Infrared Intensities as a Quantitative Measure of Intramolecular Interactions. Part XXIX.[1] Methyl Phenyl Sulphones and Sulphoxides

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The integrated i.r. intensities of the ν_8 band for series of *meta*- and *para*-substituted methyl phenyl sulphoxides and sulphones show that whereas $MeSO_2$ is a resonance acceptor σ°_R + 0·06, MeSO is a net resonance donor σ°_R − 0·07. However. when *para* to a strong donor group, both $MeSO_2$ and MeSO become resonance acceptors of considerable magnitude. Intensities of *as* and *s* ν_{SO_2} are correlated by σ^+ values of *meta*- and *para*-substituents.

THE methylthio- and t-butylthio-groups act as resonance acceptors of electrons by delocalisation into the empty *d*-orbitals of the sulphur when *para* to donor groups on a benzene ring.[1] We have now examined by our i.r. spectral technique [2] the properties of the methylsulphonyl and methylsulphinyl groups.

X-Ray [3] and dipole moment studies [4] have shown that methyl phenyl sulphones adopt conformation (1a) preferentially. No similar studies have been carried out on methyl phenyl sulphoxides although diphenyl sulphoxide assumes a conformation in the crystalline [5] and liquid [6] states similar to those of diphenyl sulphones.[7]

Most workers have concluded, from experimental evidence to be discussed later, that *d*-orbitals are involved in sulphoxide and sulphone bonding. In the theory developed by Craig and his co-workers,[8] certain substituents cause *d*-orbitals to contract in size and drop in energy so as to be available for bonding. The perturbing ability of the substituent is linked to the effective nuclear charge of the ligand and also to the internuclear bond distance.[8c,d,9] Since these two factors are in opposition, the perturbing powers of fluorine, chlorine, oxygen, and carbon are similar, whereas hydrogen has much less effect. Hybridisation of the 3*d*- and 4*p*-orbitals probably occurs to a certain extent.[8,10] In agreement with these general considerations, specific calculations [9,11] on sulphoxides and sulphones show that there is substantial *d*-orbital character in the sulphur–oxygen bonds.

The methylsulphonyl group is a resonance electron acceptor, presumably acting by delocalisation into the *d*-orbitals, as indicated by dipole moments,[12] u.v. spectroscopy,[12c,13] acidity constants,[14] and ^{19}F n.m.r. spectroscopy.[15] Methylsulphonyl groups interact with phenyl rings with bulky *ortho*-substituents to the same extent as with unhindered phenyl rings.[13a,16] This evidence supports *d*-orbital bonding of the sulphur to the benzene ring, since such bonding is not affected by rotation [16a,17] [if the parent methyl phenyl sulphone

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TABLE 1

Properties of *meta*-substituted methyl phenyl sulphones and sulphoxides

Substituents		M.p. or b.p. (°C) [mmHg]	Lit. m.p.[a] or b.p. (°C) [mmHg]	σ°_R (2)	1600—1585 cm^{-1} band			$\left(\frac{A - 340}{19,000}\right)^{1/2}$	f_m [d]
1	2				A [b]	ν	ε_A [c]		
SOMe	OMe [e]	112 [0·2]	111—112 [0·2—0·3] [f]	−0·43	4770	1593	240	0·48	0·46—0·48 [g]
						1579	110		
	F [e]	74—76 [0·5]	103—106 [3] [h]	−0·34	3270	1597	85	0·25	0·25
						1589	110		
						1577	116		
	Cl [e]	111—112 [0·3]	100—101 [0·1] [i]	−0·22	1500	1574	90	0·39	0·38
	Me [j]	112—114 [1·8]	126—127 [3] [i]	−0·10	650	1596	32	0·13	0·15
						1574	6		
SO_2Me	OMe [e]	140—142 [0·3]	140—150 [0·2—0·3] [f]	−0·43	3460	1599	196	0·40	0·39—0·41 [g]
						1582	71		
	F [e]	39—40 ‡	39—41 ‡ [h]	−0·34	2240	1593	105	0·32	0·31
						1586			
	Cl [e]	106 ‡	105—106 ‡ [k]	−0·22	1045	1586	65	0·19	0·19
						1574			
	Me [e]	100—102 [0·25—0·3]	137—138 [3] [k]	−0·10	400	1599	15	0·06	0·09
						1579	7		
SO_2Me	F [j]	*l*	*l*	−0·34	2220	1593	120	0·31	0·31
						1586			
	Cl [j]	*l*	*l*	−0·22	970	1581	59	0·18	0·19
						1576			
	Me [j]	*l*	*l*	−0·10	425	1599	15	0·07	0·09
						1579	9		
	NO_2 [j]	147—148 ‡	146 ‡ [m]	+0·17	1695	1606	89	0·27	0·21
						1586	19		

[a] M.p. indicated by ‡. [b] Integrated intensity of the 1600—1585 cm^{-1} band. [c] Peak extinction coefficient; $\varepsilon_A = a_{max.}/cl$, where $a_{max.}$ is absorbance at peak maximum, c the concentration in mol l^{-1}, and l the cell path length in cm. [d] $\{[\sigma^\circ_R(1)]^2 + [\sigma^\circ_R(2)]^2 + \sigma^\circ_R(1)\,\sigma^\circ_R(2)\}^{1/2}$. [e] Measured in CCl_4–C_6H_6 (9 : 1). [f] Ref. 14*c*. [g] Corrected for asymmetry as in ref. 1. [h] R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *J. Amer. Chem. Soc.*, 1963, **85**, 709. [i] A. Cerniani and G. Modena, *Gazzetta*, 1959, **89**, 843. [j] Measured in $CHCl_3$. [k] W. E. Truce and C. W. Vriesen, *J. Amer. Chem. Soc.*, 1953, **75**, 5032. [l] As above. [m] R. F. Twist and S. Smiles, *J. Chem. Soc.*, 1925, **127**, 1248.

TABLE 2

Properties of *para*-substituted methyl phenyl sulphones and sulphoxides

Substituents		M.p.[a] or b.p. (°C) [mmHg]	Lit. m.p.[a] or b.p. (°C) [mmHg]	σ°_R (2) [b]	1600—1585 cm^{-1} band			$\left(\frac{A - 170}{15,000}\right)^{1/2}$	λ [e]	f_p
1	2				A [c]	ν	ε_A [d]			
SOMe [g]	OMe	45—46 ‡	46—47 ‡ [h]	−0·43	4350	1595	285	0·53	0·17	0·53
						1577	107			
	F	106—108 [2]	114—116 [3] [i]	−0·34	2315	1590	180	0·38	0·13	0·40
	Cl	106—108 [0·8]	135—136 [5] [j]	−0·22	702	1574	340	0·19	0·07 [k]	0·20
	Me	118—119 [2·5]	113—114 [2] [j]	−0·10	235	1596	23	0·07	0·04	0·07
	NO_2	146—147 ‡	148—149 ‡ [j]	0·17	1256	1581	112	0·27		0·24
SO_2Me [g]	NMe_2	163·5—164 ‡	165—166 ‡ [l]	−0·53	11,640	1596	785	0·87	0·26	0·88
	OMe	120—121 ‡	121·5—122 [m] ‡	−0·43	7435	1597	360	0·70	0·21	0·70
						1579				
	F	78 ‡	77—78 ‡ [n]	−0·34	3715	1592	305	0·49	0·17	0·58
	SMe	98—99 ‡	98—99 ‡ [o]	−0·25	3005	1581	185	0·43	0·12	0·42
	Cl	97—98 ‡	96·5—98 ‡ [p]	−0·22	1875	1584	130	0·34	0·11	0·39
	Me	87 ‡	88 ‡ [p]	−0·10	945	1600	55	0·23	0·05	0·21
SO_2Me [q]	NMe_2	*r*	*r*	−0·53	12,970	1596	875	0·92	0·26	0·88
	F	*r*	*r*	−0·34	3995	1591	325	0·50	0·17	0·58
	SMe	*r*	*r*	−0·25	3200	1580	220	0·45	0·12	0·42
	Cl	*r*	*r*	−0·22	1860	1583	135	0·34	0·11	0·39
	Me	*r*	*r*	−0·10	1100	1598	58	0·25	0·05	0·21
	SO_2Me	261 ‡	261 ‡ [s]	0·06	<50	1580		0·0		0·0
	NO_2	141—142 ‡	142—143 ‡ [t]	0·17	771	1606	80	0·20		0·11
	COMe	127—128 ‡	127—128 ‡ [u]	0·22	456	1573	26	0·14		0·16
						1595	16			

[a] M.p. indicated by ‡. [b] Of substituent. [c] Integrated intensity. [d] Peak extinction coefficient; $\varepsilon_A = a_{max.}/cl$, where $a_{max.}$ is absorbance at peak maximum, c concentration in mol l^{-1}, and l cell path length in cm. [e] $\lambda = K_X\,\sigma^\circ_R D$. [f] $f_p = |[\sigma^\circ_R(1) - \sigma^\circ_R(2) + K_X\sigma^\circ_R D]|$. [g] Measured in CCl_4–C_6H_6 (9 : 1). [h] S. Ghersetti and M. Pallotti, *Gazzetta*, 1963, **93**, 1000. [i] R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *J. Amer. Chem. Soc.*, 1963, **85**, 3146. [j] A. Cerniani and G. Modena, *Gazzetta*, 1959, **89**, 843. [k] Corrected for second *d*-orbital interaction, $K_X = 0{\cdot}22$ for Cl (ref. 27). [l] A. Dondoni and P. E. Todesco, *Boll. sci. Fac. Chim. ind. Bologna*, 1962, **20**, 79. [m] Ref. 14*c*. [n] H. Zahn and H. Zuber, *Chem. Ber.*, 1953, **86**, 172. [o] H. Burton and P. F. Hu, *J. Chem. Soc.*, 1948, 604. [p] W. E. Truce and C. W. Vriesen, *J. Amer. Chem. Soc.*, 1953, **75**, 5032. [q] Measured in $CHCl_3$. [r] See above. [s] O. Manoušek, O. Exner, and P. Zuman, *Coll. Czech. Chem. Comm.*, 1968, **33**, 3988. [t] K. B. Shaw and R. K. Miller, *Canad. J. Chem.*, 1970, **48**, 1394. [u] G. B. Bachman and C. L. Carlson, *J. Amer. Chem. Soc.*, 1951, **73**, 2857.

adopts conformation (1a) little change in conjugation is to be expected]. E.s.r. studies of methyl phenyl sulphone and methyl *para*-nitrophenyl sulphone [18] indicated that the phenyl ring is conjugated only with a sulphur *d*-orbital and not with the oxygen atoms. However, frequency [19] and intensity [12b,20] correlations for *para*-substituted methyl phenyl sulphones, particularly when the substituents are strong donors, indicate that some interaction with the S–O bonds is occurring even if it is a second-order effect.[21] The methylsulphinyl group, which has been studied considerably less, might be expected to show resonance properties which are a blend of lone-pair donation and *d*-orbital acceptance. Evidence for *d*-orbital acceptance by sulphur has been obtained from the dipole moments [22] of several methyl phenyl sulphoxides, from ^{19}F n.m.r.,[15] and from pK_a values.[14] The small changes in effective σ-constants for RSO groups observed when hindered sulphoxides were compared with non-hindered analogues [16a] also supports *d*-orbital acceptance. The i.r. spectral method [2] appeared well suited to determine the precise resonance properties of this group.

EXPERIMENTAL

Compounds were prepared by the literature methods indicated (Tables 1 and 2), and purities were checked by g.l.c. or m.p. and by spectroscopy. Chloroform was passed through alumina immediately prior to use. Spectroscopic grade CCl_4 was stored over molecular sieves (4A). Benzene was dried over sodium wire, redistilled, and stored over molecular sieves (4A).

I.r. spectra for solutions in CCl_4–benzene (9 : 1) were measured as previously [23] on a Perkin-Elmer 125 spectrophotometer. In $CHCl_3$ the spectral technique was identical except that the variable and fixed path length cells were balanced by using the 2400 cm^{-1} band of $CHCl_3$. Integration techniques were identical with those previously [23] outlined. Reproducibilities in $(A - 340)^{1/2}$ or $(A - 170)^{1/2}$ values are ±1 intensity units for compounds where A is greater than 400 l mol^{-1} cm^{-2} but are greater for lower values; in such cases the actual value is also less accurate because of uncertainty in the value of the overtone correction. For the sulphone stretching vibrations, integration is complicated by the close proximity of other bands and errors in $A^{1/2}$ are estimated as ±3.

RESULTS AND DISCUSSION

Monosubstituted Compounds.—Equation (1), which has been previously [2] derived, relates the intensity of the ν_8 (ν_{16} in Herzberg's notation) i.r. band of monosubstituted benzenes to (σ°_R). The results obtained for the monosubstituted compounds are listed in Table 3. The intensity of methyl phenyl sulphone agrees satisfactorily with the value of 185 previously [23] measured. By using equation (1), values of $\pm\sigma^{\circ}_R$ of 0·06 and 0·07 were obtained for the methylsulphonyl and methylsulphinyl groups respectively.

TABLE 3

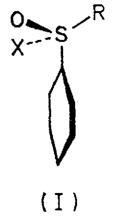
Properties of monosubstituted benzenes

Compound	M.p.[a] or b.p. (°C) [mmHg]	Lit. m.p.[a] or b.p. (°C) [mmHg]	1600—1585 cm^{-1} band ν	ε_A [b]	A	$\pm\sigma^{\circ}_R$ [c]
PhSOMe	105—106 [0·7]	144 [15] [d]	1583 [e]	15	200	0·07
$PhSO_2Me$	88 ‡	88 ‡ [f]	1587 [g]	18	170	0·06
$PhSOBu^t$	57—58 ‡	58—59 ‡ [h]	1582 [g]	8	88	0·0
$PhSO_2Bu^t$	98 ‡	98—99 ‡ [i]	1585 [g]	21	264	0·10
$PhSO_2Bu^t$	[j]	[j]	1585 [e]	23	250	0·09

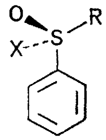
[a] M.p. indicated by ‡. [b] Peak extinction coefficient, $\varepsilon_A = a_{max.}/cl$, where $a_{max.}$ is absorbance at peak maximum, c is concentration in mol l^{-1}, and l is cell path length in cm. [c] Calculated from equation (1). [d] G. Leandri, A. Mangini, and R. Passerini, *J. Chem. Soc.*, 1957, 1386. [e] Measured in CCl_4–C_6H_6 (9 : 1). [f] J. Böeseken and H. W. van Ockenburg, *Rec. Trav. chim.*, 1914, **33**, 317. [g] Measured in $CHCl_3$. [h] I. V. Baliah and R. Varadachari, *J. Indian Chem. Soc.*, 1960, **37**, 321. [i] W. Hahn, G.P. 1,110,631/1961 (*Chem. Abs.*, 1962, **56**, 3416*e*). [j] As above.

$$A = 17{,}600\,(\sigma^{\circ}_R)^2 + 100 \qquad (1)$$

In comparison with the methyl derivatives, phenyl t-butyl sulphone and sulphoxide should favour conformation (I) because of additional steric hindrance in conformation (II). The similar σ°_R values observed for



(I)



(II)

a; X = O (sulphone)
b; X = lone pair of electrons (sulphoxide)

the methyl phenyl (±0·07) and phenyl t-butyl sulphone ±0·09) support the previous assignment [3,4] of conformation (Ia) to alkyl phenyl sulphones. In conformation (Ib), the sulphoxide lone pair is more orthogonal to the

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phenyl ring and therefore, $\sigma^{\circ}_{\mathrm{R}}$ for conformation (Ib) would be more negative than that for (IIb). The algebraic increase in $\sigma^{\circ}_{\mathrm{R}}$ of the alkylsulphinyl group on changing the alkyl substituent from methyl [−0·06 (see later for sign of $\sigma^{\circ}_{\mathrm{R}}$)] to t-butyl (0·0) indicates that methyl phenyl sulphoxide adopts conformation (Ib) to some extent.

meta-*Substituted Methyl Sulphones and Sulphoxides.*—The results for these compounds are listed in Table 1. Measurements were made both in the normal non-polar solvent CCl_4 containing 10% benzene as an aid to cell balancing and in $CHCl_3$ since some compounds were not sufficiently soluble in CCl_4. In previous papers,[24] the intensity of the ν_8 band of *meta*-disubstituted benzenes has been related to $\sigma^{\circ}_{\mathrm{R}}$ terms as in equation (2). This relationship has been used [25] previously to determine the sign of $\sigma^{\circ}_{\mathrm{R}}$ constants since the $\sigma^{\circ}_{\mathrm{R}}$ (1) $\sigma^{\circ}_{\mathrm{R}}$ (2) term depends on the sign of the unknown $\sigma^{\circ}_{\mathrm{R}}$ constant. Plotting $[(A - 340)/19{,}000]^{1/2}$ against $\{[\sigma^{\circ}_{\mathrm{R}}(1)]^2 + [\sigma^{\circ}_{\mathrm{R}}(2)]^2 + \sigma^{\circ}_{\mathrm{R}}(1)\,\sigma^{\circ}_{\mathrm{R}}(2)\}^{1/2}$ yielded a line of unit slope only when $\sigma^{\circ}_{\mathrm{R}}$ values of −0·07 and +0·06 for the SOMe and SO_2Me groups were used (Figure 1). Asymmetric corrections [24] were not made for the SO_2Me and SOMe groups because the values of the observed $\sigma^{\circ}_{\mathrm{R}}$ constants were too small for the corrections to be significant; this is supported by the low intensity found for *p*-bismethylsulphonylbenzene. For the methylsulphinyl group *p*-orbital donation is evidently stronger than *d*-orbital acceptance.

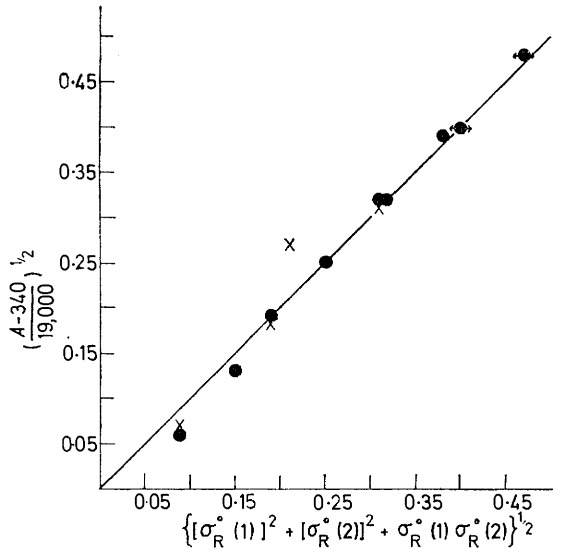

FIGURE 1 Plot of $[(A - 340)/19{,}000]^{1/2}$ against $\{[\sigma^{\circ}_{\mathrm{R}}(1)]^2 + [\sigma^{\circ}_{\mathrm{R}}(2)]^2 + \sigma^{\circ}_{\mathrm{R}}(1)\,\sigma^{\circ}_{\mathrm{R}}(2)\}^{1/2}$ for *meta*-substituted methyl phenyl sulphones and methyl phenyl sulphoxides (*a*) in CCl_4–C_6H_6 (9 : 1) (●), (*b*) in $CHCl_3$ (×); the line shown has unit slope

$$A = 19{,}000\,\{[\sigma^{\circ}_{\mathrm{R}}(1)]^2 + [\sigma^{\circ}_{\mathrm{R}}(2)]^2 + \sigma^{\circ}_{\mathrm{R}}(1)\,\sigma^{\circ}_{\mathrm{R}}(2)\} + 340 \qquad (2)$$

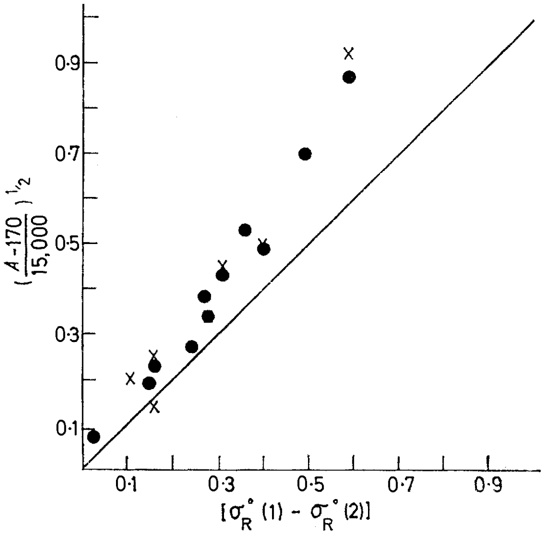

FIGURE 2 Plot of $[(A - 170)/15{,}000]^{1/2}$ *vs.* $[\sigma^{\circ}_{\mathrm{R}}(1) - \sigma^{\circ}_{\mathrm{R}}(2)]$ for *para*-substituted methyl phenyl sulphones and methyl phenyl sulphoxides (*a*) in CCl_4–C_6H_6 (9 : 1) (●), (*b*) in $CHCl_3$ (×); the line shown has unit slope

para-*Substituted Methyl Phenyl Sulphones and Sulphoxides.*—Table 2 gives the i.r. spectral results for the ν_8 bands of these compounds. The measurements were carried out in both $CHCl_3$ and CCl_4–benzene (9 : 1) as for the *meta*-substituted compounds. Treatment of the data by using equation (3), which has been developed[26,27] for compounds where there is no direct interaction between substituents, gave Figure 2. The large deviations observed may be interpreted as evidence for

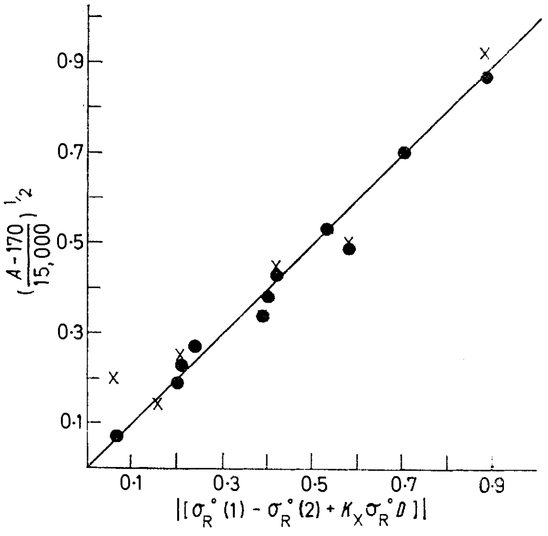

FIGURE 3 Plot of $[(A - 170)/15{,}000]^{1/2}$ *vs.* $[\sigma^{\circ}_{\mathrm{R}}(1) - \sigma^{\circ}_{\mathrm{R}}(2) + K_X\sigma^{\circ}_{\mathrm{R}}D]$ for *para*-substituted methyl phenyl sulphones and methyl phenyl sulphoxides (*a*) in CCl_4–C_6H_6 (9 : 1) (●), (*b*) in $CHCl_3$ (×); the line shown has unit slope

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Table 4

Spectral data [a] for the sulphone stretching vibrations for methyl phenyl sulphones

			1150 cm^{-1} band				1330 cm^{-1} band			
Substituent	σ^{+} [b]	σ [b]	ν	ε_A [c]	A [d]	$A^{1/2}$	ν	ε_A [c]	A [d]	$A^{1/2}$
H	0·0	0·0	1156	850	11,000	105	1325	565	11,570	107
para-NMe$_2$	−1·70	−0·83	1144	1540	25,500	160	1312	925	19,410	140
-OMe	−0·78	−0·27	1149	1330	17,900	134	1325	780	14,840	122
-F	−0·07	0·06	1162 [e] 1151	420 870	11,300	106	1329	500	11,440	107
-SMe	−0·60	0·0	1156	900	14,500	120	1325	650	12,120	110
-Cl	0·11	0·23	1158	675	10,500	102	1330	560	9980	100
-Me	−0·31	−0·17	1153	755	12,300	111	1325	510	12,130	110
-COMe	0·50 [f]	0·50	1155	748	8740	93	1330	708	8620	93
meta-OMe	0·05	0·12	1149	615	11,400	107	1314 [g]			
-F	0·35	0·34	1158 [e] 1150	190 710	9800	99	1332 [g]			
-Cl	0·40	0·37	1158	820	9200	96	1331	720	9720	99
-Me	−0·07	−0·07	1148	800	12,300	111	1327	675	10,740	104

[a] Measured in CCl$_4$–C$_6$H$_6$ (9 : 1). [b] Taken from C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, 1964, **2**, 323. [c] Peak extinction coefficient, $\varepsilon_A = a_{max.}/cl$, where $a_{max.}$ is absorbance at peak maximum, c concentration in mol l^{-1}, and l cell path length in cm. [d] Integrated intensity. [e] This peak is split, possibly owing to Fermi resonance, and this was left off with the frequency correlation graphs. [f] Taken equal to σ. [g] These peaks were not integrated because they overlapped considerably with neighbouring peaks.

through-conjugation using the *d*-orbitals of sulphur. Applying equation (4) as previously [27] to describe these

$$A = 15{,}000\,[\sigma^{\circ}_{R}\,(1) - \sigma^{\circ}_{R}\,(2)]^2 + 170 \qquad (3)$$

$$A = 15{,}000\,[\sigma^{\circ}_{R}\,(1) - \sigma^{\circ}_{R}\,(2) + K_X\sigma^{\circ}_{R}D]^2 + 170 \qquad (4)$$

interactions (where K_X is the ability of the sulphur atom to accept electrons and $\sigma^{\circ}_{R}D$ is the σ°_{R} constant of donor compounds) gave Figure 3.

The values of K_X were obtained as previously [1] by plotting the difference between $[(A - 170)/15{,}000]^{1/2}$ and $[\sigma^{\circ}_{R}\,(1) - \sigma^{\circ}_{R}\,(2)]$ against $\sigma^{\circ}_{R}\,D$. K_X Values were 0·38 ± 0·03 for the methylsulphinyl and 0·49 ± 0·03 for the methylsulphonyl group in CCl$_4$. These values are in the same range as K_X found for other sulphur substituents [1] (SH, 0·34; SMe, 0·51; SBu^t, 0·40) and for the heavy halogens [1] (Cl, 0·22; Br, 0·32; I, 0·43). The satisfactory correlation of the data gives confidence in the treatment.

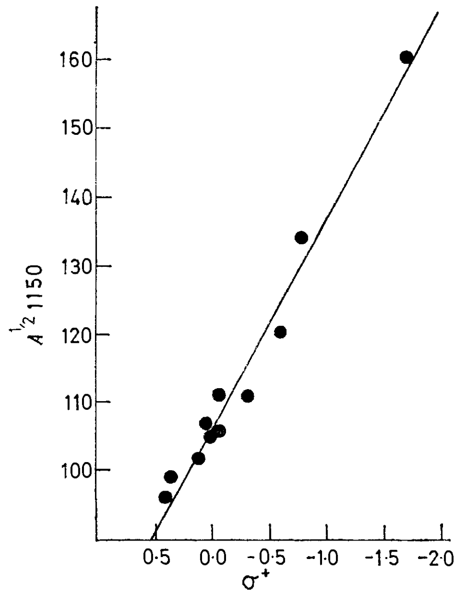

Figure 4 Plot of $A^{1/2}_{1150}$ *vs.* σ^{+} for methyl phenyl sulphones

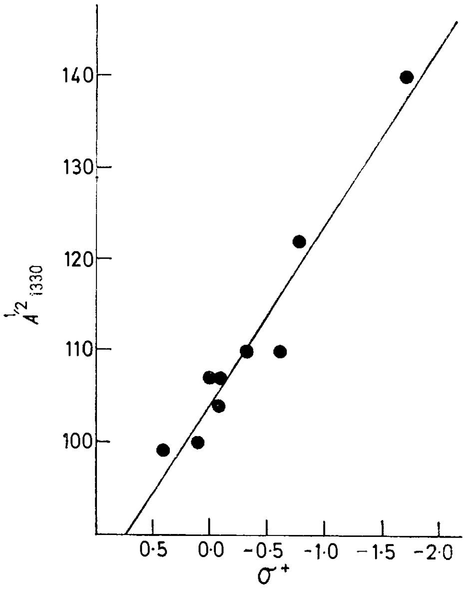

Figure 5 Plot of $A^{1/2}_{1330}$ *vs.* σ^{+} for methyl phenyl sulphones

Sulphone Stretching Vibrations at 1150 *and* 1330 *cm*$^{-1}$.—(a) *Frequencies*. The spectral data for these vibrations are listed in Table 4. In agreement with previous work,[19a,b] frequencies of the sulphone asymmetric and symmetric stretching vibrations are roughly correlated with σ substituent constants only for the *para*-compounds.

(b) *Intensities*. The square roots of the intensities of these bands are related in a linear fashion to σ^{+} as in equations (5) and (6) and Figures 4 and 5. As shown by

$$A^{1/2}_{1150} = 107 - 30{\cdot}1\sigma^{+}\ (r = 0{\cdot}99) \qquad (5)$$

$$A^{1/2}_{1330} = 104 - 20{\cdot}2\sigma^{+}\ (r = 0{\cdot}98) \qquad (6)$$

TABLE 5

Comparison of the spectral data for the 1150 cm^{-1} band of methyl phenyl sulphones

Sulphone	This work ν	This work $A \times 10^{-4}$	Bordwell *et al.*[a] ν	Bordwell *et al.*[a] $A^{b} \times 10^{-4}$
$PhSO_2Me$	1156	1·10	1161	0·91
p-$MeO{\cdot}C_6H_4{\cdot}SO_2Me$	1149	1·78	1154	1·3
m-$MeO{\cdot}C_6H_4SO_2Me$	1149	1·13	1155	0·91

[a] Ref. 12*b*. [b] Converted to I.U.P.A.C. standard units.

these equations and Table 4 the actual variation in intensity is small. Of the previous studies of sulphone intensities [12*b*, 20] only Bordwell *et al.* have examined similar compounds. Their intensities are smaller than those reported here (Table 5) but are of the same order.

The square root of the intensity of a stretching vibration for electron attracting groups attached to substituted benzene rings was suggested [28] to be correlated by σ^+ and this has also been observed for substituted *phenyl*-acetylenes [29] and substituted benzonitriles.[30] It appears that this is a general phenomenon.

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