NMR Study of Substituent Effects in 4-Substituted and 4,4'-Disubstituted Diphenyl Sulphoxides and Sulphones

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The proton and carbon NMR spectra of nine 4-X-diphenyl sulphoxides, seven 4-X-4'-NO₂-diphenyl sulphoxides, eight 4,4'-X₂-diphenyl sulphoxides, eight 4-X-diphenyl sulphones, seven 4-X-4'-NO₂-diphenyl sulphones and eight 4,4'-X₂-diphenyl sulphones have been obtained. Correlation of the ¹³C chemical shifts with the appropriate substituent chemical shifts (SCS) for monosubstituted benzenes (Lynch plots) does not show the enhancement of substituent effect at C-1 (*para* to the substituent) that was a feature of the corresponding sulphides studied earlier. Dual substituent parameter (DSP) correlations of the ¹³C chemical shifts with σ_1/σ_R^0 are excellent for carbons *meta* (C-2,6) and *para* (C-1) to the substituent. The trends for the series sulphides, sulphoxides, sulphones, where a decreasing response to the change of substituent is the general observation, are discussed. Changes of molecular conformation may also influence the transmission of electronic effects to the ring not carrying the variable substituent X.

KEY WORDS ¹H NMR ¹³C NMR Diphenyl sulphoxides Diphenyl sulphones Substituent effects

INTRODUCTION

We recently reported¹ the effect of substituents on the ¹H and ¹³C chemical shifts of 4-substituted and 4,4'disubstituted diphenyl sulphides. We concluded that there were resonance and π -polarization interactions between the rings of 4-X-diphenyl sulphides and 4-X-4'-NO₂-diphenyl sulphides, but not 4,4'-X₂-diphenyl sulphides.

We considered correlations of ¹³C chemical shifts with benzene substituent chemical shifts (Lynch plots²) and dual substituent parameter correlations using the σ_{I} and σ_{R}^{0} values derived by Bromilow *et al.*,³ and compared the slopes of the Lynch plots with the ratio $\rho_{R}^{Y}/\rho_{R}^{H}$, where ρ_{R}^{Y} is the resonance transmission coefficient for C-1 (formula 1), the carbon bearing the fixed substituents, and ρ_{R}^{H} is the resonance transmission coefficient (21.5) for the *para*-carbon of monosubstituted benzenes, as derived from DSP correlations.

In continuation of this work, we now report the ¹H and ¹³C NMR spectra of similar series of diphenyl sulphoxides and diphenyl sulphones. The compounds used, and the numbering system, are shown in the formulae below.

EXPERIMENTAL

Diphenyl sulphoxide, 4,4'-dibromo-, 4,4'-dichloro-, 4,4'difluoro-, 4,4'-dimethoxy- and 4,4'-dimethyl-diphenyl sulphoxides were prepared by Friedel-Crafts reaction of thionyl chloride with the corresponding monosubstituted benzene in the presence of aluminium chloride.⁴ All the 4-substituted diphenyl sulphoxides, 4-methoxy-4'-nitro-, 4-methyl-4'-nitro- and 4,4'-diacetyldiphenyl sulphoxides were prepared by oxidation of the appropriate sulphide with potassium dichromate⁵ (one third molar equivalent) in acetic acid at 40 °C for 24 h. 4-Bromo-4'-nitro-, 4-chloro-4'-nitro- and 4-fluoro-4'nitro-diphenyl sulphoxides were prepared by the oxidation of the sulphides with potassium peroxydisulphate⁶ (1:1 molar ratio) in aqueous acetonitrile. 4,4'-Dinitrodiphenyl sulphoxide was obtained from the sulphide by oxidation with potassium peroxydisulphate in aqueous acetic acid containing ca. 0.1 M perchloric acid. Methyl 4-phenylsulphinylbenzoate was prepared by oxidation of the sulphide (from esterification of 4-phenylthiobenzoic acid⁷) with potassium dichromate in acetic acid.

Diphenyl sulphone, 4,4'-dibromo-, 4,4'-dichloro-, 4,4'-difluoro-, 4,4'-dimethoxy- and 4,4'-dimethyl-diphenyl sulphones were prepared by oxidation of the sulphoxides with hydrogen peroxide in acetic acid and all the other sulphones were obtained by oxidation of the sulphides with an excess of hydrogen peroxide⁸ in acetic acid.

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^a Series 1 (2, G = S), 2 (3, G = S) and 3 (4, G = S) (Ref. 1, in which each substituent has the same letter as here, except for COOCH₃, which was not available in the earlier series, where g had X = NHCOCH₃).

All the sulphones were crystallized from ethanol; the sulphoxides were purified either by repeated crystallization or by column chromatography. The observed and literature m.p. (or b.p.) of the sulphoxides and sulphones are given in Table 1, and for those five compounds for which such data could not be found, and one other, analyses are reported in Table 2.

The ¹H NMR spectra were obtained at 360 MHz (Bruker WM-360) for approximately 0.03 M solutions in CDCl₃ with TMS as internal reference. Broad-band and off-resonance decoupled ¹³C NMR spectra were obtained at 90.56 MHz (Bruker WM-360) for approximately 0.5 M solutions in CDCl₃ with TMS as internal reference. A pulse angle of 37.5° (5 μ s) and a repetition time of 3.72 s were used, collecting 32K data points in the quadrature detection mode for a spectral width of 22 700 Hz, at room temperature (20-21 °C). ¹H-coupled ¹³C NMR spectra were obtained similarly for a spectral width of 5000 Hz. 2D C/H shift correlated spectra were obtained using the standard Bruker program (XHCORRD), with a spectral width of 1200 Hz in the ¹H direction (resolution 2.34 Hz per point) and 5400 Hz in the carbon direction (resolution 5.25 Hz per point).

RESULTS AND DISCUSSION

Assignment of the ¹H and ¹³C chemical shifts was straightforward, using considerations of peak intensity, peak multiplicity under off-resonance ¹H decoupling and with full ¹H coupling, $^{n}J(CF)$ (for 4e, 5e, 6e, 7e, 8e

and **9e**), 2D C/H shift correlation, and magnitudes of ${}^{3}J(CH)$ as before.¹ The ¹H chemical shifts are given in Tables 3–8 and are considered to be accurate to 0.02 ppm and the ¹³C chemical shifts are given in Tables 9–14, and are considered to be accurate to 0.05 ppm.

Correlations with benzene substituent chemical shifts (Lynch plots)

The correlation of ¹³C chemical shifts in 1,4-disubstituted benzenes with the SCS values for monosubstituted benzenes^{2,27} has shown that the fixed substituent (1, Y) has an effect on its carbon of attachment, *para* to X. This is measured by the slope b of the Lynch equation [Eqn (1)] and for some fixed substituents b can be as large as 1.64 (Y = SPh).

Shift
$$C_x(Y) = a + bSCS C_x(H)$$
 (1)

There is no agreement on the cause of this enhancement of SCS effect, but it has been discussed in terms of the shift-to-charge ratio, approximated²⁸ as $\rho_R^{Y}/\rho_R^H \times 189$ ppm per electron, where ρ_R^{Y} and ρ_R^{H} (21.5) are the resonance transmission coefficients obtained from DSP correlations (C-1 in 1 and *para*-carbon in C₆H₅X, respectively). We noted that for a number of substituents Y = SR, the slope of the Lynch plot, b and ρ_R^{Y}/ρ_R^{H} showed good agreement. What has not been pointed out is that if, in the DSP correlation in Eqn (2), the term ρ_1^{Y} can be neglected in comparison with ρ_R^{Y}/ρ_R^{H} .

$$\delta C_{\mathbf{X}}(\mathbf{Y}) - \delta C_{\mathbf{H}}(\mathbf{Y}) = \rho_{\mathbf{I}}^{\mathbf{Y}} \sigma_{\mathbf{I}} + \rho_{\mathbf{R}}^{\mathbf{Y}} \sigma_{\mathbf{R}}^{\mathbf{0}}$$
(2)

Compound	×	Observed	Literature	Bof
	u ^	EDE 71	70 71	0
4a 46		69.5-71	70-71	10
40		09-70.5 AF F	1-12	10
40		40.0	40-40	11
40	E E	/155 157/	(1/9 1/9/	
-+0	,	(155~157/ 5 mmHa)	(140-145/ 3 mmHa)	12
٨f	004	97	96 96	10
	соосн	121		
-79 4h	COCH.	99-100	100-101	13
4i	NO.	96-97	106-107	10
5b	CH.	124-125	125.5-126.5	14
5c	CI	117-118		_
5d	Br	128-129	129–131	15
5e	F	119-121		_
5f	OCH2	119-120	122	14
5 i	NO	174-175	173	16
6b	СН	94.5	93	4
6c	CI	142–143	143	17
6d	Br	150-151	153	4
6e	F	5152	50.5	18
6f	OCH₃	47	46	4
6h	COCH3	154–156	-	
7a	н	122–124	125.5-126	19
7b	CH₃	123–124	124.5-125.5	19
7c	CI	91.5	92–93	20
7d	Br	104–106	108.5–109.5	19
7e	F	110–111	109–110	21
7f	OCH₃	120122	130	7
7h	COCH3	135137	136–137	22
7i	NO ₂	139-140	143	16
8b	CH₃	167	171–172	23
8c	CI	174–176	182–183	23
8d	Br	179–181	180–182	24
8e	F	159-161		_
18	OCH ₃	158-160	162-163.5	14
81		244-245	254	18
90		155-156	158	4
96		144-146	148-149	25
90	br E	1/0	1/2	4
0f 26	r OCH	39-101 100 100ª	90 90	21
31 0h		120-122-	30 300	4
Эn	COCH3	203-205	208-209	26

Table 1. Melting and boiling points of sulphoxides and sulphones

Table 3. ¹H chemical shifts ($\delta_{\rm H}$) for 4-X-diphenyl sulphoxides (series 4)

			Prot	on		
Compound	2,6	3,5	2′,6′	3',5'	4′	Others
X = H	7.66	7.45	7.66	7.45	7.45	
CH3	7.54	7.26	7.63	7.45	7.45	2.35
CI	7.58	7.44	7.64	7.47	7.47	
Br	7.52	7.60	7.63	7.47	7.47	
F	7.65°	7.15ª	7.63	7.47	7.47	
OCH3	7.57	6.96	7.61	7.46	7.46	3.82
COOCH3	7.73	8.12	7.66	7.47	7.47	3.92
COCH3	7.77	8.03	7.67	7.47	7.47	2.60
NO ₂	7.84	8.32	7.68	7.5 [⊾]	7.5 [⊳]	
^a Confirmed by ^b Approximate v	³ J(HF) = /alues.	9 Hz, ⁴J((HF) = 5	Hz.		

Table 4. ¹H chemical shifts ($\delta_{\rm H}$) for 4-X-4'-NO₂-diphenyl sulphoxides (series 5)

			Proto	in	
Compound	2,6	3,5	2',6'	3',5'	Others
X = H	7.68	7.5°	7.84	8.32	7.5ª (H-4)
CH₃	7.56	7.30	7.81	8.31	2.37
CI	7.63	7.47	7.82	8.33	
Br	7.55	7.64	7.84	8.32	
F	7.69	7.20	7.83	8.33	
OCH ₃	7.59	6.98	7.79	8.30	3.82
NO ₂	7.96	8.36	7.96	8.36	

^a Approximate value.

Table 5.	¹ H chemical 4,4'-X ₂ -diphenyl	shifts	$(\delta_{\rm H})$ for sulphoxides	
	(series 6)		-	

Proton				
2,6	3,5	Others		
7.66	7.45	7.45 (H-4)		
7.52	7.26	2.35		
7.58	7.45			
7.50	7.61			
7.63	7.17			
7.54	6.95	3.82		
7.77	8.04	2.58		
7.96	8.36			
	2,6 7,66 7,52 7,58 7,50 7,63 7,54 7,77 7,96	Prote 2,6 3,5 7.66 7.45 7.52 7.26 7.58 7.45 7.50 7.61 7.63 7.17 7.54 6.95 7.77 8.04 7.96 8.36		

Table 2.	Elemental analyses for compounds without literature	
	melting and boiling point data	

 $^{\rm a}$ Although the m.p. is much above that previously reported, the elemental analysis, the infrared spectrum and the $^1{\rm H}$ and $^{13}{\rm C}$ NMR

spectra confirm the structure.

	Fo	und	Req	uired	
Compound	C (%)	H (%)	Formula	C (%)	H (%)
4g	64.4	4.5	C14H12O3S	64.6	4.6
5c	50.9	2.7	C12H8CINO3S	51.2	2.8
5e	54.1	2.9	C ₁₂ H ₈ FNO ₃ S	54.3	3.0
6h	66.9	4.7	C ₁₆ H ₁₄ O ₃ S	67.1	4.9
8e	60.8	3.6	C ₁₂ H ₈ FNO₄S	61.0	3.8
9f	63.8	5.1	$C_{14}H_{14}O_{4}S$	64.1	5.3

Table 6. ¹H chemical shifts $(\delta_{\rm H})$ for 4-X-diphneyl sulphones (series 7)

			Pro	oton		
Compound	2,6	3,5	2′,6′	3′,5′	4′	Others
X = H	7.95	7.50	7.95	7.50	7.57	
СН3	7.83	7.29	7.93	7.48	7.55	2.42
CI	7.88	7.48	7. 9 4	7.52	7.5 9	
Br	7.80	7.64	7.93	7.52	7.58	
F	7.96	7.18	7.94	7.52	7.58	
OCH₃	7.88	6.97	7.92	7.48	7.54	3.85
COCH₃	8.05	8.05	7.96	7.53	7.61	2.64
NO ₂	8.13	8.34	7.97	7.57	7.64	

Table 7. ¹ H pho	chemica nes (seri	l shifts (ð es 8)	_H) for 4-X-4	l'-NO ₂ -dip	henyl sul-		Table 8. 1 4	H chemica ,4′-X ₂ -diphe	ıl shifts nyl sulphon	(δ _H) for es (series 9)
			Proton						Proton	
Compound	2,6	3,5	2',6'	3',5'	Others		Compound	2,6	3,5	Others
X = H	7.97	7.57	8.13	8.34 7.0	64 (H-4)		X = H	7.95	7.50	7.57 (H-4)
CH2	7.85	7.36	8.12	8.33 2.4	44		CH3	7.81	7.28	2.39
ເັ	7.92	7.54	8.13	8.36			ເັ	7.86	7.49	
Br	7.84	7.70	8.13	8.36			Br	7.79	7.66	
F	8.00	7.24	8.13	8.36			F	7. 9 5	7.19	
OCH ₂	7.89	7.01	8.09	8.33 3.	87		OCH3	7.85	6.95	3.84
NO	8.18	8.40	8.18	8.40			сосй	3 8.07°	8.05ª	2.65
							NO ₂	8.18	8.40	
							^a Alternativ	e assignment	possible.	
Table 9. ¹³ C	chemic	al shifts (d	ა _H) for 4-X-d	liphenyl sul	phoxides (serie	s 4)	· · · · · · · · · · · · · · · · · · ·		<u></u>	<u> </u>
						Carbon				
Compound		1	2,6	3,5	4	1'	2',6'	3′,5′	4'	Others
X = H		145.45	124.58	129.18	3 130.91	145.45	124.58	129.18	130.91	
CH3		142.47	124.99ª	130.04	4 141.64	145.80	124.69°	129.27	130.89	21.45
CI		144.14	126.03	129.5	5ª 137.18	145.19	124.63	129.43ª	131.30	
Br		144.82	126.24	132.54	4 125.56	145.19	124.73	129.51	131.40	
F۵		141.03	126.95	116.43	3 164.03	145.16	124.39	129.23	131.02	
OCH ₂		136.67	127.12	114.7	5 161.92	145.72	124.47	129.12	130.65	55.43
соосн	, c	150.55	124.36	130.4	1 132.39	145.02	124.84	129.52	131.50	52.47
										165.93
COCH3	c	150.60	124.56	129.08	3 138.81	144.97	124.82	129.54	131.53	26.77

^a Alternati	ve assigr	nment pos	ssible.	
h1		2		3

 ${}^{b}{}^{1}J(CF) = 251 \text{ Hz}; {}^{2}J(CF) = 23 \text{ Hz}; {}^{3}J(CF) = 9 \text{ Hz}.$

152.94

° By 2D C/H correlation.

NO₂ °

Table 10. ¹³C chemical shifts (δ_c) for 4-X-4'-NO₂-diphenyl sulphoxides (series 5)

125.25

					Carbon				
Compound	1	2,6	3,5	4	1'	2',6'	3',5'	4'	Others
X = H	144.39	124.85	129.78	131.99	152.94	125.25	124.41	149.20	
CH _a ^a	142.88	125.17	130.52	141.30	153.27	125.27	124.39	149.17	21.54
CI	142.97	126.23	130.14	138.39	152.56	125.23	124.62	149.44	
Br	143.52	126.18	132.88	126.47	152.37	125.14	125.45	149.26	
F	140.05	127.43	117.19	164.72	152.72	125.22	124.51	149.33	
ОСН.	135.32	127.41	115.17	162.59	153.24	125.17	124.20	148.96	55.51
NO ₂	151.11	124.95	124.36	149.12	151.11	124.95	124.36	149.12	

149.20

124.41

144.39

124.85

^a By 2D C/H correlation.

Table 11. ¹³C chemical shifts (δ_c) for 4,4'-X₂-diphenyl sulphoxides (series 6)

			Carbon		
Compound	1	2,6	3,5	4	Others
X = H	145.45	124.58	129.18	130.91	
CH	142.64	124.78	129.90	141.34	21.34
Cl	143.80	126.00	129.74	137.57	
Br	144.35	126.16	132.70	125.93	
F	140.99	127.03	116.72	164.28	
OCH ₂	136.98	126.81	114.69	161.74	55.45
сосй	149.85	124.58	129.24	139.15	26.72
5					196.75
NO ₂ ª	151.11	124.95	124.36	149.12	

^a As in nitrobenzene, for carbon *ortho* to the nitro group ${}^{1}J(CH)$ is larger and ${}^{3}J(CH)$ is smaller than for the carbon meta to the nitro group.

196.97

131.99

129.78

Compound	Carbon									
	1	2,6	3,5	4	1′	2',6'	3′,5′	4,7	Others	
X = H	141.51	127.58	129.26	133.18	141.51	127.58	129.26	133.18		
CH3 *	138.51	127.58	129.84	144.11	141.85	127.35	129.15	132.95	21.48	
CI	140.09	129.09	129.59	139.83	141.14	127.60	129.40	133.44		
Br	140.58	129.12	132.53	128.36	141.01	127.56	129.38	133.43		
F	137.67	130.47	116.60	165.40	141.34	127.55	129.38	133.34		
OCH ₂	132.98	129.80	114.49	163.33	142.28	127.21	129.17	132.83	55.64	
COCH ₃ ^{a,b,c}	145.33	127.91	129.04	140.29	140.70	127.78	129.46	133.64	26.88 196.66	
NO ₂	147.30	128.98	124.54	150.31	139.95	128.01	129.70	134.14	. 30.00	

Table 12. ¹³C chemical shifts ($\delta_{\rm C}$) for 4-X-diphenyl sulphones (series 7)

^a C-2.6 and C-2'.6' distinguished by their multiplicities with full ¹H coupling.

^bC-4 and C-1' identified by the latter being a resolved triplet whereas the former was an unresolved signal under full ¹H coupling, as in the 4-NO₂ analogue.

° C-3,5 and C-3',5' distinguished by comparison of ¹J(CH) and ³J(CH) with those of the 4-NO₂ analogue (cf. footnote to Table 11).

					Carbon				
Compound	1	2,6	3,5	4	1′	2',6'	3′,5′	4′	Others
X = H	139.95	128.01	129.70	134.14	147.30	128.98	124.54	150.31	
СН,	136.99	128.10	130.36	145.42	147.75	128.84	124.50	150.21	21.72
Cl	138.51	129.51	130.09	141.06	146.93	129.04	124.69	150.47	
Br	139.12	129.57	133.12	129.73	146.93	129.06	124.71	150.53	
F	136.12	131.00	117.15	165.9 9	147.19	128.96	124.66	150.44	
OCH,	131.30	130.36	114.98	164.14	148.15	128.64	124.49	150.12	55.84
NO ₂	145.82	129.50	124.95	150.94	145.82	129.50	124.95	150.94	

Table 14.	¹³ C	chemical	shifts	$(\delta_{\rm C})$	for	4,4'-X ₂ -diphenyl	sul
	nhon	es (series '					

Compound	1	2,6	3,5	4	Others
X = H	141.51	127.58	129.26	133.18	
CH3	139.01	127.53	129.58	143.93	21.56
CI	140.20	129.13	129.77	139.73	
Br	140.23	129.19	132.76	128.80	
F	137.50	130.37	116.67	165.39	
OCH ₃	133.88	129.45	114.41	163.06	55.53
COCH3	144.64	128.26	129.26	140.73	26.98
_					196.55
NO₂	145.82	129.50	124.95	150.94	

Table 15 gives the Lynch correlations for the six series of compounds reported here, with the previous three series for comparison.

It has already been pointed out³ that for 1,4-disubstituted benzenes, the DSP correlations for the carbon bearing the fixed substituent (1, C-1) $\rho_R \gg \rho_I$. Indeed, using literature results^{1,3,29,30} for 24 different series of 1,4-disubstituted benzenes, it is found that for C-1 Eqn (3) applies:

$$\rho_{\mathbf{R}}^{\mathbf{Y}} / \rho_{\mathbf{R}}^{\mathbf{H}} = 0.945b + 0.055 \quad (r = 0.992)$$
(3)

This relationship may be more conveniently used in the form of Eqn (4) as a means of finding ρ_{R}^{Y} without doing a complete DSP correlation:

$$\rho_{\rm R}^{\ \rm Y} = 20.32b + 1.18 \tag{4}$$

It is clear from Table 15 that an enhancement of SCS for substituent X is experienced at C-1 when Y is SPh, $SC_6H_4NO_2$ -*p*, and SCH=CH₂.^{2,31} However, there is a

monosubstituted benzenes									
Carbon	Series	а	Expti. a	b	rª	$\rho_{R}^{Y} / \rho_{R}^{H}$			
C-1	1	137.30	135.72	1.64		1.68			
	2	131.66	130.33	1.53		1.47			
	3	135.63	135.72	1.04		1.09			
	4	145.81	145.45	1.12	0.997	1.12			
	5	144.81	144.39	1.09	0.985	1.14			
	6	145.34	145.45	0.99	0.996	1.01			
	7	141.45	141.51	0.97	0.992	0.98			
	8	140.04	139.95	1.01	0.991	1.03			
	9	141.13	141.51	0.82	0.990	0.84			
C-3,5	1	129.00	129.10	0.95					
	2	129.84	129.97	0.99					
	3	120.09	129.10	0.97					
	4	129.24	129.18	1.00	0.997				
	5	129.72	129.78	1.00	0.999				
	6	129.30	129.18	1.00	0.995				
	7	129.23	129.26	1.00	0.999				
	8	129.80	129.70	1.00	0.999				
	9	129.39	129.26	1.01	0.999				
C-4	1	126.50	126.93	1.03					
	2	129.68	129.61	0.97					
	3	127.01	126.93	1.00					
	4	131.03	130.91	0.97	0.998				
	5	132.05	131.99	0.95	0.998				
	6	131.36	130.91	0.95	0.998				
	7	133.61	133.18	0.92	0.996				
	8	135.07	134.14	0.90	0.9 9 6				
	9	133.81	133.18	0.92	0.998				
C-1′	1	134.47	135.72	-0.56					
	4	145.18	145.45	-0.07	0.794				
	5	152.34	152.94	-0.15	0.859				
	7	140.99	141.51	-0.16	0.927				
	8	146.88	147.30	-0.16	0.904				
^a Correla	ation coe	fficient.							

Table 15. Correlations of ¹³C chemical shifts with SCS for

clear trend that b decreases as the central group changes $-S \rightarrow -SO \rightarrow -SO_2$ (comparing series 1, 4, 7 with 2, 5, 8 and 3, 6, 9). Both the decrease in polarizability of the fixed substituent and reduction of the interaction between the two rings may contribute to this trend. There is a similar, but much smaller, trend for C-4.

Dual substituent parameter correlations

As with the diaryl sulphides,¹ the sulphoxides and sulphones show good correlations for H-3,5 with the results given in Table 16. The consistency of the correlations for H-3,5 in all nine series and the results of the Lynch plots for C-3,5 (Table 15) together show the absence of significant effect at these positions of the C-1 substituent. It may be that these substituents are all too similar to expect observable differences at these *meta* positions, for there are *meta* effects to be observed with a wider range of substituents.³²

Table 16. DSP correlations of chemical shifts for H-3,5 with Taft's σ_1 and σ_R^0 values

Series	ρ_1	$ ho_{R}$	٨٩	nъ	r°	Range of <i>δ</i> /ppm
1	0.62	1.92	3.10	8 ^d	0.993	1.05
2	0.64	1.78	2.79	7	0.988	1.22
3	0.75	2.34	3.12	7	0.989	1.23
4	0.69	2.10	3.04	9	0.986	1.36
5	0.72	2.00	2. 9 1	7	0.987	1.38
6	0.76	2.06	2.72	8	0.988	1.41
7	0.70	2.03	2.90	8	0.989	1.37
8	0.69	2.04	2.97	7	0.988	1.36
9	0.78	2.10	2.70	8	0.990	1.38
a Ratio	$\rho_{\rm R}/\rho_{\rm I}$.	anaunda				
° Numo ° Correl	er or con	npounas. Afficient				

^d Omitting NHCOCH₃ substituent.

For ready comparison, the successful DSP correlations of carbons for all nine series of compounds are given in Table 17.

Table 17.	DSP corr	elations of ¹	¹³ C chemica	ıl shifts wi	th Taf	t's $\sigma_{\rm I}$ and σ	[°] values
Carbon	Series	$\boldsymbol{\rho}_1$	$\rho_{\rm R}$	٨°	nь	r°	Range of <i>6</i> /ppm
C-1	1	10.5	36.2	3.5	9	0.999	34.4
	2	9.5	31.5	3.3	7	0.999	21.7
	3	4.7	23.4	5.0	8	0.979	12.2
	4	6.0	24.2	4.0	9	0.999	16.27
	5	4.0	24.0	6.0	7	0.990	15.79
	6	4.2	21.7	5.2	8	0.997	14.13
	7	4.9	21.1	4.3	8	0.995	14.32
	8	4.9	21.6	4.4	7	0.993	14.52
	9	3.3	18.1	5.6	8	0.994	11.92
C-2,6	1	-2.8	-14.1	5.0	9	0.990	8.7
	2	-1.4	-10.3	7.4	7	0.992	6.2
	4	2.0	-4.2	-2.2	9	0.990	2.79
	5	1.7	-5.5	-3.4	7	0.992	2.58
	6	1.9	-4.2	-2.2	8	0.979	2.45
	7	3.1	-3.2	-1.1	8	0.962	2.22
	8	3.2	-3.8	-1.2	7	0.962	2.99
	9	3.5	-2.0	-0.6	8	0.960	2.84
C-1′	1	-5.0	-11.7	2.3	9	0.993	6.3
	4	-1.4	-1.4	1.0	9	0.991	1.41
	5	-2.0	-2.5	1.3	7	0.990	2.16
	7	-1.9	-3.0	1.6	8	0.978	2.63
	8	-1.8	-2.8	1.5	7	0.993	2.33
C-2′,6′	1	3.5	8.8	2.5	9	0.990	5.8
	2	3.6	7.3	2.0	7	0.970	5.4
	7	0.53	1.0	1.9	8	0.986	0.80
	8	0.56	1.1	2.0	7	0.996	0.86
C-3′,5′	1	0.9	2.1	2.3	9	0.936	1.9
	2	0.3	0.5	1.7	7	0.994	0.4
	4	0.56	0.78	1.4	9	0.942	0.66
	7	0.56	0.56	1.0	8	0.997	0.55
	8	0.49	0.47	1.0	7	0.997	0.46
C-4′	1	2.7	5.4	2.0	9	0.997	4.0
	4	1.1	1.6	1.4	9	0.981	1.34
	7	1.2	1.5	1.3	8	0.998	1.29
	8	0.7	0.9	1.2	7	0.995	0.82
^{a,b,c} As in	Table 16.						

C-1. The structural change $-S-Ar \rightarrow -SO-Ar$ results in a large decrease in both ρ_1 and ρ_R when Ar is phenyl and p-nitrophenyl, whereas the change $-SO-Ar \rightarrow -SO_2$ -Ar results in smaller decreases (indeed, ρ_1 actually increases slightly when Ar is pnitrophenyl). When the molecules are symmetrical (series 3, 6, 9) the corresponding structural changes lead to small decreases in ρ_1 and ρ_R . These results are, of course, reflected in the Lynch slopes (Table 15).

Bromilow et al.²⁸ introduced a non-linear resonance variation to the normal DSP correlation method (DSP-NLR). They employed an electron-demand parameter ε for the fixed substituent Y, and used Eqn (5) to find a value for ε that optimizes the correlation using $\sigma_1/\bar{\sigma}_R$. Within the range of substituents that they tested,

$$\bar{\sigma}_{\mathbf{R}} = \sigma_{\mathbf{R}}^{0} / (1 - \varepsilon \sigma_{\mathbf{R}}^{0}) \tag{5}$$

the electron-demand parameter fitted Eqn (6) with few exceptions.

$$\varepsilon = -0.9\sigma_{\rm I}({\rm Y}) - 1.6\sigma_{\rm R}({\rm Y}) \tag{6}$$

Although it was argued that extremely polarizable groups, such as SCH_3 , must be excluded from such a treatment, we have calculated values for ε from Eqn (6) and also determined values for ε that give optimum correlations of our data for the three substituents PhS, PhSO and PhSO₂, with the following results:

	Phs	PhSO	PhSO ₂
Calculated ε from Eqn (6)	-0.07	-0.44	-0.69
Experimental ε	+0.2	-0.2	-0.4

The experimental set of results seem to constitute a sensible set, going from overall electron donation to electron acceptance.

C-2,6. We previously discussed the negative values of ρ_1 and ρ_R for these carbons of series 1 and 2 in terms of the involvement of sulphur lone-pair electrons.¹ It is not then surprising to find marked differences in the sulphoxide and sulphone series, where ρ_1 is now positive and ρ_R is still negative, but with the trend $|\rho_R^S| > |\rho_R^{SO}| > |\rho_R^{SO_2}|$. What is surprising is to find that $\rho_R^{SO_2}$ is still negative. Whereas the sulphoxides could be accommodated by the same explanation as that advanced for the sulphides, but with a much reduced effect because of the oxygen atom, this would not be acceptable for the sulphones.

However, in the diaryl sulphoxides and sulphones two aspects of structure make comparison with the sulphides difficult. The planes of the two aryl rings are approximately perpendicular to the C-1—S—C-1' plane,³³ in contrast to the rings being about 35° from coplanarity in the sulphides, and the oxygen atoms and polar S=O bonds at approximately tetrahedral sulphur provide an opportunity to influence the chemical shifts of nuclei *ortho* to the sulphur group. It would be expected that if some shielding or deshielding of C-2,6 by the S=O bonds, as modified by the C-4 substituents, accounted for the trends mentioned above, similar trends should also be evident at C-2',6'. The results for C-2',6' do not support such an explanation.

C-1' to C-6'. Such correlations as we find result in values for ρ_1 and ρ_R that are smaller for the sulphoxides and sulphones than for the sulphides, although the signs are the same, viz. negative for C-1' and positive for all the other carbons. Indeed, correlations for the sulphoxides and sulphones are similar to those for the corresponding carbons of the unsubstituted rings of 4-X-azobenzenes,³⁴ 4-X-stilbenes³⁴ and 4-X-benzophenones³⁵ (see Table 18). This may indicate a similarity in the trans-

Table 18. DSP correlations of ¹³C chemical shifts for azobenzenes, stilbenes, benzophenones, diphenyl sulphoxides and diphenyl sulphones

	C-1'		C-2',6'		C-3',5'		C-4'	
Series	$\boldsymbol{\rho}_{\mathrm{I}}$	$ ho_{_{\sf P}}$	$\boldsymbol{\rho}_{i}$	$ ho_{R}$	ρ	$ ho_{\scriptscriptstyle R}$	ρ	$ ho_{ m R}$
X	-0.6	-0.3ª	0.6	0.8ª	0.2	0.3	1.7	1.9 ⁶
хСн=сн(С)	-1.4	-1.1	0.5	0. 9	0.3	0.3	1.4	1.9
x-{O}-co-{O}	-1.6	-1.8	-	_	-	-	1.4	1.3
x-{>-so-{>	-1.4	-1.4			0.6	0.8	1.1	1.6
x-O-so-ONO	₂ -2.0	-2.5	-		-	_	-	
x-{>-so ₂ -{>>	-1.9	-3.0	0.5	1.0	0.6	0.6	1.2	1.5
X	₂ -1.8	-2.8	0.6	1.1	0.5	0.5	0.7	0.9
^a Correlation with $\sigma_{\rm R}^+$. ^b Correlation with $\sigma_{\rm R}^{\rm BA}$.								

mission of electronic effects from the substituted to the unsubstituted ring in all these compounds, with the 4-Xdiphenyl sulphides showing evidence of a mechanism of transmission not available to the other compounds. This generality of transmission is clearly discussed by Craik.²⁷

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