

## Long-range Substituent Effects in $^{13}\text{C}$ Chemical Shifts of Arylcarbenium Ions. Evidence of Large Substituent-Substituent Interactions between Remote Groups

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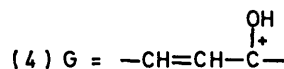
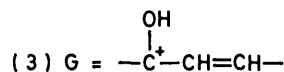
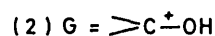
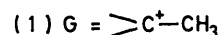
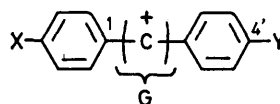
For dinuclear arylcarbenium ions of the type  $p\text{-XC}_6\text{H}_4\text{-G}\cdot\text{C}_6\text{H}_4\text{-Y-p}$  (protonated 1,1-diphenylethylenes, benzophenones, and *trans*-chalcones)  $^{13}\text{C}$  chemical shifts were used to examine the transmission of substituent effects across the bridge G. For monosubstituted ions ( $\text{Y} = \text{H}$ ), linear relationships are obtained between the long range substituent chemical shifts (s.c.s.) observed at the *para*'-position of the remote unsubstituted ring and the *para*-s.c.s. of monosubstituted benzenes. The fact that similar correlations are also observed for the *para*-position of the X-substituted ring but not for the carbenium site, suggests that the bridge G acts only as a relay in the transmission of electronic effects, with an efficiency increasing with the electron demand of the carbenium centre. For disubstituted ions ( $\text{Y} \neq \text{H}$ ) the X-induced s.c.s. at the *para*'-position largely depend on the nature of the Y groups. It is established that these s.c.s. are linearly related to the shifts observed in the corresponding monosubstituted ions. These substituent-substituent interactions between the remote X and Y groups can be satisfactorily accounted for by using the proportionality relationship  $(\Delta\delta\text{C-4}')_{\text{X}^{\text{Y}}} = b_{\text{Y}}(\Delta\delta\text{C-4}')_{\text{X}^{\text{H}}}$  with the  $b_{\text{Y}}$  values previously proposed for cationic *para*-substituted benzenes. This treatment makes it possible to divide the observed long-range s.c.s. into three independent terms which characterize the magnitude of the structural perturbation, the efficiency of the relay by the bridge G, and the susceptibility of the site of observation of the s.c.s. to its environment.

THE mode of transmission of long-range substituent effects in interconnected dinuclear aromatic compounds has received considerable attention in recent years. Using  $^{19}\text{F}$  n.m.r. and a large variety of bridged dinuclear systems, Phillips *et al.*<sup>1</sup> have shown that a distinction must be made between 'transmission effects' in which electron density is transferred from one ring to another and 'relay effects' reflecting  $\pi$ -polarization. Taft *et al.*<sup>2</sup> have also concluded that the increase in  $\pi$ -bonding between the two rings results not only in an increased transmission but also in an increased  $\pi$ -induction effect. In contrast, the importance of field-effects in  $^{19}\text{F}$  chemical shifts of 4'-substituted 4-fluorobiphenyls was also emphasized by Adcock and Khor.<sup>3a</sup> This apparent controversy has been resolved by Reynolds and Hamer<sup>4</sup> who pointed out that long-range substituent effects in  $^{19}\text{F}$  shifts are due essentially to field-induced polarization of the intervening  $\pi$ -system.

Recent results of Adcock *et al.*<sup>3b</sup> give further support to the dominant intervention of  $\pi$ -polarization effects in benzene and naphthalene rings while Ewing and Toyne<sup>5</sup> developed a unified model for the  $\pi$ -polarization effect in  $^{13}\text{C}$  and  $^{19}\text{F}$  n.m.r. Indeed, in a previous  $^{13}\text{C}$  study of diarylcarbenium ions,<sup>6</sup> we observed a fairly effective relay in the transmission of substituent effects from one ring to another, and we suggested that these long-range effects are mainly  $\pi$ -inductive without any important charge transfer between the substituent and the remote carbon atom.

In this paper we report evidence that large electronic interactions between the remote groups X and Y modulate the transmission of the X substituent effect at the Y-substituted carbon in 4-X,4'-Y-disubstituted diarylcarbenium ions (1)–(4) which correspond to protonated 1,1-diphenylethylenes, benzophenones, and *trans*-chalcones. An assessment of the magnitude of the interaction is proposed on the basis of 'proportionality rela-

tionships' introduced by Lynch<sup>7</sup> in disubstituted benzenes which we have recently extended to a large variety of arylcarbenium ions.<sup>8</sup>



### EXPERIMENTAL

Sample preparations<sup>9</sup> and recording of  $^{13}\text{C}$  spectra<sup>6</sup> have been described elsewhere. Chemical shifts were measured from internal  $\text{CH}_2\text{Cl}_2$  and are quoted relative to  $\text{Me}_4\text{Si}$  (downfield values positive).

### RESULTS AND DISCUSSION

In this study,  $(\Delta\delta\text{C-4}')_{\text{X}^{\text{Y}}}$  substituent chemical shifts (s.c.s.),<sup>6</sup> induced at the *para*'-position by changing the X substituent while the Y group remains fixed in each family of carbenium ions (1)–(4), are considered. The experimental values of the  $(\Delta\delta\text{C-4}')_{\text{X}^{\text{Y}}}$  are listed in Table I. For direct comparison chemical shifts at the *para*'-position of the unsubstituted parent ions are also listed in Table I.

*Monosubstituted Ions* ( $\text{Y} = \text{H}$ ).—For monosubstituted ions, reasonably good linear correlations are obtained between the s.c.s. observed at C-4', and at C-1 for each family (1)–(4). For instance, for ions (1),  $\Delta\delta\text{C-4}' = 0.91, \Delta\delta\text{C-1} + 13.6$  ( $r$  0.92,  $s$  1.8,  $n$  7) and for ions (2),  $\Delta\delta\text{C-4}' = 0.35, \Delta\delta\text{C-1} + 61.8$  ( $r$  0.97,  $s$  0.4,  $n$  8). Good

TABLE I  
Long-range s.c.s. at C-4' (in p.p.m. positive values downfield from Me<sub>4</sub>Si)

Ion	X	Y					
		H	Me	OMe	CF <sub>3</sub>	F	NO <sub>2</sub>
(1)	H	92.7	166.4	180.4	142.6	176.0	155.2
	Me	-2.6	-4.1 (-3.5)	-2.3 (-2.3)			
	OMe	-7.8	-10.9 (-10.5)	-6.0 (-6.7)	-5.4 (-5.3)		-3.8 (-3.2)
	F	-0.9					-0.6 (-0.6)
	CF <sub>3</sub>	4.2		2.3 (3.6)	3.9 (2.9)		
	NO <sub>2</sub>	5.0		4.1 (4.3)			
(2)	H	143.0	158.6	173.7	141.1	172.7	153.4
	Me	-1.0	-1.6 (-1.4)	-1.2 (-0.9)			-0.2 (-0.4)
	OMe	-2.8	-3.7 (-3.8)	-3.0 (-2.4)	-2.1 (-1.9)	-2.0 (-1.8)	-1.1 (-1.1)
	F	-0.4		-0.3 (-0.3)		-0.3 (-0.3)	
	CF <sub>3</sub>	1.6		1.8 (1.4)			
	NO <sub>2</sub>	2.4	3.9 (3.3)	2.8 (2.1)			1.5 (1.0)
(3)	H	139.3	153.6	169.2		169.8	151.2
	Me	-0.6	-1.1 (-0.8)	-0.7 (-0.5)		-0.6 (-0.4)	-0.4 (-0.2)
	OMe	-1.2	-2.4 (-1.6)	-2.0 (-1.0)		-1.2 (-0.8)	-0.8 (-0.5)
	F	-0.7	-0.8 (-0.9)	-0.4 (-0.6)		-0.1 (-0.4)	-0.1 (-0.3)
	NO <sub>2</sub>	2.6	4.1 (3.5)			1.9 (1.7)	0.7 (1.0)
	H	142.2	157.3	172.2		171.0	153.2
(4)	Me	-0.7	-0.8 (-0.8)	-0.8 (-0.6)		-0.4 (-0.4)	-0.5 (-0.4)
	OMe	-1.6	-2.3 (-2.2)	-1.3 (-1.4)		-0.8 (-1.0)	
	F	-0.1	-0.2 (-0.1)	-0.3 (-0.1)		-0.8 (0)	-0.1 (0)
	NO <sub>2</sub>	2.0	2.9 (2.7)	2.3 (1.7)			0.8 (0.8)

$\Delta\delta$  C-4' observed or, in parentheses, calculated by using equation (4). The entries for X = H correspond to  $\delta$ C-4' for each family (1)–(4), see text. Data from this work and ref. 6 for ions (1) and (2).

linear correlations\* are also obtained by direct comparison of each s.c.s. with the s.c.s. observed for the *para*-carbon in monosubstituted benzenes ( $S_{p,X}$ ).<sup>10</sup> The latter

The linear relationship (1) for families (1)–(4), with a

$$\Delta\delta\text{C-4}' = \alpha_G S_{p,X} \quad (1)$$

slope  $\alpha_G$  which varies with the nature of the bridge G, is illustrated in Figure 1.

Figure 2, which is for ions (2), illustrates the fact that the carbenium site C<sub>α</sub> exhibits a strikingly different response to X-induced electronic perturbations,<sup>6</sup> especially a nearly zero s.c.s. for electron-withdrawing substituents.

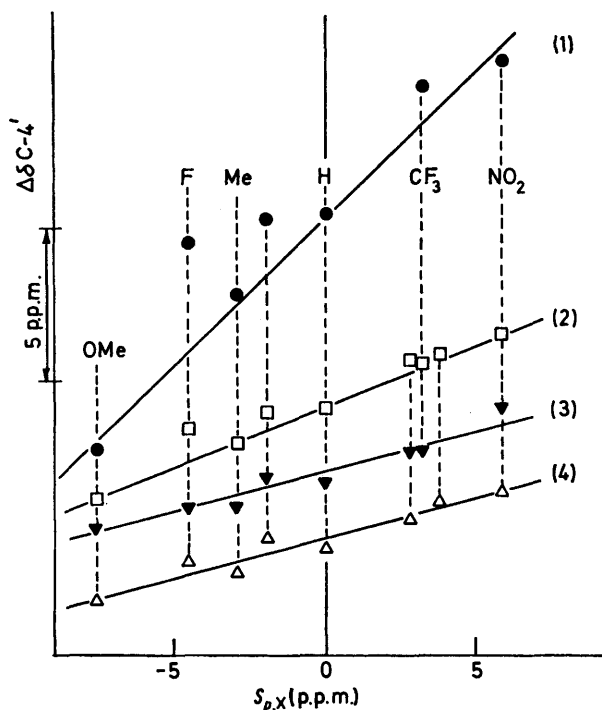


FIGURE 1 Plot of s.c.s. observed at C-4' ( $\Delta\delta\text{C-4}'$ ) versus monosubstituted benzene s.c.s.  $S_{p,X}$  for monosubstituted ions (1)–(4). Points corresponding to X = Cl ( $S_{p,X} -1.9$ ),  $\text{NH}_3^+$  (2.9), and  $\text{NMe}_2\text{H}^+$  (3.6) not used in the study of disubstituted ions are also indicated

are generally accepted as reflecting the overall electronic influence of the X substituent on the aromatic ring.

\* With  $r > 0.94$ . Small deviations are however evident for halogens and particularly for X = F. Excluding these points,  $r = 0.95$  [ions (3)] and  $0.98$  [ions (1), (2), or (4)].

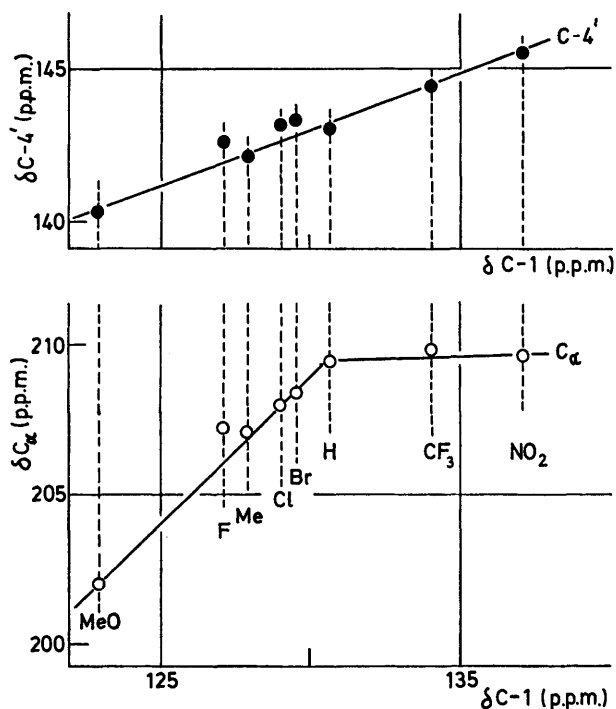


FIGURE 2 Plot of s.c.s. observed at C-4' and at C<sub>α</sub> versus s.c.s. at C-1 for ions (2)

A dual substituent parameter (DSP) treatment using Taft  $\sigma_i$  and  $\sigma_{R^+}$  parameters satisfactorily accounts for the s.c.s. observed at C-1,  $C_\alpha$ , and C-4' in each family. For instance, for ions (1)  $\Delta\delta C_\alpha = -0.5 + 6.6\sigma_i + 18.3\sigma_{R^+}$  ( $r$  0.96,  $s$  2.9);  $\Delta\delta C-1 = 0.2 + 5.1\sigma_i + 9.2\sigma_{R^+}$  ( $r$  0.97,  $s$  1.4);  $\Delta\delta C-4' = 0.1 + 6.9\sigma_i + 8.9\sigma_{R^+}$  ( $r$  0.99,  $s$  0.7). The relative weights of Taft  $\sigma_i$  and  $\sigma_{R^+}$  parameters in these correlations confirm the increased importance of charge transfer interactions for  $C_\alpha$  compared with C-1 and -4'. It is also noteworthy (and fully consistent with the proposed interpretation) that for both C-1 and -4', but not at all for  $C_\alpha$ ,  $\sigma_{R^+}$  constants given nearly as good a fit as  $\sigma_{R^+}$ .

As we have previously shown by both  $^1H$  and  $^{13}C$  n.m.r. of ions (1),<sup>6,11</sup> the only important charge transfer from the X substituent to the substrate occurs between the appropriate  $2p_z$  substituent orbital and the empty  $2p_z$  orbital of the  $C_\alpha$  cationic carbon. This orbital in turn polarizes the second aromatic ring thereby indicating that the  $C^+$  bridge acts only as a relay.

The effect of the  $\pi$ -charge at the carbenium site  $C_\alpha$  on the transmission of electronic perturbations can be elucidated by comparing, for each of the sites C-1,  $C_\alpha$ , and C-4', the s.c.s. induced in families (1)–(4). From correlation (1) it appears that the susceptibility of C-4' to electronic perturbations induced by remote substituents at C-4', as expressed by the  $\alpha_G$  coefficients 0.88, 0.35, 0.26, and 0.25 for ions (1)–(4) respectively, largely increases with the  $\pi$ -electron deficiency at  $C_\alpha$ . Quite similar behaviour is also detected for  $C_\alpha$  sites, *i.e.* their sensitivity is parallel to that of C-4' in the four families. For instance comparison of the s.c.s. observed in protonated 1,1-diphenylethylenes and benzophenones leads to linear correlations of slope 2.7 for the shifts induced at  $C_\alpha$  and 2.6 for those at C-4'.<sup>6</sup> In contrast, for C-1 nearly equal effects are observed, regardless of the charge at the  $C_\alpha$  position.

Table 2 lists the  $\pi$ -electron densities at the carbenium

TABLE 2  
Relative sensitivity of sites C-1,  $C_\alpha$ , and C-4' to X-induced s.c.s.

Site	Ion			
	(1)	(2)	(3)	(4)
C-4'	2.61	1	0.75	0.72
$C_\alpha$	2.70	1	0.93	0.90
C-1	0.94	1	1.02	0.90
$q_\pi$ at $C_\alpha$	0.506	0.619	0.649	

For INDO calculations and parameters used see ref. 6.

sites (INDO calculations) for unsubstituted ions (1–4; X = H), and the relative sensitivity of C-1,  $C_\alpha$ , and C-4' to structural perturbations. These sensitivities are defined by the slopes of the linear correlations obtained for each site by comparing the s.c.s. in families (1), (3), and (4) with the corresponding s.c.s. in family (2), the arbitrary reference scale.

These results clearly show that the positive charge at  $C_\alpha$  (carbenium site) reflects both the extent of electron migration to this position and the efficiency of the relay  $C_\alpha$  in the transmission of long-range effects to C-4'.

These results are in full agreement with the observations of Phillips and his co-workers<sup>1</sup> and with the theoretical predictions of Murrell<sup>12</sup> and Godfrey.<sup>13</sup>

**Disubstituted Ions (Y  $\neq$  H).**—The same pattern is qualitatively observed in disubstituted compounds. However, experimental results in Table 1 clearly indicate that, in each family the X-induced shifts at C-4' largely depend on the nature of the fixed Y groups directly bonded to observation site C-4'.

For instance, in diarylmethylcarbenium ions (1), a methoxy-substituent induces an upfield shift of  $-10.9$  p.p.m. at methyl-substituted C-4', but only an s.c.s. of  $-3.8$  p.p.m. if C-4' is bonded to a nitro-group. These electronic interactions between the remote X and Y groups clearly provoke significant deviations from strict additivity of the s.c.s. at the C-4' position.

Comparison of  $(\Delta\delta C-4')_{X^Y}$  observed for each family of disubstituted compounds (with fixed Y) indicates that these s.c.s. are linearly related to the shifts measured for the corresponding monosubstituted compounds (Y = H), and lead to correlations of the form (2) with slopes  $b$  much

$$(\Delta\delta C-4')_{X^Y} = b_Y(\Delta\delta C-4')_{X^H} \quad (2)$$

different from unity (as would occur in the absence of substituent–substituent interactions, *i.e.* if the effects of X and Y were independent and additive). It is note-

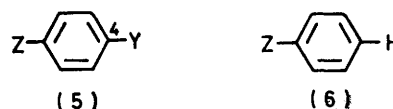
TABLE 3

Proportionality relationships $(\Delta\delta C-4')_{X^Y} = b_Y(\Delta\delta C-4')_{X^H}$						
Y	$n$	$b$	$i$	$r$	$s$	$b_Y$
Me	16	1.44	0.02	0.99	0.32	1.35
OMe	16	0.82	-0.05	0.97	0.58	0.87
CF <sub>3</sub>	4	0.77	0.33	0.99	0.43	0.68
F	10	0.70	0.02	0.98	0.23	0.65
NO <sub>2</sub>	12	0.46	-0.02	0.98	0.26	0.41

$n$  = Number of points,  $b$  and  $i$  = slope and intercept derived from least squares treatment  $(\Delta\delta C-4')_{X^Y} = b_Y(\Delta\delta C-4')_{X^H} + i$ ,  $r$  = correlation coefficient;  $s$  = standard deviation,  $b_Y$  from ref. 8.

worthy (Figure 3) that for each fixed Y group, whichever ions are considered, the points fall on the same correlation line, *i.e.* the  $b$  values depend only on the nature of Y.

These results can be easily rationalized by referring to the 'proportionality relationships' recently proposed by Lynch.<sup>7</sup> In *para*-disubstituted benzenes (5), the *para*-



s.c.s. at C-4 can be expressed as a function of the shifts observed in monosubstituted benzenes (6). Thus, equation (3) applies where  $S_{p,Z}^Y$  and  $S_{p,Z}^H$  are the substituent shifts induced by the variable Z groups in the

$$S_{p,Z}^Y = b_Y S_{p,Z}^H \quad (3)$$

*para*-position in (5) and (6), respectively. The coefficient  $b_Y$  characterizes the susceptibility of the C-4 site (bonded to Y) to these intramolecular interactions.\*

The cationic systems under study here are relevant to

\* This form is strictly equivalent to the expression  $S_{i,Y}^Z = S_{i,Y}^H + (b_Y - 1)S_{p,Z}^H$  proposed in our previous work<sup>8</sup> where the 'ipso-shifts'  $S_{i,Y}^Z$  and  $S_{i,Y}^H$  are used.

this model if we consider the whole group ( $\text{XC}_6\text{H}_4\text{-G}$ ) as a single substituent Z. With this model, equation (3) leads directly to (4) since  $(\Delta\delta\text{C-4}')_{\text{X}^{\text{Y}}}$  and  $(\Delta\delta\text{C-4}')_{\text{X}^{\text{H}}}$  represent the shifts induced at C-4' when substituent Z

$$(\Delta\delta\text{C-4}')_{\text{X}^{\text{Y}}} = b_{\text{Y}}(\Delta\delta\text{C-4}')_{\text{X}^{\text{H}}} \quad (4)$$

varies as a function of group X. Equation (4) is consistent with the experimental observation of linear relationships, for each given Y group, between the s.c.s. observed in mono- and di-substituted compounds. Furthermore, it is noteworthy that the slopes  $b$  obtained here for the  $(\Delta\delta\text{C-4}')_{\text{X}^{\text{Y}}}$  versus  $(\Delta\delta\text{C-4}')_{\text{X}^{\text{H}}}$  correlations (cf. Table 3) are in very close agreement with the  $b_{\text{Y}}$  values which we previously proposed in a study of *para*-substituted benzenes.<sup>8</sup>

The efficiency of this model for interpreting intramolecular interactions in long-range substituent effects can also be illustrated by comparing the experimental s.c.s.  $(\Delta\delta\text{C-4}')_{\text{X}^{\text{Y}}}$  to those calculated by using equation (4), starting from the  $(\Delta\delta\text{C-4}')_{\text{X}^{\text{H}}}$  observed in mono-substituted ions, and the  $b_{\text{Y}}$  values determined in our previous work.<sup>8</sup> For 48 points over a range of 15 p.p.m.,

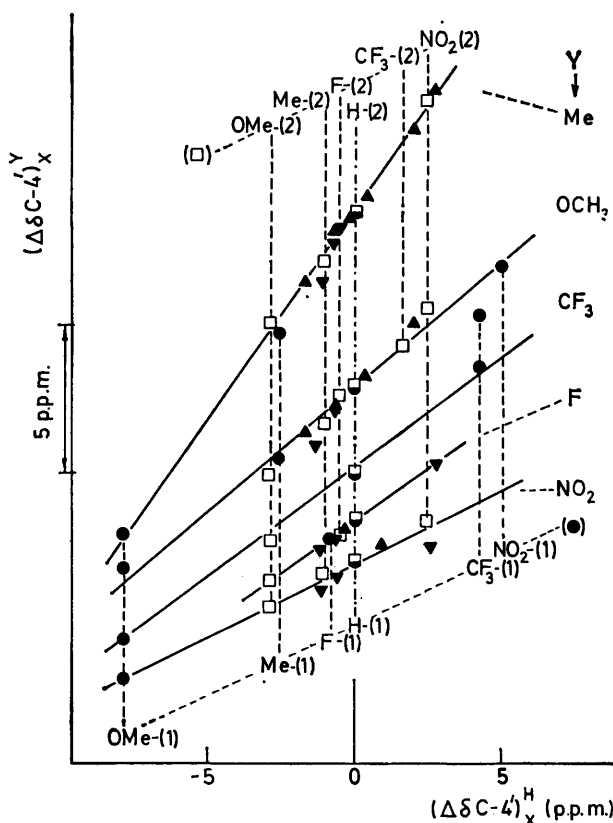


FIGURE 3 Plot of  $(\Delta\delta\text{C-4}')_{\text{X}^{\text{Y}}}$  for disubstituted ions versus  $(\Delta\delta\text{C-4}')_{\text{X}^{\text{H}}}$  observed in monosubstituted ions, for various Y groups. For clarity, only points corresponding to ions (1) and (2) are recorded [and indicated as X-(1) or X-(2), respectively]

the correlation  $(\Delta\delta\text{C-4}')_{\text{obs.}}$  versus  $(\Delta\delta\text{C-4}')_{\text{calc.}}$  (cf. Figure 4) has  $r$  0.985 and  $s$  0.4.

**Conclusions.**—Factorization of s.c.s. observed in long-range effects. Using equations (1) and (4), the s.c.s. induced by one aromatic ring on the *para*-position of the

other can be expressed by the general relation (5) which can be divided into three independent terms,  $S_{p,x}$ ,  $\alpha_G$ ,

$$(\Delta\delta\text{C-4}')_{\text{X}^{\text{Y}}} = \alpha_G b_{\text{Y}} S_{p,x} \quad (5)$$

and  $b_{\text{Y}}$ , respectively, characterizing the magnitude of the perturbation, the efficiency of the relay by the bridge G,

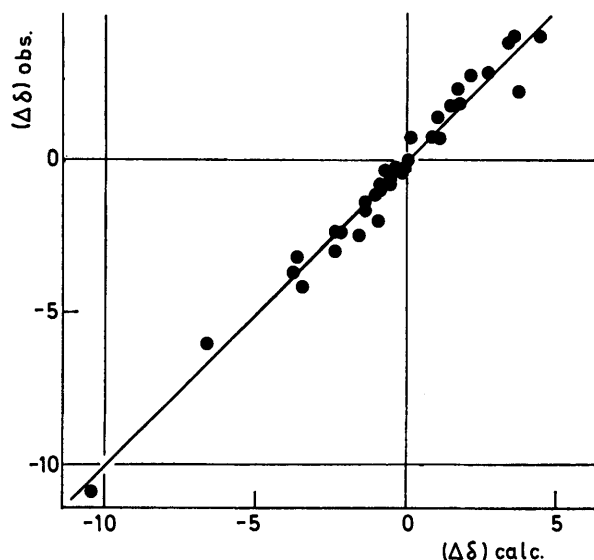


FIGURE 4 Plot of  $(\Delta\delta)_{\text{obs.}}$  versus  $(\Delta\delta)_{\text{calc.}}$  for the C-4' position of disubstituted ions (1)–(4)

and the susceptibility of the observation site (C-4') to its environment (*i.e.* as a function of the nature of the Y group bonded to C-4'). Comparison of the s.c.s. induced at C-1, C $_{\alpha}$ , and C-4' of the carbon chain also makes it possible to assess the relative magnitude of the various contributions intervening in the overall process of transmission of structural influences *via* a concerted  $\pi$ -inductive electron transfer mechanism.

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