CARBON-13 SUBSTITUENT-INDUCED CHEMICAL SHIFTS: MONOSUBSTITUTED BENZENE DERIVATIVES

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Carbon-13 NMR spectra of twelve monosubstituted benzene derivatives were measured in deuterochloroform. Together with the literature data a set of 35 systematically chosen substituents was obtained on which some thirty correlation equations were tested. As anticipated only substituent chemical shifts (SCS) in the position 4 are controlled by inductive and resonance effects, and can be correlated by dual substituent parameters (DSP). For the other positions DSP were not successful and more sophisticated equations are not much telling. On the other hand, the direct relations between two series of SCS are usually more precise and simple to understand. It is concluded that SCS in benzene ring need not be controlled by too complex mechanism but simply by different factors than by inductive and resonance effects.

Benzene derivatives represent a classical model for defining and evaluating substituent effects[1,2]. In the field of ^{13}C substituent induced chemical shifts (SCS) both extraannular and intraannular carbon atoms have been used as probe by many authors[2-4]; a more complete bibliography was given in our previous communications[5-7]. The most widespread interpretation is correlation with dual substituent parameters[8] (DSP), Eq. (*1*). It can yield some information as far as the relative importance of inductive and resonance effects is concerned[9,10], it was advocated several times as the most efficient approach[11,12], and was also refined to account for the variable electron demand[9] (DSP-NLR, non-linear resonance), Eq. (*2*). Nevertheless, we have challenged[5] this approach as overparametrized (particularly for meta derivatives) and sometimes insufficiently precise. This follows immediately from comparison with principal component analysis (PCA) which yields a better fit with less parameters: for the proof[5-7] longer series of compounds were needed and more systematic choice of substituents than usual. Untill now PCA was carried out only on a restricted series for extraannular carbon atoms[5], and in addition on many monó derivatives for intraannular atoms[13]. A more fundamental DSP approach would require several series of disubstituted compounds with different constant groups: to date two long series are available with a constant acceptor group[5,6] (CN and $COOCH_3$) and one with a constant donor group[7] (NH_2). The series of mono derivatives (constant group H) is in our opinion so important that we decided to

complete the available experimental material to be comparable with the mentioned series. In the present work we started from an extensive study of Glukhikh and Voronkov[14], checked the compatibility with our measurements, and measured further compounds with substituents used in the previous work[5-7]. In this way a data set was obtained, measured in two laboratories in the same solvent ($CDCl_3$) and under identical conditions. It is more reliable than in the previous DSP treatment[13] where data from a review[15], measured in two solvents, were used.

$$\delta = \delta^0 + \varrho_I\sigma_I + \varrho_R\sigma_R \qquad (1)$$

$$\delta = \delta^0 + \varrho_I\sigma_I + \varrho_R\sigma_R/(1 - \varepsilon\sigma_R) \qquad (2)$$

$$\delta = \delta^0 + \varrho_I\sigma_I + \varrho_R\sigma_R + \varrho_X X \quad (X = I, O, M) \qquad (3)$$

$$\sigma_{I,R} = a(\delta_m - \delta^0) + b(\delta_p - \delta^0) \qquad (4)$$

$$\delta = \delta^0 + \varrho_I\sigma_I + \varrho_d\sigma_d + \varrho_e\sigma_e \qquad (5)$$

$$\delta = \delta^0 + \varrho_I\sigma_I + \varrho_R\sigma_R + \varrho_E\sigma_E \qquad (6)$$

SCS of monosubstituted benzenes gave us also the opportunity to test several new theories on a long series of consistent data. Two of these theories were suggested just for ^{13}C shifts in benzene derivatives: one extending the DSP equation by an additional term[16] (EDSP), Eq. (*3*), the other combining two experimental data values (in the *meta* and *para* position, respectively) in one equation[14], Eq. (*4*). Two further correlations are general and were derived from reactivity data[17,18] (three-parameter equations, 3PE): while σ_I, σ_d, and σ_e in Eq. (*5*) were derived successively from models and theoretical considerations[17], σ_I, σ_R, and σ_E in Eq. (*6*) were obtained[18] at once from PCA. Still another correlation[19] cannot be described by a simple equation, better by a graph, since it assumes a bilinear dependence (two straight lines or say a curve passing over into its two asymptotes).

EXPERIMENTAL

Proton decoupled ^{13}C NMR spectra were recorded in deuteriochloroform under the same conditions as previously reported[5]. ^{13}C chemical shifts, relative to internal TMS, are listed in Table I. The SCS, relative to benzene, are given in Table II. They are based partly on our measurements from Table I, partly on a selected data of ref.[14], the selection was carried out to get a similar set as used in our previous work[5-7]. The compatibility of the two data series was tested on three compounds denoted in Table I and on benzene: there is a systematic shift of 0·02 ppm (which is cancelled in the SCS) and root-mean-square deviation of 0·029 ppm. The latter value does not include the NH_2 derivative which shows worse reproducibility as already described[7]. There is a worse agreement between ref.[14] and the values from a review[15] considered as most reliable ("class A"): 0·09 ppm in the positions 2—4, twice more in the position 1.

The linear regression was carried out as previously[5] with a freely fitted intercept, but the values of the intercept were not significant and are not given. Of many correlations carried out only those are listed in Table III which are of some relevance to the following discussion.

RESULTS AND DISCUSSION

We discussed several times[5-7,20] the reasons why some substituents are to be eliminated from the correlations. In our opinion this should be done with great responsibility, only if the reasons are quite evident. One such reason was dimerization in solution[6], spectroscopically proven, another is the less reliable values of constants σ. For the latter reason we excluded in this work the substituents $OCOCH_3$ and NCS as previously[5,7,20] but they are included in the mutual correlations of SCS, not involving any σ. On the other hand, the basic data set was broadened in the

TABLE I

Carbon-13 chemical shifts in some monosubstituted benzenes in deuteriochloroform

Substituent	C-1	C-2	C-3	C-4	Other carbons
H	128·35	128·35	128·35	128·35	—
H[a]	128·29	128·29	128·29	128·29	—
$CH_2C_6H_5$	141·01	128·91	128·43	126·04	CH_2: 41·95
$CH_2OC_6H_5$	137·13	127·44	128·55	127·90	CH_2O: 69·95, C_6H_5: 158·83(1′); 114·90(2′, 6′); 129·46(3′, 5′); 120·94(4′)
$CH_2SO_2C_6H_5$	128·15	130·80	128·62	128·73	CH_2: 62·91, C_6H_5: 137·94(1′); 128·55(2′, 6′); 128·85(3′, 5′); 133·66(4′)
COOH	129·39	130·23	128·48	133·81	COOH: 172·54
$COOCH_3$[b]	130·24	129·58	128·35	132·88	C=O: 167·07, CH_3: 52·04
$COOCH_2CH_3$	130·60	129·55	128·31	132·78	CO: 166·60, OCH_2: 60·92, CH_3: 14·34
CN[c]	112·45	132·12	129·14	132·79	CN: 118·81
$OCH_2C_6H_5$	158·83	114·90	129·46	120·94	OCH_2: 69·95, C_6H_5: 137·13(1′); 127·44(2′, 6′); 128·55(3′, 5′); 127·90(4′)
NH_2[d]	146·40	115·08	129·25	118·48	—
$NHCOCH_3$	138·05	120·17	128·89	124·28	CO: 168·92, CH_3: 24·38
NCS	131·30	125·68	129·51	127·25	NCS: 135·54
$N{=}NC_6H_5$	152·69	122·83	129·05	130·93	—
$SO_2CH_2C_6H_5$	137·94	128·55	128·85	133·66	CH_2: 62·91, C_6H_5: 128·15(1′); 130·80(2′, 6′); 128·62(3′, 5′); 128·73(4′)
SO_2NH_2[a]	143·54	126·00	128·74	131·86	—

[a] The mixture of $CDCl_3$ with CD_3SOCD_3 (10%) was used as solvent; [b] ref.[6]; [c] ref.[5]; [d] ref.[7].

TABLE II

Substituent effects in ^{13}C NMR spectra of monosubstituted benzenes[a]

Substituent	C-1	C-2	C-3	C-4
H	0	0	0	0
CH_3	9·41	0·73	−0·07	−2·96
$CH_2C_6H_5$	12·75	0·56	0·08	−2·31
$CH_2OC_6H_5$	8·78	−0·91	0·20	−0·45
$CH_2SO_2C_6H_5$	−0·20	2·45	0·27	0·38
CH_2Cl	9·13	0·16	0·28	−0·08
CF_3	2·68	−2·96	0·56	3·57
C_6H_5	12·88	−1·23	0·35	−1·17
$COCH_3$	8·89	−0·06	0·19	4·63
COC_6H_5	9·19	1·58	−0·16	3·94
COOH	1·04	1·88	0·13	5·46
$COOCH_3$	1·89	1·23	0·00	4·53
$COOCH_2CH_3$	2·25	1·18	−0·04	4·43
COCl	4·88	3·01	0·63	6·99
CN	−15·90	3·77	0·79	4·44
F	34·87	−12·91	1·72	−4·28
Cl	5·97	0·26	1·33	−1·96
Br	−5·86	3·12	1·59	−1·58
I	−34·02	8·98	1·70	−1·11
OH	26·57	−12·86	1·43	−7·26
OCH_3	31·41	−14·38	1·11	−7·70
OCH_2CH_3	30·73	−13·83	1·05	−7·84
$OCH_2C_6H_5$	30·48	−13·45	1·11	−7·41
$OCOCH_3$	22·55	−6·73	1·02	−2·62
NH_2	18·05	−13·27	0·90	−9·87
$N(CH_3)_2$	22·27	−15·74	0·65	−11·74
$NHCOCH_3$	9·70	−8·18	0·54	−4·07
NO_2	19·95	−4·92	1·05	6·35
NCS	2·95	−2·67	1·16	−1·10
$N{=}NC_6H_5$	24·34	−5·52	0·70	2·58
SCH_3	10·14	−1·75	0·38	−3·44
SO_2CH_3	12·28	−1·15	0·97	5·28
$SO_2CH_2C_6H_5$	9·59	0·20	0·50	5·31
SO_2NH_2	15·25	−2·29	0·45	3·57
SO_2F	4·72	0·08	1·54	7·51
SO_2Cl	15·82	−1·52	1·42	7·07

[a] From data of Table I and of ref.[14].

TABLE III
Correlation of ^{13}C SCS in monosubstituted benzenes

	Correlation	Explanatory variables	Regression coefficients			s^a	R^b
	C-1:						
1	DSP	σ_I σ_R^0	6·52[c]	−28·58[c]		12·50 (31)	0·468
2		σ_I σ_R^+	7·64[c]	−12·85[c]		12·39 (31)	0·482
3	EDSP	σ_I σ_R^0 I	9·42	−37·36	0·981	1·54 (13)	0·9966
4		σ_R^0 I	−35·28	0·943		2·66 (14)	0·989
5	δ–δ	δ_{C1} (anilines)	0·994[d]			0·39 (25)	0·9996
6		δ_{C1} (nitriles)	1·01[d]			0·89 (26)	0·998
	C-2:						
7	DSP	σ_I σ_R^0	−4·71[c]	21·55[e]		4·22 (31)	0·764
8		σ_I σ_R^+	−5·70[c]	9·86[e]		3·91 (31)	0·801
9	EDSP[f]	σ_R^0 O	21·62	1·01		0·88 (13)	0·994
10	δ–δ	δ_{C2} (anilines)	0·980[d]			0·99 (25)	0·989
11		δ_{C2} (nitriles)	0·959			0·65 (26)	0·995
	C-3:						
12	DSP	σ_I σ_R^0	2·35	−1·74		0·28 (31)	0·879
13		σ_I σ_R^+	2·26[e]	−0·63[e]		0·35 (31)	0·800
14	EDSP	σ_I σ_R^0 M	1·84	−1·42	0·811	0·12 (13)	0·989
15		σ_R^0 M	−0·821[c]	1·46		0·39 (14)	0·860
16	δ–δ	δ_{C3} (anilines)	1·17			0·14 (24)[g]	0·967
17		δ_{C3} (nitriles)	0·784			0·27 (26)	0·881
18	Eq. (*4*), ref.[14]	σ_I δ_{C4}	2·81	−0·083[e]		0·30 (31)	0·860
19		σ_R^0 δ_{C4}	−8·04	0·324		0·32 (31)	0·839
	C-4:						
20	DSP	σ_I σ_R^0	5·90	19·85		0·68 (31)	0·992
21		σ_R^0	21·80			1·32 (32)	0·970
22		σ_I σ_R^+	5·78[e]	8·33		1·38 (31)	0·968
23	DSP-NLR	σ_I σ_R^+	5·90	19·83	(ε −0·006)	0·69 (30)	0·992
24	3PE[h]	σ_I σ_d σ_e	5·71	1·58	5·44[c]	0·61 (22)	0·994
25		σ_I σ_d	5·95	16·03		0·67 (23)	0·991
26	3PE[i]	σ_I σ_R	5·77	19·75		0·67 (14)[i]	0·990
27	δ–δ	δ_{F4} (fluorobenzenes)[j]	0·654			0·79 (18)[j]	0·994
28		δ_{C4} (anilines)	1·07			0·24 (25)	0·9989
29		δ_{C4} (nitriles)	1·03			0·36 (25)[k]	0·998

TABLE III
(*Continued*)

Correlation	Explanatory variables		Regression coefficients		s^a	R^b
Others:						
30 σ_I, Eq. (*4*), ref.[14]	δ_{C3}	δ_{C4}	0·259	0·027	0·092 (31)[l]	0·902
31 σ_R^0, Eq. (*4*), ref.[14]	δ_{C3}	δ_{C4}	−0·086	0·041	0·033 (31)[l]	0·991
32 Differences between laboratories					0·029[m]	

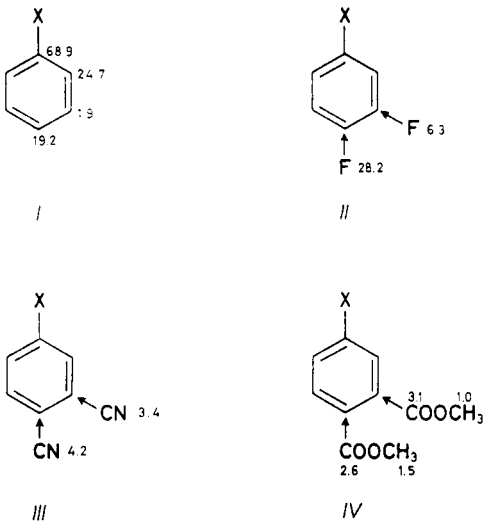
[a] Standard deviation in ppm (in parentheses degrees of freedom); [b] multiple correlation coefficient or absolute value of the simple correlation coefficient; [c] partial correlation coefficient less than 0·5 (absolute value); [d] not significantly different from unity; [e] partial correlation coefficient less than 0·8 (absolute value); [f] the term with σ_I excluded as insignificant according to the *t*-test ($\alpha = 0{\cdot}05$); [g] substituent COC_6H_5 eliminated, with it *s* would increase to 0·23; [h] ref.[17], the term with σ_e still significant according to the *t*-test ($\alpha = 0{\cdot}05$); [i] ref.[18], the term with σ_E excluded as insignificant according to the *t*-test, substituent OCH_3 eliminated — with it *s* would increase to 1·67; [j] ref.[21], in tetrachlormethane; substituents CN and $N(CH_3)_2$ eliminated, with them *s* would increase to 1·02; [k] substituent $NHCOCH_3$ eliminated, with it *s* would increase to 0·44; [l] *s* in sigma units; [m] not including NH_2 derivatives for which the difference might be 2—3 times larger.

EDSP correlations, Eq. (*3*), by the substituents $C(CH_3)_3$ and $Si(CH_3)_3$ (data from ref.[14]) in order to exploit all parameters given in the literature[16]. Similarly[18] with Eq. (*6*) the substituents C_2H_5, $CH(CH_3)_2$ and $C(CH_3)_3$ were added. In this way the correlations with few items were somewhat improved, in all cases it was checked that addition and elimination of some compounds do not affect significantly the results. In few cases some items were eliminated from a posteriori grounds, as outliers. It was done only in mutual corelations of two SCS where the reason is evident and independent of any σ values. The substituets OH and COOH were eliminated from all direct correlations of SCS, additional outliers are given in the footnotes to Table III together with the consequences for the fit. One can conclude that with the relatively broad material we have, the results are not sensitive to the presence or absence of particular compounds.

In general, the results on monosubstituted benzenes confirmed those on *meta*- and *para*-substituted anilines[7] or those obtainable on substituted benzonitriles and methyl benzoates for which only the data were hitherto published by us[5,6]. The simplest proof is a direct correlation of SCS in the same position in two series, we can call it a δ–δ correlation. According to Table III these correlations are acceptable for the position 3 (lines 16, 17) and very good to excellent for the positions 1, 2, and 4, although the reasons may be different. For instance in the position 1 the substi-

tuent effect is evidently very strong and little affected by the remote constant group: due to the strong effect the correlations are excellent according to the correlation coefficient but the standard deviations exceed still very distinctly the experimental error (lines 5, 6). As already observed several times[7,9,16]. SCS in the position 4 are most regular and controlled mainly by the classical electronic substituent effects. The δ–δ correlations (lines 28, 29) show also high correlation coefficients and in addition smaller standard deviations than in the position 1. Just a little worse are the δ–δ correlations of SCS in the position 2 (lines 10, 11) which themselves are less understandable[7,16]. In the position 3 the SCS were mostly considered inexplicable[7,9], striking are mainly their small values. The δ–δ correlations (lines 16, 17) reveal though a regular behaviour of some kind. An important feature in all δ–δ correlations is the appearance of outliers. According to preliminary results we eliminated the substituents OH and COOH from all such correlations since each appeared as outlier three times. The reasons of deviations are very probably association of the solute and solvent effects, both being more important in bis derivatives. Nevertheless, these effects are relatively small and are detected only in δ–δ correlations, not in less precise DSP treatment. The slopes of δ–δ correlations are always near to unity, although some deviations are statistically significant (Table III).

The ^{13}C SCS could be also correlated with SCS of other nuclei in suitable benzene bis derivatives. We examined only ^{19}F SCS in substituted fluorobenzenes[21,22] (in tetrachloromethane) which are available in a sufficient number and have been very important in the correlation analysis. As expected, correlation in the position 4 is very close but some outliers are of interest (Table III, line 27). One possible reason could be in different solvents. We have reexamined the ^{19}F NMR spectrum of 4-fluorobenzonitrile in deuteriochloroform (δ −103·53 ppm relative to CF_3Cl, in reasonable agreement with ref.[23]): the resulting SCS would be 10·3 ppm as in methanol[22], the deviation is not improved. The sensitivity of ^{19}F SCS to solvent effects[21,22] is a complicating factor but cannot be responsible for all the observed deviations: for the measurement in cyclohexane we obtained the same picture as in Table III while in methanol the deviations for CN, $N(CH_3)_2$ were still greater. Interesting results were obtained by comparison ^{13}C and ^{19}F SCS in the position 3: they cannot be described by an equation but are shown in a graph (Fig. 1). The points for acceptor substituents define a straight line with the slope of 0·30 while the points for donors, particularly for those bearing a lone electron pair in the α-position, are situated above this line. This may suggest that C-3 SCS are composed of two effects: one connected with the common inductive effect and transmitted (very efficiently) to the adjoining atoms, the other of unknown nature (not very close to the common resonance effect since there is no DSP correlation). This picture may help a little in understanding the almost mysterious SCS in the position 3. Their feature which is not easy to understand is the small range of values (given in ppm at the formula *I*) since the SCS of adjoining atoms are of the same order



in the positions 3 and 4 (formulas *II*, *III*, *IV*). Similar pictures as Fig. 1 were already observed in many plots of two experimental quantities[5,6,24]: they confirm the general statement[1,24] that the complex behaviour of substituents on benzene ring is due practically only to the donors.

The DSP correlations in Table III agree essentially with previous observations on other series of compounds[5-7,9-12], although the subjective evaluation of various authors was sometimes different. The correlation is satisfactory only in the position 4 with normal constants σ_R^0: SCS are clearly controlled by the classical electronic effects (Table III, line 20). Although the resonance effect is much more important (the ratio of the ϱ constants 0·30, see also the correlation with σ_R^0 separately), there is no improvement in the DSP-NLR treatment, accounting for a possibly enhanced resonance (the ε value, measuring the electron demand, equals exactly zero, line 23).

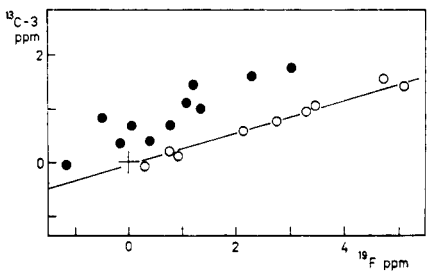


FIG. 1

Plot of ^{13}C SCS in the position 3 of monosubstituted benzene derivatives vs ^{19}F SCS in *meta*-substituted fluorobenzenes (ref.[21], in tetrachloromethane): ○ acceptor substituents, ● donor substituents

In the remaining positions the DSP treatment fails completely whatever type of resonance constant is used (lines 1, 2, 7, 8, 12, 13).

Of the three-parameter equations three kinds were examined. The EDSP treatment was specially devised[16] for SCS in the positions 1, 2, and 3: the additional specialized terms, denoted *I*, *O*, and *M*, respectively, were derived from ^{13}C SCS in aliphatic compounds. The overall fit is excellent for C-1 and very good for C-2 or C-3. However, there are some hints that the correlation with three parameters might be overparametrized. Clearly it was the case for C-2 (Table III, line 9) where the term with σ_I was insignificant and had to be eliminated, for C-1 it was significant (line 3) but the correlation with σ_R^0 and *I* is olso satisfactory (line 4). More definite statistical results cannot be obtained with the relatively small number of items which is restricted by the available *I*, *O*, and *M* constants[16]. The same restriction applies to the possible relationship[7] to the electronegativities[25]. We are of the opinion that SCS in these positions can be rationalized in a simpler way than by a three-parameter equation.

The two other three-parameter equations represent general refinements of the DSP treatment without any reference to SCS or to the positions 1 or 2 on the benzene ring. Therefore, they were applied only to SCS in the position 4 where already simple DSP is reasonably successful. No significant improvement was reached. In the Charton treatment[17], Eq. (*5*), the third term is still significant (Table III, line 24) according to the *t*-test but if it is omitted (line 25), the fit is almost unchanged and practically the same as with the classical DSP. Similar results were obtained with the Charton's constants[17] for extraannular SCS in substituted benzonitriles and methyl benzoates (refs[5,6]). Within the framework of Charton's theory[17] such a result is quite possible, it means only that the electron demand is normal (corresponding to the σ_R^0 constants and to $\varepsilon = 0$ in the DSP-NLR). In Eq. (*6*) the terms were derived[18] by PCA and particularly the third does not have any physical meaning. It was just this term which was found insignificant and omitted: the correlation with the remaining two (line 26) is again the same as with classical DSP. The data matrix on which PCA was based[18] was rather inhomogeneous and had little relation to NMR shifts.

Equation (*4*) could be derived from two DSP equations – for *meta* and *para* derivatives, respectively (e.g. ref.[24]) – by eliminating once σ_I, once σ_R. It was suggested[14] particularly for SCS in benzene derivatives, probably with the idea that some specific effects may cancel. A test on 14–18 compounds yielded a good fit but several outlers had to be eliminated[14]. Our repetition on a larger data set gave somewhat worse fit without outliers (Table III, lines 30, 31). However the problem is in the wrong choice what is the response function and what are the explanatory variables, and in the incomplete statistical treatment, not testing significance of individual terms. The fit in the case of σ_R^0 – much better than for σ_I – is caused by the rather close correlation of σ_R^0 and δ_{C4} (see the separate simple regression in

Table III, line 21): the added term with δ_{3C} represents a very small improvement. If one wants to test Eq. (*4*) for σ_R^0, the response function should be δ_{3C} which is not correlated with the other two. Table III, line 19 reveals no correlation. Even in the case of σ_I the choice of δ_{C3} as response function is physically most meaningful: prediction of just this quantity would be more valuable than prediction of σ_I with a low accuracy ($\pm 0{\cdot}09$, line 30). Table III, line 18 reveals again no correlation. Equation (*4*) is thus another example of misusing linear regression[26], this time by incorrect choice of response function.

The theory of Fadhil and Godfrey[19] is a new alternative to DSP. The traditional bisection into two terms is abandoned and *meta* and *para* derivatives plotted together into one graph which is, however, not linear but reveal an abrupt change of mechanism at a given point. As the explanatory variable new constants σ_{ST} were devised, derived from SCS in substituted styrenes. Figure 2 reveals that the theory does not apply to our SCS: instead of two straight lines rather a triangular area is obtained, evidently also δ_{C3} and δ_{C4} cannot be treated together. The idea of abrupt change of mechanism is certainly not applicable to all cases although bilinear graphs have been already observed[27] in the field of SCS.

CONCLUSIONS

We have essentially confirmed what has been already observed on several smaller series that ^{13}C SCS in the benzene ring show completely different behaviour according to the position. From the tests of several more sophisticated equations and from simple relations between two series of SCS we come to the conclusion that this behaviour is not in principle so complex. It can be hardly explained by competition of many effects but more probably by a few mechanism but different in individual positions and also different from the classical concepts of inductive and resonance effects. Further progress is thus expected merely from PCA than from the DSP treatment.

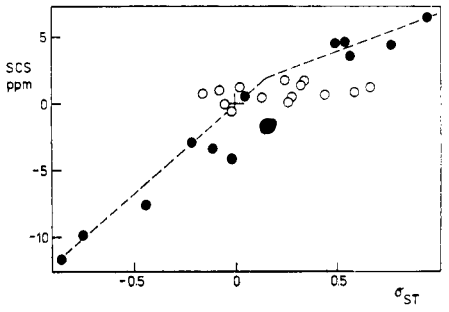


FIG. 2
Fadhil–Godfrey[19] plot of ^{13}C SCS in monosubstituted benzene derivatives vs the constants σ_{ST}: ○ position 3, ● position 4

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