MAGNETIC RESONANCE IN CHEMISTRY, VOL. 33, 779–790 (1995)

^{1}H and ^{13}C NMR Study of Substituent Effects in 2- and 3-Substituted Diphenyl Sulphides and Sulphones and 4-Substituted 2′,6′-Dimethyldiphenyl Sulphides

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The proton and carbon NMR spectra of nine 2-substituted diphenyl sulphides (S-2-X), seven 3-substituted diphenyl sulphides (S-3-X), nine 2-substituted diphenyl sulphones (SO_2-2-X), nine 3-substituted diphenyl sulphones (SO_2-3-X) and nine 4-substituted-2′,6′-dimethyldiphenyl sulphides (Me_2-S-4-X) were obtained. Correlations of the ^{1}H and ^{13}C chemical shifts were made with benzene substituent-induced chemical shifts (Lynch plots) and Hammett and dual-substituent parameters and the results were compared with those of 4-substituted diphenyl sulphides (S-4-X) and sulphones (SO_2-4-X). The main conclusions are as follows: (i) the transmission of the substituent effects in substituted diphenyl sulphides decreases in the order S-4-X ≈ S-2-X > Me_2-S-4-X > S-3-X; (ii) the inductive effects are transmitted to a larger extent than the resonance effects to the unsubstituted ring in 3-substituted diphenyl sulphides, while the reverse trend is observed in other substituted diphenyl sulphides; (iii) in 2-methoxy-, 2-chloro-, 2-bromo- and 2-nitrodiphenyl sulphides, an increase in the size of the substituent causes an upfield shift for H-6 ascribable to the repulsion between the lone pairs of electrons on the sulphur and the substituent and its influence on the conformation; (iv) the diminished transmission of substituent effects to the remote rings in 4-substituted 2′,6′-dimethyldiphenyl sulphides is probably due to the orthogonal orientation of the rings; and (v) the signal due to the H-6 of 2-substituted diphenyl sulphones suffers a downfield shift with an increase in the size of the substituent, this being ascribable to the increasing steric interaction between the 2-substituent and the sulphonyl oxygen and consequent changes in the conformation.

KEY WORDS NMR; ^{1}H NMR; ^{13}C NMR; diphenyl sulphides; diphenyl sulphones; π-polarization

INTRODUCTION

Recently, we reported[1,2] the effect of substituents on the ^{1}H and ^{13}C chemical shifts of 4-substituted and 4,4′-disubstituted diphenyl sulphides, sulphoxides and sulphones. Correlation analyses of ^{13}C chemical shifts of 4-substituted and 4,4′-disubstituted diphenyl sulphides showed that (i) there is transmission of inductive (field) and resonance effects from one aryl ring to the other, except when both rings carry substituents of the same electronic character, (ii) the resonance effects are transmitted to a larger extent than the inductive effects from the substituted ring to all the carbons of the remote ring, (iii) transmission of both inductive and resonance effects diminishes with increasing distance between the substituent and the carbon nuclei from C-1′ to C-4′, except C-3′, 5′, which are least influenced by substituent effects, and (iv) C-1′ shows an 'inverse' substituent effect whereas all other carbons show 'normal' effects. These results suggested that substituent effects between the rings in sulphides are transmitted by conjugative interactions and π-polarization. In sulphoxides and sulphones π-polarization interactions between the rings predominate and the transmission follows the order —S— ⩾ —SO— ≈ —SO_2—.

The above results prompted us to investigate the transmission of substituent effects via the sulphur atom in 3-substituted diphenyl sulphides wherein the substituent *meta* to sulphur could substantially alter the extent and composition of resonance and inductive effects transmitted to the unsubstituted ring relative to S-4-X series.

It is known that diphenyl sulphide exists in a non-planar (screw) conformation with both phenyl rings being twisted out of the C_1—S—C_1, plane by about 35° because of the steric interaction between the *ortho* hydrogens.[3] This suggests that the introduction of groups at one or both of the *ortho* positions of a phenyl ring of diphenyl sulphide would increase the steric interaction, which could influence the conformation of the sulphides and the consequent overlap of the orbitals of sulphur with those on the adjacent carbons. This could, in turn, influence the transmission of electronic effects. These considerations prompted us to undertake a detailed ^{1}H and ^{13}C NMR spectral and correlation study of 2-substituted and 4-substituted 2′,6′-dimethyldiphenyl sulphides. The NMR spectra of 3- and 2-

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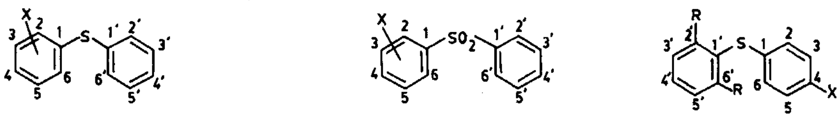
CCC 0749–1581/95/100779–12

Received 4 October 1994
Accepted (revised) 15 April 1995



Series

	S-4-X	S-3-X	S-2-X	SO_2-4-X	SO_2-3-X	SO_2-2-X	Me_2-S-4-X
NH_2	a	–	a	–	–	–	a
OCH_3	b	b	b	b	b	b	b
$NHCOCH_3$	c	–	c	–	–	–	c
CH_3	d	d	d	d	d	d	d
H	e	e	e	e	e	e	e
F	f	f	f	f	f	f	f
Cl	g	g	g	g	g	g	g
Br	h	h	h	h	h	h	h
$COOCH_3$	i	–	–	–	i	–	–
$COCH_3$	j	–	–	j	–	–	–
NO_2	k	k	k	k	k	k	k
CHO	–	–	–	–	–	l	–
CN	–	–	–	–	m	m	–

Scheme 1. Compounds studied.

substituted diphenyl sulphones were also measured with a view to studying the electronic and/or steric effects of the substituents on the chemical shifts, conformation and transmission of substituent effects. The compounds investigated are shown in scheme 1.

EXPERIMENTAL

Materials

Diphenyl sulphide was prepared from benzenethiol and iodobenzene by the method of Mauthner.[4] The 3- and 2-substituted diphenyl sulphides (X = F, Cl, Br, CH_3 and OCH_3) were prepared by the method of Hilbert and Johnson[5] by reaction of the corresponding substituted benzenediazonium chloride with sodium thiophenolate. 2-Nitrodiphenyl sulphide was prepared by a literature method.[6] 2-Acetamidodiphenyl sulphide was prepared from 2-nitrodiphenyl sulphide as reported earlier.[1] 2-Aminodiphenyl sulphide was prepared by the hydrolysis of 2-acetamidodiphenyl sulphide. The other sulphides were purified by distillation under reduced pressure, crystallization or column chromatography.

Most of the 4-substituted 2′,6′-dimethyldiphenyl sulphides reported in this study were hitherto unknown. 2,6-Dimethyldiphenyl sulphide (b.p. 137–138 °C/3 mmHg; lit.[7] 112–122 °C/1 mmHg) and 4-chloro- (b.p. 168–169.5 °C/3 mmHg), 4-bromo- (m.p. 65–67 °C), 4-fluoro- (b.p. 134–136 °C/3 mmHg), 4-methyl- (b.p. 153–155 °C/3 mmHg) and 4-methoxy- (m.p. 49.5–50.5 °C) 2′,6′-dimethyldiphenyl sulphides were prepared by the reaction of the sodium salts of corresponding substituted benzenethiols and 2,6-dimethylphenyl diazonium chloride at 70 °C. Unreacted benzenethiols and diphenyl disulphides were removed by steam distillation in the presence of zinc and HCl and the products purified by column chromatography. 4-Nitro-2′,6′-dimethyldiphenyl sulphide was prepared from the sodium salt of 2,6-dimethyl benzenethiol by refluxing with 4-chloronitrobenzene in ethanol and recrystallizing from ethanol, m.p. 105–107 °C.

4-Acetamido-2′,6′-dimethyldiphenyl sulphide was obtained by refluxing 4-nitro-2′,6′-dimethyldiphenyl sulphide (4.0 g) with zinc dust (3.5 g) in acetic acid (80 ml) for 3 h and crystallizing from light petroleum, m.p. 172–173.5 °C. 4-Amino-2′,6′-dimethyldiphenyl sulphide was obtained by the reduction of 4-nitro-2′,6′-dimethyldiphenyl sulphide (1 g) with iron filings (20 g) and concentrated hydrochloric acid (2 ml) for 3 h in methanol (20 ml) under reflux. The product worked up in the usual way was purified by column chromatography on silica gel using light petroleum –benzene (3 : 1, v/v) as eluent. This afforded an oily product.

Most of the 2- and 3-substituted diphenyl sulphones (X = OCH_3, CH_3, H, F, Cl, Br and NO_2) were prepared from the corresponding sulphides by oxidation with a slight excess of hydrogen peroxide in acetic acid. 3-Cyanodiphenyl sulphone was prepared by the reaction of 3-bromodiphenyl sulphone with copper(I) cyanide in DMF. Methyl 3-phenylsulphonyl benzoate was prepared from 3-cyanodiphenyl sulphone by hydrolysis followed by esterification with methanol. 2-Phenylsulphonyl benzaldehyde was prepared by the oxidation of 2-methyldiphenyl sulphide with chromium trioxide in acetic anhydride. 2-Cyanodiphenyl sulphone was prepared by the reaction of 2-bromodiphenyl sulphone with copper(I) cyanide in DMF. The new compounds, 3-bromo-, 2-amino- and 2-chlorodiphenyl sulphides and 3-cyano-, 3-ethoxycarbonyl- and 2-formyldiphenyl sulphones, gave satisfactory CH analyses. The observed b.p./m.p. of the sulphides and sulphones given in Table 1 are uncorrected.

Spectra

The ^1H and ^{13}C NMR spectra of 4-substituted 2′,6′-dimethyl diphenyl sulphides were measured at 300 and 75 MHz, respectively (Varian VXR-300). The ^1H and ^{13}C NMR spectra of all other compounds were measured at 360 and 90.56 MHz, respectively (Brucker WM-360). All the ^1H NMR spectra were obtained for approximately 0.03 M solutions in $CDCl_3$ with TMS as internal reference and broadband and off-resonance decoupled ^{13}C NMR spectra were obtained for approximately 0.5 M solutions in $CDCl_3$ with TMS as internal reference. A pulse angle of 37.5° (5 μs) and a repetition time of 3.72 s were used, collecting 32 K data points in the quadrature detection mode for a spectral width of 22 700 Hz at room temperature (20–21 °C). 2D C/H shift correlated spectra were obtained using the standard Bruker program (XHCORRD) or HETCOR pulse sequence of the Varian software. The ^1H and ^{13}C chemical shifts of the sulphides and sulphones are presented in Tables 2–11.

Table 1. Boiling and melting points of 3- and 2-substituted diphenyl sulphides and sulphones

Series	Substituent	Observed b.p/mmHg (m.p) (°C)	Literature b.p/mmHg (m.p) (°C)	Ref.
S-3-X	OCH_3	162–164/5.5	156/4	5
	CH_3	158–160/6	112–113/2	8
	H	115/3	115/3	9
	F	129–131/3–4	112–113/2	10
	Cl	148–150/2.5	186/30	11
	Br[a]	151–153/3	—	—
	NO_2	(41.5–42.5)	(41–42)	12
S-2-X	NH_2 [a]	Semi-solid	—	—
	OCH_3	154/3	150–152/3	5
	NHAc	(88.5–89)	(86)	4
	CH_3	142–144/5	164/12	12
	F[a]	117–120/2.5	—	—
	Cl	153–155/3.5	150/4	11
	Br	174–176/12	175–177/12	13
	NO_2	(78.5–80)	(77)	12
SO_2-3-X	OCH_3	84–86	90.5	14
	CH_3	119–121.5	121–122	12
	H	122–124	125.5–126	15
	F	95.5–97	96–97	16
	Cl	108–110	110–111	17
	Br	121–122.5	121.6–123	18
	NO_2	83–84.5	84–85	12
	CN	90–92	—	—
	$COOC_2H_5$	58.5	—	—
SO_2-2-X	OCH_3	138–140	141–142	12
	CH_3	76–78	81–82	12
	F	103–104	—	—
	Cl	105–107	103.5	19
	Br	116–117.5	117–119	18
	NO_2	143–145	147	12
	CHO	92–93.5	—	—
	CN	101.5–103	99–102	20

[a] These compounds gave satisfactory C, H analyses.

Assignment of ^{1}H and ^{13}C chemical shifts

Assignments of ^{1}H chemical shifts were made using considerations of splitting patterns, spin decoupling, 2D C/H correlations and additivity of chemical shifts. The ^{13}C chemical shifts were assigned by intensity, peak multiplicity under off-resonance decoupling and completely decoupled spectra, SCS considerations and 2D C/H correlated spectra. The $^nJ_{CF}$ values for fluoro-substituted sulphides were also used in the assignments. The ^{1}H and ^{13}C chemical shifts of the compounds are considered to be accurate to 0.02 and 0.05 ppm, respectively.

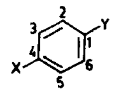
RESULTS AND DISCUSSION

2- and 3-substituted diphenyl sulphides

Lynch correlations. Correlation of ^{1}H and ^{13}C chemical shifts of nuclei of the substituent bearing phenyl ring in S-3-X and S-2-X series with the SCS values of corresponding monosubstituted benzenes were performed using the Lynch equation[21,22] [Eqn (1)] and the results are given in Table 12.

$$\text{Shift } C_X(Y) = a + b \text{ SCS } C_X(H) \qquad (1)$$

The correlation of ^{13}C chemical shifts in 1,4-disubstituted benzenes with the SCS values for monosubstituted benzenes showed that the fixed substituent (Y in **1**) 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).



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The correlation of ^{13}C chemical shifts for the 4-substituted diphenyl sulphides (S-4-X) showed that the fixed phenylthio substituent (Y = PhS) undergoes an amplification of the substituent effect on C-1, as is evident from the *b* value of 1.64.[1] In the S-3-X series, C-2, C-3 and C-4 have almost unit slopes whereas the carbon *para* to the variable substituent (C-6) has a Lynch slope of 0.83, indicating that the fixed PhS substituent significantly diminishes the substituent effect. In the series S-2-X, only C-2 and C-3 afford good Lynch correlations.

Table 2. ^{1}H chemical shifts of 2-substituted diphenyl sulphides (S-2-X)

	δ (ppm)							
X	H-3	H-4	H-5	H-6	H-2′,6′	H-3′,5′	H-4′	Others
NH_2	6.69	7.17	6.72	7.42	7.15	7.05[a]	7.05[a]	—
OCH_3 [b]	6.89	7.22	6.87	7.08	7.34	7.30	7.25	—
$NHCOCH_3$	8.44	7.45	7.13	7.58	7.08	7.25	7.17	3.87
CH_3 [a]	7.20	7.20	7.20	7.20	7.20	7.20	7.20	8.18, 2.06
H	7.28	7.24	7.28	7.33	7.33	7.28	7.24	7.33 (H-2)
F	7.11	7.23	7.07	7.26	7.32	7.31	7.28	—
Cl[b]	7.39	7.13[c]	7.11[c]	6.97	7.45	7.38	7.36	—
Br[b]	7.56	7.02	7.14	6.92	7.45	7.40	7.37	—
NO_2	8.23	7.22	7.34	6.86	7.59	7.48	7.49	—

[a] Approximate values.
[b] By 2D C/H shift correlation.
[c] Alternative assignments possible.

Table 3. ^1H chemical shifts of 3-substituted diphenyl sulphides (S-3-X)

	δ (ppm)							
X	H-2	H-4	H-5	H-6	H-2′,6′	H-3′,5′	H-4′	Others
OCH_3	6.86	6.77	7.21	6.91	7.37	7.32	7.27	3.76
CH_3	7.18	7.06	7.16	7.15	7.33	7.28	7.22	2.30
H	7.33	7.24	7.28	7.33	7.33	7.28	7.24	7.28 (H-6)
F	6.93	6.88	7.23	7.04	7.42	7.34	7.36	—
Cl[a]	7.12	7.14	7.27	7.26	7.41	7.30	7.14	—
Br	7.40	7.30	7.12	7.18	7.39	7.33	7.33	—
NO_2	8.03	8.00	7.41	7.49	7.49	7.41	7.41	—

[a] By 2D C/H shift correlation.

Table 4. ^1H chemical shifts of 4-substituted 2′,6′-dimethyldiphenyl sulphides (Me_2-S-4-X)

	δ (ppm)					
X	H-2,6	H-3,5	H-3′,5′	H-4′	2′,6′-Dimethyl	Others
NH_2	6.84	6.53	7.14[a]	7.14[a]	2.45	3.36
OCH_3	6.90	6.73	7.14	7.16	2.42	3.72
$NHCOCH_3$	6.86	7.30	7.15	7.19	2.40	2.08
CH_3	6.97	6.83	7.15	7.17	2.42	2.24
H	7.18[b]	7.17[b]	6.92	7.05	2.44	7.22 (H-4)
F	6.88	6.86	7.16	7.18	2.41	—
Cl	6.82	7.11	7.15	7.20	2.40	—
Br	6.76	7.25	7.17	7.20	2.40	—
NO_2	6.97	8.02	7.23	7.29	2.40	—

[a] Approximate values.
[b] Interchangeable.

Table 5. ^1H chemical shifts of 2-substituted diphenyl sulphones (SO_2-2-X)

	δ (ppm)							
X	H-3	H-4	H-5	H-6	H-2′,6′	H-3′,5′	H-4′	Others
OCH_3	6.91	7.55	7.11	8.16	7.97	7.48	7.55	3.76
CH_3	7.23	7.50	7.40	8.22	7.86	7.50	7.57	2.44
H	7.50	7.57	7.50	7.95	7.95	7.50	7.57	7.95 (H-2)
F[a]	7.12	7.58	7.33	8.12	8.02	7.53	7.63	—
Cl	7.52	7.54	7.45	8.37	7.96	7.52	7.61	—
Br	7.67	7.44	7.56	8.42	7.96	7.52	7.62	—
CN[b]	7.82	7.71	7.80	8.36	8.09	7.57	7.65	—
CHO[b]	8.03	7.75[c]	7.78[c]	8.22	7.91	7.56	7.63	—
NO_2	7.76	7.76	7.77	8.37	7.98	7.57	7.65	—

[a] Confirmed by $^nJ_{HF}$ values: $^3H_{HF} = 9.0$ Hz (H-3), $^4J_{HF}$ and $^5H_{HF} = 7.5$ Hz (H-5).
[b] By 2D C/H shift correlation.
[c] Alternative assignments possible.

Table 6. ^1H chemical shifts of 3-substituted diphenyl sulphones (SO_2-3-X)

	δ (ppm)							
X	H-2	H-4	H-5	H-6	H-2′,6′	H-3′,5′	H-4′	Others
OCH_3	7.45	7.07	7.40	7.52	7.95	7.53	7.57	3.84
CH_3	7.76	7.36	7.38	7.74	7.95	7.50	7.57	2.41
H	7.95	7.57	7.50	7.95	7.95	7.50	7.57	7.50 (H-3)
F	7.65	7.27	7.49	7.74	7.95	7.53	7.60	
Cl[a]	7.93	7.52	7.45	7.84	7.95	7.54	7.61	
Br	8.09	7.68	7.38	7.87	7.95	7.53	7.60	
CN[a]	8.22	7.84	7.66	8.18	7.96	7.56	7.64	
$COOC_2H_5$	8.60	8.24	7.60	8.13	7.97	7.53	7.60	1.42 4.42
NO_2	8.78	8.42	7.74	8.28	7.99	7.57	7.64	

[a] By 2D C/H shift correlation.

Table 7. ^{13}C **chemical shifts for 2-substituted diphenyl sulphides (S-2-X)**

	δ (ppm)										
X	C-1	C-2	C-3	C-4	C-5	C-6	C-1′	C-2′,6′	C-3′,5′	C-4′	Others
NH_2[a]	114.12	148.72	115.21	130.99	118.54	137.31	136.69	126.31	128.86	125.26	—
OCH_3[a]	123.93	157.23	110.81	128.30	121.16	131.55	134.46	131.31	129.06	126.96	55.77
$NHCOCH_3$	120.01	139.82	120.94	126.32	124.41	136.32	135.64	130.86	129.31	127.21	24.72, 168.29
CH_3	133.74	136.16	130.58	126.30	127.89	132.98	139.91	129.58	129.10	126.71	20.63
H	135.72	130.94	129.10	126.93	129.10	130.94	135.72	130.94	129.10	126.93	—
F[b]	122.74	161.11	151.91	124.72	133.38	129.38	134.15	130.92	129.27	127.29	—
Cl[a]	132.69	133.23	129.74	127.72	127.25	130.10	136.52	133.23	129.59	128.32	—
Br[a]	138.69	122.97	132.92	127.17	127.74	129.66	132.77	133.39	129.57	128.38	—
NO_2[a]	130.92	144.91	125.70	124.95	133.45	128.30	139.42	135.86	130.10	130.03	—

[a] By 2D C/H shift correlation.

[b] Confirmed by $^{n}J_{CF}$ values: $^{1}J_{CF} = 246.8$ Hz (C-2), $^{2}J_{CF} = 22.3$ Hz (C-3), $^{2}J_{CF} = 17.4$ Hz (C-1), $^{3}J_{CF} = 2.9$ Hz (C-4) and $^{3}J_{CF} = 9.7$ Hz (C-6).

Table 8. ^{13}C **chemical shifts of 3-substituted diphenyl sulphides (S-3-X)**

	δ (ppm)										
X	C-1	C-2	C-3	C-4	C-5	C-6	C-1′	C-2′,6′	C-3′,5′	C-4′	Others
OCH_3	137.10	115.86	159.95	112.63	129.86	122.83	135.20	131.26	129.11	127.12	55.05
CH_3	136.13	131.82	138.95	128.33	129.02	128.00	135.24	130.70	129.09	126.79	21.29
H	135.72	130.94	129.10	126.93	129.10	130.94	135.72	130.94	129.10	126.93	—
F[a]	139.36	116.41	163.04	113.47	130.30	125.18	133.87	132.58	129.47	128.06	—
Cl[b]	138.83	130.02	133.85	126.64	129.37	127.80[c]	134.82	132.24	129.42	127.91[c]	—
Br	138.98	132.09	122.91	129.46	130.24	128.23	133.81	132.09	129.33	127.79	—
NO_2	140.44	123.00	148.56	120.82	129.59	134.17	132.03	133.33	129.73	128.87	—

[a] Confirmed by $^{n}J_{CF}$ values: $^{1}J_{CF} = 248.4$ Hz (C-3), $^{2}J_{CF} = 23.3$ Hz, $^{2}J_{CF} = 21.2$ Hz (C-4), $^{3}J_{CF} = 8$ Hz (C-1) and $^{3}J_{CH} = 8.3$ Hz (C-5).

[b] Assigned by 2D C/H shift correlation.

[c] Alternative assignments possible.

Table 9. ^{13}C **chemical shifts[a] of 4-substituted-2′,6′-dimethyldiphenyl sulphides (Me_2-S-4-X)**

	δ (ppm)								
X	C-1	C-2,6	C-3,5	C-4	C-1′	C-2′,6′	C-3′,5′	C-4′	2′-6′-Dimethyl	Other
NH_2	125.49	128.59	115.83	144.20	132.52	143.13	128.23	128.23	22.04	—
OCH_3	128.57	127.90	114.64	157.49	131.86	143.47	128.34	128.86	21.90	55.24
$NHCOCH_3$	133.50	128.43	120.85	135.15	131.20	143.67	126.60	129.16	21.75	24.28, 168.30
CH_3	134.34	125.87	129.64	134.38	130.99	143.75	128.35	129.03	21.84	20.81
H	138.03	128.90	128.46	124.62	130.50	143.87	125.63	129.26	21.84	—
F[b]	132.97	127.47	115.93	160.68	130.90	143.64	128.50	129.28	21.79	—
Cl	136.63	126.82	128.96	130.37	130.07	143.77	128.55	129.48	21.75	—
Br	137.31	127.09	131.82	118.08	129.88	143.76	128.54	129.51	21.74	—
NO_2	144.79	124.81	124.06	148.13	128.03	143.86	128.85	130.28	21.54	—

[a] Chemical shifts of all compounds except NH_2 assigned with the help of 2D C/H HETCOR spectra.

[b] Confirmed by $^{n}J_{CF}$ values: $^{1}J_{CF} = 244$ Hz, $^{2}J_{CF} = 22$ Hz, $^{3}J_{CF} = 7.7$ Hz and $^{4}J_{CF} = 3.4$ Hz.

Table 10. ^{13}C **chemical shifts of 2-substituted diphenyl sulphones (SO_2-2-X)**

	δ (ppm)										
X	C-1	C-2	C-3	C-4	C-5	C-6	C-1′	C-2′,6′	C-3′,5′	C-4′	Others
OCH_3	128.71	156.93	112.46	135.55	120.39	129.62	141.31	128.21	128.40	132.87	55.78
CH_3	138.67	137.86	129.28	133.61	126.42	132.64	141.12	127.52	128.98	133.01	20.14
H	141.51	127.58	129.26	133.18	129.26	127.58	141.51	127.58	129.26	133.18	—
F[a]	129.36	159.17	117.30	136.04	124.65	129.72	140.85	128.11	129.13	133.70	—
Cl	138.28	132.80	130.93	134.69	127.30	132.00	139.99	128.43	128.84	133.46	—
Br	134.67	121.14	131.42	135.63	127.94	128.85	139.82	128.61	128.85	133.44	—
CN[b]	143.47	111.21	133.37	133.47	135.64	129.76	139.42	128.55	129.40	134.21	115.62
CHO[b]	142.21	133.64	129.50	133.90[c]	133.75[c]	129.54	141.38	127.42	129.64	133.80	189.30
NO_2	134.44	148.43	124.71	132.54	133.81	131.55	140.37	128.18	129.10	134.64	—

[a] Confirmed by $^{n}J_{CF}$ values: $^{1}J_{CF} = 257.1$ Hz (C-2), $^{2}J_{CF} = 14$ Hz (C-1), $^{2}J_{CF} = 21.1$ Hz (C-3), $^{3}J_{CF} = 8.4$ Hz (C-4), $^{4}J_{CF} = 3$ Hz (C-5) and $^{3}J_{CF} = 0$ Hz (C-6).

[b] By 2D C/H shift correlation.

[c] Alternative assignments possible.

Table 11. ^{13}C chemical shifts of 3-substituted diphenyl sulphones (SO_2-3-X)

	δ (ppm)										
X	C-1	C-2	C-3	C-4	C-5	C-6	C-1′	C-2′,6′	C-3′,5′	C-4′	Others
OCH_3	142.66	112.31	159.99	119.45[a]	130.39	119.84[a]	141.49	127.59	129.26	133.21	55.68
CH_3	141.36[a]	127.87	139.53	134.00	129.12	124.78	141.69[a]	127.55	129.22	133.09	21.31
H	141.51	127.58	129.26	133.18	129.26	127.58	141.51	127.58	129.26	133.18	—
F[b]	143.72	114.87	162.37	120.46	131.20	123.40	140.79	127.71	129.42	133.58	—
Cl[c]	143.32	127.62	135.41	133.33	130.64	125.76	140.81	127.75	129.45	133.61	—
Br	143.49	130.48[a]	123.24	136.28	130.89[a]	126.24	140.83	127.80	129.49	133.64	—
CN[c]	143.37	131.14	113.85	136.25	130.42	131.50	140.11	127.84	129.63	133.98	116.97
$COOC_2H_4$	142.35	128.71	131.96	134.06	129.48	131.57	141.09	127.80	129.48	133.51	164.82, 61.76, 14.32
NO_2	143.91	122.71	148.40	127.71	130.85	134.15	140.09	127.96	129.73	133.11	—

[a] Alternative assignments possible.
[b] Confirmed by $^nJ_{CF}$ values: $^1J_{CF} = 252$ Hz (C-3), $^2J_{CF} = 24.3$ Hz (C-2), $^2J_{CF}$ 21.3 (C-4), $^3J_{CF} = 7.7$ Hz (C-5) and $^4J_{CF} = 2.4$ Hz (C-6).
[c] By 2D C/H shift correlation.

Table 12. Lynch correlations of ^1H and ^{13}C chemical shifts of 4-, 3- and 2-substituted diphenyl sulphides

Series	Nucleus	Benzene SCS (*S*)	Slope (*b*)	Intercept (*a*) Calculated	Intercept (*a*) Observed	*r*	*n*
S-4-X	C-1	S_p	1.64	137.36	135.72	0.991	9
	C-2,6	S_m		Scattered plot			
S-2-X	C-1/C-3	S_o		Scattered plots			
	C-4/C-6	S_m		Scattered plots			
	C-5	S_p		Scattered plot			
S-3-X	C-1/C-5	S_p		Scattered plots			
	C-2	S_o	0.98	129.94	130.94	0.979	7
	C-6	S_p	0.83	129.65	130.94	0.978	7
S-2-X	C-2	S_i	0.91	128.65	130.94	0.993	8
S-4-X	C-3,5	S_o	0.93	129.10	129.10	0.994	9
S-3-X	C-3	S_i	0.98	128.75	129.10	0.999	7
S-2-X	C-3	S_o	1.10	129.83	129.10	0.984	8
S-4-X	C-4	S_i	1.01	126.50	126.93	0.997	9
S-3-X	C-4	S_o	0.99	126.84	126.93	0.989	7
S-4-X	H-3,5	S_o	0.83	7.32	7.28	0.994	9
S-2-X	H-3	S_o	0.92	7.36	7.28	0.997	8
S-3-X	H-2	S_o	0.82	7.24	7.33	0.975	7
	H-4	S_o	0.86	7.18	7.24	0.993	7
	H-5	S_m		Scattered plot			
S-2-X	H-6	S_p	0.71	7.26	7.33	0.953	7
	H-4/H-6	S_m		Scattered plots			
	H-5	S_p		Scattered plot			

Hammett and dual-substituent parameter correlations. The ^1H and ^{13}C chemical shifts of the remote ring atoms of the S-2-X series afford several reasonable correlations using Hammett substituent parameters [Eqn (2)] and the data are given in Table 13 along with the results for the S-4-X series.

$$\delta = \rho\sigma + \delta_0 \qquad (2)$$

The ρ values for the nuclei of the unsubstituted phenyl ring show that the extent of transmission is almost the same in both the S-4-X and S-2-X series.

The results of correlations of ^1H and ^{13}C SCS values of the S-4-X, S-3-X and S-2-X series with σ_I and $\sigma_R{}^0$ constants[23] according to the equation

$$\delta = \rho_I\sigma_I + \rho_R{}^0\sigma_R{}^0 + \delta_0 \qquad (3)$$

are presented in Tables 14 and 15. That the fixed phenylthio substituent diminishes the substituent effects on the carbon *para* to the variable substituent (C-6) in

Table 13. Hammett correlations[a] of ^1H and ^{13}C chemical shifts of remote rings of 4- and 2-substituted diphenyl sulphides with σ_p

Series	Nuclei	ρ	*r*	Range, δ (ppm)
S-4-X	C-2′,6′	5.68	0.970	5.80
S-2-X	C-2′,6′	6.42	0.950	9.55
S-4-X	C-3′,5′	1.39	0.918	1.84
S-2-X	C-3′,5′	0.91	0.958	0.24
S-4-X	C-4′	3.68	0.990	3.94
S-2-X	C-4′	3.29	0.977	4.77
S-4-X	H-2′,6′	0.34	0.942	0.40
S-2-X	H-2′,6′	0.31	0.935	0.51
S-4-X	H-3′,5′	0.24	0.954	0.36
S-2-X	H-3′,5′	0.29	0.934	0.43
S-4-X	H-4′	0.32	0.981	0.35
S-2-X	H-4′	0.30	0.970	0.44

[a] Number of substituents *n* = 9 in both series.

Table 14. DSP correlations[a] of ^{13}C chemical shifts of 4-, 3- and 2-substituted diphenyl sulphides

Series	Carbon	ρ_I	ρ_R^0	λ[b]	R[c]	Range, δ (ppm)	n[d]
S-4-X	C-1	10.46 ± 0.61	36.24 ± 0.70	3.46	0.999	24.17	9
S-3-X	C-1	6.61 ± 0.59	0.90 ± 0.82	0.14	0.985	4.72	7
S-4-X	C-2,6	−2.80 ± 0.71	−14.10 ± 0.82	6.48	0.990	8.69	9
S-3-X	C-6	0.95 ± 0.27	19.40 ± 0.38	20.42	0.999	11.34	7
S-4-X	C-1′	−4.96 ± 0.53	−11.71 ± 0.62	2.36	0.993	8.24	9
S-3-X	C-1′	−3.89 ± 0.94	−2.56 ± 1.31	0.66	0.920	3.69	7
S-4-X	C-2′,6′	3.53 ± 0.48	8.79 ± 0.56	2.48	0.990	5.80	9
S-3-X	C-2′,6′	3.45 ± 0.28	1.10 ± 0.39	0.32	0.988	2.63	7
S-2-X	C-2′,6′	6.82 ± 0.19	7.72 ± 2.29	1.13	0.928	9.55	8
S-4-X	C-3′,5′	0.94 ± 0.31	2.10 ± 0.36	2.23	0.936	1.84	9
S-3-X	C-3′,5′	0.81 ± 0.11	0.45 ± 0.15	0.56	0.973	0.64	7
S-2-X	C-3′,5′	1.08 ± 0.16	1.05 ± 0.18	0.97	0.997	1.24	8
S-4-X	C-4′	2.68 ± 0.18	5.37 ± 0.21	2.00	0.997	2.72	9
S-3-X	C-4′		Poor correlation				
S-2-X	C-4′	3.61 ± 0.61	3.98 ± 0.72	1.10	0.972	4.77	8

[a] Acetamido group was excluded from correlation because of poor results.
[b] Ratio ρ_R^0/ρ_I.
[c] Correlation coefficient.
[d] Number of compounds.

the series S-3-X is evident from the low ρ_I (0.95) and ρ_R^0 (19.40) values relative to those for the C-4 of monosubstituted benzenes ($\rho_I = 4.6$; $\rho_R^0 = 21.5$). This is also reflected by the low values of Lynch slopes for C-6 (0.83) and H-6 (0.71) (Table 12). This can probably be ascribed to the saturation effect resulting from the + M effects of PhS group on C-6.

An 'inverse' substituent effect is evident for C-1′ of the S-3-X series from the negative regression coefficients, ρ_I and ρ_R^0 (Table 14), suggesting that the transmission of substituent effects between phenyl rings occurs via π-polarization[24–26] interactions as observed in the S-4-X series. The low values of ρ_R^0 and λ for the nuclei of unsubstituted ring (C-1′; C-2′,6′; C-3′,5′; H-2′,6′; and H-3′5′) in the S-3-X series (relative to the S-4-X or S-2-X series suggest the absence of significant conjugative interactions between the rings via sulphur in the S-3-X series. This is unsurprising as the PhS group is *meta* to the substituent in the S-3-X series.

The data in Tables 14 and 15 show that, in general, inductive effects are transmitted more in the S-2-X than in the S-4-X series, ascribable to the proximity of the substituent to the unsubstituted ring in the former. The diminution in the transmission of resonance effects to the remote ring atoms in the S-2-X series relative to the S-4-X series may presumably be attributed to the pos-

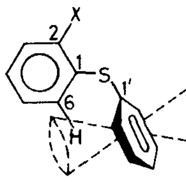
Table 15. DSP correlations[a] of ^{1}H chemical shifts of 4-, 3- and 2-substituted diphenyl sulphides

Series	Carbon	ρ_I	ρ_R^0	λ[b]	R[c]	Range, δ (ppm)	n[d]
S-4-X	H-2,6		Poor correlation				
S-3-X	H-2	0.43 ± 0.21	1.85 ± 0.29	4.30	0.960	1.17	7
	H-4	0.59 ± 0.15	1.86 ± 0.20	3.15	0.982	1.23	7
	H-6	0.10 ± 0.08	0.97 ± 0.11	9.70	0.978	0.58	7
S-4-X	H-3,5	0.20 ± 0.05	1.92 ± 0.13	3.10	0.993	1.20	8
S-2-X	H-3	0.79 ± 0.17	1.73 ± 0.20	2.19	0.981	1.54	8
	H-5	−0.02 ± 0.10	0.93 ± 0.12	−51.67	0.961	0.60	8
S-4-X	H-2′,6′	0.19 ± 0.02	0.56 ± 0.03	3.03	0.993	0.40	9
S-3-X	H-2′,6′	0.20 ± 0.02	0.07 ± 0.03	0.35	0.973	0.16	7
S-2-X	H-2′,6′	0.40 ± 0.08	0.33 ± 0.09	0.83	0.950	0.44	8
S-4-X	H-3′,5′	0.17 ± 0.03	0.37 ± 0.04	2.17	0.980	0.31	9
S-3-X	H-3′,5′	0.09 ± 0.01	0.03 ± 0.01	0.33	0.950	0.07	7
S-2-X	H-3′,5′	0.33 ± 0.10	0.32 ± 0.12	0.97	0.912	0.43	8
S-4-X	H-4′	0.25 ± 0.03	0.47 ± 0.38	1.88	0.986	0.37	9
S-3-X	H-4′		Poor correlation				
S-2-X	H-4′	0.34 ± 0.07	0.35 ± 0.08	1.03	0.955	0.44	8

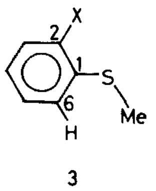
[a] Acetamido group excluded because of poor correlation.
[b] Ratio ρ_R^0/ρ_I.
[c] Correlation coefficient.
[d] Number of compounds.

sible steric constraints arising from the *ortho* substituents in the former impeding the conjugative interations of sulphur orbitals with the phenyl rings. Fortuitously, the enhancement in inductive effects and diminution in resonance interactions in the S-2-X series relative to those in the S-4-X series appear to balance each other, resulting in an almost equal extent of transmission of substituent effects to the remote ring in both the S-4-X and S-2-X series (Table 13).

Effect of substituents on the chemical shift of H-6 in series S-2-X series. The steric and polar influences of the substituent X on the chemical shift of H-6 in the S-2-X series deserves comment. From the differences between the chemical shifts of H-6 of *ortho*-substituted diphenyl sulphides (viz. 2-nitrodiphenyl sulphide, 2,4-dinitrodiphenyl sulphide and some tri-*ortho*-substituted diphenyl sulphides) and the chemical shifts of H-6 of the corresponding 2-substituted phenyl methyl sulphides (MPS-2-X), Montaudo and co-workers[27–29] concluded that there is a preference for conformation **2** in these 2-substituted diphenyl sulphides where the *ortho* aromatic hydrogen (H-6) lies within the shielding zone of the adjacent ring.



2



3

The preponderance of conformation **2** for tri-*ortho*-substituted diphenyl sulphides has been ascribed to steric repulsion among *ortho* substituents forcing the molecule to adopt the less hindered form.[30,31] The driving force for the preference of conformation **2** in the case of 2,4-dinitrodiphenyl sulphide was attributed to the increase in the double bond character in the C_1—S bond (arising from the concerted electron-withdrawing effect of the two nitro groups). This increase in the double bond character was suggested to cause the dinitrophenyl ring to lie in the C_1—S—C_1, plane, forcing the unsubstituted ring to go out-of-plane.

The data in Table 16 compare the chemical shifts and the corresponding SCS values of H-6 of the series S-2-X with those of H-6 of 2-substituted phenyl methyl sulphides (MPS-2-X),[32] with a view to understanding the dependence of the shielding of H-6 on the nature of the substituents. The difference between these SCS values (ΔSCS) listed in Table 16 suggests large upfield shifts for H-6 by groups containing a lone pair of electrons (such as OCH_3, F, Cl, Br and NO_2 in the S-2-X series) relative to those in the MPS-2-X series. These ΔSCS values were correlated with the van der Waals radii (r_w) of the 2-substituents. This correlation shown in Fig. 1, is linear for all substituents except fluoro and methyl.

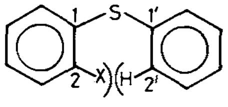
Although the shielding of H-6 in 2-nitrodiphenyl sulphide is explicable by the conjugative interactions suggested by Montaudo *et al.*[28] for 2,4-dinitrodiphenyl sulphide, the shielding of H-6 by + M groups (OCH_3, F, Cl and Br) may arise from factors other than conjugative interactions.

Table 16. Chemical shifts (δ), SCS and ΔSCS values for H-6 in 2-substituted diphenyl sulphides and 2-substituted phenyl methyl sulphides

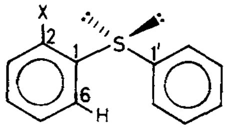
	S-2-X		MPS-2-X[a]		
X	δ_{H-6} (ppm)	SCS (ppm)	δ_{H-6} (ppm)	SCS (ppm)	ΔSCS[b]
NH_2	7.42	0.09	—[c]	—	—
$NHCOCH_3$	7.58	0.25	—[c]	—	—
OCH_3	7.08	−0.25	7.16	−0.12	−0.13
CH_3	7.20	−0.13	7.15	−0.13	0.00
H	7.33	0.00	7.28	0.00	0.00
F	7.07	−0.26	7.27	−0.10	−0.25
Cl	6.97	−0.36	7.15	−0.13	−0.23
Br	6.92	−0.41	7.13	−0.15	−0.26
NO_2	6.86	−0.47	7.38	+0.10	−0.57

[a] MPS-2-X: 2-substituted phenyl methyl sulphides.[32]
[b] ΔSCS = SCS_{H-6} (S-2-X) − SCS_{H-6} (MPS-2-X).
[c] The δ_{H-6} values for NH_2 and $NHCOCH_3$ in the MPS-2-X series are not available.
[d] From a 60/100 MHz NMR study of 2-chlorodiphenyl sulphide, Montaudo *et al.*[28] were unable to find a significant upfield shift.

Although several conformations with a wide range of torsional angles could be visualized for 2-substituted diphenyl sulphides, in order to understand the influence of X on the conformations, two extreme conformations, **4a** and **4b**, or conformations approximating to these (**4a**-like and **4b**-like) can be considered.



4a



4b

Whereas **4a**-like conformations would be destabilized by steric interaction between X and the *ortho*-hydrogens of the unsubstituted ring, H-2' or H-6', the **4b**-like conformations would be rendered unstable by repulsion between electron pairs on X and those on sulphur. The steric interactions in **4a**-like conformations could be

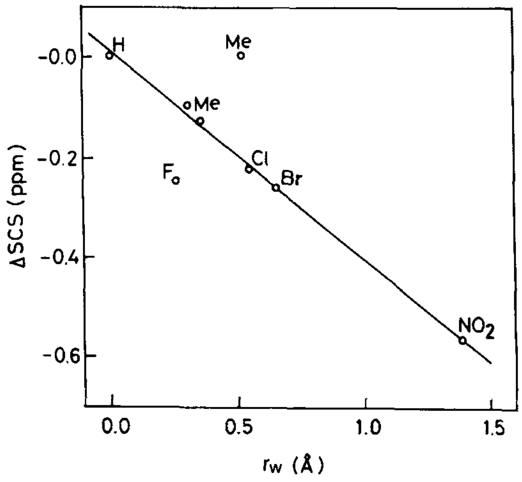


Figure 1. Plot of ΔSCS_{H-6} (ppm; S-2-X) *vs.* r_w (van der Waals radii).

Table 17. Lynch correlations[a] of ^1H and ^{13}C chemical shifts of 4-substituted 2′,6′-dimethyldiphenyl sulphides

Nucleus	Benzene SCS (*S*)	Slope (*b*)	Intercept (*a*) Calculated	Observed	*r*
C-1	S_p	1.06	138.23	138.03	0.989
		(1.64)[b]	(137.36)	(135.72)	(0.991)
C-3,5	S_o	0.93	128.94	128.46	0.995
		(0.93)	(129.10)	(129.10)	(0.994)
C-4	S_i	1.05	124.25	124.62	0.998
		(1.01)	(126.50)	(126.93)	(0.997)
H-3,5	S_o	0.85	7.12	7.17	0.982
		(0.83)	(7.32)	(7.28)	(0.994)

[a] Number of substituents $n = 9$.
[b] Values for 4-substituted diphenyl sulphides in parentheses.

minimized by the rotation around either of the C—S bonds or both in opposite directions, while the attenuation in the repulsive interactions between the electron pair in **4b**-like conformations would require the rotation of the C_1—S bond. These rotations around the C—S bonds will bring the H-6 into the shielding zone of the unsubstituted ring, causing shielding.

It appears that in the absence of lone pair–lone pair repulsions, **4b**-like conformations are not significantly destabilized, as is evident from the ΔSCS value (0.0) for the methyl group. The large deviation in the upfield direction for the fluoro substituent (Fig. 1) suggests stronger electronic repulsion than that predicted by its size.

For NH_2 and $NHCOCH_3$ groups in the S-2-X series, the repulsion between the lone pairs of electrons on sulphur and nitrogen may not be significant, since (i) the nitrogen lone pair can be oriented away from the sulphur lone pairs and (ii) the hydrogen(s) attached to nitrogen in these groups could possibly form H-bonds with the sulphur lone pair, providing some stability for **4b**-like conformations. This appears to be consistent with positive SCS values observed for these groups in S-2-X series in Table 16.

4-Substituted 2′,6′-dimethyldiphenyl sulphides

Lynch correlations. The results of Lynch correlations of the chemical shifts of C-1 to C-4 in the Me_2-S-4-X series with the SCS of monosubstituted benzenes are listed in Table 17. The data reveal that the Lynch slopes for C-3, 5 and C-4 in the Me_2-S-4-X and S-4-X series do not differ significantly. All carbons, except C-2,6 of the variable substituent-bearing ring of the Me_2-S-4-X series, afford good Lynch correlations with slopes close to unity. These Lynch slopes were compared with those for the S-4-X series.[1] Previously, it has been found that the Lynch slopes of the C-1 of 4-substituted phenyl vinyl sulphides ($b = 1.54$), 4-substituted diphenyl sulphides ($b = 1.64$) and 4-substituted 4′-nitrodiphenyl sulphides ($b = 1.53$) showed amplification of the substituent effects at C-1 by the fixed substituents viz. —SCH=CH_2, —SPh, —SC_6H_4X-4′ (considering these sulphides as 1,4-disubstituted benzenes). However, the Lynch slopes for the C-1 of 4-substituted phenyl methyl sulphides ($b = 1.14$) and symmetrically 4,4′-disubstituted diphenyl sulphides ($b = 1.04$) remain close to unity. These results led us to conclude that 'the amplification at the *para* carbon (C-1) would seem to require the polarizable sulphur atom and an attached π-system capable of conjugating with the ring via sulphur.' As a corollary, from the almost unit slope of C-1 ($b = 1$) for the Me_2-S-4-X series, it may be inferred that conjugative interactions between the aryl rings via sulphur might have been significantly diminished, as shown by DSP correlations (see below).

Hammett and dual-substituent parameter correlations. The results of correlations of ^1H and ^{13}C chemical shifts of the Me_2-S-4-X series using the Hammett equation [Eqn (2)] and Taft's DSP equation [Eqn (3)] are listed in Table 18. One feature then emerges from the Hammett and DSP correlations: the ρ, ρ_I and $\rho_R{}^0$ values obtained for C-1′ and C-4′ of the Me_2-S-4-X series and those of the S-4-X series (Table 18) reveal a decrease in the transmission of substituent effects to the remote ring of the Me_2-S-4-X series relative to the S-4-X series, as suggested by Lynch correlations.

The ρ_I and $\rho_R{}^0$ values for C-1′ are negative in the Me_2-S-4-X series, showing 'inverse' substituent effects as found with the S-4-X series. This inverse substituent effect for C-1′ and the λ values (>2) for C-1′ and C-4′ in the Me_2-S-4-X series appear to be consistent with either or both π-polarization and conjugative interactions between the rings via sulphur.

The diminished transmission of substituent effects and the absence of amplification of substituent effects at

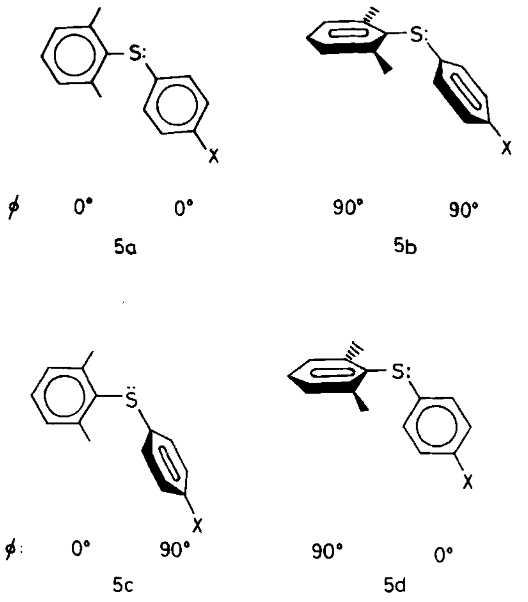
Table 18. Hammett and DSP correlations for 4-substituted 2′,6′-dimethyldiphenyl sulphides

Nucleus	Hammett ρ	r[a]	DSP ρ_I	$\rho_R{}^0$	λ[b]	*R*[c]	Range, δ (ppm)
C-1	13.29	0.939	5.91	25.36	4.29	0.996	19.30
	(21.53)[d]	(0.940)	(10.46)	(35.24)	(3.46)	(0.999)	(24.17)
C-1′	−3.17	0.973	−2.41	−5.04	2.09	0.995	3.83
	(−7.67)	(0.976)	(−4.96)	(−11.71)	(2.36)	(0.993)	(8.24)
C-4′	1.38	0.996	0.83	2.21	2.67	0.954	1.42
	(3.68)	(0.990)	(2.68)	(5.37)	(2.00)	(0.997)	(3.94)

[a] Number of substituents $n = 9$.
[b] Ratio $\rho_R{}^0/\rho_I$.
[c] Correlation coefficient.
[d] Values for S-4-X series in parentheses.

C-1 in the Me_2-S-4-X series may presumably be ascribed to the steric crowding in these compounds.

If one considers conformations of the two rings relative to the C_1—S—$C_{1'}$ plane, viz. rotamers about the C_1—S and S—$C_{1'}$ bonds, four extreme conformations (**5a–d**) are possible (Scheme 2). Inspection of molecular models show that the conformations **5a–c** have severe steric interactions. It is likely that the Me_2-S-4-X sulphides adopt the less sterically congested conformation with orthogonal orientation of aryl rings (**5d**).



Scheme 2. Conformations of 4-substituted 2′,6′-dimethyldiphenyl sulphides; φ refers to angles of rotation of phenyl rings relative to the C_1—S—$C_{1'}$ plane.

The diminished transmission of substituent effects in 2′,6′-dimethyldiphenyl sulphides can probably be ascribed to the orthogonal orientation of the aryl rings in conformation **5d**, which could impede conjugation and also π-polarization interactions between the rings. It is pertinent to note that extended π-polarization interactions diminish when the unsaturated groups take up an orthogonal orientation.[33]

2- and 3-substituted diphenyl sulphones

Lynch correlations The results of Lynch correlations of ^1H and ^{13}C chemical shifts of nuclei of the substituent-bearing ring in the SO_2-3-X and SO_2-2-X series are listed in Table 19. For several carbons and protons of the substituent-bearing phenyl ring of these compounds Lynch slopes close to unity are obtained, suggesting the applicability of additivity relationships as found earlier for the SO_2-4-X series.

Dual-substituent parameter correlations. The results of correlations of ^1H and ^{13}C SCS values with σ_I and $\sigma_R{}^0$ constants are presented in Tables 20 and 21. An examination of the regression coefficients (ρ_I and $\rho_R{}^0$) presented in Table 20 for the atoms of remote rings of the diphenyl sulphones reveals an inverse substituent effect for C-1′ of the SO_2-3-X and SO_2-2-X series, suggesting π-polarization interactions as proposed previously for the SO_2-4-X series.

Correlations of H-6 chemical shift in SO_2-2-X. The chemical shifts of H-6 in the SO_2-2-X series, which failed to afford any satisfactory Lynch or DSP correlation (see

Table 19. Lynch correlations of ^1H and ^{13}C chemical shifts in 4-, 3- and 2-substituted diphenyl sulphones

Series	Nuclei	Benzene SCS (S)	Slope (b)	Intercept (a) Calculated	Observed	r
SO_2-4-X	C-1	S_p	0.97	141.45	141.51	0.992
	C-3,5	S_o	1.00	129.23	129.26	0.999
	C-4	S_i	0.92	133.61	133.16	0.996
	C-2,6	S_m		Scattered plots		
	H-3,5	S_o	0.94	7.47	7.50	0.998
SO_2-2-X	C-2	S_i	0.96	126.98	127.58	0.997
	C-3	S_o	0.95	128.86	129.26	0.994
	C-5	S_p	0.99	128.98	129.26	0.982
	H-3	S_o	1.08	7.45	7.50	0.997
	H-4	S_m	0.76	7.57	7.57	0.957
	H-5	S_p	0.83	7.53	7.50	0.979
SO_2-3-X	C-1,5	S_m		Scattered plots		
	C-2	S_o	0.97	127.48	127.58	0.995
	C-3	S_i	0.96	129.26	129.26	0.999
	C-4	S_o	0.92	133.07	133.18	0.994
	C-6	S_p	0.96	127.54	127.58	0.996
	H-2	S_o	0.92	7.92	7.95	0.999
	H-4	S_o	0.94	7.53	7.57	0.998
	H-5	S_m	0.98	7.49	7.50	0.993
	H-6	S_p	0.89	7.93	7.95	0.997

Table 20. DSP correlations of ^{13}C chemical shifts of 4-, 3- and 2-substituted diphenyl sulphones

Series	Carbon	ρ_I	ρ_R^0	R	λ^a	Range,δ (ppm)	n^b
SO_2-4-X	C-1	4.97 ± 0.83	20.91 ± 0.99	0.995	4.20	14.32	8
SO_2-3-X	C-1	3.81 ± 0.24	− 0.54 ± 0.29	0.998	−0.14	2.55	9
SO_2-4-X	C-2,6	3.05 ± 0.52	−3.20 ± 0.62	0.962	−1.05	2.89	8
SO_2-3-X	C-5	2.92 ± 0.26	−1.49 ± 0.31	0.980	−0.51	2.08	9
	C-6^c	4.68 ± 0.37	21.05 ± 0.45	0.999	4.50	14.27	9
SO_2-2-X	C-5^{c,d}	4.59 ± 1.88	21.42 ± 2.15	0.974	4.67	15.25	8
SO_2-4-X	C-1′	−1.83 ± 0.15	−2.73 ± 0.18	0.993	1.49	2.33	8
SO_2-3-X	C-1′	−2.09 ± 0.16	−1.06 ± 0.19	0.987	0.51	1.60	9
SO_2-3-X	C-2′,6′	0.44 ± 0.05	0.35 ± 0.06	0.973	0.80	0.41	9
SO_2-4-X	C-2′,6′	0.53 ± 0.07	1.00 ± 0.09	0.986	1.88	0.80	8
SO_2-4-X	C-3′,5′	0.56 ± 0.03	0.56 ± 0.03	0.997	1.00	0.55	8
SO_2-3-X	C-3′,5′	0.57 ± 0.03	0.44 ± 0.03	0.995	0.77	0.51	9
SO_2-4-X	C-4′	1.15 ± 0.04	1.48 ± 0.05	0.998	1.28	1.31	8
SO_2-2-X	C-4′	1.67 ± 0.26	1.57 ± 0.29	0.965	0.94	1.77	8

[a] Ratio ρ_R^0/ρ_I.
[b] Number of substituents.
[c] These carbons are *para* to the variable substituent.
[d] In the SO_2-3-X series, $NHCOCH_3$ is excluded from correlation.

above), were correlated well with σ_I, σ_R^0 and van der Waals radius r_w (steric) parameters using the multiparameter equation[34]

$$\delta_{H\text{-}6} = \rho_I\sigma_I + \rho_R^0\sigma_R^0 + Ar_w + \delta_0 \qquad (4)$$

where σ_I, σ_R^0 and r_w are the inductive, resonance and steric susceptibility parameters, respectively. The results of this correlation are expressed in the equation

$$\begin{aligned}\delta_{H\text{-}6} &= (0.23 \pm 0.04)\sigma_I + (0.26 \pm 0.05)\sigma_R^0 \\ &+ (0.64 \pm 0.05)r_w + 7.95 \qquad (5) \\ R &= 0.993, \quad n = 8\end{aligned}$$

In this correlation, the r_w value corresponding to the orthogonal orientation of the NO_2 group afforded a better correlation [Eqn (5)] than that corresponding to the planar orientation. This suggests that the NO_2 group is probably twisted out-of-plane by the bulky $PhSO_2$ group at the *ortho*-position. That the NO_2 group actually takes an out-of-plane orientation is evident from the SCS value (7.76 − 7.50 = 0.26 ppm) of the NO_2 group on the *ortho*-proton (H-3) of 2-nitrodiphenyl sulphone, in contrast to the SCS value of about 0.8 ppm for the NO_2 group remaining in the plane of the ring on the *ortho*-protons (H-2 and H-4) in 3-nitrodiphenyl sulphone (see above) or that in nitrobenzene (0.95 ppm).[35]

The larger value of A (0.64) than either the ρ_I (0.23) or the ρ_R^0 (0.26) reveals that the size of the substituent influences $\delta_{H\text{-}6}$ to a larger extent than the electronic effects. The positive values of ρ_I, ρ_R^0 and A in Eqn (5) show that $\delta_{H\text{-}6}$ increases with increase in the electron-withdrawing ability (inductive and resonance effects) and increase in the size of the substituent. The deshielding of H-6 with increase in the size of X can be interpreted in terms of the conformation of diphenyl sulphone.

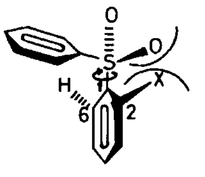
It is known that the conformation adopted by diphenyl sulphone is strongly biased towards forms in

Table 21. DSP correlations of ^1H chemical shifts of 4-, 3- and 2-substituted diphenyl sulphones

Series	Proton	ρ_I	ρ_R^0	R	λ^a	Range, δ (ppm)	n^b
SO_2-4-X	H-3,5	0.70 ± 0.12	2.03 ± 0.15	0.989	2.90	1.37	8
	H-2,6,2′,6′		Poor correlations				
	H-3′,5′	0.09 ± 0.01	0.09 ± 0.01	0.995	1.02	0.09	8
	H-4′	0.08 ± 0.01	0.12 ± 0.01	0.991	1.46	0.69	8
SO_2-3-X	H-2	0.50 ± 0.22	1.89 ± 0.27	0.953	3.78	1.33	8
	H-6	0.10 ± 0.08	0.97 ± 0.11	0.978	9.70	0.58	8
	H-2′,6′	0.20 ± 0.02	0.07 ± 0.03	0.973	0.35	0.16	9
SO_2-2-X	H-5	0.26 ± 0.08	0.99 ± 0.09	0.976	3.81	0.69	9
	H-3′5′	0.08 ± 0.01	0.11 ± 0.01	0.963	1.38	0.09	9
	H-4′	0.11 ± 0.02	0.08 ± 0.03	0.935	0.73	0.10	9

[a] Ratio ρ_R^0/ρ_I.
[b] Number of substituents.

which the C_1—S—$C_{1'}$ plane lies almost perpendicular to the planes of the two aryl rings, the sulphur atom being approximately tetrahedral[36] as in SO_2-2-X (a) (**6**).



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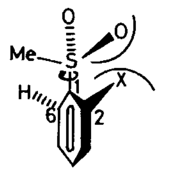
SO_2-2-X (a)



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$MPSO_2$-2-X (a)

The downfield shift for H-6 with increase in the size of X can probably be attributed to an increase in the steric interaction between X and the proximate sulphonyl oxygen causing rotation around the C_1—S bond. This moves H-6 away from the unsubstituted phenyl ring but towards the sulphonyl oxygens, resulting in van der Waals deshielding for H-6. That a similar dependence of deshielding of H-6 exists in 2-substituted phenyl methyl sulphones[32] and that the variation in the deshielding for H-6 in SO_2-2-X does not significantly depend on the unsubstituted phenyl ring is evident from the approximately linear relationship between the chemical shifts of H-6 in both the SO_2-2-X and $MPSO_2$-2-X series (Fig. 2). This is in sharp contrast to the upfield shift observed for the H-6 in 2-substituted diphenyl sulphides, attributed to the rotation of the C—S bond (with an increase in size of X) bringing H-6 into the shielding zone of the unsubstituted ring. It may be noted that steric interaction has been suggested between sulphonyl oxygen and H-2,6 even in unsubstituted diphenyl sulphone from the ^{17}O chemical shifts of sulphonyl oxygens,[37] supporting the above conclusion.

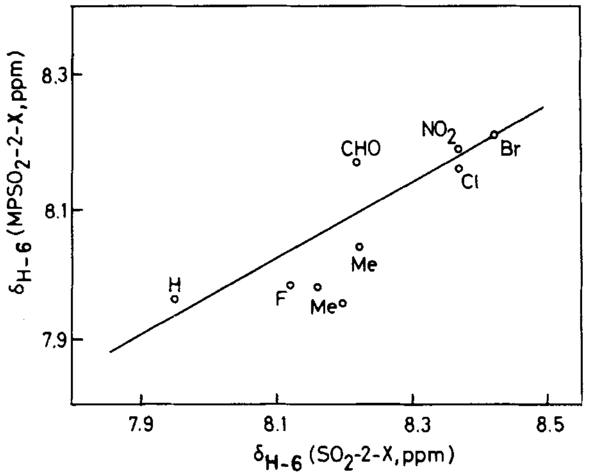

Figure 2. Plot of δ_{H-6} (ppm MPSO$_2$-2-X) *vs.* δ_{H-6} (ppm, SO$_2$-2-X).

Acknowledgements

We are grateful to CSIR, New Delhi, for the award of a Research Associateship (to R.C.) and for a major research project and to Mrs M. Dowsett for measuring many of the spectra.

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