Tetrahedron Letters No. 46, pp 4547 - 4550.

0040-4039/78/1108-4547$02.00/0

EFFECTS OF FIXED SUBSTITUENTS UPON SUBSTITUENT CHEMICAL SHIFTS OF THE C-1 ATOM IN m- AND p-DISUBSTITUTED BENZENES. CORRELATION WITH INDUCTIVE SUBSTITUENT PARAMETER ($\underline{\iota}$)

Naoki Inamoto,* Shozo Masuda, Kazuo Tori+ and Yohko Yoshimura+
Department of Chemistry and Research Centre for Spectrochemistry,
Faculty of Science, The University of Tokyo, Hongo, Tokyo 113,
Japan, and +Shionogi Research Laboratory, Shionogi & Co., Ltd.,
Fukushima-ku, Osaka 553, Japan

Bromilow, Brownlee, Topsom and Taft[1] reported that the effect of a fixed substituent (Y) on the substituent ^{13}C-chemical shifts of the C_1 atom directly bonded to the Y group (C_1-SCS) in p-substituted benzenes (p-X-C_6H_4-Y) is controlled by the σ-charge density at the C_1-atom on the basis of their dual substituent parameter approach. Recently, Lynch[2] concluded that the slope parameter ($\underline{b}$ in equation: $\delta = a_o + \underline{b}\delta_o$) depends on the ionization potential of the key atom in the Y group, examining a wider variety of systems by the single parameter approach using the shift-shift relationship of C_1-SCS (δ) with the corresponding C_p-SCS (δ_o) in monosubstituted benzenes (XC_6H_5).

We[3] have also treated C_1-SCS in disubstituted benzenes with the same method as that reported by Lynch.[2] This communication describes our finding that the slope parameters ($\underline{b}$) in the m- and p-series are linearly correlated with the inductive substituent parameter[4] ($\underline{\iota}$:Iota) of the group Y.

Our new observed data on C_1-SCS as well as those selected from the literature[5-12] were treated with the shift-shift relationship using the data on monosubstituted benzenes recommended by Lynch.[2] The results are summarized in the TABLE.

The slope parameters ($\underline{b}$) obtained here and reported by Lynch[2] were plotted against parameter $\underline{\iota}$ and linear relationships were obtained in the p- and m-series as shown in Figs. 1 and 2, respectively. Deviations for the Cl, Br, I, CN, C≡CH and CF_3 groups in the p-series are attributed to the spin-orbit coupling for the heavy halogen atoms,[13] the magnetic anisotropies for the C≡CH and CN groups,[14] and the unsuitable $\underline{\iota}$ value for the CF_3 group probably owing to an overestimation of the electronegativity (the correct $\underline{\iota}$ value can be estimated

TABLE. Shift-shift relationships of C_1-SCS in m- and p-XC_6H_4Y to the corresponding ^{13}C-SCS in XC_6H_5

	p-Series Fixed substituent, Y	n[a]	a_o	b	r^b	ref.
1	NMe_2	5	150.7	0.58	0.979	c
2	F	10	163.0	0.62	0.993	2
3	OMe	10	160.2	0.71	0.995	2
4	OMe	12	160.0	0.77	0.992	c
5	$OCH=CH_2$	8	156.4	0.77	0.996	2
6	CHO	10	135.9	0.80	0.991	c
7	NO_2	10	147.8	0.82	0.989	2
8	NO_2	9	147.6	0.89	0.981	c
9	NH_2	10	147.0	0.83	0.993	2
10	NH_2	7	147.3	0.92	0.986	c
11	COMe	10	136.8	0.84	0.991	c
12	$CH=CH_2$	11	137.4	0.92	0.998	2
13	$C(Me)=CH_2$	8	141.0	0.96	0.999	2
14	Ph	8	141.6	0.98	0.998	2
15	COPh	9	137.4	0.98	0.994	6
16	$CONH_2$	7	134.3	0.99	0.992	2
17	$C(^tBu)=CH_2$	9	143.1	0.99	0.999	2
18	SO_2Me	7	141.2	0.99	0.988	7
19	C≡CH	11	122.4	1.03	0.998	2
20	CF_3	9	131.1	1.05	0.997	2
21	CMe_3	8	151.0	1.07	0.996	2
22	CMe_3	19	151.7	1.11	0.993	10
23	Et	9	141.6	1.09	0.999	2
24	Et	5	144.8	1.10	0.998	c
25	Me	10	138.1	1.10	0.998	2
26	Me	16	138.7	1.16	0.996	9
27	Cl	10	134.8	1.12	0.999	2
28	SMe	7	138.8	1.12	0.988	7
29	SMe	7	139.7	1.16	0.951	c
30	CH_2F	7	136.6[d]	1.15	0.995	8
31	CN	10	113.0	1.16	0.992	2
32	CN	10	111.8	1.17	0.993	9
33	SOMe	7	146.8	1.16	0.996	7
34	COOH	7	131.6	1.18	0.980	5b
35	Br	10	122.6	1.24	0.998	2
36	$SiMe_3$	7	140.0	1.25	0.997	2
37	$GeMe_3$	6	142.2	1.31	0.9998	2
38	$SnMe_3$	7	142.0	1.35	0.997	2
39	I	8	94.3	1.47	0.997	2
40	$SCH=CH_2$	9	134.8	1.54	0.998	2
41	$SeCH=CH_2$	9	129.8	1.54	0.999	2

	m-Series Fixed substituent, Y	n[a]	a_o	b	r^b	ref.
1	OMe	10	159.9	0.53	0.707	c
2	NMe_2	5	150.8	0.63	0.693	c
3	NO_2	7	148.4	0.71	0.760	c
4	COMe	7	137.5	0.89	0.955	c
5	CN	11	112.8[d]	0.85	0.636	12
6	CN	5	112.6	1.36	0.768	c
7	CHO	8	136.7	0.95	0.910	c
8	$CH=CH_2$	5	136.4[e]	0.99	0.920	11
9	Me	14	138.0	1.39	0.904	9
10	COOH	6	131.5	1.54	0.906	5b
11	CMe_3	13	151.4	1.55	0.915	10

[a] No. of substituents used. [b] Correlation coefficients. [c] This work. ^1H Noise-decoupled ^{13}C FT NMR spectra were recorded on a Varian NV-14 FT NMR spectrometer at 15.087 MHz using 8-mm spinning tubes at 30°. Sample concentrations were 1 mmol/cm^3 in $CDCl_3$ with TMS(δ 0) as an internal reference. Accuracies of chemical shifts δ are ±0.07(ppm). The full data will be reported elsewhere. [d] Data converted using $\delta_C(CHCl_3)$=77.2 ppm. [e] Data converted using $\delta_C(CS_2)$=192.8 ppm.

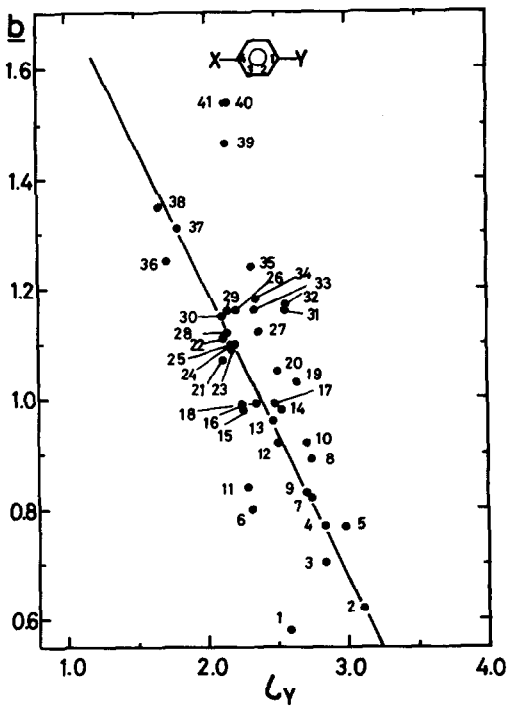

Fig. 1. Plot of b against ι in the p-series.

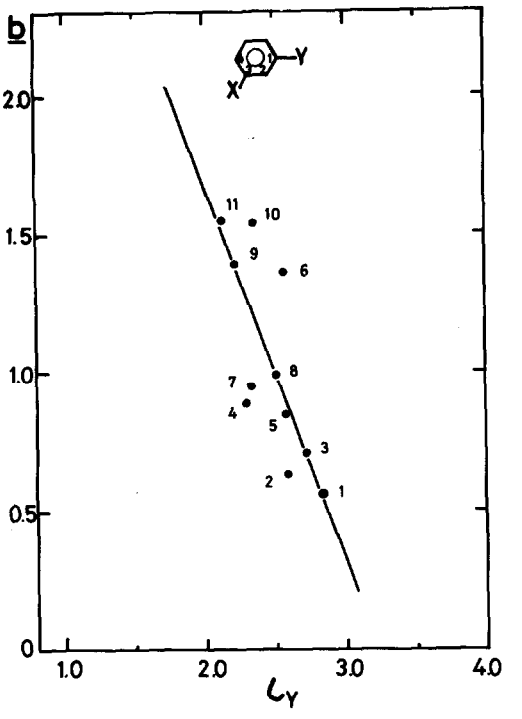

Fig. 2. Plot of b against ι in the m-series.

to be ca. 2.5, by judging from many plots of ^{13}C-SCS in various systems against ι).

In the m-series, the shift-shift relationships were found to have not enough high r values (see the TABLE) because of the small ^{13}C-SCS. Therefore, plot of b against ι is scattered more than those in the p-series.

The features of the plots shown in Figs. 1 and 2 are quite similar to that of the C_α-SCS in substituted alkanes against ι reported previously.[4] This fact indicates that the slope parameters are controlled by the σ-electron density at the C_1 atom as suggested by Bromilow et al.[1]

Moreover, Lynch's result[2] implies that both electron density and excitation energy terms in the paramagnetic shielding expression in ^{13}C chemical shift formalism[15] are reflected in parameter ι; the latter energy term is considered to depend on ionization potential.

In conclusion, we have succeeded in unifying the two different interpretations by Bromilow et al.[1] and Lynch,[2] employing the ι parameter. Thus, the ι parameter should be very useful for interpreting ^{13}C-SCS.[4,16] The applications of the inductive substituent parameter ι to other linear free-energy relationships are in progress.[17]

REFERENCES

1. J. Bromilow, R. T. C. Brownlee, R. D. Topsom and R. W. Taft, J. Am. Chem. Soc. 98, 2020 (1976).
2. B. M. Lynch, Can. J. Chem. 55, 541 (1977).
3. N. Inamoto, S. Masuda, Y. Takayama, K. Tokumaru, K. Tori and M. Yoshida, presented partly in the 34th Annual Meeting of the Chemical Society of Japan, Hiratsuka, Abstracts II, p. 549 (1976).
4. N. Inamoto and S. Masuda, Tetrahedron Lett. 3287 (1977). The ι values for the other substituents are as follows: CH_2F(2.12), $SeCH{=}CH_2$(2.15), $SCH{=}CH_2$(2.16), $CONH_2$(2.25), SOMe(2.33), SO_2Me(2.35), $C(Me){=}CH_2$(2.47), $C(^tBu){=}CH_2$(2.48) and $OCH{=}CH_2$(2.98).
5. a) J. Niwa and M. Yamazaki, Chem. Lett. 765 (1974); b) C. Nagata, H. Nagata and S. Tanaka, Nippon Kagaku Kaishi 2045 (1975).
6. M. J. Shapiro, Tetrahedron 33, 1091 (1977).
7. G. W. Buchanan, C. Reyes-Zamora and D. E. Clarke, Can. J. Chem. 52, 3895 (1974).
8. J. Bromilow, R. T. C. Brownlee and A. V. Page, Tetrahedron Lett. 3055 (1976).
9. N. Inamoto, S. Masuda, K. Tokumaru, K. Tori, M. Yoshida and Y. Yoshimura, ibid. 3707 (1976).
10. S. Berger, Tetrahedron 32, 2451 (1976).
11. K. S. Dhami and J. B. Stothers, Can. J. Chem. 43, 510 (1965).
12. J. Bromilow and R. T. C. Brownlee, Tetrahedron Lett. 2113 (1975).
13. I. Morishima, K. Endo and T. Yonezawa, J. Chem. Phys. 59, 3356 (1973).
14. I. Morishima, A. Mizuno and T. Yonezawa, Chem. Phys. Lett. 7, 633 (1970).
15. M. Karplus and J. A. Pople, J. Chem. Phys. 38, 2803 (1963).
16. N. Inamoto and S. Masuda, Chem. Lett. 177 (1978).
17. N. Inamoto and S. Masuda, presented preliminarily in the 37th Annual Meeting of the Chemical Society of Japan, Yokohama, Abstracts II, P. 636 (1978).

(Received in Japan 12 August 1978)