Infrared Intensities as a Quantitative Measure of Intramolecular Interactions. Part XXVIII.[1] Benzenethiols and Methyl and t-Butyl Phenyl Sulphides

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I.r. intensities of series of *meta*-substituted benzenethiols and methyl phenyl and phenyl t-butyl sulphides confirm the following order of resonance donation: SMe > SH ≫ SBu^t. The intensities of the *para*-substituted benzenethiols and phenyl sulphides are interpreted in terms of sulphur *d*-orbital acceptance when the divalent sulphur opposes a donor substituent. A scale of *d*-orbital-acceptor ability is given for a range of substituents.

FOR a number of years there has been controversy as to the importance of *d*-orbital participation in the bonding of sulphides attached to π-bonded systems. The frequencies of bands in u.v. spectra of alkyl aryl sulphides have been quoted as evidence for *d*-orbital participation,[2] as evidence against [3] for simple sulphides or as contradictory when strong donors are present,[3] and as inconclusive.[4,5] Acidity values (pK_a) of substituted phenols and benzenethiols have also been quoted as evidence against [6] or for [7] *d*-orbital participation or as inconclusive.[8] The application of Goodman's substituent interference experiment [9] to the intensities of the ($A' - {}'L_b$) bands of benzenethiols has been used in turn as evidence for [10] and against [11] *d*-orbital bonding in these molecules. Photoelectron spectroscopy has suggested that the effect of *d*-orbital bonding in benzenethiol and some related compounds on the π-orbitals of the benzene ring is small.[12] The discrepancies between the additive dipole moments and the observed ones for *para*-*NN*-dimethylaminophenyl methyl sulphide and the corresponding methyl ether are 0·58 and 0·05 D, respectively.[12] This is good evidence that, at least where strong donors are *para* to the sulphide group,[13,14] *d*-orbital acceptance is important. Kinetics of H–D exchange in aromatic sulphides also provide evidence [15] for (*p*–*d*)π bonding.

Steric Considerations.—It is experimentally observed that in sterically twisted anisoles there is less conjugation.[16,17] This is because, when one of the lone pair orbitals of oxygen is removed from conjugation, it is

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[1] Part XXVII, G. Butt, M. Davis, Y. T. Pang, R. D. Topsom, and A. R. Katritzky, preceding paper.

[2] E. A. Fehnel and M. Carmack, *J. Amer. Chem. Soc.*, 1949, **71**, 2889.

[3] J. Degani, A. Mangini, A. Trombetti, and C. Zauli, *Spectrochim. Acta*, 1967, **23A**, 1351.

[4] E. L. Wehry, *J. Amer. Chem. Soc.*, 1967, **89**, 41.

[5] A. Mangini, *Pure Appl. Chem.*, 1963, **7**, 103.

[6] F. G. Bordwell and P. J. Boutan, *J. Amer. Chem. Soc.*, 1956, **78**, 854.

[7] R. R. Beishline, *J. Org. Chem.*, 1961, **26**, 2533.

[8] G. Chuchani and A. Frohlich, *J. Chem. Soc.* (*B*), 1971, 1417.

[9] L. Goodman, A. H. Konstam, and L. H. Sommer, *J. Amer. Chem. Soc.*, 1965, **87**, 1012.

[10] L. Goodman and R. W. Taft, *J. Amer. Chem. Soc.*, 1965, **87**, 4385.

[11] G. di Lonardo and C. Zauli, *J. Chem. Soc.* (*A*), 1969, 1305.

[12] D. C. Frost, F. G. Herring, A. Katrib, C. A. McDowell, and R. A. N. McLean, *J. Phys. Chem.*, 1972, **76**, 1030; H. Bock, G. Wagner and J. Kroner, *Tetrahedron Letters*, 1971, 3713.

[13] V. Baliah and M. Uma, *Tetrahedron*, 1963, **19**, 455.

[14] H. Lumbroso and R. Passerini, *Bull. Soc. chim. France*, 1955, 1179.

[15] A. I. Shatenshtein and H. A. Gvozdeva, *Tetrahedron*, 1969, **25**, 2749.

[16] See the section on durenes in R. T. C. Brownlee, R. E. J. Hutchinson, A. R. Katritzky, T. T. Tidwell, and R. D. Topsom, *J. Amer. Chem. Soc.*, 1968, **90**, 1757.

[17] A. R. Katritzky, R. F. Pinzelli, and R. D. Topsom, *Tetrahedron*, 1972, **28**, 3441.

not replaced by the other to the same extent, since the σ framework hybridization causes considerable angular deformation of the in-plane *p*-orbital. However, when *d*-orbitals are involved, as in thioanisole, one orbital of the appropriate symmetry replaces another in a bonding position as the group is rotated. Hence consideration of steric effects is a potential method of observing *d*-orbital effects. Phenyl methyl sulphides have been shown to be near planar.[18] The effect has been previously observed in comparison [10] of the ^{19}F n.m.r. spectra of 2,6-dimethyl-4-fluorothioanisole and 1,3-dimethyl-5-fluorobenzene; in the former the twisted methylthio-group behaves as a weak acceptor.[4] Similar conclusions have been drawn from dipole moment studies of sterically hindered aryl methyl sulphides.[13] The pK_a values of phenols with sterically hindered *para*-methylthio-substituents have been quoted as evidence for *d*-orbital participation.[4] Consideration of u.v. intensities and frequencies [3,4] and i.r. intensities [17] of the series of compounds PhSR, where R = Me, Et, Pr^i, or Bu^t, and of the pK_a values of similarly *para*-substituted benzoic acids,[19] all of which change uniformly, indicate clearly that $(p\text{–}p)\pi$ overlap has diminished but do not provide positive evidence for $(p\text{–}d)\pi$ resonance interactions.

TABLE 1

Physical and spectral properties of benzenethiols and methyl and t-butyl sulphides substituted in the *meta*-position

Substituents					1600—1585 cm^{-1} band				
1	2	B.p. (°C) [mmHg]	Lit. b.p. (°C) [mmHg]	$\sigma°_R(2)$	ν	ε_A [a]	A [b]	$\left(\frac{A-340}{19,000}\right)^{\frac{1}{2}}$	f_m [c]
SH	Me	*d*	*d*	−0·10	1593	112	1650	0·26	0·26
					1574	33			
	Cl	70[4·8]	205[207] [e]	−0·22	1578	269	3045	0·38	0·36
					1566	114			
	F	67[23]	157[740] [f]	−0·34	1599	300	4985	0·49	0·47
					1587	146			
					1580	207			
	OMe	87—89[5·7]	78[4] [g]	−0·43	1588	360	6600	0·57	0·54—0·57†
					1577	197			
SMe	Me	95—97[15]	96[15] [h]	−0·10	1592	95	2090	0·09	0·08—0·10†
					1576	34			
					1574	42			
	Cl	44[0·08]	112[16] [j]	−0·22	1578	214	3280	0·15	0·13—0·19†
					1562	90			
					1558	77			
	F	43[1·7]	186—187[740] [f]	−0·34	1600	235	5755	0·28	0·22—0·30†
					1584	85			
					1578	228			
	OMe	104—106[7·1]	125—127[16—17] [k]	−0·43	1590	339	6985	0·35	0·27—0·42†
					1574	184			
	NMe$_2$	63—64[0·03]	165—167[10] [l]	−0·53	1587	519	11215	0·57	0·40—0·54†
					1563	149			
					1558	106			
SBu^t	Me	72·5[2·3]	‡	−0·10	1589	75	910	0·17	0·15
					1572	20			
	Cl	57—59[0·05]	‡	−0·22	1573	107	2095	0·30	0·26
					1560	15			
	F	50[0·9]	‡	−0·34	1596	120	3740	0·42	0·39
					1588	120			
					1576	160			
	OMe	68[0·12]	‡	−0·43	1587	273	5445	0·52	0·46—0·48†
					1573	176			

[a] Peak extinction coefficient, $\varepsilon_A = a_{max.}/cl$, where $a_{max.}$ is the absorbance at peak maximum, c is concentration in mol l^{-1}, and l is cell path length in cm. [b] The integrated intensity of the 1600—1585 cm^{-1} band, in l mol^{-1} cm^{-2}. [c] $f_m = [\sigma°_R(1)]^2 + [\sigma°_R(2)]^2 + \sigma°_R(1)\sigma°_R(2)$. [d] From Kodak Limited. [e] G. Daccomo, ' Jahres Bericht uber die Fortshcritte der Chemie,' 1891, 1375. [f] 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. [g] D. S. Tarbell and A. H. Herz, *J. Amer. Chem. Soc.*, 1953, **75**, 1668. [h] G. Modena and L. Maioli, *Gazzetta*, 1957, **87**, 1306. [j] G. Leandri, A. Mangini, and R. Passerini, *Gazzetta*, 1954, **84**, 3. [k] F. G. Bordwell and P. J. Boutan, *J. Amer. Chem. Soc.*, 1957, **79**, 717. [l] M. T. Zincke and J. Muller, *Ber.*, 1913, **46**, 775.

† Corrected for asymmetry. ‡ New compound.

It has been previously demonstrated [20] that the i.r. intensities of ν_8 bands (ν_{16} in Herzberg's notation) of benzenes may be related both to the overall resonance effect of a group and to its ability to accept electrons into its *d*-orbitals. A re-analysis [21] has established equation (1) for *para*-disubstituted benzenes, where λ is a

$$A = 15,000\,[\sigma°_R(1) - \sigma°_R(2) + \lambda] + 170 \quad (1)$$

measure of the electronic interaction additional to that based on additivity of substituent effects.

We have studied the i.r. intensities of the ν_8 bands of substituted benzenethiols, methyl phenyl sulphides, and

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[18] M. J. Aroney, R. J. W. Le Fèvre, R. K. Pierens, and M. G. N. The, *J. Chem. Soc.* (*B*), 1971, 1132.

[19] N. H. P. Smith, *Nature*, 1966, **211**, 186; N. H. P. Smith, personal communication of the pK_a of *p*-t-butylthiobenzoic acid; V. Baliah, Sp. Shanmuganathan, and R. Varadachari, *J. Phys. Chem.*, 1957, **61**, 1013.

[20] A. R. Katritzky and R. D. Topsom, *Angew. Chem. Internat. Edn.*, 1970, **9**, 87.

[21] R. T. C. Brownlee, D. G. Cameron, R. D. Topsom, A. R. Katritzky, and A. F. Pozharsky, *J.C.S. Perkin II*, 1974, 247.

t-butyl phenyl sulphides. We also reconsider results for other substituents in order to provide a relative order of *d*-orbital acceptor abilities. We had earlier [22] used an equation of type (1) but with a value of 11,800 instead of 15,000; we therefore also show, as in a preceding paper,[21] that our previous conclusions are still valid.

TABLE 2

Physical and spectral properties of benzenethiols and methyl and t-butyl sulphides substituted in the *para*-position

Substituents 1	2	M.p. [B.p.](°C)	Lit. m.p. [b.p.] (°C)	$\sigma^\circ_R(2)$	1600—1585 cm^{-1} band ν	ε_A [a]	A [b]	$\left(\frac{A-170}{15,000}\right)^{\frac{1}{2}}$	λ [c]	f_p [d]
SH	Me	[48 at 0·1 mmHg]	[195] [e]	−0·10	1599	3	185	0·03	0·03	0·06
	Cl	52—53	53 [f]	−0·22	1573	1	210	0·05	0·04§	0·08
	F	[29—30 at 2·3 mmHg]	[64—65 at 12 mmHg] [g]	−0·34	1591	115	1140	0·25	0·12	0·27
	OMe	[57—59 at 0·7 mmHg]	[227—229] [h]	−0·43	1593	120	2370	0·38	0·15	0·39
					1573	56				
SMe	Me	[72 at 3·8 mmHg]	[104—105 at 20 mmHg] [j]	−0·10	1604	10	295	0·08‡	0·05	0·10
	Cl	[44 at 0·08 mmHg]	[112 at 18 mmHg] [k]	−0·22	1576	3	290	0·06‡	0·06§	0·04
	SMe	[83—84·5]	[85] [l]	−0·25	1578	10	305	0·00‡		0·00
	F	[65 at 7·7 mmHg]	[74 at 10 mmHg] [m]	−0·34	1589	60	1120	0·24‡	0·18	0·27
	OMe	[48—49 at 0·07 mmHg]		−0·43	1594	87	2755	0·40‡	0·22	0·40
		25—26	25—26 [n]		1571	58				
	NMe$_2$	[112—114 at 3 mmHg]	[159—160 at 20 mmHg] [o]	−0·53	1596	240	5120	0·57‡	0·28	0·57
	NO$_2$	68—69	70·5—71·5 [p]	+0·17	1595	190	6400	0·64‡		
					1583	295				
	COMe	81—82	79—80 [q]	+0·22	1591	470	4815	0·56 ‡	0·09	0·58
	SO$_2$Me	98—99	98—99 [r]	+0·07	1581	185	3005	0·43‡	0·12	0·43
SBu^t	Me	[59 at 0·6 mmHg]	[142 at 50 mmHg] [s]	−0·10	1596	15	295	0·09	0·04	0·07
	Cl	[92 at 1·1 mmHg]	[75 at 0·6 mmHg]	−0·22	1571	47	670	0·18	0·07§	0·23
	F	[64—66 at 3·1 mmHg]	†	−0·34	1588	180	2630	0·41	0·14	0·41
	OMe	(77—79 at 0·3 mmHg]	[86 at 0·6 mmHg] [t]	−0·43	1590	230	4260	0·52	0·17	0·53
					1569	70				
	NO$_2$	[86—88 at 1·15 mmHg]		0·17	1597	180	2270	0·37		
		37	39 [t]		1576	77				

[a] Peak extinction coefficient; $\varepsilon_A = a_{max.}/cl$, where $a_{max.}$ is absorbance at peak maximum, c is concentration in mol l^{-1}, l is cell path length in cm. [b] The integrated intensity of the 1600—1585 cm^{-1} band in l mol^{-1} cm^{-2}. [c] $\lambda = K_X\sigma^\circ_R D$ where SR is *para* to a donor; $\lambda = K_A(\sigma^+ - \sigma)$ where SR is *para* to an acceptor (see ref. 21). [d] $f_p = [\sigma^\circ_R(1) - \sigma^\circ_R(2) + \lambda]$. [e] E. Bourgeois, *Rec. Trav. chim.*, 1899, **18**, 426. [f] H. J. Backer and N. D. Dijkstra, *Rec. Trav. chim.*, 1933, **52**, 701. [g] G. Olah and A. Pavlath, *Acta Chim. Acad. Sci. Hung.*, 1954, **4**, 111. [h] F. Taboury, *Ann. Chim.* (*France*), 1908, **15**, 21. [j] H. Gilman and N. J. Beaber, *J. Amer. Chem. Soc.*, 1925, **47**, 1449. [k] H. Lumbroso and G. Dumas, *Bull. Soc. chim. France*, 1955, 651. [l] T. Zincke and W. Frohneberg, *Ber.*, 1909, **42**, 2721. [m] H. Zahn and H. Zuber, *Chem. Ber.*, 1953, **86**, 172. [n] F. G. Bordwell and P. G. Boutan, *J. Amer. Chem. Soc.*, 1957, **79**, 717. [o] Ref. 23. [p] B. J. Lindberg and B. Schroder, *Acta Chem. Scand.*, 1970, **24**, 3089. [q] L. C. King, M. McWhirter, and R. L. Rowland, *J. Amer. Chem. Soc.*, 1948, **70**, 239. [r] H. Burton and P. F. Hu, *J. Chem. Soc.*, 1948, 604. [s] W. Hahn, G.P. 1,110,631/1961 (*Chem. Abs.*, 1962, 56, 3416*e*). [t] G. Maccagnani and F. Taddei, *Boll. sci. Fac. Chim. ind. Bologna*, 1965, **23**, 381 (*Chem. Abs.*, 1966, **64**, 17395).

† New compound. ‡ Corrected for asymmetry. § Also corrected for *d*-orbital interaction with Cl.

EXPERIMENTAL

With the exception of certain phenyl t-butyl sulphides, the compounds were commercial samples or were prepared by literature methods. Their physical and spectral properties are described in Tables 1 and 2. Their purities were checked by g.l.c., by m.p. determination, and by standard spectroscopic methods. Benzene was dried with sodium wire. Spectroscopic grade carbon tetrachloride was stored over molecular sieves.

The new phenyl t-butyl sulphides were prepared by a standard method, illustrated for t-butyl *m*-tolyl sulphide.

t-Butyl m-*Tolyl Sulphide*.—t-Butyl alcohol (2·4 g) was slowly added to stirred concentrated sulphuric acid (20 ml; 15%) at 0—5°, and the mixture was stirred for 30 min. Toluene-*m*-thiol (1·5 g) was slowly added dropwise over 15 min, and the mixture was maintained between 0 and 5° for 1 h, and then at room temperature for 3 h. It was then poured onto crushed ice (50 g) and extracted with ether (3 × 25 ml). The combined extracts were washed with dilute aqueous sodium hydroxide (2 g in 30 ml) and water (25 ml), then dried ($MgSO_4$) and evaporated. The product was distilled to give *t-butyl* m-*tolyl sulphide* (0·4 g, 20%), as an oil, b.p. 72·5° at 2·3 mmHg (Found: C, 73·2; H, 8·9. $C_{11}H_{16}S$ requires C, 73·2; H, 8·9%). The following were prepared similarly: m-*chlorophenyl t-butyl sulphide*, oil, b.p. 57—59° at 0·05 mmHg (Found: C, 60·0; H, 6·9; Cl, 17·7. $C_{10}H_{13}ClS$ requires C, 59·9; H, 6·6; Cl, 17·7%); m-*fluorophenyl t-butyl sulphide*, oil, b.p. 50° at 0·9 mmHg (Found: C, 64·9; H, 7·2. $C_{10}H_{13}FS$ requires C, 65·2; H, 7·1%); m-*methoxyphenyl t-butyl sulphide* (the reaction mixture was kept at 0—5° for 3 h and then worked up), oil, b.p. 68° at 0·12 mmHg (Found: C, 67·3; H, 8·3. $C_{11}H_{16}OS$ requires C, 67·3; H, 8·2%); and p-*fluorophenyl t-butyl sulphide*, oil, b.p. 64—66° at 3·1 mmHg (Found: C, 65·6; H, 7·1. $C_{10}H_{13}FS$ requires C, 65·2; H, 7·1%).

p-NN-*Dimethylaminophenyl Methyl Sulphide*.—A literature method [23] gave the title compound, b.p. 112—114° at 3 mmHg (lit.,[23] 159—160° at 20 mmHg) (Found: C, 64·5; H, 8·0; N, 8·6. Calc. for $C_9H_{13}NS$: C, 64·6; H, 7·8; N, 8·4%).

The intensities of the i.r. vibrations were measured as described previously [24] on dilute solutions of compounds in carbon tetrachloride containing 10% benzene. Reproducibilities in $(A - 340)^{\frac{1}{2}}$ or $(A - 170)^{\frac{1}{2}}$ values are ±1 intensity

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[22] P. J. Q. English, A. R. Katritzky, T. T. Tidwell, and R. D. Topsom, *J. Amer. Chem. Soc.*, 1968, **90**, 1767.

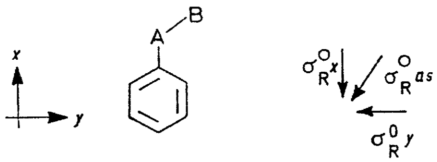
[23] H. Gilman and F. J. Webb, *J. Amer. Chem. Soc.*, 1949, **71**, 4062.

[24] R. T. C. Brownlee, A. R. Katritzky, and R. D. Topsom, *J. Amer. Chem. Soc.*, 1966, **88**, 1413.

units for compounds where A is greater than 400 l mol^{-1} cm^{-2} but greater for lower values; in such cases the actual value is also less accurate because of uncertainty in the value of the overtone correction.

RESULTS AND DISCUSSION

Asymmetry.—Compounds of type (I) have intensities made up of contributions in both x and y directions.[22]



(I)

For the compounds at present considered B = H, Me, or Bu^t. Thiols have not been corrected for asymmetry. The σ°_R value for SBu^t (0·07) is too small for the asymmetric contribution to be significant; in addition SBu^t is twisted into a non-planar conformation[17] which will decrease $\sigma^\circ_R y$. The $\sigma^\circ_R x$ and $\sigma^\circ_R y$ values for SMe have been calculated as previously[22] from the intensity of p-bis(methylthio)benzene to be ±0·24 and ±0·07, respectively (*cf.* ±0·42 and ±0·06 for[21] OMe). Corrections for the intensities of *meta*- and *para*-substituted methyl phenyl sulphides have been applied[22,25] as necessary.

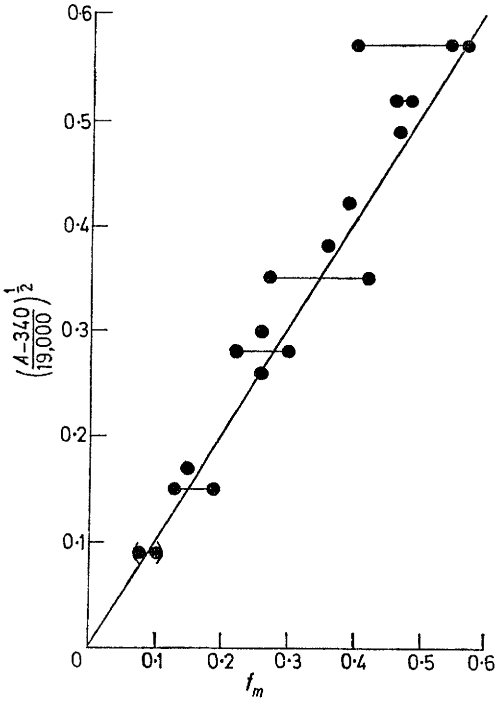


FIGURE 1 Plot of $[(A - 340)/19{,}000]^{\frac{1}{2}}$ against $\{[\sigma^\circ_R(1)]^2 + [\sigma^\circ_R(2)]^2 + \sigma^\circ_R(1)\sigma^\circ_R(2)\}$ for *meta*-substituted benzenethiols and alkyl phenyl sulphiddes

meta-*Disubstituted Benzenes*.—Table 1 contains the spectral data for the *meta*-substituted alkyl phenyl sulphides and benzenethiols. Equation (2) has been developed previously[25] to relate the combined intensity of 1600 and 1585 cm^{-1} bands of *meta*-disubstituted benzenes to σ°_R terms. Application of this equation to the *meta*-substituted sulphur compounds with an

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

asymmetry correction[25] in the case of methyl phenyl sulphides using the previously determined σ°_R values (SH, −0·19;[16] SMe, −0·25;[16] SBu^t, −0·07[17]) gave a good straight line (Figure 1), thus confirming the values adopted.

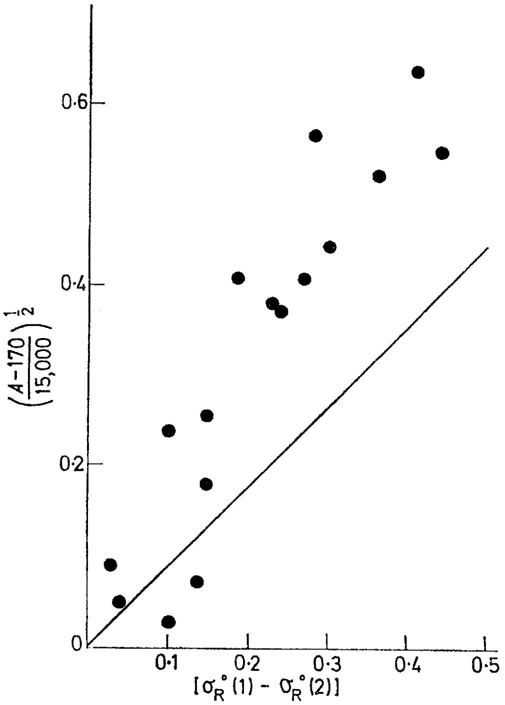


FIGURE 2 Plot of $[(A - 170)/15{,}000]^{\frac{1}{2}}$ against $[\sigma^\circ_R(1) - \sigma^\circ_R(2)]$ for *para*-substituted benzenethiols and alkyl phenyl sulphides

para-*Disubstituted Benzenes*.—Table 2 contains the spectral data for the *para*-substituted alkyl phenyl sulphides and benzenethiols. The intensities of the chloro- (290; lit.,[22] <50) and fluoro-(methylthio)-benzenes (1120; lit.,[22] 895) differ from previous values because in the present study the intensity of an overtone at 1640 cm^{-1} was included in the integration. The intensity of *para*-dimethylamino(methylthio)benzene also differs considerably (5120; lit.,[22] 3107). Since the present compound gave good analytical figures and was homogeneous by g.l.c., we conclude that there was an error in the previous calculation or that the previous sample was impure.

Equation (1)[21] describes the intensities of *para*-disubstituted benzenes; $\lambda = 0$ where there is no inter-

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[25] A. R. Katritzky, M. V. Sinnott, T. T. Tidwell, and R. D. Topsom, *J. Amer. Chem. Soc.*, 1969, **91**, 628.

action between substituents. Figure 2 shows a plot of $[(A) - 170)/15{,}000]^{\frac{1}{2}}$ against $[\sigma^{\circ}_{R}(1) - \sigma^{\circ}_{R}(2)]$ and the line drawn assumes a linear relationship of unit slope. There are significant deviations from this line for the derivatives of all three sulphur substituents. This type of behaviour has been previously [22] observed for benzene derivatives with strong donors *para* to substituents with available *d*-orbitals, and the correction term λ † has been introduced and analysed in terms of equation (3); K_X is

$$\lambda = K_X\sigma^{\circ}_{R}D \qquad (3)$$

an empirical measure of the electron-accepting power of the *d*-orbital substituent determined by plotting Δ,* obtained from $\{[(A - 170)/15{,}000]^{\frac{1}{2}} - [\sigma^{\circ}_{R}(1) - \sigma^{\circ}_{R}(2)]\}$, against $\sigma^{\circ}_{R}D$ where D refers to an opposing electron donating substituent. Application of this treatment to the data in Table 2 gave K_X values of 0·34 ± 0·03, 0·51 ± 0·02, and 0·40 ± 0·03 for SH, SMe, and SBu^t, respectively.

TABLE 3

Resonance interactions in *para*-disubstituted benzenes containing one resonance-donating substituent and one *d*-orbital Acceptor (A in l mol^{-1} cm^{-2})

		$\sigma^{\circ}_{R}(2)$	$A - 170$ [a]	$\left(\frac{A - 170}{15{,}000}\right)^{\frac{1}{2}}$	$[\sigma_{R}(1) - \sigma_{R}(2)]$	λ [c]	f_p [d]
Cl	NMe_2	0·54	2780	0·43	0·32	0·12	0·44
	NHMe	0·52	2760	0·43	0·30	0·12	0·42
	ND_2	0·47	1850	0·35	0·25	0·10	0·35
	OMe	0·43	1454	0·31	0·21	0·09	0·30
	F	0·34	440	0·17	0·12	0·07	0·19
	Me	0·10	110	0·09	−0·12	0·02	0·10
Br	NMe_2	0·54	3350	0·47	0·31	0·17	0·48
	NHMe	0·52	2970	0·44	0·29	0·17	0·46
	ND_2	0·47	2450	0·40	0·24	0·15	0·39
	OMe	0·43	1694	0·34	0·20	0·14	0·34
	F	0·34	630	0·20	0·11	0·11	0·22
	Me	0·10	70	0·07	−0·13	0·03	0·10
I	NMe_2	0·54	4610	0·55	0·32	0·23	0·55
	ND_2	0·47	3050	0·45	0·25	0·20	0·45
	OMe	0·43	2294	0·39	0·21	0·18	0·39
	F	0·34	690	0·21	0·12	0·15	0·27
	Me	0·10	0	0·00	−0·12	0·03	0·09
$SiMe_3$	NMe_2	0·54	9930 [b]	0·81	0·56	0·23	0·79
	OMe	0·43	5830 [b]	0·62	0·45	0·18	0·63
	F	0·34	3190 [b]	0·46	0·36	0·15	0·51
	Cl	0·23	1270 [b]	0·29	0·25	0·10	0·35
	Me	0·10	550 [b]	0·19	0·12	0·03	0·15

[a] From ref. 22 unless otherwise stated. [b] Ref. **26**. [c] $K_X\sigma^{\circ}_{R}D$. [d] $|[\sigma^{\circ}_{R}(1) - \sigma^{\circ}_{R}(2) + \lambda]|$.

The K_X values for the SR groups (R = Me or Bu^t) differ much less than their σ°_{R} values (−0·25 and −0·07 respectively). The ability of the sulphur atom to accept electrons into its vacant *d*-orbitals under the influence of *para*-donor substituents is thus much less affected by rotation of the alkyl sulphur group out of the plane of the benzene ring than the overlap of the sulphur lone-pair orbitals with the π-systems.

The K_X value for the SH group (0·34) is smaller than that of the methylthio-substituent (0·51). This is in agreement with the theory of Craig,[26] who considered the effects of substituents on sulphur on the availability of *d*-orbitals for bonding. He found that alkyl substituents, in comparison to hydrogen, caused the *d*-orbitals to contract in size and drop in energy so as to be more available for bonding.

Relative d-*Orbital Acceptor Abilities.*—In Table 3 we list the previous published i.r. intensity data and derived σ values for *para*-donor-substituted chlorobenzenes,[22] bromobenzenes,[22] iodobenzenes,[22] and trimethylphenylsilanes.[26] Use of equations (1) and (3) allows the calculation of K_X values, and thus of the overall *d*-orbital acceptor abilities as follows:

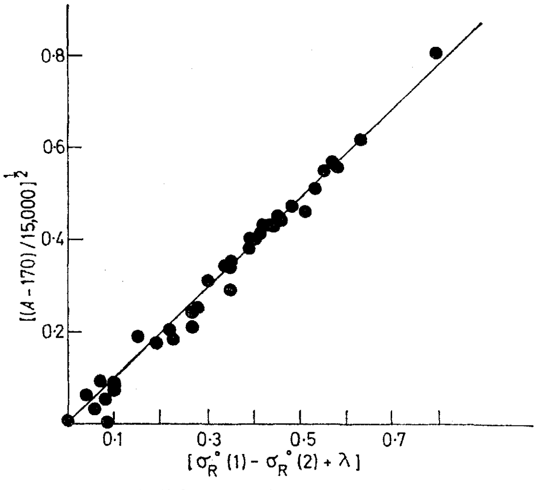

FIGURE 3 Plot of $[(A - 170)/15{,}000]^{\frac{1}{2}}$ against $[\sigma^{\circ}_{R}(1) - \sigma^{\circ}_{R}(2) + \lambda]$ for *para*-substituted benzenethiols, alkyl phenyl sulphides, and trimethylsilyl-, chloro-, bromo-, and iodo-benzenes

Group:	SMe	$SiMe_3$	I	SBu^t	SH	Br	Cl
K_X	0·51	0·43	0·43	0·40	0·34	0·32	0·22
Range	±0·02	±0·04	±0·02	±0·04	±0·04	±0·02	±0·01

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* We use the term λ to denote the calculated correction term and Δ to denote the measured difference between $[(A - 170)/15{,}000]^{\frac{1}{2}}$ and $[\sigma^{\circ}_{R}(1) - \sigma^{\circ}_{R}(2)]$.

[26] N. C. Cutress, A. R. Katritzky, C. Eaborn, D. R. M. Walton, and R. D. Topsom, *J. Organometallic Chem.*, 1972, **43**, 131.

Figure 3 shows the good relation obtained by plotting $[(A - 170)/15{,}000]^{\frac{1}{2}}$ against $(\sigma^{\circ}{}_{R}D - \sigma^{\circ}{}_{R}X + K_{X}\sigma^{\circ}{}_{R}D)$ for the compounds in Tables **2** and **3**. The values for $SiMe_3$, I, Br, and Cl are all lower than previously reported (0·62,[26] 0·55,[22] 0·42,[22] and 0·32 [22]) as a result of the more definite value of the constant in equation (1). The numerical values provide an albeit approximate quantitative measure of *d*-orbital acceptance by the substituents.

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