166.30	52.30	COOH 167.58
$COOCH_3$	133.96	129.55	129.55	133.96	166.18	52.38	—
COCl	136.63	131.17	130.00	135.93	165.59	52.71	COCl 167.85
CN	116.45	132.23	130.11	133.98	165.41	52.70	CN 117.93
F[b]	165.79 (253.8)	115.51 (22.0)	132.14 (9.3)	126.51 (2.9)	166.11	52.15	—
Cl	139.38	128.71	130.98	128.71	166.18	52.23	—
Br	128.02	131.71	131.11	129.10	166.32	52.25	—
I	100.65	137.73	131.02	129.67	166.57	52.25	—
OH	160.39	115.33	131.98	122.26	167.54	52.09	—
OCH_3	163.37	113.63	131.59	122.68	166.84	51.81	OCH_3 55.40
OCH_2CH_3	162.79	114.07	131.58	122.45	166.86	51.76	OCH_2 63.68; CH_3 14.68
$OCOCH_3$	154.34	121.59	131.15	127.74	166.29	52.16	CO 168.78; CH_3 21.11
NH_2	150.90	113.80	131.60	119.72	167.17	51.57	—
$N(CH_3)_2$	153.33	110.73	131.25	117.08	167.46	51.44	$N(CH_3)_2$ 40.03
$NHCOCH_3$	142.42	118.99	130.76	125.48	166.78	52.04	CO 169.06; CH_3 24.62
NO_2	150.61	123.55	130.73	135.55	165.17	52.83	—
NCS	135.75	125.63	131.05	128.74	165.88	52.34	NCS[c]
$N=N-C_6H_5$	155.16	122.63	130.60	131.83	166.49	52.28	C_6H_5 152.60 (1'), 123.14 (2', 6'), 129.16 (3', 5'), 131.66 (4')
SCH_3	145.42	125.01	129.88	126.36	166.83	51.98	SCH_3 14.87
SO_2CH_3	144.35	127.49	130.54	134.91	165.42	52.73	SO_2CH_3 44.32
SO_2NH_2 [a]	147.57	126.14	129.92	132.94	165.66	52.44	—
SO_2F	137.03	128.53	130.73	136.56	164.92	52.96	—
SO_2Cl	147.49	127.07	130.85	136.11	164.89	52.95	—
Aza	—	150.65	122.83	137.30	165.52	52.66	—

[a] A mixture of $CDCl_3$ with DMSO-d_6 (10%) was used as solvent.
[b] J(CF) values are given in parentheses.
[c] The signal was not observed (probably owing to a long relaxation time).

latter is evidently different in character and deviates in all correlations (see Figs 1 and 2); in addition, the values of the σ constants are uncertain.[39] For methyl 3-hydroxybenzoate, its association in solution is revealed by the strong concentration dependence of its CO shifts (Table 1). The formation of a 14-membered ring with two hydrogen bonds was established by IR spectroscopy for 3-hydroxyacetophenone[40] and ethyl 4-methyl-3-hydroxybenzoate.[41] Although methyl 4-hydroxybenzoate behaves normally, we eliminated the OH substituent completely. A similar dimerization is also possible with the 3-COOH substituent, but the low solubility of 3-methoxycarbonylbenzoic acid prevented us from studying the concentration dependence. The corresponding point seems to deviate in Figs 1 and 2, but the statistical characteristics of the correlations are not affected.

Table 3 confirms the results obtained previously[3] on substituted benzonitriles. The Hammett equation in its original form, Eqn (1), is evidently invalid, mainly because of the unequal slopes for the *meta* and *para* derivatives. Separate correlation for the *meta* derivatives is better, but it is still far from the required precision. The DSP treatment, Eqn (2), does not bring any improvement, in spite of the increased number of parameters. By far the best fit was obtained with new

Table 3. Regression analysis of the ^{13}C SCS values in substituted methyl benzoates, the $\underline{C}OOCH_3$ carbon atom[a]

Type of regression	Substituents	Explanatory variables	Regression coefficients		s^b	r^c	n
Hammett	*meta* + *para*	$\sigma_{m,p}$	−1.907		0.338	0.887	65
Hammett	*meta*	σ_m	−2.924		0.253	0.949	33
Hammett	*meta*	σ_m	−3.175		0.234	0.966	16
DSP	*meta*	σ_I, σ_R^0	−3.102	−0.938[d]	0.254	0.951	33
DSP	*meta*	σ_I, σ_R^0	−3.327	−1.063[d]	0.234	0.968	16
DSP	*meta*	σ_I, σ_R^+	−3.060	−0.510[d]	0.226	0.963	32
DSP	*meta*	σ_I, σ_R^+	−3.157	−0.478	0.198	0.977	16
DSP	*meta*	σ_I, σ_R^0 corr[e]	−3.418	−1.083[d]	0.240	0.957	33
Afanas'ev[f]	*meta*	σ^*, σ^r	−1.072	−0.644	0.283	0.957	14
PCA const.[g]	*meta*	B^m	−2.968		0.055[h]	0.998[h]	14
PCA const.[g]	*meta*	D^m	−3.319		0.160	0.985	13
Hammett	*para*	σ_p	−1.501		0.267	0.917	33
Hammett	*para*	σ_p	−1.446		0.256	0.932	16
Yukawa–Tsuno	*para*	σ_p, $\Delta\sigma_p^+$	−2.007	0.876 (r − 0.44)	0.236	0.940	31
DSP	*para*	σ_I, σ_R^0	−2.408	−1.158	0.169	0.968	33
DSP	*para*	σ_I, σ_R^0	−2.431	−1.121	0.122	0.986	16
DSP	*para*	σ_I, σ_R^{Bz}	−2.438	−0.832	0.181	0.964	32
DSP	*para*	σ_I, σ_R^+	−2.413	−0.454	0.196	0.958	32
DSP	*para*	σ_I, σ_R^0 corr[e]	−2.715	−1.104	0.174	0.966	33
DSP	*para*	σ_I, σ_R^0 corr[e]	−2.699	−1.066	0.131	0.984	16
Afanas'ev[f]	*para*	σ^*, σ^r	−0.825	−0.551	0.191	0.970	14
DSP-NLR[i]	*para*	σ_I, σ_R^0	−2.341	−1.316 (ε 1.34)	0.177	0.968	33
DSP-NLR	*para*	σ_I, σ_R^0	−2.406	−1.473 (ε 0.51)	0.111	0.989	16
PCA const.[g]	*para*	B^p, C^p	−2.608	−0.032[d,j]	0.127	0.973	14
PCA const.[g]	*para*	D^p, E^p	−1.883	0.409[k]	0.305	0.918	13
meta–para[l]	*para vs. meta*	δ^m	0.849		0.045	0.998	15

[a] The broader set consisted of all substituents except OH and Aza (n = 33, see Discussion), and the narrower set only of substituents for which original values of σ_I and σ_R (Ref. 15) are available (n = 16); the remaining constants are from Ref. 37. The latter set is listed only if there is an important difference. No data are excluded for *a posteriori* grounds.
[b] Standard deviation in ppm.
[c] Correlation coefficient (absolute value) or multiple correlation coefficient.
[d] The corresponding partial correlation coefficient $|r| < 0.8$.
[e] Values from Refs 34 and 37.
[f] Ref 30, improved values of σ^* and σ^r.
[g] Regression with components obtained previously by PCA of eight series (Ref. 3).
[h] Without iodine the regression is improved to s = 0.031, r = 0.9995.
[i] Reference 38.
[j] The term is insignificant at any confidence level.
[k] The term is insignificant at α = 0.05.
[l] Without donor substituents and without $COCH_3$, COC_6H_5, COOH, $COOCH_3$; with the latter four substituents the correlation is slightly worse (s = 0.053, r = 0.997).

constants, designated B^m, derived by PCA on eight series.[3] These constants, valid for the α-carbon on an α,β-multiple bond, seem to incorporate some effects, specific for SCS, due to which some substituents (Br, I, SCH_3, CF_3, OC_6H_5, COR) have often been excluded from the correlations.[17,20,21,38,42,43] Nevertheless, some deviations are still observable (see footnote h in Table 3); this shows that our model is obviously local in terms of the recent discussion.[44,45] Since PCA yielded the B^m values for only 13 substituents, we calculated additional mean values from the series of nitriles[3] and methyl benzoates (Table 5). Although they are similar to the common σ_m values, some differences are sufficient to improve the fit significantly. The greatest deviations are observed for I, $N(CH_3)_2$, SO_2NH_2, COOH, $N{=}NC_6H_5$ and $CH_2SO_2C_6H_5$ substituents, but not for other substituents with an additional benzene ring which could modify the SCS through the ring current. These differences are probably not due to solvent effects as they cannot be qualitatively explained by particular constants[21] valid for chloroform solution.

$$\delta_{m,p} = \delta^0 + \rho\sigma_{m,p} \quad (1)$$

$$\delta_m = \delta^0 + \rho_I{}^m\sigma_I + \rho_R{}^m\sigma_R \quad (2a)$$

$$\delta_p = \delta^0 + \rho_I{}^p\sigma_I + \rho_R{}^p\sigma_p \quad (2b)$$

$$\delta_p = \delta^0 + \rho_I{}^p\sigma_I + \rho_R{}^p\sigma_R/(1 - \varepsilon\sigma_R) \quad (3)$$

With *para* substituents the results are less clear as they depend more on the size of the sample set. For a narrower set several correlations are of comparable quality: DSP, its non-linear extension[38] [DSP-NLR, Eqn (3)] or B^p and C^p constants[3] from PCA. The merit of the last correlation is not so evident as the regression

Table 4. Regression analysis of the ^{13}C SCS values in substituted methyl benzoates, the COOC̲H$_3$ carbon atom[a]

Type of regression	Substituents	Parameters	Regression coefficients		s^b	r^c	n
Hammett	*meta* + *para*	$\sigma_{m,p}$	0.966		0.053	0.986	65
Hammett	*meta*	σ_m	1.025		0.056	0.979	33
DSP	*meta*	σ_I, σ_R^0	0.993	0.491[d]	0.057	0.979	32
DSP	*meta*	σ_I, σ_R^+	1.001	0.189[d]	0.071	0.967	32
DSP	*meta*	σ_I, σ_R^0 corr[e]	1.118	0.478[d]	0.056	0.980	33
Afanas'ev[f]	*meta*	σ^*, σ^r	0.332	0.213	0.067	0.976	14
PCA const.[g]	*meta*	B^m	0.862		0.078	0.959	14
PCA const.[g]	*meta*	D^m	1.055		0.018	0.998	13
Hammett	*para*	σ_p	0.939		0.047	0.992	33
Hammett	*para*	σ_p	0.907		0.039	0.996	16
Yukawa–Tsuno	*para*	σ_p, $\Delta\sigma_p^+$	0.978	−0.071[d,j] (r − 0.07)	0.047	0.993	31
DSP	*para*	σ_I, σ_R^0	0.994	1.099	0.046	0.993	33
DSP	*para*	σ_I, σ_R^0	1.016	1.075	0.037	0.996	16
DSP	*para*	σ_I, σ_R^{Bz}	1.024	0.805	0.049	0.992	32
DSP	*para*	σ_I, σ_R^+	0.993	0.446	0.078	0.979	32
DSP	*para*	σ_I, σ_R^0 corr[e]	1.282	1.050	0.057	0.989	33
Afanas'ev[f]	*para*	σ^*, σ^r	0.223	0.458	0.077	0.986	14
DSP-NLR[i]	*para*	σ_I, σ_R^0	1.021	0.963 (ε − 0.36)	0.044	0.994	30
PCA const.[g]	*para*	B^p, C^p	1.090	0.266	0.053	0.993	14
PCA const.[g]	*para*	D^p, E^p	1.001	−0.107[d,k]	0.061	0.991	13
meta–para[a]	*para vs. meta*	δ^m	1.117		0.031	0.997	15

[a–j] See footnotes in Table 3.
[k] Insignificant at α = 0.025.
[l] Without donor groups and without $COCH_3$, COC_6H_5, COOH, $COOCH_3$; with the latter four the correlation is slightly worse (s = 0.039, r = 0.993).

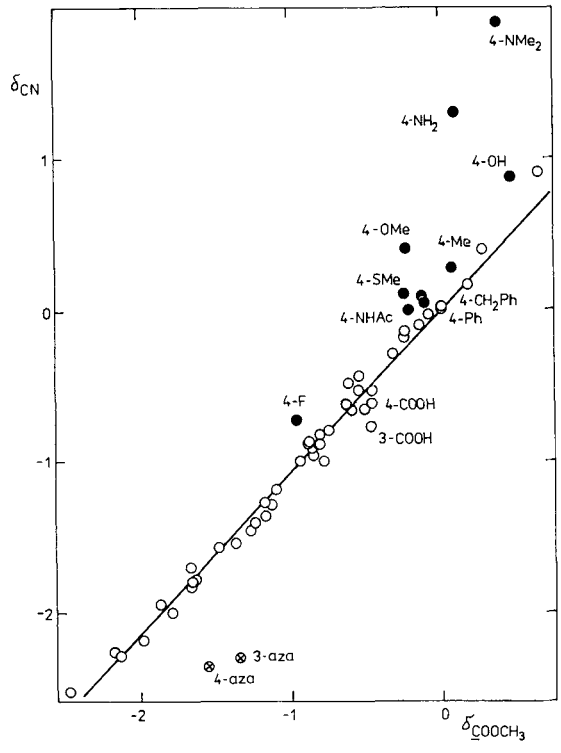


Figure 1. Comparison of the SCS of the α-carbon atoms in the two series methyl benzoates and benzonitriles; ○, all *meta* derivatives and *para* acceptors; ●, *para* donors; ⊗, aza substituent.

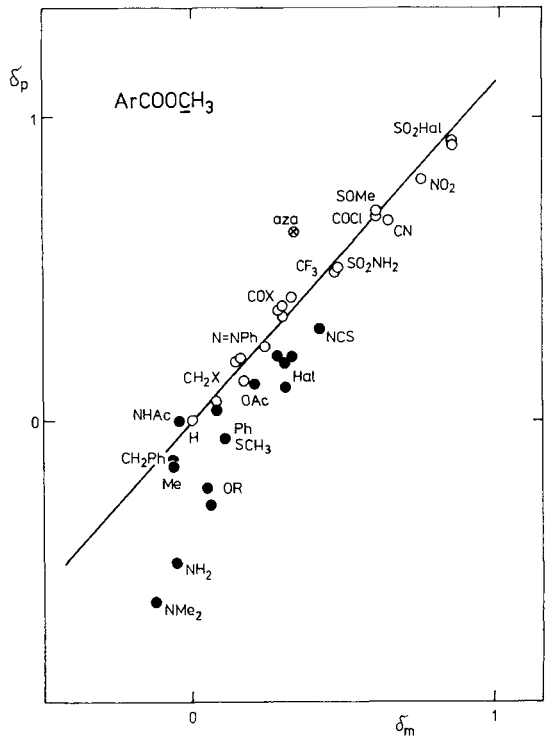


Figure 2. Comparison of SCS of the $COOCH_3$ carbon atom in methyl benzoates: the *meta–para* plot; designation of points as in Fig. 1.

Table 5. Substituent parameters describing the ^{13}C SCS on the α-carbon atom of an α,β-double bond[a]

Substituent	B^m	B^p	C^p	Substituent	B^m	B^p	C^p
H	0	0	0	$NHCOCH_3$	0.09	(0.11)	(−0.32)
CH_3	−0.061	−0.005	−0.357	NCS	(0.49)	(∼0.45)	(0)
$CH_2C_6H_5$	0.00	(0.05)	(∼−0.2)	$N{=}NC_6H_5$	(0.19)	0.22	0[c]
$CH_2OC_6H_5$	0.07	(0.09)	(∼−0.1)	NO_2	0.710	0.710	0[b]
$CH_2SO_2C_6H_5$	0.27	0.23	0[c]	OH	(0.05)	(−0.18)	(−0.35)
CH_2Cl	0.17	0.20	(∼−0.05)	OCH_3	0.021	0.096	−0.964
CH_2Br	0.20	0.22	(∼−0.05)	OCH_2CH_3	(0.02)	—	—
CF_3	0.431	0.463	0[b]	$OCOCH_3$	0.31	0.31	(∼0)
C_6H_5	0.02	(0.04)	(−0.20)	SCH_3	0.16	0.09	−0.39
$COCH_3$	0.268	0.347	0.091	SO_2CH_3	0.60	0.63	0[c]
COC_6H_5	0.28	0.30	(∼0.05)	SO_2NH_2	0.39	0.42	0[c]
COOH	(0.23)	(0.19)	(∼0.08)	SO_2F	(0.80)	0.81	0[c]
$COOCH_3$	0.285	0.307	0.094	SO_2Cl	(0.80)	0.81	0[c]
$COOCH_2CH_3$	(0.28)	(0.29)	(0.08)	F	0.371	0.359	−0.652
COCl	0.53	(0.56)	0[c]	Cl	0.421	0.378	−0.401
CN	0.681	0.615	0[b]	Br	0.453	0.351	−0.266
NH_2	−0.093	−0.038	−1.535	I	0.492	0.340	−0.463
$N(CH_3)_2$	−0.236	−0.133	−1.898	Aza	(∼0.6)	—	—

[a] Values from PCA (Ref. 3) are given to 3 places of decimals, although this does not express the actual 'precision;' average values from two series are given to two places of decimals, and values from one series or estimates are in parentheses.
[b] Zero values obtained by rounding off.
[c] Zero values assumed.

coefficient for C^p is near to zero just in the case of methyl benzoates. The variability of this coefficient, or of ρ_R, has been explained by variable proportions of the local and direct polarization.[3] This variability is caused exclusively by donor substituents, as can be seen from a *meta* vs. *para* plot (not shown); if restricted to acceptors the fit exceeds all other correlations in precision (Table 3, bottom). Further proof follows from a comparison of the two series, methyl benzoates and benzonitriles (Fig. 1). Fadhil and Godfrey[46] recently advocated separation of donors and acceptors, placing each group on a separate straight line, and the *meta* and *para* derivatives together. According to our more extensive plot, all the meta derivatives together with *para* acceptors lie on a common straight line with high accuracy, whereas *para* donors deviate but do not define an additional line. When two series which are even more similar are compared, for example, methyl benzoates and ethyl benzoates,[47] all points are situated on a straight line with unit slope (not shown); the root mean square deviation of 0.046 is probably mainly due to the experimental error and can be taken as the lower limit for any correlation. The separation of acceptors and donors is also observed in Table 5, where we have attempted to calculate provisional values of B^p and C^p from the available data, assuming that $C^p = 0$ for strong acceptors. Although imprecise, these values allow a clearer recognition of the separation of substituents into classes than that observed previously.[48] The four classes of acceptors, donors, alkyls and halogens are evident in a plot C^p vs. B^p (not shown); nevertheless, some of them are spread over a large area and cannot be considered as clusters. According to common methods of cluster analysis, the OCH_3 substituent and the NH_2–$N(CH_3)_2$ pair form separate clusters, a further four clusters being the halogens, stronger donors, strong acceptors and a cluster containing weak acceptors, weak donors and alkyls together. These results are sensitive to the exact values of B^p and C^p. In our opinion, such a clustering cannot invalidate the results of PCA or linear regression analysis.

The CH_3 carbon

As expected according to its distance, the ^{13}C shifts of this carbon are less sensitive to substitution. Nevertheless, the correlations are both simpler and more precise, in spite of the less favourable ratio to the experimental error. The simple Hammett equation, Eqn (1), holds well with a common slope for *meta* and *para* substituents, and no efficient refinement was found (Table 4). Note, for example, the equal values of ρ_I and ρ_R in the attempted DSP treatment, or the insignificant value of ε in the DSP-NLR variant. The positive ρ value is in agreement with the proposed general rules[49] and possibly with the much discussed principle of charge alteration.[50] One could even suggest this CH_3 carbon as a secondary standard for estimating σ constants, but the values would not be more precise than those from pK values in mixed solvents.

In conclusion, the SCS of more distant and nonconjugated carbon atoms are more regular and can be expressed by a single constant which does not require any DSP treatment. This means that the Hammett equation holds as long as its original range of validity[51] is strictly retained.

Acknowledgement

Thanks are due to Mrs P. Marešovská for skilful preparative work.

REFERENCES

1. D. J. Craik and R. T. C. Brownlee, *Prog. Phys. Org. Chem.* **14**, 1 (1983).
2. H.-O. Kalinowski, S. Berger and S. Braun, *^{13}C NMR-Spektroskopie*, Ch. 3.3 and 3.4. Georg Thieme, Stuttgart (1984).
3. O. Exner and M. Buděšínský, *Magn. Reson. Chem.* **27**, 27 (1989).
4. W. F. Reynolds, R. H. Kohler and G. K. Hamer, *Tetrahedron Lett.* 4671 (1976).
5. W. Adcock, W. Kitching, V. Alberts, G. Wickham, P. Barron and D. Doddrell, *Org. Magn. Reson.* **10**, 47 (1977).
6. V. I. Glukhikh and M. G. Voronkov, *Dokl. Akad. Nauk SSSR* **248**, 142 (1979).
7. K. Suda, T. Tsujimoto and M. Yamauchi, *Bull. Chem. Soc. Jpn.* **60**, 3607 (1987).
8. C. N. Robinson, J. L. Horton, D. O. Fosheé, J. W. Jones, S. H. Hanissian and C. D. Slater, *J. Org. Chem.* **51**, 3535 (1986).
9. R. Noto, L. Lamartina, C. Arnone and D. Spinelli, *J. Chem. Soc., Perkin Trans. 2* 887 (1988).
10. I. Danihel, P. Kristian, S. Böhm and J. Kuthan, *Chem. Zvesti* **38**, 539 (1984).
11. F. Guillaume, J. P. Seguin, L. Nadjo, R. Uzan, F. Membrey and J. P. Doucet, *J. Chem. Soc., Perkin Trans. 2* 1139 (1984).
12. D. A. R. Happer and B. E. Steenson, *J. Chem. Soc., Perkin Trans. 2* 19 (1988).
13. H. M. Hutton, K. R. Kunz, J. D. Bozek and B. J. Blackburn, *Can. J. Chem.* **65**, 1316 (1987).
14. D. Johnels, U. Edlund, E. Johansson and M. Cocchi, *J. Chem. Soc., Perkin Trans. 2*, submitted.
15. S. Ehrenson, R. T. C. Brownlee and R. W. Taft, *Prog. Phys. Org. Chem.* **10**, 1 (1973).
16. U. Edlund and S. Wold, *J. Magn. Reson.* **37**, 183 (1980).
17. D. Johnels, U. Edlund, H. Grahn, S. Hellberg, M. Sjöström, S. Wold, S. Clementi and W. J. Dunn, *J. Chem. Soc., Perkin Trans. 2* 863 (1983).
18. N. Inamoto and S. Masuda, *Chem. Lett.* 1007 (1982).
19. M. Schindler, *J. Am. Chem. Soc.* **109**, 5950 (1987).
20. D. A. R. Happer and B. E. Steenson, *J. Chem. Soc., Perkin Trans. 2* 843 (1983).
21. D. A. R. Happer, *J. Chem. Soc., Perkin Trans. 2* 1673 (1984).
22. C. Yijima, T. Tsujimoto, K. Suda and M. Yamauchi, *Bull. Chem. Soc. Jpn.* **59**, 2165 (1986).
23. E. Barchiesi, S. Bradamante and G. A. Pagani, *J. Chem. Soc., Perkin Trans. 2* 1091 (1987).
24. F. Membrey and E. Steiner, *Spectrochim. Acta, Part A* **43**, 593 (1987).
25. F. Membrey and J. P. Doucet, *J. Chim. Phys.* **73**, 1024 (1976).
26. W. F. Reynolds, P. Dais, D. W. MacIntyre, G. K. Hamer and I. R. Peat, *J. Magn. Reson.* **43**, 81 (1981).
27. S. Datta, A. De, S. P. Bhattacharyya, C. Medhi, A. K. Chakravarty, J. S. A. Brunskill, S. Fadoujou and K. Fish, *J. Chem. Soc., Perkin Trans. 2* 1599 (1988).
28. D. A. R. Happer, *Aust. J. Chem.* **29**, 2607 (1976).
29. D. J. Craik, R. T. C. Brownlee and M. Sadek, *J. Org. Chem.* **47**, 657 (1982).
30. I. B. Afanas'ev, *J. Chem. Soc., Perkin Trans. 2* 1589 (1984).
31. F. A. Bottino, G. Musumarra and Z. Rappoport, *Magn. Reson. Chem.* **24**, 31 (1986).
32. J. I. DeGraw, P. H. Christie, E. G. Brown, L. F. Kelly, R. L. Kisliuk, Y. Gaumont and F. M. Sirotnak, *J. Med. Chem.* **27**, 376 (1984).
33. H. Meerwein, G. Dittmar, R. Gollner, K. Hafner, F. Mensch and O. Steinfort, *Chem. Ber.* **90**, 841 (1957).
34. O. Exner, *Collect. Czech. Chem. Commun.* **31**, 65 (1966).
35. O. Exner and E. Svátek, *Collect. Czech. Chem. Commun.* **36**, 534 (1971).
36. Y. Tashika, Y. Nitta and J. Yomoda, *J. Chem. Soc. Jpn.* **74**, 1193 (1954).
37. O. Exner, *Correlation Analysis of Chemical Data*, Ch. 2.2, 5.1 and 5.2. Plenum Press, New York (1988).
38. J. Bromilow, R. T. C. Brownlee, D. J. Craik, M. Sadek and R. W. Taft, *J. Org. Chem.* **45**, 2429 (1980).
39. Reference 37. Ch. 4.3.
40. Š. Kováč and G. Eglinton, *Tetrahedron* **25**, 3599 (1969).
41. Š. Kováč, M. Dandárová and A. Piklerová, *Tetrahedron* **27**, 2831 (1971).
42. D. A. Dawson and W. F. Reynolds, *Can. J. Chem.* **53**, 373 (1975).
43. J. Bromilow, R. T. C. Brownlee, D. J. Craik and M. Sadek, *Magn. Reson. Chem.* **24**, 862 (1986).
44. B. Eliasson, D. Johnels, S. Wold, U. Edlund and M. Sjöström, *Acta Chem. Scand., Ser. B* **41**, 291 (1987).
45. M. J. Kamlet, R. M. Doherty, G. R. Famini and R. W. Taft, *Acta Chem. Scand., Ser. B* **41**, 589 (1987).
46. G. F. Fadhil and M. Godfrey, *J. Chem. Soc., Perkin Trans. 2* 133 (1988).
47. J. Bromilow, R. T. C. Brownlee, D. J. Craik, P. R. Fiske, J. E. Rowe and M. Sadek, *J. Chem. Soc., Perkin Trans. 2* 753 (1981).
48. S. Aluni, S. Clementi, U. Edlund, D. Johnels, S. Hellberg, M. Sjöström and S. Wold, *Acta Chem. Scand., Ser. B* **37**, 47 (1983).
49. R. G. Jones and G. Allen, *Org. Magn. Reson.* **19**, 196 (1982).
50. J. Klein, *Tetrahedron* **44**, 503 (1988).
51. Reference 37, Ch. 2.5.